Acta Chemica Scandinavica, 1999: 53: 263–268
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Studies on a Chiral (*N,P*) Ligand Containing a C_2-Symmetric Aziridine Unit

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Tanner, D., Wyatt, P., Johansson, F., Bertilsson, S. K. and Andersson, P. G., 1999. Studies on a Chiral (*N,P*) Ligand Containing a C_2-Symmetric Aziridine Unit. – Acta Chem. Scand. 53: 263–268. © Acta Chemica Scandinavica 1999.

As part of a program on the use of chiral aziridines in asymmetric synthesis and catalysis, the enantiopure (*N,P*) ligand **1**, consisting of a C_2-symmetric chiral aziridine and a triarylphosphine unit, was prepared. The synthesis was convergent and efficient, proceeding in five steps and 37% overall yield from 2-bromotoluene. The ligand was designed (a) for a study of the asymmetric Pd-catalyzed allylic substitution reaction, (b) in an attempt to obtain a measure of the *trans* effect of phosphorus relative to an aziridine nitrogen, and (c) to compare its performance with the corresponding chiral phosphinooxazoline species (computational studies having indicated certain similarities between the two ligand types). However, the new aziridine species did not provide levels of enantioselectivity comparable to those obtained with the phosphinooxazoline analogs, and our results serve to underline once more the difficulties associated with the rational design of ligands for asymmetric catalysis.

We have earlier reported on the synthesis and use of bis(aziridines) as chiral ligands for metal mediated reactions.[1] Especially encouraging results[1b] were obtained for the asymmetric palladium catalyzed allylic alkylation[2] shown below (>99% ee for the 'standard' reaction with 1,3-diphenylpropenyl acetate). However, for this particular reaction, it quickly became apparent that these ligands were somewhat limited in scope, NMR studies of putative catalytic intermediates showing in most cases only weak coordination between ligand and metal. As a result, only 'activated' substrates in which the leaving group was in a benzylic position gave satisfactory levels of conversion and enantioselectivity.

Other research groups have also studied chelating *N,N*-ligands for palladium catalysis, with varying degrees of success,[3] but one of the most exciting recent developments has involved ligands containing two different heteroatoms exerting different *trans* effects on the metal. In this respect, both *N,S*-[4] and *N,P*-ligands[5] have been used, the latter being generally the more successful. Encouraged by these observations, we decided to prepare some ligands such as **1** containing both a chiral aziridine and a phosphine.

Our design was based on inspection of molecular models of possible catalytic intermediates, i.e. square planar Pd(II) π-allyl complexes. One such structure is shown below, together with the corresponding six-membered chelate implied in the reaction catalyzed by the phosphinoaryldihydrooxazole ligands introduced by the groups of Pfaltz,[5a] Helmchen[5b] and Williams[5c]

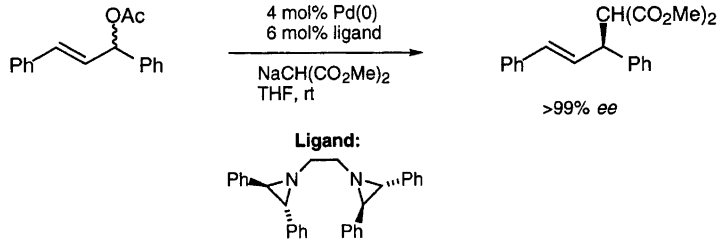

Fig. 1. Palladium-catalyzed allylic alkylation using chiral bis(aziridines) as ligands.

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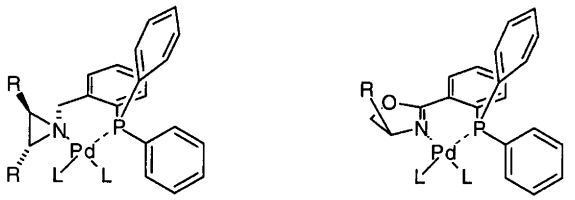
and shown to be highly efficient for the allylic alkylation reaction.

The present project was also expected to provide some measure of the *trans* effect of phosphorus relative to an aziridine nitrogen and, in order to compare the two types of ligand in this respect, calculations[6] were performed on the model π-allyl complexes shown below.

