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trans-2,5-Dialkylpyrrolidinyl-containing phosphinamines. Synthetic and mechanistic studies in Pd-catalysed asymmetric allylic alkylation

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Abstract

The preparation of new phosphinamine ligands possessing an enantiopure *trans*-2,5-dialkylpyrrolidinyl unit linked by a rigid *o*-phenylene bridge to a diphenylphosphine is described. Only that route forming the *trans*-2,5-dialkylpyrrolidine in the final step from (2-aminophenyl)diphenylphosphine proved successful. The cyclocondensation proceeded in 48% and 27% yields, respectively, for the dimethyl- and diethyl-analogues. Their palladium complexes were prepared and applied to the test of enantioselective alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate in high chemical yields but with moderate enantioselectivities of up to 34% ee.

^{1}H NMR spectra of the η^3-allyl Pd complexes of four *trans*-2,5-dialkylpyrrolidine-containing ligands were analysed in an attempt to explain the results obtained. In the cases of the 1,3-diphenylallyl complexes, two diastereomers were observed for all four ligands and their configurations were assigned with the aid of COSY and NOESY experiments. The catalytic results obtained are best interpreted by the reaction proceeding with nucleophilic attack on the allyl *trans* to the phosphorus donor atom of the major diastereomer.

1. Introduction

The ability of enantiopure, heterobidentate ligands to induce asymmetry by exerting a combination of steric and electronic effects on reactions occurring within the co-ordination sphere of the transition metal to which they are bound has led to the development of an active area of research in their design and application in asymmetric catalysis. Of the possible mix of donor atoms the phosphinamine class has received most attention and examples possessing different chiral elements and backbone scaffolding have been designed and applied with success in catalytic asymmetric synthesis.[1–4] The majority of examples utilise an sp^2 nitrogen and ligands possessing an sp^3 nitrogen donor atom have only recently

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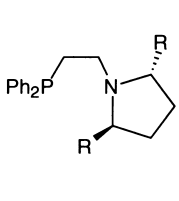
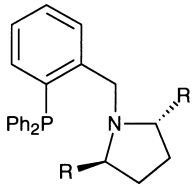
been reported. Koga prepared diphenylphosphinopyrrolidines of type **1** which form five-membered chelates but gave poor ees of 11–20% when applied to the palladium-catalysed reaction between sodium dimethylmalonate and 1,3-diphenylpropenyl acetate.[5]

We have recently reported the preparation of phosphinamine ligands of type **2** and **3**,[6] bearing an enantiopure *trans*-2,5-disubstituted pyrrolidine unit, and have described their application in iridium-catalysed enantioselective imine reduction[7] and in the palladium-catalysed asymmetric intermolecular Heck reaction.[8] Our optimum enantioselectivity in the test palladium-catalysed allylic substitution was 90% for ligand **3**.[9] This increased ee value, compared to those obtained with **1**, can be attributed to an increase in chelate ring size from five to six or to a more rigid backbone between the donor atoms. Decreasing the chelate size again to five and having an *o*-phenylene backbone, present in the successful DuPhos ligands of type **4**,[10] leads to the design of ligands **5** and **6**, which would allow us to determine whether chelate ring size or backbone rigidity was more important in the design of such ligand systems. We now report the preparation of these new phosphinamine ligands **5**–**6**, their application in palladium-catalysed enantioselective allylic substitution and our mechanistic studies in this reaction using ligands **2**–**3** and **5**–**6**.

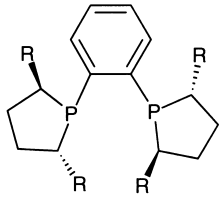


1

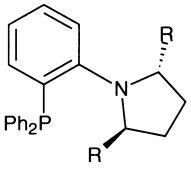
R = Me, Et, Bn.



2: R = Me; **3**: R = Et.



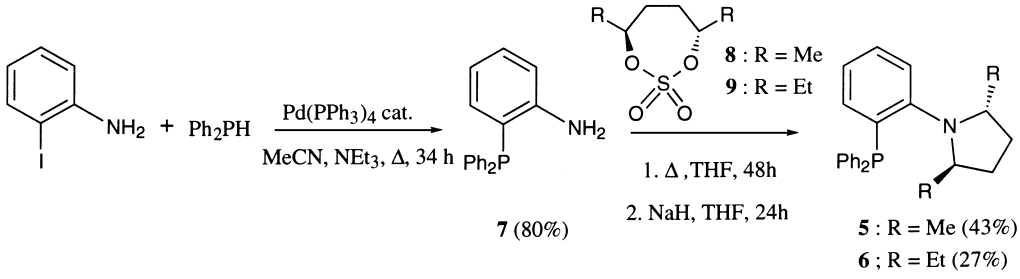
4: R = Me, Et.



5: R = Me; **6**: R = Et.

2. Ligand preparation

The key step in our synthesis of phosphinamines **3** and **4** was the cyclocondensation of an amine with enantiopure 2,5-dimethyl- or 2,5-diethyl-1,4-diol cyclic sulfate and similar, successful routes to *trans*-2,5-disubstituted pyrrolidines have used appropriately substituted 1,4-dimesylates[11] or 1,4-diacetates.[12] We investigated a pathway in which the diphenylphosphino group was already in place prior to the cyclocondensation, a strategy already successfully used in the synthesis of ligands of class **3** and **4**.[9] The required (2-aminophenyl)diphenylphosphine **7** was prepared in 80% yield, according to the method of Stetzer, by refluxing diphenylphosphine, 2-iodoaniline and triethylamine in acetonitrile for 34 h in the presence of 1 mol% of tetrakis(triphenylphosphine)palladium, Scheme 1.[13] Using the standard procedure for pyrrolidine ring formation, **7** was reacted with (2*S*,5*S*)-hexanediol cyclic sulfate **8** to give (−)-[2-((2*R*,5*R*)-2,5-dimethylpyrrolidinyl)phenyl]diphenylphosphine **5** in an optimised 43% yield.[14] Each proton associated with the pyrrolidine ring resonates at a different frequency in the ^{1}H NMR spectrum, implying restricted rotation about the aryl–nitrogen bond. The methyl groups at the 2,5-positions resonate as doublets at 1.18 ppm and 0.70 ppm suggesting that the latter is shielded by ring current effects. Similarly, that methine coupled to the methyl at 1.18 ppm appears at an unusually high field resonance of 0.50 ppm. Using the optimised conditions for the preparation of **5**, **7** was reacted with (3*S*,6*S*)-octanediol cyclic sulfate **9** to give (−)-[2-((2*R*,5*R*)-2,5-diethylpyrrolidinyl)phenyl]diphenylphosphine **6** in 27% yield, Scheme 1. The moderate yields presumably reflect the steric congestion about the reacting nitrogen.



Scheme 1.

The enantioselective substitution of allylic acetates is an important asymmetric carbon–carbon bond forming process[1] catalysed by diphosphine complexes of palladium, and more recently with phosphinamine ligands.[15] We wished to compare the enantiodifferentiating ability of ligands **5–6** with ligands **3–4** in this transformation and our results using in situ prepared palladium η^3-allyl complexes are given in Table 1.

