Efficient asymmetric hydrogenation of olefins with hydrazine-derived diphosphoramidites†

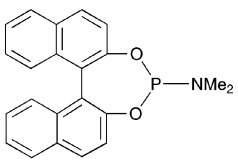
Luc Eberhardt,[a] Dominique Armspach,*[a] Dominique Matt,*[a] Benoît Oswald[b] and Loic Toupet[c]

Received 10th July 2007, Accepted 5th September 2007
First published as an Advance Article on the web 14th September 2007
DOI: 10.1039/b710576b

Enantiopure, BINOL-derived diphosphoramidites built upon an achiral *hydrazine* spacer are efficient ligands for the hydrogenation of 2-(acetylamino)-3-(aryl)-propenoic methyl esters. The activity and enantioselectivity of the hydrazine derivatives were shown to be markedly influenced by the nature of the two NR substituents, symmetrical but bulky R groups leading to the best results. A diphosphosphoramidite obtained from ^{t}BuHNNH^{t}Bu resulted in ee's as high as 95%. The present results contradict previous reports on "short" diphosphoramidites.

Introduction

Over the past decade, many studies have focused on the synthesis and use of BINOL-derived monophosphoramidites,[1–6] of which compound **1** is a prominent representative.[7] Compounds of this family are nowadays regarded as cheap, readily available and powerful ligands for asymmetric catalysis, notably for the rhodium-catalysed hydrogenation of prochiral olefins.[8]

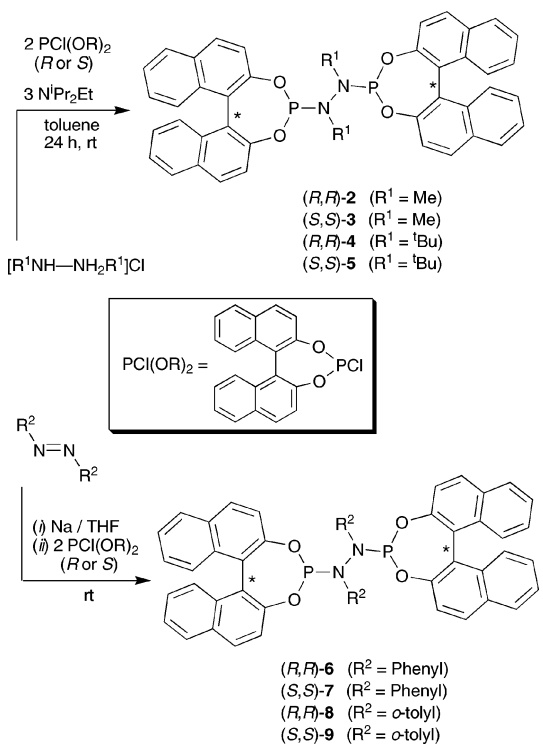


1

When used for the first time, their effectiveness was rather unexpected, their monodentate nature being considered a deficiency. Similarly, chiral diphosphoramidites built upon an achiral backbone were long considered unsuited for enantioselective catalysis but it was very recently found that such ligands may also lead to high ee's in asymmetric olefin hydrogenation, provided the phosphorus atoms are separated by a rather long spacer (for example –N(CH$_2$)$_n$N-where $n \geq 2$) which allows for a high degree of ligand flexibility.[9] Surprisingly, chiral diphosphoramidites with spacers having less than two carbon atoms have not been considered yet. We have therefore investigated the catalytic behaviour of some very short and incidentally rigid diphosphoramidites, namely built upon a *N*,*N*′-dialkyl or diaryl hydrazine unit. Their properties have been compared to those of related, mixed phosphoramidite–aminophosphine ligands, the synthesis of which is also reported herein.

Results and discussion

The diphosphoramidites **2–5** were prepared in *ca.* 30–40% yield by reacting a dialkylhydrazine hydrochloride, [R^{1}NH–NHR^1]·HCl, with 3 equiv. of diisopropylethylamine and 2 equiv. of the appropriate enantiopure chlorophosphite, *R*- or *S*-PCl(OR)$_2$ [(HOR)$_2$ = BINOL) (Scheme 1). The arylhydrazine derivatives **6–9** were obtained by reduction of an azobenzene with sodium in THF followed by reaction with the corresponding optically pure chlorophosphite (Scheme 1) (yields *ca.* 50%). We found that the procedure applied for the preparation of **2–5** could not be applied to arylhydrazines, since in the latter case no reaction occurred. The ^{31}P NMR spectra of all these compounds reveal the presence



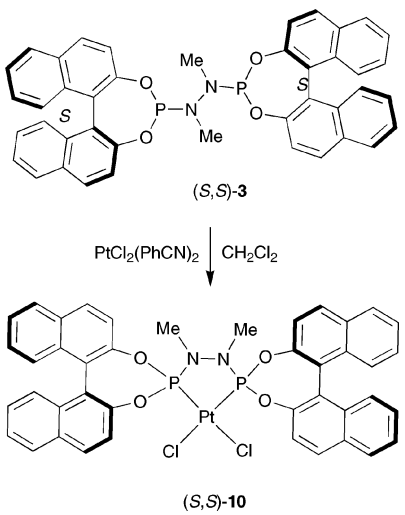
Scheme 1 Synthesis of the diphosphoramidites **2–9**.

