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New chiral phosphole ligands: their coordination behaviour and application in palladium-catalysed asymmetric allylic substitution

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Abstract—1-Pyrrolidinophospholes, new chiral phosphorus ligands have been synthesised. These phospholes behave as monodentate ligands towards transition metal centres giving mononuclear disubstituted phosphole complexes of the type [M(phosphole)$_2$Cl$_2$] with palladium(II) and platinum(II) precursors. In the palladium-catalysed asymmetric allylic substitution of 1,3-diphenyl-2-enylacetate with the anion of dimethylmalonate, the palladium and platinum complexes of these ligands proved to be efficient catalysts for the alkylation reaction, but provided only moderate enantioselectivities.

1. Introduction

As part of our continuing interest in the design and synthesis of new phosphole-containing ligands with applications in asymmetric catalysis,[1] we have investigated the synthesis of a new class of chiral monophosphole ligand. Although the chemistry of phospholes has been investigated extensively and reviewed,[2] little attention has been paid to chiral monophospholes. Indeed to our knowledge, most of the chiral phospholes reported in the literature are diphospholes with chiral *P*-substituents.[3] The first synthesis of a chiral monophosphole, the 1-oxazolinodibenzophosphole,[4] and its use as a catalytic ligand in asymmetric hydrosilylation[5a] and transfer hydrogenation protocols[5b] was reported in 1996 by Helmchen and co-workers. More recently, another example of a chiral monophosphole in which chiral substituents are directly attached to the carbon of the phosphole ring has been reported.[6]

Herein, we report the synthesis of 1-pyrrolidinophospholes as a new class of chiral ligand, their coordination behaviour towards transition metals such as palladium(II) and platinum(II) and their use in palladium-catalysed asymmetric allylic substitution.

2. Results and discussion

2.1. Preparation and characterisation of chiral 1-pyrrolidinophospholes

For the preparation of 1-pyrrolidinophospholes, the most convenient route to introduce the pyrrolidino group on the phosphorus atom seem to be the procedure reported by Mathey in 1988,[7] which involved nucleophilic substitution reaction of a 1-cyanophosphole. Thus, we have investigated the reactions of various pyrrolidine derivatives with different 1-cyanophosphole compounds.

In a preliminary experiment, we attempted to synthesise the 1-pyrrolidino-3,4-dimethylphosphole using the (*S*)-2-methoxymethylpyrrolidine and the 1-cyano-3,4-dimethylphosphole **1** which has been already described in the literature.[7a] At room temperature in the presence of a large excess of Et_3N, phosphole **1** reacted with (*S*)-2-methoxymethylpyrrolidine in 24 h to give the corresponding chiral phosphole **3a** in 52% yield (Scheme 1). However, nucleophilic substitution with the preformed amide salt, obtained by action of *n*-BuLi on (*S*)-2-methoxymethylpyrrolidine, on the phosphole **1** was more rapid (2 h) at −78°C in THF and afforded the phosphole **3a** in better yield (63%) (Scheme 2).

The utility of the reaction could be extended by using a different pyrrolidine, the 1-(*S*,*S*)-[2,5-(bis-methoxymethyl)]pyrrolidine. Using the same conditions, the treatment of the 1-cyanophosphole **1** with the corre-

