PERKIN 1

Coordination of (β-*N*-sulfonylaminoalkyl)phosphines and their analogous arsines to Pd^{II} and Pt^{II}. Application of the Pd-complexes as chiral catalysts in asymmetric hydrosilylation of 1,3-dienes †

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Optically active ligands **2** and **3** were synthesised from phenylglycine and the coordination of ligand **2** to $PdCl_2(CH_3CN)_2$ and $PtCl_2(C_6H_5CN)_2$ was studied with ^1H, ^{31}P and ^{15}N–^1H-HMQC NMR spectroscopy. The results indicated P,O rather than P,N bidentate coordination. Both ligands were tested in the palladium catalysed hydrosilylation of cyclic 1,3-dienes. Asymmetric induction of up to 84% (≤25% yield), which is the hitherto highest reported ee value for asymmetric hydrosilylation of 1,3-dienes, was achieved as measured on the allylic alcohols formed after ethanolysis–oxidation of the initially formed allylic silanes.

Introduction

In connection with projects in natural product synthesis[1,2] we became interested in the synthesis and use of allylic silanes generated *via* 1,4-addition of silanes to 1,3-dienes. For unsymmetrical 1,3-dienes both regiochemistry and stereochemistry must be controlled. Although asymmetric allylic silanes in which the silicon is attached to a stereogenic carbon center are useful building blocks in organic synthesis they are rarely found in the literature. Despite many formal similarities between the catalytic version of hydrogenation and hydrosilylation, the latter reaction has received much less attention. Little is known about the mechanism and how the stereochemical information is transferred from the ligand to the substrate, although suggestions regarding the mechanism in palladium catalysed hydrosilylation of dienes have been made.[3–5] Bidentate bisphosphine ligands such as BINAP have been shown to be less efficient in the palladium catalysed asymmetric hydrosilylation due to the formation of an inactive PdL intermediate.[6] Instead, different monodentate or potentially heterobidentate ligands have been used such as 2-methoxy-2′-diphenylphosphino-1,1′-binaphthyl (MOP),[7] 2-methoxy-2′-diphenylphosphino-1,1′-biphenanthrenyl (MOP-phen),[4] (β-*N*-sulfonylaminoalkyl)phosphine,[8] phosphetanes and [2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) (Fig. 1).[3,9,10]

Hayashi *et al.* have systematically studied the asymmetric hydrosilylation of dienes, but hitherto the yields and degree of asymmetric induction have not been satisfactory.[10–12] In 1990 and 1995 Achiwa *et al.* reported that different (β-*N*-sulfonylaminoalkyl)phosphine ligands derived from amino acids showed promising activity in the hydrosilylation and the Heck reaction.[8,13] Inspired by these results and our interest in the synthesis and applications of new amino acids[14–17] we investigated these aspects further. In this paper we wish to report our results on the coordination of some new (β-*N*-sulfonylaminoalkyl)phosphines to Pd^{II} and Pt^{II}, as studied by NMR-spectroscopy, and the efficiency of the Pd-complexes of the sulfamido phosphines and their arsenic analogues as catalysts in the asymmetric hydrosilylation of cyclic dienes.

† Electronic supplementary information (ESI) available: NMR spectra. See http://www.rsc.org/suppdata/p1/b1/b101464l

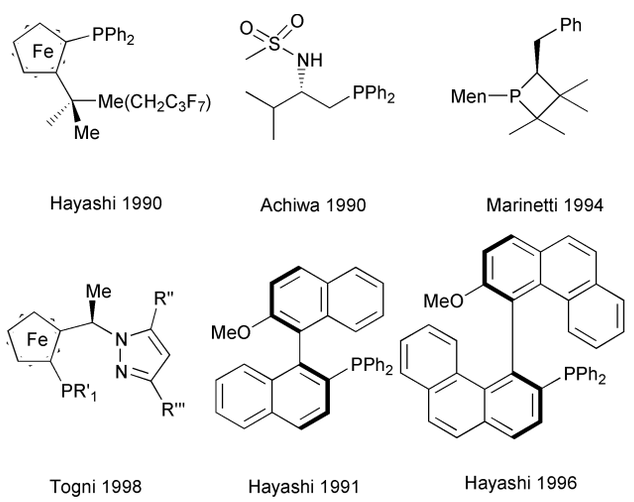

Fig. 1 Some monodentate and potentially heterobidentate ligands previously used in asymmetric hydrosilylations of alkenes and dienes.