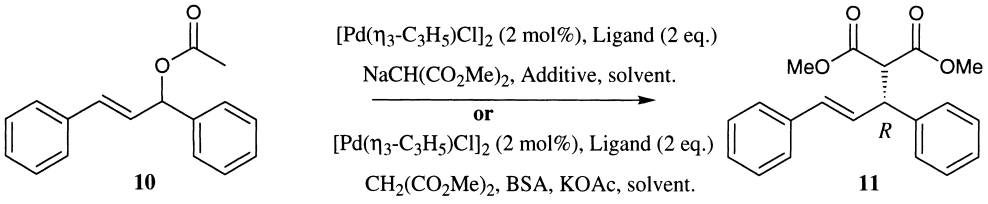


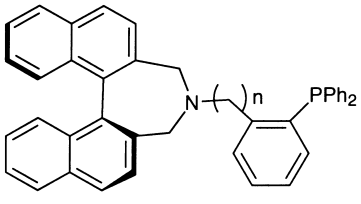
Table 1
Application of pyrrolidine-containing ligands **3–6** to the asymmetric allylic alkylation of acetate **10**[a]

Entry	Method	Ligand	Solvent	Temp. °C	% Conversion[b]	% ee[c] (config.[d])
1	NaMal	**5**	CH_2Cl_2	25	68	24 (*R*)
2	NaMal	**5**	CH_3CN	25	75	20 (*R*)
3	NaMal	**5**	DMF	25	63	34 (*R*)
4	NaMal	**5**	DMF	0	60	34 (*R*)
5	BSA	**5**	DMF	25	67	30 (*R*)
6	BSA	**5**	CH_3CN	25	69	32 (*R*)
7	BSA	**5**	CH_2Cl_2	25	65	28 (*R*)
8	BSA	**5**	CH_3CN	0	72	32 (*R*)
9	BSA	**3**	DMF	0	**62**	**55** (*R*)[9]
10	NaMal	**6**	CH_2Cl_2	25	65	10 (*R*)
11	NaMal	**6**	CH_3CN	25	87	11 (*R*)
12	NaMal	**6**	THF	25	76	16 (*R*)
13	NaMal	**6**	DMF	25	62	26 (*R*)
14	BSA	**6**	CH_3CN	25	87	18 (*R*)
15	BSA	**6**	CH_2Cl_2	25	64	16 (*R*)
16	BSA	**3**	CH_3CN	25	**89**	**90** (*R*)[9]

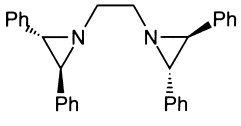
[a] The reaction was carried out over 24 h in the presence of 2 mol% of *in situ* formed catalyst using either NaMal or BSA method.
[b] Isolated yield after silica gel chromatography. [c] Enantiomeric excesses were determined by ^{1}H NMR using $Eu(hfc)_3$ as the chiral shift reagent. [d] Assignment is based on the sign of the optical rotation and comparison with lit..[16]

The malonate nucleophile can be preformed as its sodium salt (NaMal) or prepared in situ by Trost's

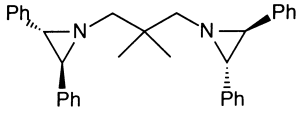
procedure using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and catalytic quantities of potassium acetate.[17] The highest enantioselectivity of 34% for the product malonate **11** was obtained by the malonate method at room temperature using ligand **5** in DMF, entry 3. Other solvents tested using the same catalyst under the same conditions gave lower ee values. The BSA method was also tested but this was found to be less effective, giving slightly lower ee values of 28–32%, entries 5–8. When the ethyl-substituted complex **6** was tested a lower enantioselectivity of 26% was obtained compared to 34% using catalyst **5** under the same conditions (compare entries 12 and 3). This was in contrast to the increase in enantioselectivity observed in ligand class **3** going from the dimethyl- to the diethyl-substituted catalyst (55–90% ee, respectively, entries 9 and 16). Varying the solvent to dichloromethane, acetonitrile and tetrahydrofuran had an adverse effect on the ee, decreasing it to 10, 11 and 16% respectively, entries 9–11. The BSA method was also tested for catalyst **6** and gave enantioselectivites of 18% in acetonitrile and 16% in dichloromethane, entries 13 and 14. Even though the diethyl-substituted complex **6** contains larger substituents at the stereogenic centres it is clear from the results that the ees obtained with it are lower. Despite this it is worth noting that palladium complexes of our ligand system gave an ee of 34% compared to the ees of 11–20% obtained by Koga with the related diphenylphosphinopyrrolidines **2**. The groups at the pyrrolidine stereocentres are similar in size, which suggests that rigidifying the backbone has only a small overall effect and is thus not as important in ligand design as an increase in chelate ring size from five to six. In related work, Widhalm has prepared ligands **12** and **13** and both ligands form a five- and six-membered chelate, respectively.[18] However, inspection of the enantioselectivities obtained in palladium-catalysed allylic substitution reveals that they afforded 96 and 95% ee, respectively. In this case the change in chelate ring size appears not to play as major a role as it does in our ligand systems. Conversely, Tanner has found that the chelate size in bis-aziridines is similarly crucial in allylic substitution as palladium complexes of ligand **14** give high yield and ee (89%, 99% ee) whilst ligand **15** gives only a 5% yield.[19]



12 : n = 0 [96% ee]
13 : n = 1 [95% ee]



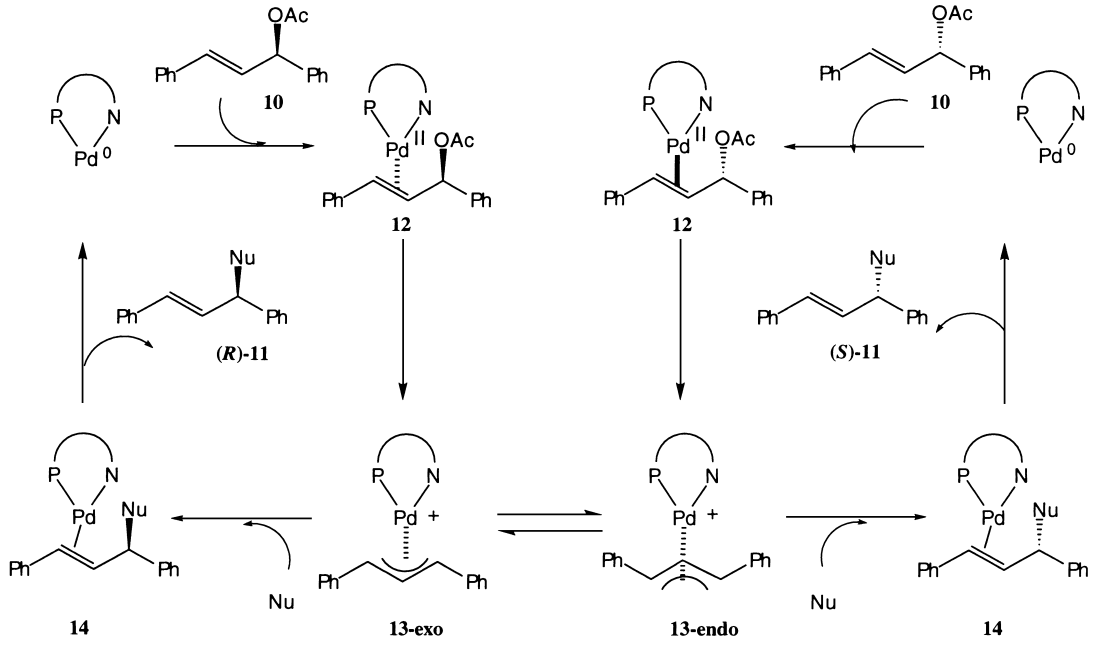
14 : [89%, > 99% ee]



15 : [5%]

3. Mechanistic studies

In an attempt to explain the stereoselectivities observed with ligands **2**, **3**, **5** and **6**, we carried out solution NMR studies on their cationic palladium(II) 1,3-diphenylallyl intermediates. The information thus garnered could be useful for future rational ligand design in this area. For palladium complexes of phosphinamine ligands the generally accepted mechanism[1e] of allylic alkylation involves the initial association of a palladium(0) phosphinamine species to the olefinic fragment of racemic 1,3-diphenylprop-2-enyl acetate **10** to give diastereomeric η^2-palladium(0) species **12**, which undergo oxidative addition to give cationic palladium(II) η^3-intermediates **13**-*endo* and **13**-*exo*, Scheme 2 [note: only two of the four possible η^2-palladium(0) species **12** are shown for clarity]. Intermediates **13** interconvert via a π–σ–π mechanism, thus allowing racemic material the possibility to afford enantiomerically enriched product. Carbon–carbon bond formation with soft nucleophiles then occurs outside the coordination sphere to afford, after olefin dissociation from **14**, the allylated product as either the (*R*)-**11** or (*S*)-**11** enantiomer.



Scheme 2.