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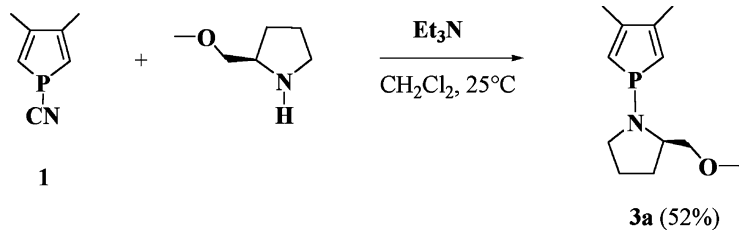
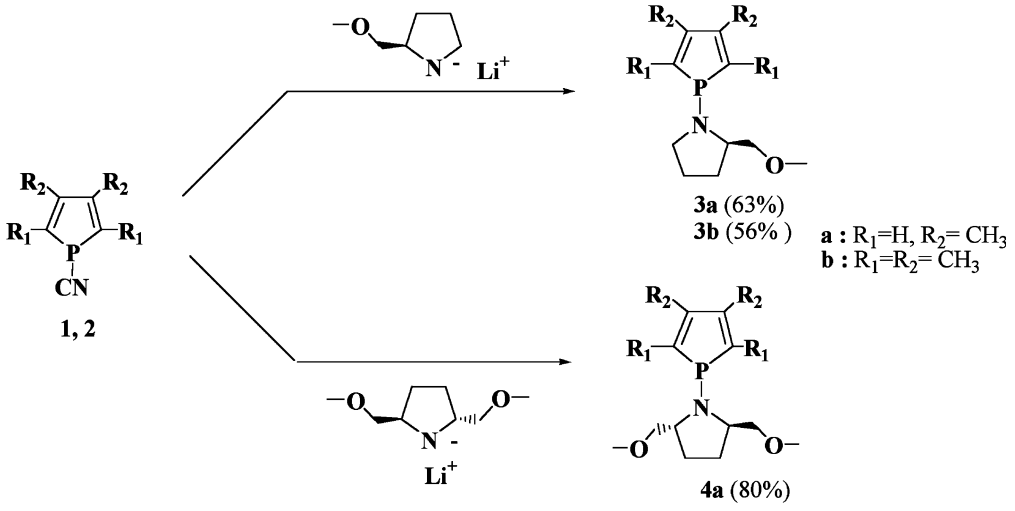


Scheme 1.



Scheme 2.

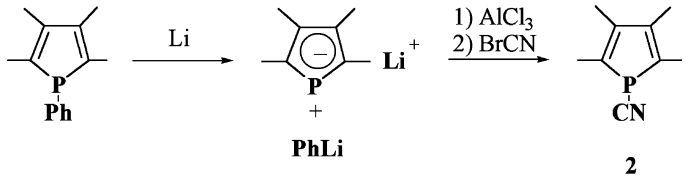
sponding lithium amide afforded phosphole **4a** in 80% yield (Scheme 2).

In addition to the 3,4-dimethylphosphole derivative, the 2,3,4,5-tetramethylphosphole compound was investigated. We obtained the 1-cyano-2,3,4,5-tetramethylphosphole **2** easily by applying Mathey's procedure described for the 1-cyanophosphole **1**.[7a] This method involved reductive cleavage of the exocyclic phosphorus–phenyl bond with an excess of metallic lithium following by addition of BrCN after neutralisation of PhLi using $AlCl_3$ (Scheme 3). The crude 1-cyanophosphole **2** was obtained in quantitative yield as an air-stable yellow powder and was characterised by ^1H, ^{31}P and ^{13}C NMR spectroscopy, and mass spectrometry. Starting from 1-cyanophosphole **2** and lithium (*S*)-2-methoxymethylpyrrolidino amide, the ligand **3b** was prepared in 56% yield according to the procedure described for ligand **3a** (Scheme 2).

2.2. Coordination behaviour of chiral pyrrolidinophosphole towards palladium(II) and platinum(II)

Before engaging in asymmetric catalysis, the coordination behaviour of these new chiral ligands was studied. Indeed, the ligand possesses two electronically distinct donor moieties and could potentially behave either as a monodentate *P*-donor or as a bidentate *P*,*O*-donor ligand. Initial complexation experiments were performed on phosphole **3a** with palladium(II) and platinum(II) precursors.

Reactions of phosphole **3a** with $[M(CH_3CN)_2Cl_2]$ (M = Pd, Pt) in dichloromethane at room temperature were examined with various ligand/precursor molar ratios. Treatment of **3a** with 1 or 2 equiv. of $[M(CH_3CN)_2Cl_2]$ led to complete consumption of the ligand to afford the mononuclear disubstituted phosphole complexes $[Pd(phosphole)_2Cl_2]$, **5** and $[Pt(phosphole)_2Cl_2]$, **6**,



Scheme 3.

respectively (Scheme 4). Neither mononuclear monosubstituted phosphole complexes [M(phosphole)Cl_2] in which the phosphole **3a** acts as a bidentate ligand, nor binuclear complexes [M(phosphole)Cl_2]$_2$ as in the case of 1-aminophosphole complex,[8] could be detected. NMR analysis indicated that the geometry of these complexes in solution is square planar with *cis*-configuration. Indeed for the complex **5**, the 1:1 doublets observed at $\delta = 6.29$ ($^2J_{H-P} = 34$ Hz) and at 6.44 ($^2J_{H-P} = 34$ Hz) in ^{1}H NMR for the two diastereotopic α-methylene resonances are consistent with *cis*-geometry in solution,[9] as observed for the 1-diisopropylaminophosphole–palladium complexes.[8] As we were unable to obtain this complex in crystalline form, its geometry in the solid state could not be confirmed.