Results and discussion

Ligands **2** and **3** were synthesised in two steps from (*S*)-phenylglycinol (Scheme 1). Reaction of the aminoalcohol with methanesulfonyl chloride and triethylamine in dichloromethane afforded **1** in 88% yield as a white solid. Treatment of **1** with $LiPPh_2$ (generated from diphenylphosphine and butyllithium)[13] or $LiAsPh_2$ (generated from triphenylarsine and lithium metal)[18] at −30 °C gave ligands **2** and **3** in 40% and 50% yield, respectively. In general the yield of ligand **3** was higher, probably owing to the better solubility of ligand **3** compared to ligand **2**, which facilitated the isolation. Two equivalents of $LiPPh_2$ or $LiAsPh_2$, respectively, were needed to get a reasonable yield due to competitive deprotonation of the acidic sulfonamide proton. It is not likely that aziridine **4** (synthesized from **1** by treatment with NaH in THF) was an intermediate in the ligand synthesis, because when **4** was reacted with $LiPPh_2$ in THF a low yield of **2** and an unknown product were formed.

It is known from the literature that a monoalkylated aminophosphine ligand, $(p\text{-}CH_3C_6H_4)_2PCH_2CH(^iPr)NHCH_2(p\text{-}OCH_3C_6H_4)$, derived from (*S*)-valine coordinates to Pd^{II} and

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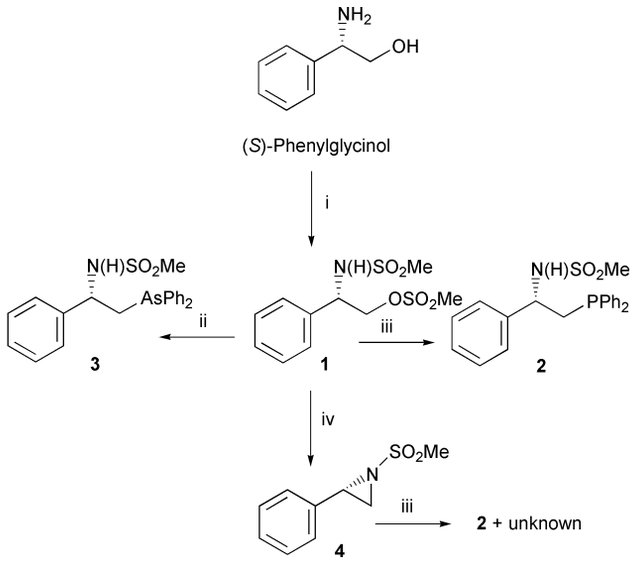


Scheme 1 *Reagents and conditions*: i) $MeSO_2Cl$, Et_3N, CH_2Cl_2; ii) $LiAsPh_2$, THF, −30 °C; iii) $LiPPh_2$, THF, −30 °C; iv) NaH, THF, rt.

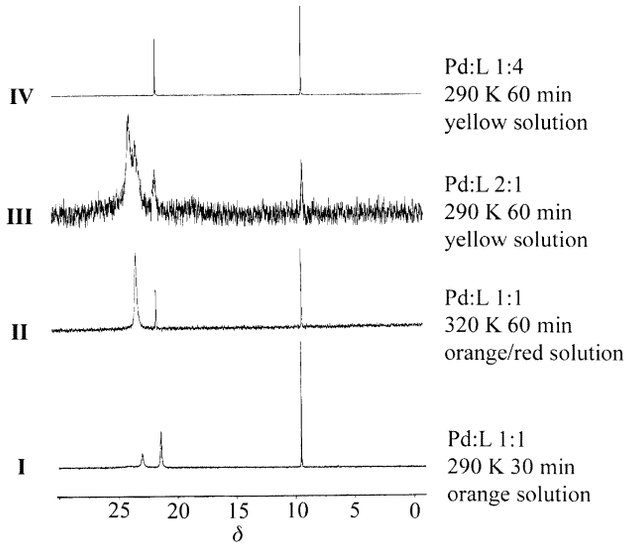


Fig. 2 ^{31}P-NMR spectra of different mixtures of $PdCl_2(CH_3CN)_2$ and ligand **2**.

Pt[II] in a bidentate fashion.[19] When the nitrogen atom binds to the metal a more or less labile stereogenic center is created at nitrogen.[20] This transfer of chirality from the backbone of the ligand closer to the metal center can be useful in asymmetric catalysis as shown by Anderson *et al.*[21] In the palladium catalysed allylic substitution these authors showed that an introduction of a potential stereogenic center on nitrogen in P,N chelating ligands affected the absolute configuration of the product. To our knowledge the coordination of the sulfonamide group to transition metals in organic solvents has been investigated to a lesser extent, although a few reports regarding *N*-sufonylamino acids and their coordination to metals have been published.[22–25]

Since all attempts to grow crystals suitable for X-ray crystallographic structure determination failed, our ligand–metal complexes were investigated by NMR-spectroscopy.