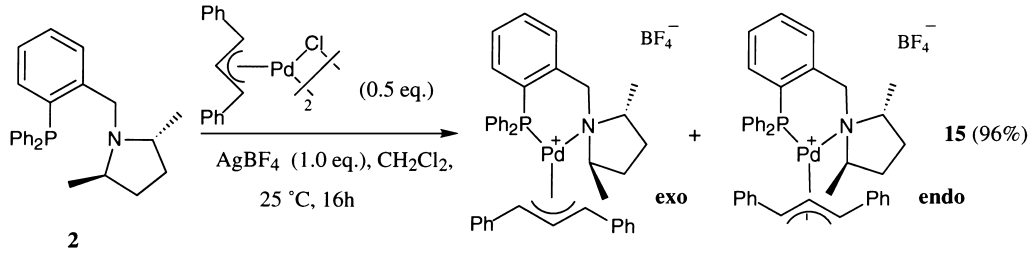
A considerable effort has been made to understand this critical enantiodifferentiating carbon–carbon bond forming step from the initial investigations of Bosnich[20] employing diphosphine ligands to the more recent work of Brown, Pfaltz, Togni and Helmchen employing phosphinamine ligands.[21–24] The key findings from the latter studies suggest that the ground state of complex **13** contains an allyl which has reoriented itself into a product-like geometry, thus facilitating nucleophilic attack on that allyl terminal carbon *trans* to the phosphorus donor atom. The labilty of the diastereomeric 1,3-diphenylallyl complexes is influenced by such electronic factors and also by intra-complex steric clashes between the ligand and the allyl. Solution NMR studies on these key intermediates would allow us to determine the ratio of *endo*- to *exo*-diastereomers and to gain some insight as to the influence of the alkyl groups at the stereogenic centres of the pyrrolidine. [Nomenclature note: the *endo*-isomer is defined as that allyl configuration in which the central allyl proton points in the same direction as the C-2′ substituent; see Fig. 2a.] In the present study it would allow a direct comparison between the solution behaviour of the 1,3-diphenylallyl complexes of our four *trans*-2,5-dialkylpyrrolidinyl-containing phosphinamine ligands.

*3.1. Solution NMR studies of palladium 1,3-diphenylallyl complexes of **2** and **3***

Hence we prepared the η^3-1,3-diphenylallyl palladium tetrafluoroborate salt **15** in 96% yield following literature precedent by the reaction of **2** with di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium, Scheme 3.[25]

In contrast to the corresponding unsubstituted π-allyl complex, which was broad,[9] the ^{1}H NMR of this complex at room temperature gave sharp peaks, Fig. 1.

It can be seen that there are two diastereomeric intermediates present in a 5:2 ratio and the full assignment is facilitated by observing the characteristic pattern (a double doublet) of that allyl proton *trans* to phosphorus, and all other allyl protons are deduced from DQF–COSY experiments. In this fashion the proton of the allyl *trans* to phosphorus of the major intermediate was assigned at 5.72 ppm (J_1=10.5, J_2=3.0), the central proton appeared as a double doublet at 6.90 ppm (J_1=10.5, J_2=7.2) and the



Scheme 3.

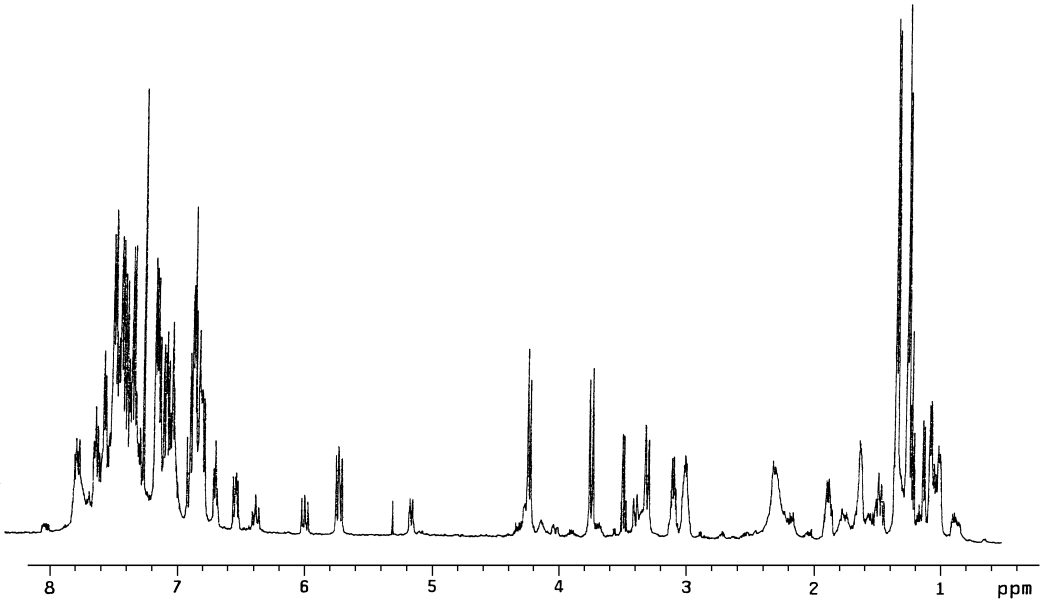


Figure 1. ^{1}H NMR spectrum of the diphenylallyl complex **15**

allyl proton *trans* to nitrogen is a doublet at 4.22 ppm with the required coupling constant of 7.2 Hz. Using similar logic the allyl protons of the minor diastereomer occurred at 6.00, 6.53 and 5.16 ppm, respectively. The ratio of diastereomeric intermediates was confirmed by ^{31}P NMR spectroscopy with resonances at 23.5 ppm (minor) and 21.2 ppm (major). Using COSY the protons of the pyrrolidine ring of the major diastereomer could also be identified; one of the methyl groups of the pyrrolidine occurs as a doublet (J 8.0) at 1.33 ppm and the other as a doublet (J 8.0) at 1.24 ppm but it is impossible to tell which is Me-2′ or Me-5′. The benzylic protons resonate at 3.39 and 3.78 ppm. The correct assignment of the doublet at 1.24 ppm, which leads to the correct assignment of the major diastereomer, was aided by obtaining a 2D-NOESY spectrum. In the published X-ray structure of the palladium dichloride complex, only Me-2′ is close in space to one of the benzylic protons and therefore the peak at 1.24 ppm is assigned to Me-2′ as it is the only methyl doublet of the major diastereomer to show an NOE with the benzylic proton at 3.39 ppm, Fig. 2a.[7] The allyl proton *trans* to nitrogen at 4.20 ppm shows a strong cross-peak to the allyl proton *trans* to phosphorus at 5.72 ppm, indicating these two protons are close together in space, thereby verifying the *syn–syn* π-allyl orientation hinted at by the vicinal coupling constants obtained. Me-5′ shows a strong cross-peak to the allyl proton *trans* to phosphorus at 5.72 ppm and to allyl phenyl protons which is only possible in the *endo*-diastereomer and thus confirms the structure of the major diastereomer, which does not interconvert to the *exo*-diastereomer on the timescale of the NOE.[26]

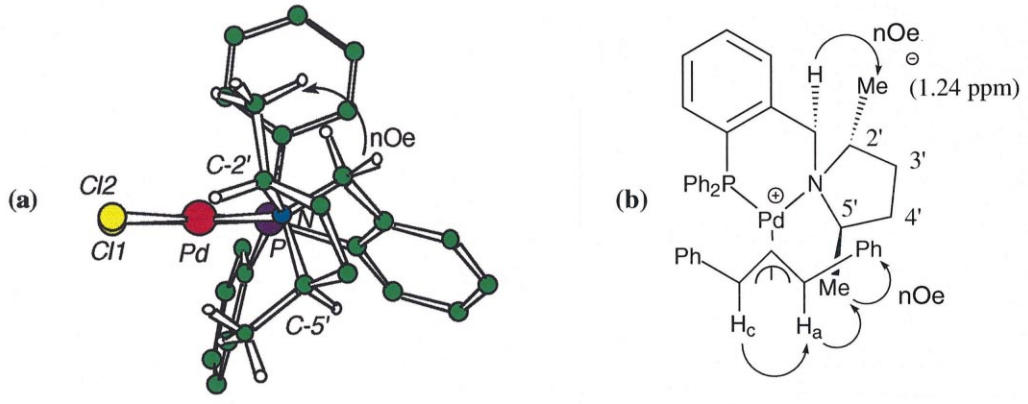
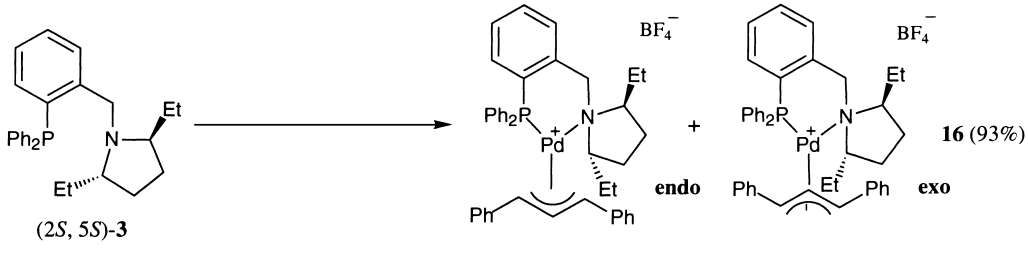


Figure 2. (a) Side view of X-ray structure of Pd dichloride complex of **2**. (b) Important NOEs allowing assignment of the major diastereomer

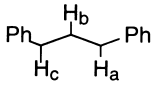
In a similar manner the *trans*-2,5-diethyl-substituted pyrrolidine 1,3-diphenyl allyl palladium complexes **16** were prepared but with the opposite hand of ligand **3** used in catalysis, i.e. 2*S*,5*S*-**3**, but the information obtained could be readily extrapolated to explain the allylic alkylation results. Thus, a mixture of diastereomeric complexes **16**-*endo* and **16**-*exo* was prepared in 93% yield, Scheme 4.