For the platinum complex **6**, the ^{31}P and ^{1}H NMR analysis are also consistent with a *cis*-square planar complex in solution. The ^{31}P{^{1}H} spectrum showed a single signal with an overlapping doublet due to the 33.8% of the phosphorus nuclei coupled to ^{195}Pt and the value of the $^1J_{P-Pt}$ ($^1J_{P-Pt} = 3596$ Hz) coupling constant is typical of *cis*-dichloro-bisphosphole–platinum complexes.[10] In addition, the two diastereotopic α-methylene resonances appear as 1:1 doublets, in ^{1}H NMR.[10] In contrast to the palladium complex **5**, the platinum complex **6** was rather unstable, air and moisture sensitive and could not be isolated in pure form.

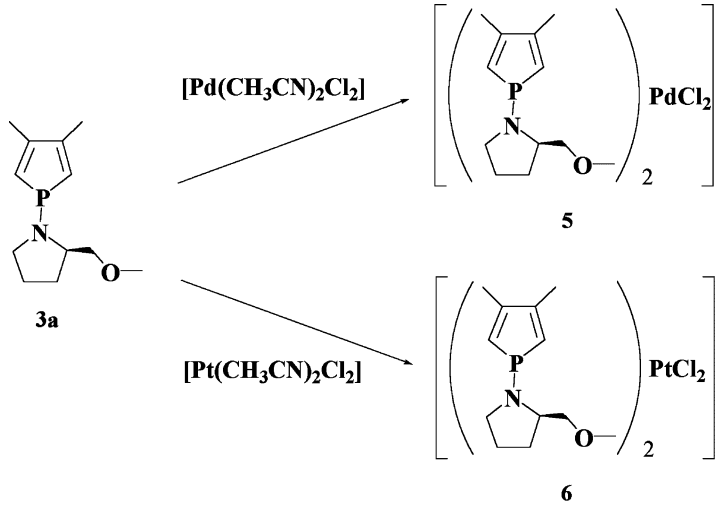
In conclusion, the coordination chemistry of the 1-pyrrolidinophosphole **3a** towards palladium(II) and platinum(II) shows a tendency to be a monodentate *P*-ligand rather than a bidentate *P*,*O*-ligand.

2.3. Application of 1-pyrrolidinophospholes 3 and 4 in palladium-catalysed asymmetric allylic substitution

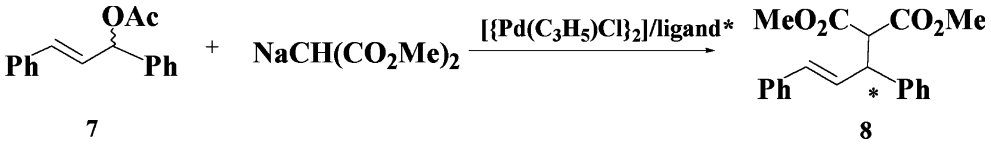
As a preliminary evaluation of the catalytic properties of the chiral 1-pyrrolidinophospholes **3** and **4**, we explored the palladium-catalysed asymmetric allylic substitution[11] of 1,3-diphenylprop-2-enylacetate **7** with the anion of dimethyl malonate.

The catalytic process was initiated by addition of a mixture of the allylic palladium chloride dimer [PdCl(μ-C_3H_5)]$_2$, the chiral ligand **3** or **4** and allylic acetate **7**, to a solution of sodium dimethyl malonate (Scheme 5). The results are summarised in Table 1. Using the ligand **3a**, the allylic acetate **7** was quantitatively converted after 5 min at room temperature in THF to the desired product (*R*)-**8** in 29% ee (entry 1). Lowering the temperature to 0°C slowed the reaction without improving the enantioselectivity (entry 2). Moreover, the enantioselectivity of the reaction was not sensitive to the stoichiometry between palladium and the chiral ligand (entries 3–4), showing that a 2:1 ligand/palladium ratio was sufficient. Furthermore, the use of CH_2Cl_2 as solvent decreased the rate of the reaction but the enantioselectivity did not increase (entry 5). These results show that the ligand **3a** has a high activity in this allylic substitution, inducing complete conversion over 5 min in THF at room temperature. Unfortunately, the levels of ee obtained so far are modest (29%) in comparison to the best values.[11]

Under similar conditions, at room temperature using CH_2Cl_2 and THF as solvents, the ligand **3b** led to the



Scheme 4.