NMR spectroscopy

The complex formed on mixing one equivalent of $PdCl_2(CH_3CN)_2$ and one equivalent of ligand **2** in $CDCl_3$ showed ^{31}P-NMR signals at 23.2, 21.6 and 9.7 ppm which integrated as 0.31, 0.42 and 0.27, respectively, at $T = 290$ K (Fig. 2, spectrum I). No free ligand (−22.8 ppm) was observed. When the sample was heated at 320 K for 30 min an apparently irreversible process took place. The peak at 23.2 ppm increased at the expense of the other two and the ratios were now 0.57 to 0.20 to 0.23, respectively. Further heating resulted in one dominant peak at 23.2 ppm (Fig. 2, spectrum II). In order to gain some information about the composition of the complexes (monomeric, dimeric, *etc.*) a few control experiments were performed. When $PdCl_2(CH_3CN)_2$ was used in excess (2 equivalents) a new signal appeared at 23.7 ppm. The integrals were 0.82 (23.7 + 3.2 ppm) to 0.13 (21.6 ppm) to 0.05 (9.7 ppm) (Fig. 2, spectrum III). When ligand **2** was in excess (2 equivalents) the resonances at 23 ppm decreased and the peaks at 21.6 and 9.7 ppm increased. When further ligand was added (4 equivalents) the resonance at 23 ppm disappeared. The signals at 21.6 ppm (0.24) and 9.7 ppm (0.33) and free ligand (not shown) at −22.8 ppm (0.43) remained (Fig. 2, spectrum IV). When a racemate of the ligand was added to $PdCl_2(CH_3CN)_2$ in a 1 : 1 ratio the signal at 9.7 ppm was split into two, indicating the presence of diastereomeric complexes, possibly containing two ligands in the same complex. The signal at 21.6 ppm was not a doublet but was broadened. A further indication that the complexes with resonances at 9.7 and 21.6 ppm may carry two ligands *e.g.* PdL_2 was indicated by the integrals in the NMR sample containing 4 equivalents of the ligand per metal atom. Both the ^{1}H-NMR spectrum and ^{31}P-NMR spectrum showed in this case that the ratio (the sum of the integrals of the resonances at 21.6 and 9.7 ppm compared to that of −22.8 ppm) between complex and free ligand was almost 1 : 1.

Pregosin *et al.* have shown that in sp^2-hybridised nitrogen ligands the ^{15}N-shift moves 40 ppm downfield upon coordination to a transition metal, in this case platinum.[26,27] We therefore recorded a ^{15}N–^{1}H-HMQC spectrum of the sample containing 3–4 equiv. of the ligand to $PdCl_2(CH_3CN)_2$, which revealed three nitrogen–proton correlations well in agreement with the ^{31}P-NMR data mentioned. ^{15}N-resonances from the free ligand appeared at 84.5 ppm ($J_{(N,H)} = 87$ Hz) and from the complex at 80.6 ppm ($J_{(N,H)} = 89$ Hz) and 87.4 ppm ($J_{(N,H)} = 88.0$ Hz) (Fig. 3, spectrum b). The small shift difference between free ligand and the complexed ligands indicated that the nitrogens may not be directly coordinated to Pd in these complexes.

For comparison the corresponding Pt-complexation was examined. Thus, when one equivalent of $PtCl_2(PhCN)_2$ and one equivalent of ligand **2** were mixed and stirred in CH_2Cl_2 at rt for one hour a complex was formed showing only one ^{31}P signal at 5.7 ppm. The ^1J(Pt,P) was 2526 Hz in good agreement with known *trans* Pt-bisphosphine complexes.[28] The ^{15}N-shift, 79.7 ppm ($J_{(N,H)} = 88$ Hz), of our complex was close to the shift of the free ligand (84.5 ppm) indicating also in this case that the ligand probably did not coordinate to the metal *via* its nitrogen atom. The ^{1}H-set for the Pt-complex was very similar to that of the Pd-complex having ^{31}P at 9.7 ppm.

In the light of these results, we suggest that when one equivalent of $PdCl_2(CH_3CN)_2$ and one equivalent of ligand **2** were mixed, three complexes were formed; two PdL_2 complexes (21.6 ppm and 9.7 ppm) and one PdL complex (23 ppm) (Fig. 4). In the two PdL_2 complexes the ligands should coordinate in a monodentate fashion *via* the phosphorus atom. Compared with the platinum complex (*trans*-PtL_2) it seems reasonable to assume that the PdL_2 at 9.7 ppm is the *trans* complex, while the 21.6 ppm signal belongs to the *cis* complex. The complexes having resonances at 23 ppm may coordinate in a bidentate fashion *via* P and O of the ligand. A P,N bidentate coordination is not likely due to the fact that the ^{15}N-shift differences for the PdL complex and free ligand was only 1–2 ppm (Fig. 3, spectrum a and b). The complex showing a ^{31}P-signal at 23.7 ppm is probably a kinetically formed complex, which on heating converts to a new complex having a ^{31}P-signal at 23.2 ppm.