Scheme 4.

The ^{1}H NMR spectrum of this complex at room temperature was sharp and again showed that one of the two possible diastereomeric intermediates was favoured, in this case in a 3:1 ratio. The key peaks of both diastereomers, which were assigned using similar techniques as for complex **15**, are given in Table 2.

Table 2
^{1}H NMR chemical shifts of allylic protons in complexes **16** in $CDCl_3$. Peaks of the major diastereomer are given above the minor

P-------N	H_a	H_b	H_c	2'-Et	5'-Et	Benzylic
	6.02	6.80	4.19	0.71 (Me) 1.76-1.85 1.91-2.00 (CH_2)	0.89 (Me) 1.36-1.41 1.42-1.48 (CH_2)	3.38, 3.72
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	6.32	6.48	3.95	0.55 (Me) 1.38-1.44 1.42-1.48 (CH_2)	0.68 (Me) 0.82-0.86 1.08-1.15 (CH_2)	3.46, 4.26

There were two critical NOEs in the major diastereomer which allowed its unambiguous assignment. Firstly between one of the benzylic protons at 3.38 ppm and an ethyl methylene proton at 1.42–1.48 ppm which specifies this methylene as CH_2-6′, thus allowing complete assignment of the two ethyl substituents. The second key NOE was between the allyl proton *trans* to phosphorus at 6.02 ppm and an ethyl methylene proton at 1.76–1.85 ppm, which specifies the major diastereomer as **16**-*endo*, Fig. 3.

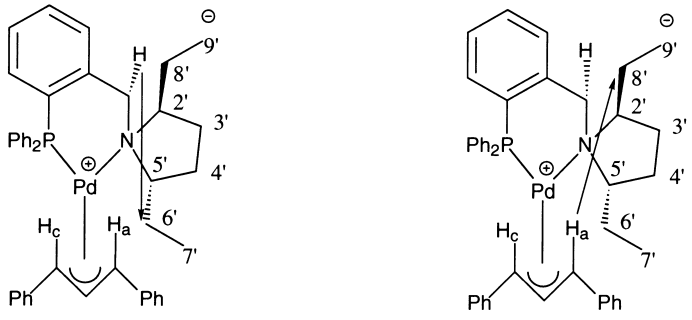
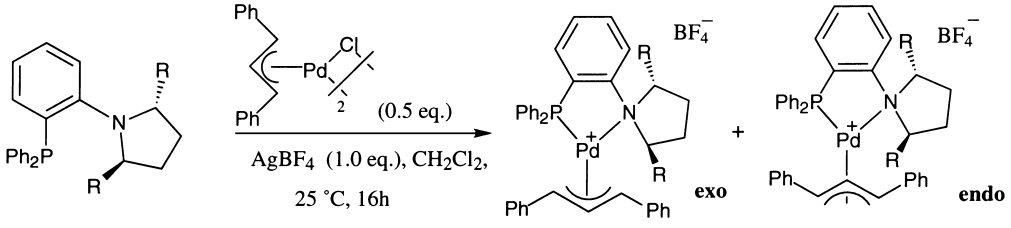


Figure 3.

3.2. Solution NMR studies of palladium 1,3-diphenylallyl complexes of **5** and **6**

The 1,3-diphenylallyl palladium complexes **17** and **18** were prepared in an analogous manner from ligands **5** and **6** in 86 and 87% yields, respectively.



5 : R = Me
6 : R = Et

17: R = Me (86%).
18: R = Et (87%).

The ^{1}H NMR spectrum of **17** at room temperature was sharp and showed a slight preference (3:2 ratio) for one of the two possible diastereomeric intermediates, Fig. 4.

The key peaks of both *E*,*E*-diastereomers, which were assigned using similar techniques as for complexes **15**–**16**, are given in Table 3. The four methyl peaks are well-separated and only one of the peaks in the major diastereomer shows an NOE with a multiplet centred at 6.25 ppm assigned to H-3 on the aryl ring. Only Me-2′ can show such an NOE and hence Me-2′ and Me-5′ can be distinguished. Similarly for the minor diastereomer, Me-2′ resonates at 0.78 ppm as it shows an NOE with a multiplet at 6.54 ppm due to H-3 of the minor aryl ring. One cross-peak exists between Me-5′ of the minor pyrrolidine and an allyl proton *trans* to phosphorus. As the two diastereomeric allyl protons *trans* to phosphorus resonate at 6.02 ppm we cannot distinguish between the major and the minor allyl partners. In contrast to complexes **15** and **16** the two species interconvert on the timescale of the NOE and specifically link the allyl proton H_a in one diastereomer with the allyl proton H_c in the other, due to rotation about the Pd–C bond in a σ-allyl intermediate.[15a]

[{(−)-[2-((2*R*,5*R*)-2,5-Diethylpyrrolidinyl)phenyl]diphenylphosphine}-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate complexes **18** were obtained as a 1:1 mixture of diastereomers. The key allyl peaks of both diastereomers, which were assigned using similar techniques as for complex **18**, are given in

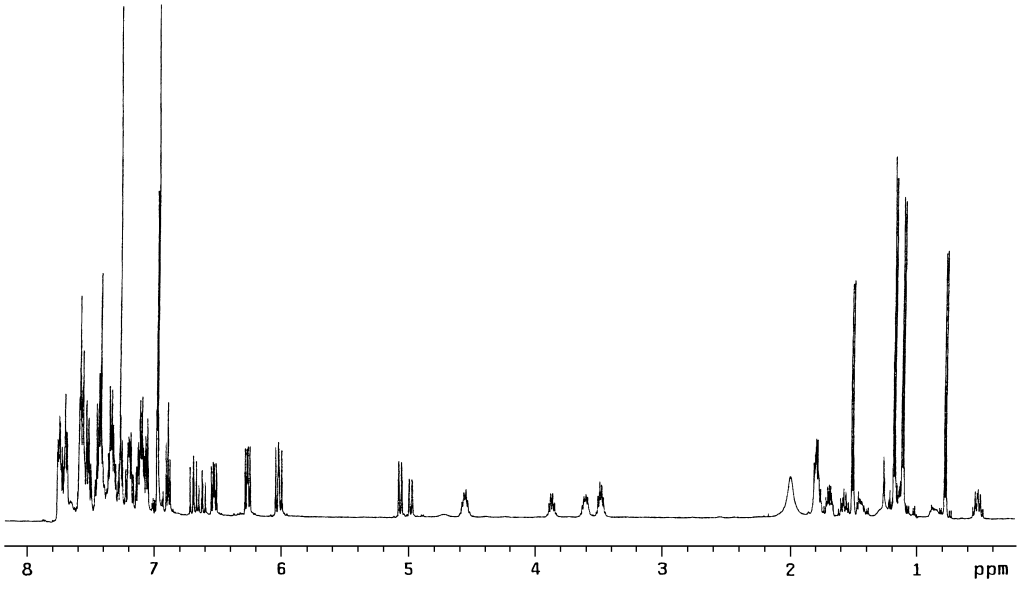
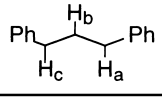


Figure 4. ^{1}H NMR spectrum of complex **17**

Table 3
^{1}H NMR chemical shifts of allylic protons in complexes **17** in $CDCl_3$. Peaks of the major diastereomer are given above the minor

P-------N	H_a	H_b	H_c	2'-Me	5'-Me
	6.02	6.69	5.08	1.18	1.11
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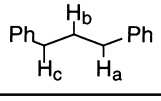
	6.02	6.62	4.99	0.78	1.51

Table 4. The complete assignment of the protons in the pyrrolidine ring of either diastereomers was not possible due to the occurrence of a series of complicated multiplets in the aliphatic region from 0.40 to 2.20 ppm. However, a number of NOEs allowed structural assignment of the two diastereomeric intermediates. The proton *trans* to phosphorus in one of the diastereomers appears at 5.93 ppm and has an NOE with a methine proton of a pyrrolidine which appears at 4.41 ppm. The methine proton is assigned as H-2′ and hence the allyl must be *endo*. As with complex **17** the two species diastereomers interconvert by a similar mechanism on the timescale of the NOE.