The calculations suggested fairly similar structures for the π-allyl species, with considerable differences in the N–Pd–C_{trans} and P–Pd–C_{trans} distances in both cases. Although this seemed promising, we were aware that the greater conformational freedom of the aziridine ligand could pose problems concerning the enantioselectivity of the reaction (*vide infra*).

Results and discussion

For the synthesis of the ligand we considered the two retrosynthetic analyses shown below. The first route we tried (A) relied on the nucleophilic aromatic substitution of fluorine by phosphorus in the first step, but we were unfortunately unable to reproduce the high yields reported in the literature for the reaction involving 2-fluorobenzaldehyde.[7] We then turned to the second approach (B) involving electrophilic phosphorus, and a simple high-yielding route to the first example of ligands of type **1** (R = Ph) is shown below. (We found that a number of the phosphine intermediates were very sensitive towards air and required the phosphorus to be protected as the phosphine oxide.)



1 L,L = π-allyl

Fig. 2. Comparison of chiral aziridine–phosphine and oxazoline–phosphine ligands.

In the first step, the Grignard reagent from 2-bromotoluene (**2**) was allowed to react with chlorodiphenylphosphine to give **3** in good yield. Oxidation at phosphorus to give **4** was followed by standard bromination with NBS, and substitution at the benzylic position of **5** occurred smoothly upon exposure to (2*S*,3*S*)-2,3-diphenylaziridine, the synthesis of which is described in the Experimental. Phosphine oxide **6** was obtained as a stable crystalline solid. The reagent of choice for the final step proved to be alane,[8] and in this way the desired ligand **1** was obtained in 37% overall yield (five steps from 2-bromotoluene). The method of synthesis also allows equally easy access to both enantiomers of the ligand.

The new ligand was then tested in some palladium-catalyzed allylic substitution reactions, with the results shown below. Much to our disappointment, in the 'standard' reaction with 1,3-diphenylpropenyl acetate, ligand **1** proved to be catalytically incompetent (< 30% yield and < 5% ee). Use of both ligand and palladium in stoichiometric amounts improved the yield (62%) but not the enantioselectivity (ca. 8% ee). Furthermore, in contrast with the case[1b] with the bis(aziridine) ligand shown in Fig. 1, we were unable to prepare or isolate the presumed catalytic intermediate for the reaction involving **1**. The catalytic reaction involving the unsymmetrical acetate (R = Ph, R′ = Me) shown below gave an acceptable chemical yield of a single regioisomer (from attack at the non-benzylic position) but the ee was still poor (23%).

The disappointingly low levels of selectivity obtained with the new ligand are presumably due to the flexibility of the system at the N–CH_2–Aryl linkage, leading to the conformational equilibrium shown below. Allowing for different orientations of the π-allyl moiety, there would