Another observation worth mentioning is that the signals in both ^{1}H and ^{31}P NMR spectra are quite broad in the PdL complex compared to the PdL_2 complexes. If the PdL complex

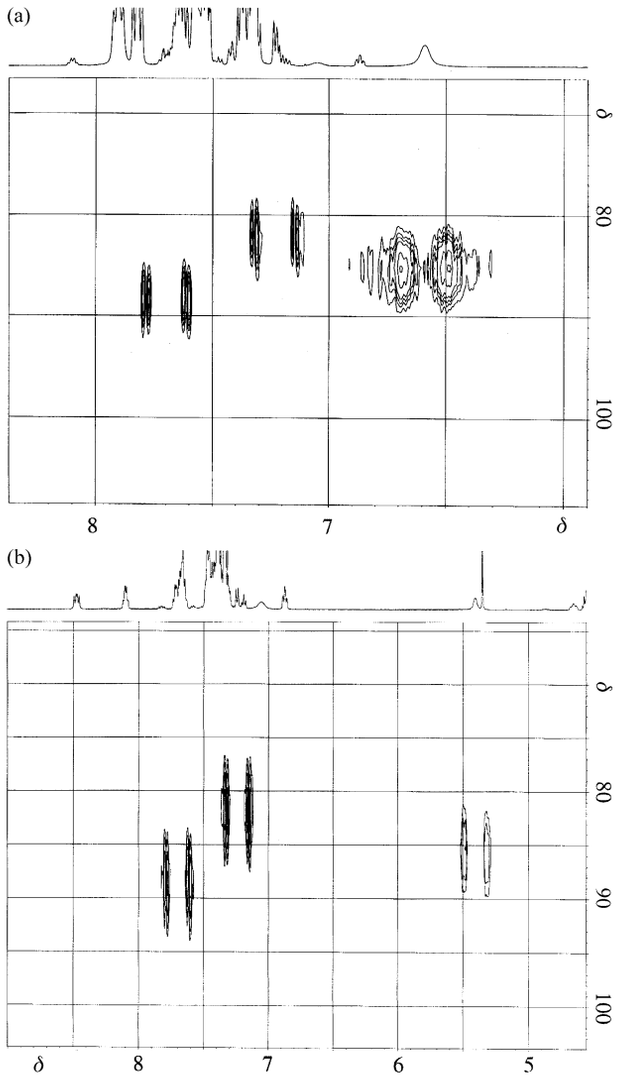


Fig. 3 ^{15}N–^{1}H-HMQC spectra of the complexes corresponding to spectra II (a) and IV (b) in Fig. 2.

coordinates in a bidentate fashion *via* the phosphorus and the nitrogen atoms, a five-membered ring would be formed, while coordination *via* the phosphorus and oxygen atoms would form a seven-membered ring. The broad signals and lack of well defined coupling patterns may be further evidence in favour of the seven-membered P,O coordination mode. One would expect a five-membered arrangement to have a more fixed structure leading to sharper lines in its NMR-spectrum than a seven-membered one.

Hydrosilylation

Asymmetric 1,4-hydrosilylation of dienes followed by oxidation may provide an interesting route to optically active allylic alcohols since it has been shown that oxidation of optically active silanes gives alcohols with complete retention of configuration.[29,30] A few such examples have been demonstrated although not with more substituted dienes.[3,4,6,8,10,13] During our studies in natural product synthesis we needed optically active cyclic allylic alcohols and we therefore reasoned that the mentioned route *via* allylic silanes could be useful. Moreover, the prognosis of chromatographic determination of the enantiomeric composition was judged better for the alcohols than for the corresponding silanes. Thus, we chose to measure the ees of the alcohols. Scheme 2 and Table 1 summarises the palladium catalysed hydrosilylation of cyclohexa-1,3-diene **5**, 1-butylcyclohexa-1,3-diene **8**, 2-methylcyclohexa-1,3-diene **11** and cyclopentadiene **14**. Several types of hydrosilanes were used but