Table 4
^{1}H NMR chemical shifts of allylic protons in complex **18** in $CDCl_3$

P-------N	H_a	H_b	H_c
	6.09	6.61	5.00
	-------	-------	-------
	5.93	6.66	5.24

3.3. Mechanism of allylic alkylation catalysed by Pd complexes of ligands 2–3 and 5–6

In the case of the 1,3-diphenylallyl complexes of ligands **2** and **3**, the implication of the NMR studies is that either the nucleophile attacks *trans* to nitrogen[27] in the minor diastereomer, or *trans* to phosphorus in the major diastereomer. A considerable body of evidence now exists on related phosphinamine examples to favour the latter possibility and in addition via a late transition-state.[21–24] The later the transition-state the greater are the steric interactions between ligand and allyl, which may explain why the asymmetric induction obtained using ligand **2** (50% ee) is lower than that obtained with **3** (90% ee), despite the ground state diastereomer ratio being so close (5:2 vs 3:1, respectively). Non-equilibration of these diastereomers on the NMR timescale suggests that the rate of nucleophilic attack is slower than the rate of diastereomer interconversion to achieve the ees observed. Using the X-ray structure of the palladium dichloride of **2** as our basis, a model for the reaction transition-state can be envisaged in which attack *trans* to phosphorus of the minor diastereomer engenders unwanted steric interactions between Me-5′ and the phenyl group of the diphenylallyl moiety as it rolls into a product-like geometry (Fig. 5a). Attack *trans* to phosphorus of the major diastereomer is not as sterically disfavoured, thus leading to the preferred (*R*)-enantiomer of **11** (Fig. 5b). The larger bulk of the 2,5-diethylpyrrolidine unit increases the difference in energy between the transition states, leading to an improved ee.

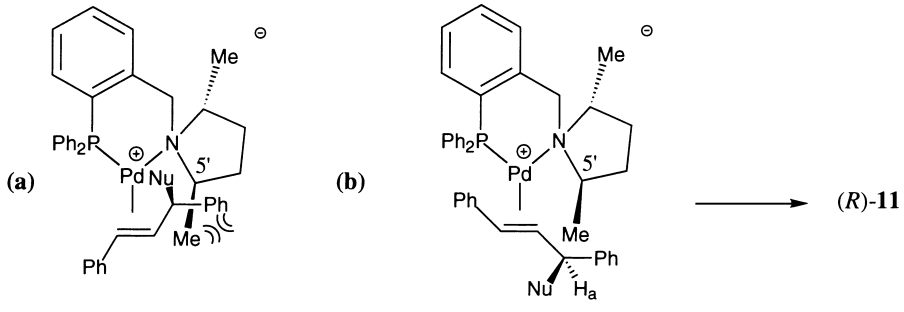


Figure 5. Model of: (a) the disfavoured diastereomer; and (b) the favoured diastereomer at a late transition-state for nucleophilic attack *trans* to phosphorus

In the case of the 1,3-diphenylallyl complexes of ligands **5** and **6**, there is little ground state discrimination between the diastereomeric allyls but, in the one case where unambiguous assignment can be made, the favoured enantiomer can again arise from attack *trans* to phosphorus of the predominant diastereomer. By virtue of having a five-membered chelate rather than a six-membered one as in the case of **2** and **3**, the pyrrolidine ring is pulled back from the allyl and the 2,5-dialkyl substituents play a less significant role in intra-complex interactions. This is seen quite clearly as both complexes **17** and **18** readily interconvert on the timescale of the NOE and in addition the ees are considerably lowered compared to ligands **2** and **3**.

The lessons for future ligand design are clear: a six-membered chelate is preferred and bulkier substituents than methyl and ethyl are necessary to give improved ees.

In conclusion, we have prepared new diphenylphosphinopyrrolidine ligands **4** and **5** and applied their palladium complexes in the test allylic alkylation with high chemical yields but moderate enantioselectivities.[28] Higher ees are obtained using palladium complexes of ligands **5** and **6**. Solution NMR studies were useful in attempting to understand the catalytic results obtained. Further work will be disclosed on related mechanistic studies in this area employing molecular modelling.[29]

4. Experimental

4.1. General

NMR spectra were recorded on a Jeol 270 MHz or a Varian Unity 500 MHz spectrometer. ^{1}H chemical shifts are reported in δ ppm relative to $CHCl_3$ (7.27 ppm), ^{13}C chemical shifts are reported relative to the central peak of $CDCl_3$ (77.0 ppm), and ^{31}P chemical shifts are reported relative to 85% aqueous phosphoric acid (0.0 ppm). Elemental microanalyses were carried out in-house using a Carlo Erba 1106 elemental analyser. Electron impact mass spectra were determined on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode unless otherwise stated. Electrospray mass spectra were recorded on a VG (Micromass) Quattro with electrospray probe. IR spectra were recorded on a Perkin–Elmer Paragon 1000 FT spectrometer. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

Solvents were dried immediately before use by distillation from standard drying agents and subjected to degassing by three freeze–thaw cycles at 0.1 mmHg. Tetrakis(triphenylphosphine)palladium, diphenylphosphine, 2-iodoaniline, sodium hydride (60% disp. in mineral oil), silver tetrafluoroborate, dimethyl malonate, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) were commercially available (Aldrich Chemical Co.) and were used as purchased. *n*-Butyllithium was used as a 1.6 M solution in hexane. (2*S*,5*S*)-Hexanediol cyclic sulfate and (3*S*,6*S*)-octanediol cyclic sulfate were purchased from Strem Chemicals. (*E*)-1,3-Diphenylprop-2-enyl acetate,[20] di-μ-chloro-bis(π-allyl)dipalladium[30] and di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium[31] were prepared according to literature procedures. $PdCl_2$ were obtained on loan from Johnson–Matthey plc. Separations by column chromatography was performed using Merck Kieselgel 60 (Art. 7734) and Merck aluminium oxide 90 (Art 1097).

4.2. (−)-[2-((2R,5R)-2,5-Dimethylpyrrolidinyl)phenyl]diphenylphosphine **4**

(2-Aminophenyl)diphenylphosphine (0.34 g, 1.22 mmol) and (2*S*,5*S*)-hexanediol cyclic sulfate (0.22 g, 1.22 mmol) were placed in a Schlenk tube. To this mixture, tetrahydrofuran (3.0 ml) was added and the reaction was refluxed for 48 h. A white precipitate formed and the reaction was cooled to 0°C. Sodium hydride (54 mg, 1.34 mmol) was added slowly to the reaction which was allowed to warm slowly to room temperature, stirred for 2 h and refluxed again for 24 h. The reaction mixture was transferred to a round-bottom flask and the solvent removed in vacuo to yield a brown oil. The oil was dissolved in ether (20 ml) and washed successively with a 10% ammonium chloride solution (20 ml), water (20 ml), and brine (15 ml). The organic layer was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. Purification by column chromatography (silica) afforded (−)-[2-((2*R*,5*R*)-2,5-dimethylpyrrolidinyl)phenyl]diphenylphosphine (185 mg, 43%) as a colourless oil which solidified overnight, m.p. 46–47°C; $[\alpha]_D^{23}$ −60.4 (*c* 1, chloroform); (found C, 80.30; H, 7.29; N, 3.87; P, 8.63. $C_{24}H_{26}NP$ requires C, 80.22; H, 7.24; N, 3.90; P, 8.64%); ν_{max} (Nujol)/cm^{-1} 2922 (Ar-H), 1463 (P-Ar) and 1242 (N-Ar); δ_H (270 MHz, $CDCl_3$) 0.50 (d, 3H, J 5.9, Me-5′), 0.70 (d, 3H, J 5.9, Me-2′), 1.06–1.24 (m, 1H, H-4a′), 1.25–1.41 (m, 1H, H-3b′), 1.76–1.93 (m, 1H, H-3a′), 1.95–2.12 (m, 1H, H-4b′), 3.51–3.66 (m, 1H, H-2′), 4.24–4.46 (m, 1H, H-5′), 6.69–6.74 (m, 1H, H-3), 6.77–6.82 (m, 1H, H-5), 6.89–6.93 (m, 1H, H-6), 7.12–7.19 (m, 6H, H-2″, H-4″, H-6″) and 7.22–7.25 (m, 5H, H-4, H-3″, H-5″); δ_C (67.8 MHz, $CDCl_3$) 18.74 (Me-5), 18.93 (Me-2), 30.14 (C-4′), 32.30 (C-3′), 53.06 (C-2′), 56.53 (C-5′), 122.37 (C-3), 123.03 (C-5), 128.04 (d, $J_{P\text{-}C}$ 7.6, C-3″), 128.43 (d, $J_{P\text{-}C}$ 6.4, C-5″), 128.83