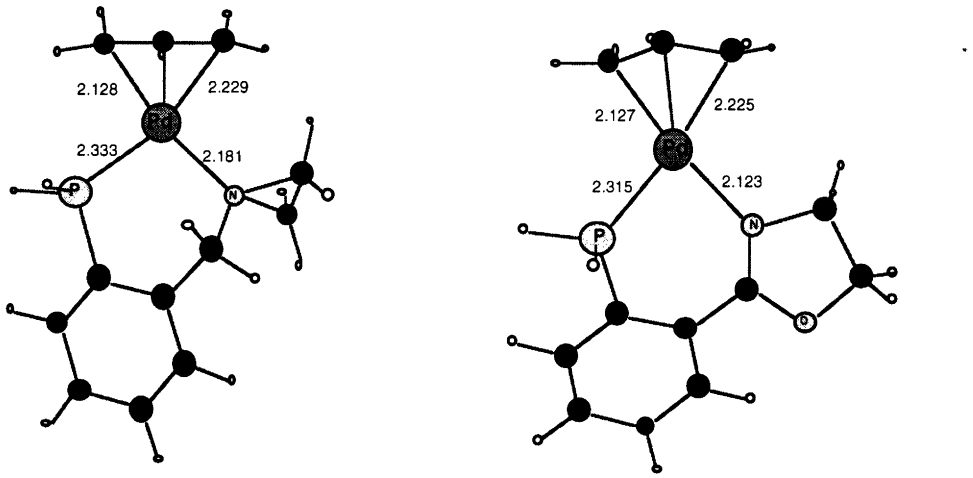
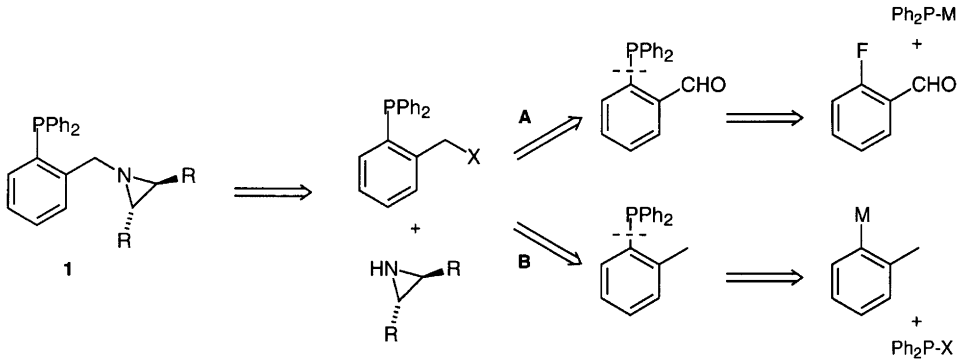
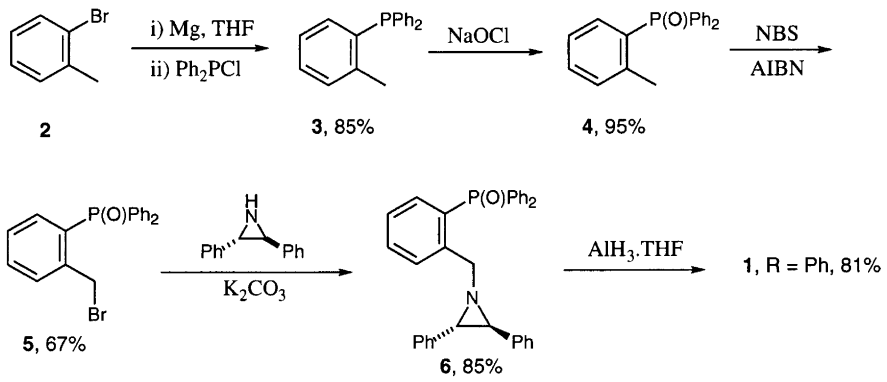


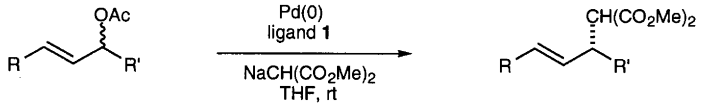
Fig. 3. Calculated structures of model π-allyl–Pd complexes with aziridine (left) and oxazoline (right) (*N,P*)-ligands (interatomic distances in Å).



Scheme 1.



Scheme 2.



R	R'	equiv. Pd	equiv. ligand	yield %	*ee* %
Ph	Ph	0.04	0.06	<30	<5
Ph	Ph	1.1	1.2	62	8 (*R*)
Ph	Me	0.04	0.06	71	23 (*R*)

Fig. 4. Asymmetric palladium-catalyzed allylic alkylation of allylic acetates using ligand **1**.

thus be four competing complexes for nucleophilic attack in the case of the 1,3-diphenyl substrate, and eight for the (phenyl, methyl) system; this obviously has a deleterious effect on the enantioselectivity of the reaction.

Although this particular chiral aziridine–phosphine species leaves a lot to be desired in terms of asymmetric induction in palladium catalysis, our efforts to develop novel (*N,P*) derivatives as chiral ligands are continuing, and results will be reported elsewhere.