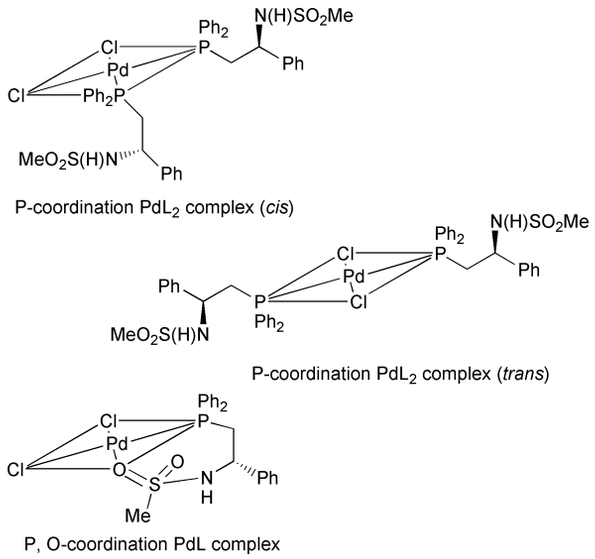
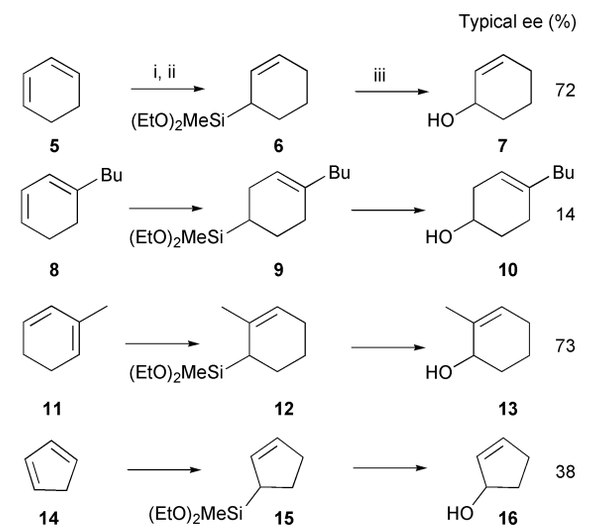


Fig. 4 Tentative coordination modes of complexes formed on mixing $PdCl_2(CH_3CN)_2$ and ligand **2**.



Scheme 2 *Reagents*: i) $HSiMeCl_2$, PdL 2 mol%; ii) EtOH, Et_3N; iii) KF, H_2O_2.

halogenated silanes were favoured due to the reported too weak coordination of trialkylsilanes to the Pd center to allow good yields.[31]

Our first choice was $HSiMe_2Cl$, which is easily handled and not very sensitive towards moisture and air. When we used this silane together with $PdCl_2(CH_3CN)_2$ and ligand **2** as catalyst in the hydrosilylation of cyclohexa-1,3-diene the yield was rather low, an average of 15% and maximum 25%, but the asymmetric induction was quite efficient resulting in the highest ee reported (84%) in asymmetric hydrosilylation of 1,3-dienes (entry 1). The low yield was probably due to the observed precipitation of Pd metal. In entries 2 and 3 a dihalogenated silane, $HSiMeCl_2$, was used. In these cases precipitation of Pd metal was not noticed. The yield was now over 80%, but the degree of asymmetric induction was lower than in entry 1, 62% ee at 20 °C and 72% ee at 0 °C. When the arsenic ligand **3** was used the ee was even lower, 40% (entry 5). No asymmetric induction was achieved when $HSiCl_3$ was used, entry 4. It has been reported that phenyl groups in the hydrosilane may play an important role in the induction.[6] We therefore tried $HSiPhCl_2$ but the ee now dropped to 34%, entry 6.

A considerable adverse effect on both the ee and yield resulted when 1-butylcyclohexa-1,3-diene was used. In fact, when ligand **2** was applied no conversion of the starting material was achieved even after 72 h (entry 7). On the other

Table 1 Results of the hydrosilylation–ethanolysis–oxidation sequence of dienes

Entry	Diene/ ligand [a]	Silane conditions [b]	Yields of alkoxysilanes (%)	Ee (%), [c] absolute configuration [d] of alcohols
1	**5/2**	$HSiMe_2Cl$	**6** <25	**7** 84 (*S*)
2	**5/2**	$HSiMeCl_2$/rt	**6** >80	**7** 62 (*S*)
3	**5/2**	$HSiMeCl_2$	**6** >80	**7** 72 (*S*)
4	**5/2**	$HSiCl_3$	**6** >80	**7** 0
5	**5/3**	$HSiMeCl_2$	**6** >80	**7** 40 (*S*)
6	**5/2**	$HSiPhCl_2$	**6** 60	**7** 34 (*S*)
7	**8/2**	$HSiMeCl_2$/50 h	**9** —	**10** —
8	**8/3**	$HSiMeCl_2$/50 h	**9** 70	**10** 14 [e]
9	**11/2**	$HSiMeCl_2$	**12** >85	**13** 73 (*S*)
10	**11/3**	$HSiMeCl_2$	**12** >85	**13** 53 (*S*)
11	**14/2**	$HSiMeCl_2$	**15** >85	**16** 37 (*S*)
12	**14/3**	$HSiMeCl_2$	**15** >85	**16** 28(*S*)