(C-4′′), 133.81 (d, $J_{P\text{-}C}$ 19.3, C-6), 133.98 (d, $J_{P\text{-}C}$ 15.0, C-2′′), 134.06 (C-4), 134.28 (d, $J_{P\text{-}C}$ 15.0, C-6′′), 134.69, 137.84 (d, $J_{P\text{-}C}$ 12.9, C-1′′), 137.92 (d, $J_{P\text{-}C}$ 10.7, C-1) and 150.62 (d, $J_{P\text{-}C}$ 19.3, C-2); δ_P (109.3 MHz, $CDCl_3$) −9.6; *m/z* (EIMS, 70 eV) 359 (M^+, 68%), 316 (94), 282 (49), 172 (100), 158 (71) and 118 (42).

4.3. (−)-[2-((2R,5R)-2,5-Diethylpyrrolidinyl)phenyl]diphenylphosphine **5**

(2-Aminophenyl)diphenylphosphine (0.25 g, 0.90 mmol) and (3*S*,6*S*)-octanediol cyclic sulfate (0.19 g, 0.90 mmol) were placed in a Schlenk tube. To this mixture, tetrahydrofuran (2.0 ml) was added and the reaction was refluxed for 48 h. A white precipitate formed and the reaction was cooled to 0°C. Sodium hydride (40 mg, 0.99 mmol) was added slowly to the reaction which was allowed to warm slowly to room temperature, stirred for 2 h and refluxed again for 24 h. The reaction mixture was transferred to a round-bottom flask and the solvent removed under reduced pressure to yield a brown oil. The oil was dissolved in ether (20 ml) and washed successively with a 10% ammonium chloride solution (20 ml), water (20 ml), and brine (15 ml). The organic layer was dried with anhydrous sodium sulfate and the solvent was removed in vacuo. Purification by column chromatography afforded (−)-[2-((2*R*,5*R*)-2,5-diethylpyrrolidinyl)phenyl]diphenylphosphine (150 mg, 27%) as a colourless oil which solidified overnight, m.p. 45–46°C; $[\alpha]_D^{23}$ −48.9 (*c* 1, chloroform); (found C, 80.68; H, 7.81; N, 3.61. $C_{26}H_{30}NP$ requires C, 80.62; H, 7.75; N, 3.62%); ν_{max} (Nujol)/cm^{-1} 2925 (Ar-H), 1461 (P-Ar) and 1238 (N-Ar); δ_H (270 MHz, $CDCl_3$) 0.50 (t, 3H, J 7.3, Me-7′), 0.67–0.73 (m, 2H, H-6′), 0.93–1.11 (m, 2H, H-8′), 1.21 (t, 3H, J 7.1, Me-9′), 1.31–1.47 (m, 2H, H-4a′, H-3b′), 1.97–2.06 (m, 2H, H-4b′, H-3a′), 3.54–3.61 (m, 1H, H-2′), 3.96–4.03 (m, 1H, H-5′), 6.77–6.82 (m, 2H, H-3), 6.94–6.98 (m, 1H, H-6), 7.12–7.21 (m, 6H, H-2′′, H-4′′, H-6′′) and 7.23–7.31 (m, 5H, H-4, H-3′′, H-5′′); δ_C (67.8 MHz, $CDCl_3$) 10.72 (Me-7′), 14.84 (C-6′), 17.53 (C-8′), 18.24 (Me-9′), 26.94 (C-4′), 31.37 (C-3′), 52.46 (C-5′), 57.64 (C-2′), 121.87 (C-3), 122.79 (C-5), 128.54 (d, $J_{P\text{-}C}$ 7.7, C-3′′), 128.65 (d, $J_{P\text{-}C}$ 6.6, C-5′′), 128.82 (C-4′′), 133.57 (d, $J_{P\text{-}C}$ 19.4, C-6), 134.17 (d, $J_{P\text{-}C}$ 14.8, C-2′′), 134.21 (C-4), 134.36 (d, $J_{P\text{-}C}$ 14.8, C-6′′), 134.87, 137.26 (d, $J_{P\text{-}C}$ 13.1, C-1′′), 137.81 (d, $J_{P\text{-}C}$ 10.7, C-1) and 151.02 (d, $J_{P\text{-}C}$ 19.3, C-2); δ_P (109.3 MHz, $CDCl_3$) −9.5; *m/z* (EIMS, 70 eV) 387 (M^+, 20%), 358 (100), 277 (24), 172 (154), and 57 (53).

4.4. Allylic alkylation procedures

4.4.1. Malonate ion procedure

Sodium dimethyl malonate (0.042 g, 0.275 mmol) was placed in a dry Schlenk which had previously been flushed with nitrogen and dry degassed acetonitrile (0.3 ml) was added to form a white suspension. To this was added a solution of in situ prepared catalyst [di-μ-chloro-bis(π-allyl)dipalladium (0.0025 mmol) and diphenylphosphinopyrrolidine (0.005 mmol)] and (*E*)-1,3-diphenylprop-2-enyl acetate (0.063 g, 0.250 mmol) in dry degassed acetonitrile (0.1 ml) to form a pale orange suspension. Reaction progress was monitored by TLC (petroleum ether 40–60°C:diethyl ether, 2:1, as the eluent). After stirring under nitrogen at room temperature for 2 days, acetic acid (0.1 ml) was added and the solvent was removed in vacuo. Water (25 ml) was added and the reaction was extracted into diethyl ether (25 ml), then washed with water (25 ml) and brine (25 ml). The solution was dried with $MgSO_4$, filtered and the solvent removed in vacuo to give an an orange oil. This was purified on silica gel plates (eluent=petroleum ether 40–60°C:diethyl ether, 2:1) to afford the product, (*R*)-methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate as a colourless oil, R_f=0.37; ν_{max} (Nujol)/cm^{-1} 1733 (C=O) and 1600 (C=C); δ_H (500 MHz, $CDCl_3$) 3.51 (s, 3H, -OMe), 3.70 (3H, s, -OMe), 3.95 (1H, d, J 11.2, $CH(CO_2Me)_2$), 4.26 (1H, dd, J 8.8,

J 11, H-1), 6.33 (1H, dd, J 8.8, 5.6, H-2), 6.47 (1H, d, J 15.6, H-3) and 7.33–7.18 (10H, m, Ph); *m/z* (EIMS, 70 eV) 324 (M^+, 5%), 193 (20), 105 (100) and 91 (27).

4.4.2. BSA procedure

A solution of catalyst [di-μ-chloro-bis(π-allyl)dipalladium (0.0025 mmol) and diphenylphosphinopyrrolidine (0.005 mmol)] in dry degassed acetonitrile (0.5 ml) was added to potassium acetate (0.005 mmol), under a nitrogen atmosphere, to form a suspension. To this suspension was then added 1,3-diphenylprop-2-enyl acetate (0.025 mmol), dimethylmalonate (0.275 mmol), and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (0.275 mmol) by syringe. The yellow suspension was allowed to stir under nitrogen at ambient temperature and the reaction rate was monitored by TLC and the reaction mixture was purified as for the malonate ion procedure.