Experimental

General remarks. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian Unity spectro-

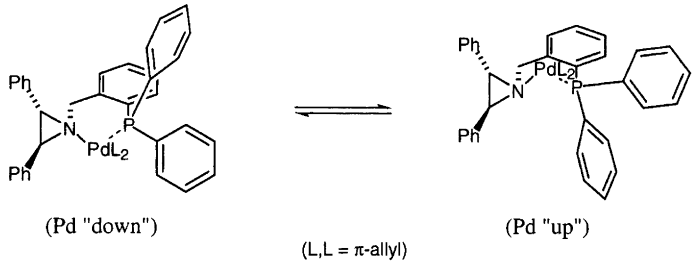


Fig. 5. Conformational isomerism of Pd-complexes with ligand **1**.

meter ($CDCl_3$–TMS unless otherwise stated). For ^{13}C NMR signals the superscripts + and − denote odd and even numbers of attached protons, respectively. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR instrument. Specific rotation values were measured at 25 °C on a Perkin-Elmer 241 polarimeter. Mass spectra were recorded on a VG Autospec-Q instrument equipped with an electrospray interface. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany. Tetrahydrofuran (THF) was distilled under nitrogen from Na–benzophenone; dichloromethane was distilled under nitrogen from calcium hydride; carbon tetrachloride was distilled immediately before use; HPLC-grade acetonitrile was used directly as received. Silica gel for flash chromatography was purchased from Grace-Amicon. All reactions involving air- or moisture-sensitive intermediates were carried out under a dry argon or nitrogen atmosphere.

2-Methylphenyl(diphenyl)phosphine **3**.[9] Dry THF (25 ml) was added to magnesium turnings (3.08 g, 128 mmol) in a 250 ml three-necked flask fitted with a reflux condenser and dropping funnel. Approximately 5 ml of a solution of dry *o*-bromotoluene (15 ml, 125 mmol) in THF (50 ml) and a crystal of iodine were added to the stirring magnesium mixture. After the reaction had started the rest of the bromotoluene solution was added dropwise over a period of 1 h. The mixture refluxed during this time without external heating. The mixture was then heated to reflux for a further 2 h. The resulting Grignard reagent was cooled to −78 °C. Freshly distilled Ph_2PCl (22.3 ml, 125 mmol) was dissolved in THF (30 ml) and added dropwise to the cooled Grignard reagent over 10 min. The reaction mixture froze after it had been stirred for 1 h and was allowed to warm to room temperature overnight. Saturated aqueous $(NH_4)_2SO_4$ solution (200 ml) was added to the stirred mixture. The layers were separated and the organic layer was washed with aqueous $(NH_4)_2SO_4$ (2 × 100 ml). The combined aqueous layers were washed with Et_2O (3 × 100 ml) and the combined organics were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting solid was recrystallized from EtOH (50 ml) to yield the phosphine (29.0 g, 85%) m.p. 68–69 °C. R_f (1:19 EtOAc-pentane) 0.58. IR: ν_{max} (KBr)/cm^{-1} 1584 (Ar), 1434 (Ph–P). ^1H NMR: 7.40–7.21 (12 H, m), 7.13 (1 H, t, *J* 7.4), 6.83 (1 H, t, ddd, *J* 6.83, $^4J_{PH}$ 4.5 and *J* 0.8, 3-ArH), 2.44 (3 H, d, $^4J_{PH}$ 0.8, Me). ^{13}C NMR: 142.2$^-$ ($^2J_{PC}$ 25.0, 2-ArC), 136.3$^-$ ($^1J_{PC}$ 9.9), 136.0$^-$ ($^1J_{PC}$ 12.1), (134.1–125.1)$^+$ (several lines), 21.2$^+$ ($^3J_{PC}$ 20.5, Me). MS: *m/z* 276 (100%, M^+). HRMS: Found: M^+ 276.1047; $C_{19}H_{17}P$ requires 276.1068.