[a] Ligand in the Pd-complex used as the catalyst 2 mol%. [b] Reaction time: 40 h, 0 °C unless otherwise indicated. [c] Determined by GC analysis on an alpha-DEX column. [d] Determined by comparison of optical rotation data. [e] Not determined.

hand and quite unexpectedly, with the use of the Pd-complex of ligand **3** as catalyst, a good yield of **9** was obtained (70%), although the ee was only 14% (entry 8). This product seems to have been formed *via* a 1,2-addition, which is rather unusual for a Pd-catalysed hydrosilylation of 1,3-dienes where *syn* 1,4-addition is the normal outcome.[4,31] An alternative route would be a 1,4-addition followed by an isomerisation, which at this stage cannot be excluded.

A methyl substituent in the 2-position as for 2-methylcyclohexa-1,3-diene was better tolerated. In this case a 1,4-addition occurred and both the yield and degree of induction were relatively high, over 80% yield and 73% ee. Cyclopentadiene gave much lower ees, 37% and 28% for **2** and **3**, respectively, than with the similar ligand used by Achiwa *et al.*, see Fig. 1.[8,13]

Other metal complexes of ligands **2** and **3** based on $Rh_2Cl_2(COD)_2$, $PtCl_2Ph(CN)_2$ and $NiCl_2$ have so far given products with ees close to 0% in the reactions of cyclohexadiene, although the yields were fairly good, 50–70%.

Conclusion

The (β-*N*-sulfonylaminoalkyl)phosphine ligand **2** coordinated to Pd^{II} in several coordination modes: both by monodentate phosphorus coordination and by bidentate coordination *via* the phosphorus and oxygen atoms. The mixture of complexes formed by combining ligand **2** and $PdCl_2(CH_3CN)_2$ in the ratio 1 : 1 was used as catalyst in the asymmetric hydrosilylation of 1,3-dienes to give optically active allylic silanes, which were oxidised to give the corresponding optically active allylic alcohols. The presence of an aromatic substituent at the 2-position of the ligand backbone improved the ee compared with other ligand structures reported in the literature. Exchanging the phosphorus for arsenic in the ligands had a positive effect only for one substrate, entry 8. Further investigations regarding the hydrosilylation and its mechanistic aspects will be reported in due course.

Experimental

GC analyses were performed with either an alpha- or beta-DEX column (Supelco, 30 m × 0.25 mm id × 0.25 μm film thickness). NMR spectra were recorded at 400 MHz (Bruker DRX NMR spectrometer), unless otherwise stated. Chemical shift data are in ppm, referenced to external TMS for ^1H and ^{13}C, H_3PO_4 for ^{31}P and CH_3NO_2 for ^{15}N. The coupling constants were measured in Hertz. Optical rotations were measured with a Perkin-Elmer 241 LC polarimeter at 23 °C and are given in 10^{-1} deg cm^2 g^{-1}. Preparative chromatographic separations were performed on Matrex Amicon normal phase silica gel 60 (0.035–0.070 mm). Thin-layer chromatography was performed on Merck precoated TLC plates with Silica gel 60 F-254, 0.25 mm. After elution, the TLC plates were visualized with UV light followed by spraying with a solution of *p*-methoxybenzaldehyde (26 mL), glacial acetic acid (11 mL) concentrated sulfuric acid (35 mL), and 95% ethanol (960 mL) followed by heating. All solvents were dried over 4 Å MS for 24 h prior to use, unless otherwise mentioned. The molecular sieves were activated at 400 °C for 6 h and then allowed to cool under argon. Cyclopentadiene **14** was prepared *via* thermal cracking of the corresponding dimer. 2-Methylcyclohexa-1,3-diene **11**[32] and 1-butylcyclohexa-1,3-diene **8**[33] were synthesised as described by Bäckvall *et al.* All other reagents were used as received.