Scheme 5.

Table 1. Results of asymmetric allylic substitution reaction of 1,3-diphenylprop-2-enylacetate with the anion of dimethyl malonate[a]

Entry	Ligand	Solvents	Temperature (°C)	Reaction time (min)	Ee % of **8**[b] (configuration[c])
1	**3a** (4%)	THF	20	5	29 (*R*)
2	**3a** (4%)	THF	0	15	29 (*R*)
3	**3a** (12%)	THF	0	15	30 (*R*)
4	**3a** (14%)	THF	20	5	28 (*R*)
5	**3a** (4%)	CH_2Cl_2	25	15	29 (*R*)
6	**3b** (4%)	THF	25	30	20 (*R*)
7	**3b** (4%)	CH_2Cl_2	25	60	8 (*R*)
8	**4a** (4%)	THF	25	30	55 (*R*)
9	**4a** (4%)	CH_2Cl_2	25	60	58 (*R*)

[a] *Reaction conditions*: [Pd] (0.005 mmol), (*E*)-1,3-diphenylprop-2-enylacetate (1 mmol), dimethylmalonate (3 mmol). The degree of conversion was evaluated by ^{1}H NMR.
[b] Determined by ^{1}H NMR using the chiral shift reagent Eu(hfc)$_3$.
[c] Determined on the basis of the sign of the specific rotation of the product.

quantitative conversion of the allylic acetate **7** to product (*R*)-**8** in 30 min in THF or 60 min in CH_2Cl_2. However, these reactions occurred with low enantioselectivity (10–20%) (entries 6–7).

More interesting results were obtained with ligand **4a**, the use of which gave the product (*R*)-**8** in quantitative yield after 30 min in THF or 60 min in CH_2Cl_2 at room temperature (entries 8–9) as with the ligand **3a**, but higher ee values were achieved. The best result was obtained using CH_2Cl_2 as solvent (58%).

In conclusion, ligands **3a**–**4a** have been shown to efficiently catalyse the asymmetric allylic substitution of the 1,3-diphenylprop-2-enylacetate **7** with the anion of dimethyl malonate to give the product (*R*)-**8** with moderate enantioselectivities.

3. Conclusions

We have developed a convenient procedure to prepare chiral 1-pyrrolidinophospholes from chiral pyrrolidines and 1-cyanophospholes. The coordination chemistry of these ligands towards palladium(II) and platinum(II) reveals their tendency to behave as *P*-monodentate rather than *P*,*O*-bidentate ligands. These ligands, evaluated in palladium-catalysed asymmetric allylic substitution, proved to be very effective catalysts with respect to the reaction rate, but induced only moderate enantioselectivities.

Investigations of these new chiral ligands in various catalytic asymmetric reactions are currently in progress.

4. Experimental

4.1. General

All reactions were carried out under an inert atmosphere of dry argon using Schlenk glassware and vacuum line techniques. 1-Cyano-2,3-dimethylphosphole[7a] and 1-phenyl-2,3,4,5-tetramethylphosphole[12] were prepared as described in the literature. Solvents were freshly distilled from standard drying agents. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H, ^{31}P} NMR spectra were recorded on a Bruker AM 250 instrument operating at 250, 101, and 63 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained on a Mermag R10-10 instrument. Elemental analyses were performed by the 'service d'analyse du Laboratoire de Chimie de Coordination' at Toulouse. Optical rotations were measured with a Perkin–Elmer 241 polarimeter.