2-Methylphenyl(diphenyl)phosphine oxide **4**.[10] The 2-methyl(phenyl)diphenylphosphine from above (10.0 g, 36.2 mmol) was dissolved in CH_2Cl_2 (50 ml). The solution was cooled to 3 °C and stirred vigorously as a solution of NaOCl (15 ml, 10% available chlorine) and water (15 ml) was added dropwise. More NaOCl (40 ml, 10% available chlorine) was added at a rate slow enough to keep the reaction mixture below 20 °C. The reaction mixture was poured into a mixture of CH_2Cl_2 (50 ml) and NaOCl solution (40 ml, 10% available chlorine). The layers were separated and the aqueous phase was further extracted with CH_2Cl_2 (50 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was recrystallised from 4:3 hexane–EtOAc (102 ml) to yield the phosphine oxide (8.39 g). Additional phosphine oxide (1.64 g) was obtained from the mother liquor, and the total product (10.03 g, 95%) was obtained as prisms m.p. 121–123 °C (from hexane–EtOAc). R_f (1:1 hexane–EtOAc) 0.20. IR: ν_{max} ($CHCl_3$)/cm^{-1} 1594 (Ar), 1438 (Ph–P), 1174 (P=O). ^1H NMR: 7.68–7.61 (4 H, m), 7.56–7.38 (7 H, m), 7.27 (1 H, ddd, *J* 7.6, $^4J_{PH}$ 4.0 and *J* 0.4, 6-ArH), 7.11 (1 H, m), 7.02 (1 H, ddd, $^3J_{PH}$ 14.0, *J* 7.6 and 1.2, 3-ArH), 2.45 (3 H, s, Me). ^{13}C NMR: 143.3$^-$ ($^1J_{PC}$ 7.6, 1-ArC), 133.4$^+$ (J_{PC} 12.1), 132.8$^-$ ($^1J_{PC}$ 102.4, *ipso*-Ph), (132.0–131.7)$^+$ several lines, 130.8$^-$ ($^1J_{PC}$ 102.5 2-ArC), 128.5$^+$ (J_{PC} 11.4), 125.1$^+$ (J_{PC} 12.9), 21.6$^+$ ($^3J_{PC}$ 4.5, Me). MS: *m/z* 292 (33%, M^+), 291 (54, $M-H$). HRMS: Found: M^+ 292.1011. $C_{19}H_{17}OP$ requires 292.1017.

2-(Diphenylphosphinoyl)-α-bromotoluene **5**.[11] The phosphine oxide from above (1.50 g, 5.14 mmol), NBS (936 mg, 5.26 mmol) and AIBN (2 mg, 0.012 mmol) were suspended in dry CCl_4 (47 ml). The mixture was refluxed overnight and allowed to cool to room temperature. Water (20 ml) and CH_2Cl_2 (20 ml) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 ml) and the combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purifed by flash chromatography eluting with 1:1 EtOAc–pentane to yield the bromide (1.28g, 67%) as plates m.p.118–120 °C (from EtOAc–pentane). R_f (1:1 EtOAc–pentane) 0.33. IR: ν_{max} (KBr)/cm^{-1} 1590 (Ar), 1508 (Ar), 1436 (Ph–P), 1187 (P=O). ^1H NMR: 7.67–7.41 (12 H, m, Ar), 7.19 (1 H, tdd, *J* 7.6, 2.0 and 1.2), 7.00 (1 H, ddd, $^3J_{PH}$ 14.0, *J* 7.6 and 1.2, 3-ArH), 4.99 (2 H, s, CH_2Br). ^{13}C NMR: 142.7$^-$ ($^2J_{PC}$ 6.8, 1-ArC), (133.3–131.8)$^+$ several lines, 131.4$^-$ ($^1J_{PC}$ 104.0), 130.6$^-$ ($^1J_{PC}$ 100.10, (128.5–127.3)$^+$ several lines and 30.9$^-$ ($^3J_{PC}$ 4.6, CH_2Br). MS: *m/z* 291 (100%, $M-Br$).

(2S,3S)-2,3-Diphenylaziridine. A solution of (1*R*,2*S*)-1,2-diphenyl-2-azidoethanol 1c (3.58 g, 15.0 mmol) and triphenylphosphine (4.83 g, 18.4 mmol) in THF (50 ml) was refluxed overnight. The reaction mixture was concentrated under reduced pressure and the residue was purifed by flash chromatography eluting with 19:1 pentane–EtOAc followed by 3:1 pentane–EtOAc to give the desired aziridine as a colorless oil (2.42 g, 82%). R_f (19:1 pentane–EtOAc) 0.12. ^1H NMR: 7.40–7.20 (10 H, m, 2 × Ph), 3.10 (2 H, br s, 2 × PhC*H*), 1.36 (1 H, br s, NH). $[\alpha]_D$ +391 (*c* 1.05, CH_2Cl_2). Anal. Calc. for

$C_{14}H_{13}N$: C, 86.12%; H, 13.10; N, 7.17. Found: C, 86.10; H, 6.68; N, 7.21.