(*S*)-2-Methylsulfonylamino-2-phenyl-1-methylsulfonyloxyethane 1

A solution of methanesulfonyl chloride (2.92 g, 25.5 mmol) in CH_2Cl_2 (10 mL) was added to a mixture of (*S*)-(+)-2-phenylglycinol (1.0 g, 7.3 mmol, 98%) and triethylamine (2.65 g, 26.6 mmol) in CH_2Cl_2 (50 ml) at 0 °C under an argon atmosphere. The resulting solution was stirred at rt for 15 h whereafter saturated $NaHCO_3$ (30 ml) was added and the reaction mixture was worked up as follows: extraction with ethyl acetate (3 × 50 ml), washing of the collected organic extracts with brine (2 × 30 ml) followed by drying (Na_2SO_4), filtration and removal of the solvent under reduced pressure. The residue, a yellow oil was column chromatographed (SiO_2, heptane–ethyl acetate 1 : 1) to give the title compound (1.89 g, 88%) as a white solid; mp 105–107 °C; $[a]_D$+47.5 (*c* 0.3, $CHCl_3$); δ_H 2.76 (3 H, s), 3.02 (3 H, s), 4.46–4.34 (2 H, m), 4.91–4.81 (1 H, m), 5.64 (1 H, d, *J* 7.2), 7.46–7.33 (5 H, m); δ_C 37.9, 42.0, 56.9, 71.0, 127.0, 129.1, 129.3, 136.3; HRMS (FAB+): (M + H); Found: *m*/*z*, 294.0481. $C_{10}H_{15}O_5NS_2$ requires *m*/*z*, 294.0470.

General procedure for the synthesis of ligands 2 and 3

A solution of **1** (one equivalent) in THF (5 ml $mmol^{-1}$) was added to a solution of either $LiPPh_2$[13] or $LiAsPh_2$[18] (two equivalents) in THF (10 ml $mmol^{-1}$) at −30 °C under an argon atmosphere. The resulting mixture was stirred at −30 °C for 20 h whereafter saturated $NaHCO_3$ was added followed by extraction with degassed toluene (or with ethyl acetate in the synthesis of ligand **2** due to the low solubility of **2** in toluene). The collected organic extracts were washed with water and brine followed by drying (Na_2SO_4), filtration and removal of the solvent under reduced pressure. The residue, a slightly yellow oil, was column chromatographed (SiO_2, toluene–ethyl acetate 4 : 1) to give ligands **2** and **3** as white solids. All operations, including the chromatography, were performed under a nitrogen gas atmosphere and using degassed solvents and solutions in order to avoid oxidation. Instead of elemental analyses we used HRMS due to the high risk of oxidation of the ligands.

[(2*S*)-2-(Methylsulfonylamino)-2-phenylethyl]diphenylphosphine (+)-2. Yield 40%. δ_H 2.56 (3 H, s), 2.58 (1 H, ddd, *J* 13.4, 6.6 and 1.0), 2.68 (1 H, ddd, *J* 13.9, 8.6 and 1.2), 4.53 (1 H, m), 5.20 (1 H, d, *J* 5.4), 7.50–7.15 (15 H, m); δ_C 38.0 (d, *J* 14.5), 42.0, 56.4 (d, *J* 17.8), 126.9, 128.4, 128.9 (d, *J* 7), 129.2, 129.4 (d, *J* 7), 133.0 (d, *J* 15.1), 133.1 (d, *J* 15.1), 141.5 (d, *J* 5); δ_P −22.8; mp 163–165 °C; $[\alpha]_D$ +18.6 (*c* 0.22, $CHCl_3$); HRMS (FAB+) Found: *m*/*z*, 383.1113. $C_{21}H_{22}O_2NSP$ requires *m*/*z*, 383.1109.

[(2*R*)-2-(Methylsulfonylamino)-2-phenylethyl]diphenylphosphine (−)-2. The ligand was prepared in 40% yield according to the general procedure above except using (*R*)-**1** synthesised from (*R*)-phenylglycinol and had the same spectroscopic data as ligand (+)-**2**. The ligand was used in the preparation of a racemic mixture of ligand **2**. $[\alpha]_D$ −18.4 (*c* 0.27, $CHCl_3$).

[(2*S*)-2-(Methylsulfonylamino)-2-phenylethyl]diphenylarsine 3. Yield 50%. δ_H 2.50 (1 H, dd, *J* 12.7 and 7.4), 2.56 (3 H, s), 2.61 (1 H, dd, *J* 12.7 and 7.9), 4.66 (1 H, q, *J* 7.4), 4.97 (1 H, d, *J* 7.1), 7.55–7.24 (15 H, m); δ_C 37.4, 42.0, 57.2, 126.7, 128.5, 128.8, 128.9, 129.0, 129.1, 129.2, 133.1 and 133.3; mp 145–147 °C; $[\alpha]_D$ +19.7 (*c* 0.25, $CHCl_3$); HRMS (FAB+) Found: *m*/*z*, 427.05823. $C_{21}H_{22}O_2NSAs$ requires *m*/*z*, 427.05872.