4.2. 1-[(*S*)-2-Methoxymethylpyrrolidino]-3,4-dimethylphosphole, 3a

To a solution of 2-(*S*)-methoxymethylpyrrolidine (0.080 mL, 0.64 mmol) in THF (2 mL) was added dropwise a 1.6 M solution of *n*-BuLi (0.400 mL, 0.64 mmol) at −20°C. The yellow reaction mixture was allowed to warm at 0°C and stirred 30 min. Then, a solution of phosphole **1** (84 mg, 0.61 mmol) in THF (2 mL) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature, stirred for 2 h and evaporated in vacuo. The residue was extracted with pentane. The combined organic extract was washed with H_2O, dried over $MgSO_4$ and evaporated to afford compound **3a** as a yellow oil (0.087 mg, 63%). $[\alpha]_D = -14.8$ (*c* 0.25, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 41.53. ^{1}H NMR ($CDCl_3$): δ 1.62 (m, 3H, CH_2), 1.78 (m, 1H, CH_2), 1.94 (dd, $^4J_{H-P}$ 4.5 Hz, $^4J_{H-H}$ 1.0 Hz, 6H, CH_3), 2.70 (ABX$_2$, $^2J_{B-A}$ 9.3 Hz, $^3J_{B-X}$ 6.8 Hz, 1H, CH_2N), 2.84 (ABX$_2$, $^2J_{A-B}$ 9.3 Hz, $^3J_{A-X}$ 6.8 Hz, 1H, CH_2N), 3.08 (ABX, $^2J_{A-B}$ 7.5 Hz, $^3J_{A-X}$ 8.9 Hz, 1H, C$\underline{H}_2$OCH$_3$), 3.19 (m, 1H, CHN), 3.27 (s, 3H, CH_3-O), 3.28 (ABX, $^2J_{A-B}$ 7.5 Hz, $^3J_{A-X}$ 8.9 Hz, 1H, C$\underline{H}_2$OCH$_3$), 5.96 (d, $^2J_{HP}$ 36 Hz, 1H, CHP), 5.99 (d, $^2J_{HP}$ 36 Hz, 1H, CHP). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.50 (d, $^3J_{C-P}$ 3.6 Hz, CH_3), 25.31 (d, $^3J_{C-P}$ 3.2 Hz, CH_2), 29.65 (d, $^3J_{C-P}$ 4.2 Hz, CH_2), 51.31 (s, CH_2N) 58.99 (s, CH_3O), 61.15 (d, $^2J_{C-P}$ 12.8 Hz, CHN), 76.06 (d, $^3J_{C-P}$ 4.6 Hz, $\underline{C}H_2OCH_3$), 127.30 (d, $^1J_{C-P}$ 2.5 Hz, CHP), 127.60 (d, $^1J_{C-P}$ 2.5 Hz, CHP), 146.20 (d, $^2J_{C-P}$ 13 Hz, $\underline{C}CH_3$), 146.50 (d, $^2J_{C-P}$ 13 Hz, $\underline{C}CH_3$). MS (DCI, NH_3); *m*/*z*

(%): 226 (100) [MH^+]. Anal. calcd for $C_{12}H_{20}NOP$: C, 63.98; H, 8.95; N, 6.22. Found: C, 64.06; H, 8.26; N, 5.89%.

4.3. 1-Cyano-2,3,4,5-tetramethylphosphole, 2

A solution of 1-phenyl-2,3,4,5-tetramethylphosphole (5 g, 23.15 mmol) in THF (20 mL) was added at room temperature to a suspension of lithium (1 g, 0.143 mol) in THF (5 mL). The reaction was monitored by ^{31}P NMR analysis. After completion of the reaction, the red suspension was filtered through Celite (to remove unreacted lithium) into another Schlenck and anhydrous $AlCl_3$ (1.03 g, 7.7 mmol) was added at 0°C. The reaction mixture was allowed to warm to room temperature, stirred for 0.5 h and then transferred by cannula to a solution of BrCN (4.88 g, 46.1 mmol) in THF (10 mL) cooled at −78°C. The mixture was stirred for 0.5 h at −78°C, then allowed to warm to room temperature and stirred at room temperature overnight. The mixture was concentrated to dryness and the resulting residue was extracted with small portions of pentane. The combined pentane extracts were filtered through Celite and the solvents were evaporated to give crude compound **2** as a white solid (2 g, 52%). This was used without further purification. ^{31}P NMR ($CDCl_3$): δ −32.17. ^1H NMR ($CDCl_3$): δ 1.91 (m, 6H, CH_3), 2.08 (d, $^3J_{HP}$ 11.0 Hz, CH_3CP).