4.4.3. Determination of enantiomeric excess

The ee was found by ^{1}H NMR spectroscopy from the spectrum obtained after adding 20–30 μl of a 0.2 M solution of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) to 10–15 mg of methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate in $CDCl_3$ (0.5 ml). The methoxy groups of methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate resonate at 3.51 ppm and 3.70 ppm. Following the addition of the chiral shift reagent and subsequent formation of diastereomers four methoxy peaks are present in the ^{1}H spectrum. The methoxy peak originally at 3.70 ppm is changed to two peaks at 3.74 ppm and 3.76 ppm and the relative integration of these peaks gives the ee value. If the right-hand peak of these two is larger then this is typical of the (*S*)-enantiomer in excess, which was confirmed by comparing the specific rotation obtained with literature values.

*4.5. [{(−)-{2-[((2′*R*,5′*R*)-2,5-Dimethylpyrrolidinyl)methyl]phenyl}diphenylphosphine}-[1,3-diphenyl-π-allyl] palladium]tetrafluoroborate* ***15***

Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (0.067 g, 0.100 mmol), (−)-{2-[((2′*R*,5′*R*)-2,5-dimethylpyrrolidinyl)methyl]phenyl}diphenylphosphine (0.075 g, 0.20 mmol) and silver tetrafluoroborate (0.078 g, 0.400 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (3.0 ml) was added via syringe to give an orange suspension which was stirred for 16 h. The suspension was filtered, the solvent removed in vacuo and diethyl ether added to precipitate a yellow solid. This solid was filtered and dried to give [{(−)-{2-[((2′*R*,5′*R*)-2,5-dimethylpyrrolidinyl)methyl]phenyl}diphenylphosphine}-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate, (0.146 g, 96%), as a mixture of two diastereomers, m.p. 115°C (dec.); $[\alpha]_D^{23}$ −57.4 (*c* 1, chloroform); (found: C, 63.47; H, 5.46; N, 2.02. $C_{40}H_{41}NPPdBF_4$ requires C, 63.40; H, 5.41; N, 1.84%); ν_{max} (KBr) 2965 (HC aliph.), 1436 (P-Ph), 1060 (B-F) cm^{-1}; δ_H (500 MHz, $CDCl_3$) major diastereomer 1.02–1.06 (m, 2H, H-3_b′, H-4_a′), 1.24 (d, 3H, J 8.0, Me-2′), 1.33 (d, 3H, J 8.0, Me-5′), 1.75–1.81 (m, 2H, H-3_a′, H-4_b′), 2.95–3.03 (m, 1H, H-5′), 3.05–3.13 (m, 1H, H-2′), 3.26 (dd, 1H, J 13.2, 0.8, benzylic-H_a), 3.72 (dd, 1H, J 13.2, 3.8, benzylic-H_b), 4.22 (d, 1H, J 7.2, allyl *trans*-N), 5.72 (dd, 1H, J 10.5, $J_{P\text{-}H}$ 3.0, allyl *trans*-P), 6.90 (dd, 1H, J 10.5, J 7.2, central allyl H) and 6.68–7.82 (m, 24H, Ar-H), minor diastereomer 1.06 (d, 3H, J 6.5, Me-2′), 1.43 (d, 3H, J 6.5, Me-5′), 1.86–1.92 (m, 2H, H-3_b′, H-4_a′), 2.26–2.34 (m, 2H, H-3_a′, H-4_b′) 3.31–3.38 (m, 1H, H-5′), 3.39 (dd, 1H, J 13.3, 0.7, benzylic-H_a), 3.42–3.51 (m, 1H, H-2′), 3.78 (dd, 1H, J 13.3, 4.0, benzylic-H_b), 5.16 (d, 1H, J 6.5, allyl *trans*-N), 6.00 (dd, 1H, J 10.0, $J_{P\text{-}H}$ 3.0, allyl *trans*-P), 6.53 (dd, 1H, J 7.0, J 4.5, central allyl H) and 6.68–7.82 (m, 24H, Ar-H); δ_C (67.8 MHz, $CDCl_3$) major diastereomer 16.12 (Me-2′), 24.25 (Me-5′), 29.58 (C-3′), 30.22 (C-4′), 56.05 (d, $J_{P\text{-}C}$ 12.9, benzylic-C), 62.17 (C-2′), 63.20 (C-5′), 72.14

(d, $J_{P\text{-}C}$ 6.5, allyl *trans*-N), 103.73 (d, $J_{P\text{-}C}$ 22.6, allyl *trans*-P) 110.34 (d, $J_{P\text{-}C}$ 5.3, central allyl), minor diastereomer 17.77 (Me-2′), 23.10 (Me-5′), 28.63 (C-3′), 29.11 (C-4′), 52.76 (d, $J_{P\text{-}C}$ 12.8, benzylic-C), 61.38 (C-2′), 63.65 (C-5′), 70.87 (d, $J_{P\text{-}C}$ 6.5, allyl *trans*-N), 101.26 (d, $J_{P\text{-}C}$ 22.5, allyl *trans*-P), 110.17 (d, $J_{P\text{-}C}$ 5.3, central allyl), major and minor diastereomers (Ar-C) 126.37, 127.10, 127.37, 127.40, 127.73, 127.78, 128.00, 128.54, 128.87, 128.90, 129.30, 129.46, 129.51, 129.55, 129.64, 129.69, 129.84, 129.93, 130.01, 130.19, 130.20, 131.23, 131.47, 131.72, 132.10, 132.84, 133.27, 133.60, 133.73, 134.63, 134.82, 135.01, 135.10, 135.15, 135.36, 136.29, 136.32, 138.57 and 138.81; δ_P (109.3 MHz, $CDCl_3$) minor diastereomer 23.5 and major diastereomer 21.2; *m/z* (ESI/pos in CH_3OH) cation 672 (100%, $M-BF_4$).

4.6. [{(−)-{2-[((2′S,5′S)-2,5-Diethylpyrrolidinyl)methyl]phenyl}diphenylphosphine}-[1,3-diphenyl-p-allyl]palladium]tetrafluoroborate ***16***

Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (0.034 g, 0.050 mmol), (−)-{2-[((2′*S*,5′*S*)-2,5-diethylpyrrolidinyl)methyl]phenyl}diphenylphosphine (0.040 g, 0.100 mmol) and silver tetrafluoroborate (0.039 g, 0.200 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (1.8 ml) was added to afford a yellow/orange suspension which was stirred for 16 h. The silver chloride which formed was removed by filtration. The solution was concentrated in vacuo and diethyl ether added to afford a yellow/orange solid which was filtered and dried to give [{(−)-{2-[((2′*S*,5′*S*)-2,5-diethylpyrrolidinyl)methyl]phenyl}diphenylphosphine}-[1,3-diphenyl-π-allyl]-palladium]tetrafluoroborate (0.075 g, 93%) as a mixture of two diastereomers, m.p. 113°C (dec.); $[\alpha]_D^{23}$ −74.8 (*c* 0.5, chloroform); (found: C, 64.82; H, 5.66; N, 1.69. $C_{42}H_{45}NPPdBF_4$ requires C, 64.04; H, 5.72; N, 1.78%); ν_{max} (KBr) 2939 (HC aliph.), 1448 (P-Ph) and 1057 (B-F) cm^{-1}; δ_H (500 MHz, $CDCl_3$) major diastereomer 0.71 (t, 3H, J 7.3, Me-9′), 0.89 (t, 3H, J 7.3, Me-7′), 1.28–1.34 (m, 2H, H-3_b′, H-4_a′), 1.36–1.41 (m, 1H, H-6_b′), 1.42–1.48 (m, 1H, H-6_a′), 1.62–1.69 (m, 2H, H-3_a′, H-4_b′), 1.76–1.85 (m, 1H, H-8_b′), 1.91–2.00 (m, 1H, H-8_a′), 2.79–2.84 (m, 1H, H-2′), 2.97–3.01 (m, 1H, H-5′), 3.38 (dd, 1H, J 12.7, 3.4, benzylic-H_b), 3.72 (d, 1H, J 12.7, benzylic-H_a), 4.19 (d, 1H, J 11.2, allyl *trans*-N), 6.02 (dd, 1H, J 13.7, $J_{P\text{-}H}$ 4.4, allyl *trans*-P), 6.78–6.82 (m, 1H, central allyl H), 6.67–7.78 (m, 24H, Ar-H), minor diastereomer 0.55 (t, 3H, J 7.3, Me-9′), 0.68 (t, 3H, J 7.3, Me-7′), 1.08–1.15 (m, 1H, H-6_b′), 0.82–0.86 (m, 1H, H-6_a′), 1.16–1.22 (m, 2H, H-3_a′, H-4_b′), 1.38–1.44 (m, 1H, H-8_a′), 1.42–1.48 (m, 1H, H-8_b′), 1.61–1.66 (m, 2H, H-3_b′, H-4_a′), 2.52–2.58 (m, 1H, H-2′), 2.63–2.66 (m, 1H, H-5′), 3.46 (dd, 1H, J 14.2, 7.3, benzylic-H_b), 3.95 (d, 1H, J 11.2, allyl *trans*-N), 4.26 (dd, 1H, J 14.2, 2.6, benzylic-H_a), 6.32 (dd, 1H, J 8.8, $J_{P\text{-}H}$ 6.8, allyl *trans*-P), 6.46–6.50 (m, 1H, central allyl H) and 6.67–7.78 (m, 24H, Ar-H); δ_P (109.3 MHz, $CDCl_3$) 21.1 and 22.3; *m/z* (ESI/pos in CH_3OH) cation 700 (100%, $M-BF_4$).