2-(Diphenylphosphinoyl)-α-[(2S,3S)-2,3-diphenylaziridin-1-yl]toluene **6**. A mixture of compound **5** (377 mg, 1.02 mmol), K_2CO_3 (156 mg, 1.13 mmol) and (2*S*,3*S*)-2,3-diphenylaziridine (218 mg, 1.12 mmol) in acetonitrile (20 ml) was stirred at 45 °C overnight and then at 65 °C for a further 24 h. The acetonitrile was then evaporated off under reduced pressure, water (10 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 10 ml). The combined organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 4:1 CH_2Cl_2–EtOAc followed by 1:1 CH_2Cl_2–EtOAc to yield an oil which was refluxed briefly in 1:2.4 EtOAc–hexane (9.8 ml). The mixture was then cooled to yield the desired product as a solid (324 mg). The mother liquor was concentrated under reduced pressure, refluxed in 1:2 EtOAc–hexane (1.8 ml) and cooled to yield additional product (97 mg). The total product (421 mg, 85%) was purified by recrystallization and was isolated as prisms, m.p. 143–145 °C (from EtOAc–hexane). R_f (4:1 CH_2Cl_2–EtOAc) 0.20. IR: ν_{max} (KBr)/cm^{-1} 1602, 1590, 1496 (Ar), 1437 (Ph–P), 1185 (P=O). ^1H NMR: 7.92 (1 H, dd, *J* 7.2 and 4.2, 6-ArH), 7.56–7.17 (21 H, m, Ar), 7.13 (1 H, td, *J* 7.4 and 1.6), 7.04 (1 H, ddd, *J* 14.0, 7.6 and 0.8, 3-ArH), 3.72 (1 H, d, *J* 16.0, $ArCH_AH_BN$), 3.57 (1 H, d, *J* 16.0, $ArCH_AH_BN$), 3.27 (1 H, br s, $PhCH_ACH_BPh$), 3.05 (1 H, br s, $PhCH_ACH_BPh$). ^{13}C NMR: 144.3$^-$ ($^2J_{PC}$ 7.6, 1-ArC), 140.0$^-$ (br, *ipso*-Ph_ACHN), 133.6$^-$ (br, *ipso*-Ph_BCHN), 132.6$^-$ ($^1J_{PC}$ 103, *ipso*-Ph_AP), 132.5$^-$ ($^1J_{PC}$ 102, *ipso*-Ph_BP), 129.8$^-$ ($^1J_{PC}$ 101, 2-ArC), (132.9–125.7)$^+$ several lines, 54.0$^-$ ($^3J_{PC}$ 4.6, CH_2N), 51.1$^+$ (NC_AHPh), 45.3$^+$ (NC_BHPh). $[\alpha]_D$ −37.4 (*c* 1.14, CH_2Cl_2). Anal. Calc. for $C_{33}H_{28}NOP$: C, 81.63%; H, 5.81; N, 2.89. Found: C, 81.59; H, 5.78; N, 2.92.

2-(Diphenylphosphino)-α-[(2S,3S)-2,3-diphenylaziridin-1-yl]toluene **1**. (*i*) *Alane*. Dry THF (10 ml) was added to concentrated sulfuric acid (0.590 g, 6.02 mmol) and cooled to 0 °C before $LiAlH_4$ (12.0 ml of a 1 M solution in THF, 12.0 mmol) was added dropwise to the stirred mixture. The mixture was allowed to warm to room temperature and stirred for 1 h. The precipitate was allowed to settle before the solution was used. The solution was used without titration within 24 h of preparation and presumed to contain approximately 0.54 M AlH_3–THF during that period.