(*R*)-*N*-(Methylsulfonyl)-2-phenylaziridine 4

NaH (30 mg, 0.75 mmol, 60% in mineral oil) was added to a solution of **1** (0.20 g, 0.68 mmol) in THF (10 ml) at rt. The reaction mixture was heated at 50 °C for 4 h. Aqueous work-up followed by filtration through a short plug of silica afforded 0.11 g, 82% of **4** as a slightly yellow solid. The compound had the same ^1H and ^{13}C spectroscopic data as previously reported.[34] Mp 43–45 °C; $[\alpha]_D$ −206.2 (*c* 0.29, $CHCl_3$); HRMS (FAB+) Found: *m*/*z*, 198.0581. $C_9H_{12}O_2NS$ (M + H) requires *m*/*z*, 198.0589.

Preparation of the catalyst

$PdCl_2(CH_3CN)_2$ (one equivalent) and the appropriate ligand (one equivalent) were mixed in benzene and heated at 50 °C for 1 h under an argon atmosphere. The solvent was evaporated under reduced pressure and the resulting yellow–orange powder was used as catalyst. The catalyst was not rigorously protected from contact with air.

General procedure for hydrosilylation of substrates 5, 8, 11 and 14 followed by ethanolysis and oxidation

Under an atmosphere of argon the catalyst (0.02 equivalents) was dissolved in a minimum amount of CH_2Cl_2. The substrate (one equivalent) was added and the mixture was cooled to 0 °C. $HSiCl_2Me$ (1.5 equivalents) was then added *via* a syringe and the mixture was allowed to stir for 40 h at 0 °C. The excess of solvent and hydrosilane was evaporated under reduced pressure and the resulting crude product was added to a solution of Et_3N in EtOH at 0 °C and stirred for 2 h. Pentane was added to the resulting mixture which was filtered through a small plug of silica to remove the precipitate. The filtrate was concentrated under reduced pressure to give the corresponding alkoxysilanes (for yields, see Table 1).

Oxidation of the alkoxysilanes was performed using a standard method: $KHCO_3$ (one equivalent), KF (one equivalent) and H_2O_2 (one equivalent) were added to the alkoxysilane in MeOH–THF 1 : 1 at room temperature and then the mixture was heated at reflux for 5 h. Aqueous work-up and filtration through a short plug of silica afforded the corresponding alcohols in 40–70% yield. The alcohols **7**, **10**, and **13** were analysed with respect to the ees using GLC analyses (alpha-DEX column). The ee of alcohol **16** and the absolute configuration of alcohols **7**, **13** and **16** were determined by comparison of optical rotation data known from the literature. Absolute configuration of **10** has not yet been determined.

3-(Diethoxymethylsilyl)cyclohexene **6**, cyclohex-2-en-1-ol **7**, 2-methylcyclohex-2-en-1-ol **13**, 3-(diethoxymethylsilyl)cyclopentene **15**, and cyclopent-2-en-1-ol **16** had NMR spectra in agreement with those reported.[13,35,36] 1-Butyl-4-(diethoxymethylsilyl)cyclohexene **9** was oxidized directly without work-up to the corresponding alcohol **10**.

4-Butylcyclohex-3-en-1-ol 10. $[\alpha]_D$ +12.5 (*c* 0.12, $CDCl_3$); δ_H 0.91 (1 H, t, *J* 7.2), 2.0–1.3 (13 H, m), 4.19 (1 H, m), 5.50 (1 H, m); δ_C 14.2, 19.3, 22.6, 28.7, 29.9, 32.2, 37.5, 66.1, 123.7, 142.9; HRMS (FAB+) Found: *m*/*z*, 154.1369. $C_{10}H_{18}O$ requires *m*/*z*, 154.1358.

3-(Diethoxymethylsilyl)-2-methylcyclohexene 12. δ_H 0.13 (s, 3 H), 1.22 (t, 3 H, *J* 7.0), 1.23 (t, 3 H, *J* 7.0), 1.99 (br m, 2 H), 1.76 (m, 3 H), 3.79 (q, 2 H, *J* 7.0), 3.80 (q, 2 H, *J* 7.0), 5.36 (m, 1 H); δ_C −5.0, 18.6, 21.6, 24.2, 24.9, 25.4, 29.6, 58.4, 120.7, 134.5; HRMS (FAB+) Found: *m*/*z*, 228.1544. $C_{12}H_{24}O_2Si$ requires *m*/*z*, 228.1546.

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