4.4. 1-[(*S*)-2-Methoxymethylpyrrolidino]-2,3,4,5-tetramethylphosphole, 3b

The same procedure as described for **3a** was used. Compound **3b** was obtained as a yellow oil in 56% yield. $[\alpha]_D = -56.0$ (*c* 0.80, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 58.57. ^1H NMR ($CDCl_3$): δ 1.74 (m, 4H, CH_2), 1.84 (s, 6H, CH_3), 1.89 (d, $^4J_{H-P}$ 11.3 Hz, 3H, CH_3P),), 1.91 (d, $^4J_{H-P}$ 11.3 Hz, 3H, CH_3CP), 2.66 (m, 2H, CH_2-O), 2.79 (m, 1H, CH_2-N), 3.15 (m, 1H, CH-N), 3.35 (s, 3H, CH_3-O), 3,39 (m, 1H, CH-N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.60 (d, $^2J_{C-P}$ 21.8 Hz, CH_3CP), 12.98 (d, $^2J_{C-P}$ 21.8 Hz, CH_3CP), 13.79 (d, $^3J_{C-P}$ 3.2 Hz, CH_3), 13.87 (d, $^3J_{C-P}$ 3.2 Hz, CH_3), 25.86 (d, $^3J_{C-P}$ 1.1 Hz, CH_2), 30.57 (d, $^3J_{C-P}$ 4.1 Hz, CH_2), 50.48 (s, CH_2N) 59.32 (s, CH_3O), 61.44 (d, $^2J_{C-P}$ 16.0 Hz, CHN), 76.81 (d, $^3J_{C-P}$ 3.9 Hz, CH_2O), 132.81 (d, $^1J_{C-P}$ 5.4 Hz, CH_3-C), 132.98 (s, CH_3-C), 139.97 (d, $^1J_{C-P}$ 17.4 Hz, CP), 140.15 (d, $^1J_{C-P}$ 17.4 Hz, CP). MS (DCI, NH_3); *m*/*z* (%): 254 (100) [MH^+].

4.5. 1-[(*S*,*S*)-2,5-Bis(methoxymethyl)pyrrolidino]-3,4-dimethylphosphole, 4a

The same procedure as described for **3a** was used. The lithium amide was prepared as previously, starting from (*S*,*S*)-2,5-bis(methoxymethyl)pyrrolidine. Compound **4a** was obtained as an orange oil in 80% yield. $[\alpha]_D = -14.2$ (*c* 0.5, $CHCl_3$). ^{31}P NMR ($CDCl_3$): δ 29.26. ^1H NMR ($CDCl_3$): δ 1.78 (m, 4H, CH_2), 1.99 (d, $^4J_{H-P}$ 4.5 Hz, 6H, CH_3), 3.10 (ABX, $^2J_{A-B}$ 7.3 Hz, $^3J_{A-X}$ 8.0 Hz, 2H, CH_2OCH_3), 3.28 (s, 6H, CH_3O), 3.30 (ABX, $^2J_{A-B}$ 7.3 Hz, $^3J_{A-X}$ 8.0 Hz, 2H, CH_2OCH_3), 5.97 (d, $^2J_{HP}$ 36.1 Hz, 1H, CHP), 6.09 (d, $^2J_{HP}$ 36.1 Hz, 1H, CHP). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.40 (s, CH_3), 27.40 (d, $^3J_{C-P}$ 2.5 Hz, CH_2), 58.90 (s, CH_3O), 61.70 (d, $^2J_{C-P}$ 5.7 Hz, CHN), 75.20 (d, $^3J_{C-P}$ 5.8 Hz, CH_2OCH_3), 127.60 (s, CHP), 128.60 (s, CHP), 143.90 (d, $^2J_{C-P}$ 14 Hz, CCH_3), 146.60 (d, $^2J_{C-P}$ 14 Hz, CCH_3). MS (DCI, NH_3); *m*/*z* (%): 270 (100) [MH^+]. Anal. calcd for $C_{14}H_{24}NO_2P$: C, 62.44; H, 8.98; N, 5.20. Found: C, 62.46; H, 9.09; N, 5.12%.