(*ii*) Compound **6** (76 mg, 0.157 mmol) was dissolved in dry THF (4 ml) and $AlH_3 \cdot$ THF (0.630 ml of a 0.54 M solution in THF, 0.34 mmol) was added to the stirred solution at room temperature. The mixture was heated at 55 °C for 30 min before MeOH (3 ml) was added and the mixture filtered through Celite. The filter cake was washed with hot THF (3 × 5 ml) and the combined organics were concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 19:1 pentane–EtOAc to give the desired phosphine **1** (59 mg, 81%) as a solid, m.p. 47–49 °C (from pentane–EtOAc). R_f (9:1 pentane–EtOAc) 0.38. IR: ν_{max} ($CHCl_3$)/cm^{-1} 1603 (Ar), 1586 (Ar), 1496 (Ar), 1434 (Ph–P). ^1H NMR: 7.59 (1 H, dd, *J* 8.0 and 4.4), 7.34–7.06 (22 H, m, Ar), 6.77 (1 H, ddd, *J* 7.6, 4.4 and 1.2), 3.70 (1 H, d, *J* 15.2, $ArCH_AH_BN$), 3.64 (1 H, dd, *J* 15.2 and $^4J_{PH}$ 2.0, $ArCH_AH_BN$), 3.28 (1 H, br s, $PhCH_ACH_BPh$), 3.07 (1 H, br s, $PhCH_ACH_BPh$). $[\alpha]_D$ −49.2 (*c* 1.05, CH_2Cl_2). The compound was not amenable to storage, and no satisfactory elemental analysis could be obtained. HRMS: Found: M^+ 469.5668; $C_{33}H_{28}NP$ requires 469.5679.

The palladium-catalyzed allylic substitution reactions were carried out as previously described[1b,c] and assignments of absolute configuration and e.e. were made by comparison of optical rotation data with those in the literature. [1b,c,12]

Acknowledgements. We thank the Danish Natural Science Research Council, the Swedish Natural Science Research Council, NORFA, and the Royal Society for financial support.

References

1. (a) Tanner, D., Andersson, P. G., Harden, A. and Somfai, P. *Tetrahedron Lett. 35* (1994) 4631; (b) Andersson, P. G., Harden, A., Tanner, D. and Norrby, P.-O. *Chem. Eur. J. 1* (1995) 12; (c) Tanner, D., Harden, A., Johansson, F., Wyatt, P. and Andersson, P. G. *Acta Chem. Scand. 50* (1996) 361; (d) Andersson, P. G., Johansson, F. and Tanner, D. *Tetrahedron 54* (1998) 11549.
2. For reviews: (a) Trost, B. M. and van Vranken, D. L. *Chem. Rev. 96* (1996) 395; (b) Williams, J. M. J. *Synlett* (1996) 705.
3. Some representative examples: (a) Hoarau, O., Ait-Haddou, H., Castro, M. and Balavoine, G. G. A. *Tetrahedron: Asymmetry 8* (1997) 3755. (b) Chelucci, G., Medici, S. and Saba, A. *Tetrahedron: Asymmetry 8* (1997) 3183; (c) Nordström, K., Macedo, E. and Moberg, C. *J. Org. Chem. 62* (1997) 1604; (d) Pfaltz, A. *Acta Chem. Scand. 50* (1996) 189. (e) Peña-Cabrera, E., Norrby, P.-O., Sjögren, M., Vitagliano, A., De Felice, V., Oslob, J., Ishii, S., O'Neill, D., Åkermark, B. and Helquist, P. *J. Am. Chem. Soc. 118* (1996) 4299; (f) Kubota, H., Nakajima, M. and Koga, K. *Tetrahedron Lett. 34* (1993) 8135; (g) Togni, A., Rihs, G., Pregosin, P. S. and Ammann, C. *Helv. Chim. Acta 73* (1990) 723; (h) general review of (*N,N*)-bidentate ligands: Togni, A. and Venanzi, L. M. *Angew. Chem., Int. Ed. Engl. 33* (1994) 497.
4. See, e.g. (a) Chesney, A., Bryce, M. R., Chubb, R. W. J., Batsanov, A. S. and Howard, J. A. K. *Tetrahedron: Asymmetry 8* (1997) 2337; (b) Morimoto, T., Tachibana, K. and Achiwa, K. *Synlett* (1997) 783; (c) Chelucci, G. and Cabras, M. A. *Tetrahedron: Asymmetry 7* (1996) 965; (d) Allen, J. V., Coote, S. J., Dawson, G. J., Frost, C. G., Martin, C. J. and Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* (1994) 2065; (e) Allen, J. V., Bower, J. F. and Williams, J. M. J. *Tetrahedron: Asymmetry 5* (1994) 1895.
5. Introduction of chiral phosphinooxazoline ligands for Pd-catalysis: (a) von Matt, P. and Pfaltz, A. *Angew. Chem., Int. Ed. Engl. 32* (1993) 566; (b) Sprinz, J. and Helmchen, G. *Tetrahedron Lett. 34* (1993) 1769;