*4.7. [{(−)-[2-((2*R*,5*R*)-2,5-Dimethylpyrrolidinyl)phenyl]diphenylphosphine}-[1,3-diphenyl-π-allyl]-palladium]tetrafluoroborate* ***17***

Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (0.037 g, 0.056 mmol), (−)-[2-((2*R*,5*R*)-2,5-dimethyl pyrrolidinyl)phenyl]diphenylphosphine (0.040 g, 0.110 mmol) and silver tetrafluoroborate (0.044 g, 0.220 mmol) were placed in a Schlenk under nitrogen. Dichloromethane (3.2 ml) was added via syringe to give an orange suspension which was stirred for 16 h. The solid was removed by filtration, the filtrate was then concentrated in vacuo and diethyl ether added to precipitate a yellow solid. The solid was filtered and dried to afford [{(−)-[2-((2*R*,5*R*)-2,5-dimethylpyrrolidinyl)phenyl]diphenylphosphine}-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate (0.075 g, 86%) as a mixture of two diastereomers, m.p.

118°C (dec.); $[\alpha]_D^{23}$ −58.3 (*c* 0.5, chloroform); (found: C, 62.48; H, 5.64; N, 1.89. $C_{39}H_{39}NPPdBF_4$ requires C, 62.82; H, 5.23; N, 1.88%); ν_{max} (KBr)/cm^{-1} 2965 and 1060 (B-F); δ_H (500 MHz, $CDCl_3$) diastereomer 1: 0.78 (d, 3H, J 6.8, Me-5′), 1.12–1.15 (m, 1H, H-3a′), 1.16–1.20 (m, 1H, H-4b′), 1.43–1.47 (m, 1H, H-4a′), 1.51 (d, 3H, J 6.3, Me-2′), 1.55–1.58 (m, 1H, H-3b′), 3.58–3.63 (m, 1H, H-2′), 4.52–4.60 (m, 1H, H-5′), 4.99 (dd, 1H, J 11.5, 13, allyl *trans*-N), 6.02 (dd, 1H, J 10.2, $J_{P\text{-}H}$ 13.4, allyl *trans*-P), 6.26 (m, 1H, H-3), 6.62 (app. tr., 1H, J 13.2, central allyl H), 7.05–7.76 (m, 23H, Ar-H); diastereomer 2: 0.50 (m, 1H, H-4b′), 1.11 (d, 3H, J 6.8, Me-5′), 1.18 (d, 3H, J 6.3, Me-2′), 1.67–1.70 (m, 1H, H-3a′), 1.73–1.77 (m, 1H, H-4a′), 1.78–1.82 (m, 1H, H-3b′), 3.45–3.51 (m, 1H, H-2′), 3.58–3.63 (m, 1H, H-5′), 5.08 (dd, 1H, J 11.2, 13.7, allyl *trans*-N), 6.02 (dd, 1H, J 10.2, $J_{P\text{-}H}$ 13.4, allyl *trans*-P), 6.26 (m, 1H, H-3), 6.69 (dd, 1H, J 13.7, 11.3, central allyl H), 6.89 (t, 1H, J 7.3, H-5) and 7.05–7.76 (m, 22H, Ar-H); δ_C (67.8 MHz, $CDCl_3$) diastereomer 1: 18.07 (Me-5′), 21.61 (Me-2′), 31.36 (C-4′), 35.26 (C-3′), 68.17 (C-5′), 69.85 (C-2′), 73.02 (d, $J_{P\text{-}C}$ 6.6, allyl *trans*-N), 105.27 (d, $J_{P\text{-}C}$ 22.5, allyl *trans*-P), 111.31 (d, $J_{P\text{-}C}$ 5.4, central allyl); diastereomer 2: 18.05 (Me-5′), 21.86 (Me-2′), 31.18 (C-4′), 34.07 (C-3′), 63.62 (C-2′), 65.28 (C-5′), 71.56 (d, $J_{P\text{-}C}$ 6.6, allyl *trans*-N), 103.46 (d, $J_{P\text{-}C}$ 22.5, allyl *trans*-P), 111.31 (d, $J_{P\text{-}C}$ 5.4, central allyl); diastereomer 1 and diastereomer 2: (Ar-C) 126.38, 126.93, 126.97, 127.35, 127.84, 128.64, 128.71, 128.90, 129.06, 129.13, 129.22, 129.65, 129.68, 129.82, 129.87, 130.42, 130.83, 131.50, 131.67, 131.89, 132.07, 132.18, 132.23, 133.92, 134.11, 134.31, 134.49, 134.66, 134.85, 135.07, 135.09, 135.19, 136.21, 136.47, 138.46 and 138.91; δ_P (109.3 MHz, $CDCl_3$) 33.3 and 34.3; *m/z* (ESI/pos in CH_3OH) 669 (100%, M−BF_4).

4.8. [{(−)-[2-((2R,5R)-2,5-Diethylpyrrolidinyl)phenyl]diphenylphosphine}-[1,3-diphenyl-π-allyl]-palladium]tetrafluoroborate ***18***

Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (0.036 g, 0.055 mmol), (−)-[2-((2*R*, 5*R*)-2,5-diethyl pyrrolidinyl)phenyl]diphenylphosphine (0.042 g, 0.110 mmol) and silver tetrafluoroborate (0.042 g, 0.220 mmol) were placed in a Schlenk under nitrogen. Dichloromethane (3.0 ml) was added via syringe to give an orange suspension which was stirred for 16 h. The solid was removed by filtration, the solvent was then reduced in vacuo and diethyl ether added to give a yellow solid. The solid was filtered and dried to give [{(−)-[2-((2*R*, 5*R*)-2,5-diethylpyrrolidinyl)phenyl]diphenylphosphine}-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate (0.074 g, 87%) as a mixture of two diastereomers, m.p. 114°C (dec.); $[\alpha]_D^{23}$ −44.2 (*c* 0.3, chloroform); (found: C, 63.52; H, 5.47; N, 1.76. $C_{41}H_{43}NPPdBF_4$ requires C, 63.65; H, 5.56; N, 1.81%); ν_{max} (KBr)/cm^{-1} 2965 and 1060 (B-F); δ_H (500 MHz, $CDCl_3$) diastereomer 1: 0.50 (t, 2H, J 6.3, Me), 0.8–2.1 (m, 12H), 3.3–3.4 (m, 1H, H-2′), 5.24 (d, 1H, J 11.2, allyl *trans*-N), 5.93 (dd, 1H, J 10.3, $J_{P\text{-}H}$ 13.7, allyl *trans*-P), 6.66 (dd, 1H, J 13.7, J 11.8, central allyl H) and 6.8–7.8 (m, 24H); diastereomer 2: 1.21 (t, 3H, J 6.4, Me), 0.8–2.1 (m, 12H), 4.3–4.4 (m, 1H, H-2′), 5.00 (d, 1H, J 9.8, allyl *trans*-N), 6.09 (dd, 1H, J 10.8, $J_{P\text{-}H}$ 13.7, allyl *trans*-P), 6.61 (m, 1H, central allyl H) and 6.8–7.8 (m, 24H); δ_P (109.3 MHz, $CDCl_3$) 33.6 and 34.5; *m/z* (ESI/pos in CH_3OH) 697 (100%, M−BF_4).[16]

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