4.6. *cis*-Dichloro-bis(1-[(*S*)-2-methoxymethylpyrolidino]-3,4-dimethylphosphole) palladium(II), 5

To a solution of phosphole **3a** (0.070 g, 0.31 mmol) in dichloromethane (5 mL) was added solid [$Pt(CH_3CN)_2Cl2$] (0.040 g, 0.154 mmol). The reaction mixture was stirred for 1 h at room temperature, filtered through a 0.45 μm PTFE filter, and then evaporated. The orange–red solid obtained was washed with pentane and dried in vacuum. Yield: 0.081 mg (83%). ^{31}P NMR ($CDCl_3$): δ 57.45. ^1H NMR ($CDCl_3$): δ 1.79 (m, 8H, CH_2), 2.05 (d, $^4J_{H-P}$ 5.3 Hz, 12H, CH_3), 3.04 (m, 2H, CHN), 3.22 (ABX, $^2J_{A-B}$ 6.7 Hz, $^3J_{A-X}$ 9.4 Hz, 2H, CH_2OCH_3), 3.28 (ABX, $^2J_{A-B}$ 6.7 Hz, $^3J_{A-X}$ 9.4 Hz, 2H, CH_2OCH_3), 3.29 (s, 6H, CH_3O), 3.38 (m, 4H, CH_2N), 6.29 (d, $^2J_{H-P}$ 34 Hz, 2H, CHP), 6.44 (d, J_{H-P} 34 Hz, 2H, CHP). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.50 (s, CH_3), 25.31 (s, CH_2), 29.65 (s, CH_2) 51.38 (s, CH_2N) 58.99 (s, CH_3O), 61.15 (d, $^2J_{C-P}$ 12 Hz, CHN), 76.06 (s, CH_2OCH_3), 122.50 (d, $^1J_{C-P}$ 60 Hz, CHP), 123. 60 (d, $^1J_{C-P}$ 60 Hz, CHP), 151.10 (d, $^2J_{C-P}$ 17 Hz, CCH_3), 151.50 (d, $^2J_{C-P}$ 17 Hz, CCH_3). MS (DCI, NH_3); *m*/*z* (%): 629 (100) [MH^+], 593 (82) [MH^+−Cl]. $[\alpha]_D = +187$ (*c* 0.24, CH_2Cl_2).

4.7. *trans*-Dichloro-bis(1-[(*S*)-2-methoxymethylpyrrolidino]-3,4-dimethylphosphole) platinum(II), 6

The same procedure as described for **5** was used. Starting from **3a** (0.110 mg, 0.49 mmol) and [$Pt(CH_3CN)_2Cl_2$] (0.85 g, 0.244 mmol), **6** was obtained as a yellow–orange solid. Yield: 0.151 mg (86%). ^{31}P NMR ($CDCl_3$): δ 35.4 (J_{P-Pt} 3596 Hz). ^1H NMR ($CDCl_3$): δ 1.80 (m, 8H, CH_2), 2.06 (b, 12H, CH_3), 3.07 (m, 2H, CHN), 3.22 (m, 4H, CH_2N), 3.29 (s, 6H, CH_3O), 3.35 (m, 4H, CH_2OCH_3), 6.18 (d, J_{HP} 30 Hz, 2H, CH-P) 6.42 (d, J_{HP} 30 Hz, 2H, CH-P). MS (DCI, NH_3); *m*/*z* (%): 716 (11) [M^+], 681 (70) [$M-Cl^+$].

4.8. Allylic substitution reactions

A mineral oil dispersion of NaH (30 mg, 80% NaH, 1.0 mmol) was washed with dry pentane (3×5 mL). The oil-free NaH was suspended in the solvent (THF or CH_2Cl_2) (3 mL), cooled to 0°C and treated dropwise with dimethyl malonate (0.085 mL, 0.75 mmol). After the reaction was complete, the resulting sodium dimethyl malonate was transferred by cannula under argon into a Schlenk tube containing a solution of the ligand, the 1,3-diphenylprop-2-enylacetate (138 mg, 0.5 mmol) and $[(Pd(C_3H_5)Cl)]_2$ (0.005 mmol, 2 mg, 1% mol) in solvent (2 mL). The reaction was monitored by TLC for disappearance of acetate. After complete reac-

tion, the resulting mixture was diluted with diethyl ether (5 mL) and quenched with a saturated aqueous solution of ammonium chloride (5 mL). The aqueous phase was extracted with Et_2O, the combined organics were dried over magnesium sulfate, filtered and evaporated. The degree of conversion was calculated from the crude reaction mixture by ^1H NMR spectroscopy. Subsequent purification by chromatography on silica eluting with ethyl acetate/pentane (15/85) afforded the product as a white solid (0.346 g, 93%). The enantiomeric excess was determined ^1H NMR using the chiral shift reagent $Eu(hfc)_3$.

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