(c) Dawson, G. J., Frost, C. G., Williams, J. M. J. and Coote, S. J. *Tetrahedron Lett. 34* (1993) 3149; for a selection of more recent work, see: (d) Schaffner, S., Müller, J. F. K., Neuburger, M. and Zehnder, M. *Helv. Chim. Acta 81* (1998) 1223; (e) Vasconcelos, I. C. F., Rath, N. P. and Spilling, C. D. *Tetrahedron: Asymmetry 9* (1998) 937; (f) Gläser, B. and Kunz, H. *Synlett* (1998) 53; (g) Prétôt, R. and Pfaltz, A. *Angew. Chem., Int. Ed. Engl. 37* (1998) 323; (h) Steinhagen, H., Reggelin, M. and Helmchen, G. *Angew. Chem., Int. Ed. Engl. 36* (1997) 2108; (i) Saitoh, A., Morimoto, T. and Achiwa, K. *Tetrahedron: Asymmetry 8* (1997) 3567; (j) Mino, T., Imiya, W. and Yamashita, M. *Synlett* (1997) 583; (k) Gilbertson, S. R. and Chang, C.-W. T. *J. Chem. Soc., Chem. Commun.* (1997) 975; (l) Koch, G. and Pfaltz, A. *Tetrahedron: Asymmetry 7* (1996) 2213; (m) Zhang, W., Hirao, T. and Ikeda, I. *Tetrahedron Lett. 37* (1996) 4545; (n) Togni, A., Burckhardt, U., Gramlich, V., Pregosin, P. S. and Salzmann, R. *J. Am. Chem. Soc. 118* (1996) 1031; (o) von Matt, P., Lloyd Jones, G. C., Minidis, A. B. E., Pfaltz, A., Macko, L., Neuburger, M., Zehnder, M., Rüegger, H. and Pregosin, P. S. *Helv. Chim. Acta 78* (1995) 265; (p) Rieck, H. and Helmchen, G. *Angew. Chem., Int. Ed. Engl. 34* (1995) 2881; (q) von Matt, P., Loiseleur, O., Koch, G., Pfaltz, A., Lefeber, C., Feucht, T. and Helmchen, G. *Tetrahedron: Asymmetry 5* (1994) 573; (r) Kubota, H. and Koga, K. *Tetrahedron Lett. 35* (1994) 6689; (s) Brown, J. M., Hulmes, D. I. and Guiry, P. J. *Tetrahedron 50* (1994) 4493; (t) Sprinz, J., Kiefer, M., Helmchen, G., Reggelin, M., Huttner, G., Walter, O. and Zsolnai, L. *Tetrahedron Lett. 35* (1994) 1523.

6. The calculations were performed using GAUSSIAN 94, with a Becke-type three-parameter hybrid functional (B3PW91) and LANL2DZ basis set, with d-polarisation on C, N, O, P and Pd. For B3PW91, see: Becke, A. D. *J. Chem. Phys. 98* (1993) 5648. For a comparison with X-ray crystallographic data for bond lengths in a π-allyl–Pd complex containing a chiral phosphinoaryldihydrooxazole ligand, see Ref. 5(t).
7. Coote, S. J., Dawson, G. J., Frost, C. G. and Williams, J. M. J. *Synlett* (1993) 509. We were able to reproduce the results reported in that paper with substrates other than 2-fluorobenzaldehyde, and we thank Prof. Williams for the detailed experimental procedure and other pertinent information.
8. Griffin, S., Heath, L. and Wyatt, P. *Tetrahedron Lett. 39* (1998) 4405.
9. Feher, K. and Kurz, D. *Z. Naturforsch., Tiel B. 24* (1969) 1089.
10. Griffin, C. E., Davison, R. B. and Gordon, M. *Tetrahedron 22* (1966) 561.
11. Tani, K., Yabuta, M., Nakamura, S. and Yamagata, T. *J. Chem. Soc., Dalton Trans.* (1993) 2781.
12. Hayashi, T., Yamamoto, A. and Hagihara, T. *J. Org. Chem. 51* (1986) 723.

Received September 4, 1998.