[a]*Laboratoire de Chimie Inorganique Moléculaire, Institut de Chimie, UMR 7177 CNRS and Université Louis Pasteur, 1 rue Blaise Pascal, F-67008, Strasbourg, Cedex, France*
[b]*Genzyme Pharmaceuticals, Eichenweg 1, CH-4410, Liestal, Switzerland*
[c]*Groupe Matière Condensée et Matériaux, UMR 6626, Université de Rennes 1, Campus de Beaulieu, F-35042, Rennes, Cedex, France*

† CCDC reference number 294863. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710576b

in unequal amounts of two conformational isomers in solution, the signals appearing in the range 135–150 ppm.

The diphosphoramidites readily form chelate complexes. Thus, for example, when (*S*,*S*)-**3** was reacted with $[PtCl_2(PhCN)_2]$, complex (*S*,*S*)-**10** was formed quantitatively (Scheme 2). The NMR spectra, which are consistent with a C_2-symmetrical structure, reveal the presence of a single isomer in this case. The observed *J*(PPt) coupling constant, 5609 Hz, is typical for a platinum complex with two *cis*-disposed phosphoramidites.[10–12] The X-ray structure of (*S*,*S*)-**10** (Fig. 1) reveals a ligand bite angle of 84.4° and an almost planar PtP_2Cl_2 unit (maximum deviation from this plane: 0.093 Å). The five-membered chelate ring displays a classic open envelope shape, with the N(2) atom lying 0.38 Å above the coordination plane. As found in other five-membered PNNPM metallacycles, one of the two nitrogen atoms (N(2)) is planar, the other being slightly pyramidal.[13] Unsurprisingly for such a cycle, the two nitrogen atoms come close to the coordination plane, their distances to this plane being +0.26 Å and −0.38 Å, respectively. Thus, the position of the nitrogen atoms in (*S*,*S*)-**10** contrasts with that found in the *cis*-$[MX_2(monophosphoramidite)_2]$ complexes for which an X-ray structure was established.[11,14,15] In the latter the N atoms, which are located on both sides of the metal plane, are considerably more remote from this plane (>1 Å). Clearly, this minimizes the steric repulsions between the two phosphorus ligands. The dihedral angle between the naphthyl units linked to P(1) is 54.0°, whereas that between the naphthyls connected to P(2) is 56.1°.



Scheme 2 Quantitative synthesis of complex (*S*,*S*)-**10**.

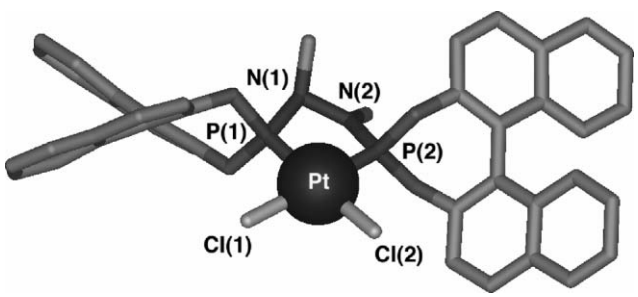


Fig. 1 X-Ray structure of complex (*S*,*S*)-**10**. Important distances (Å) and angles (°): P(1)N(1) 1.666(6); P(2)N(2) 1.660(7); N(1)N(2) 1.464(9); PtP(1) 2.174(2); PtP(2) 2.184(2); PtCl(1) 2.336(2); PtCl(2) 2.333(2). P(1)N(1)N(2)P(2) 42.3(6); P(1)PtP(2) 84.42(7).

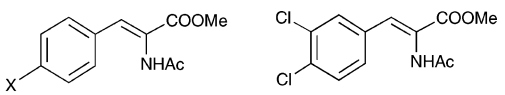
The phosphoramidites were assessed in the rhodium-catalysed hydrogenation of the 2-(acetylamino)-3-(aryl)-propenoic methyl esters **11a–d**. As precatalyst, a dichloromethane solution containing $[Rh(COD)_2]BF_4$ (COD = 1,5-cycooctadiene) and 1.1 equivalent of the bidentate ligand was used. As revealed by a separate study, the complex [Rh(COD){(*R*,*R*)-**2**}]BF_4 was formed as a single product when sub-stoichiometric amounts of the corresponding diphosphoramidite were used. Its ^{31}P NMR ($CDCl_3$) spectrum displays a doublet at 155.8 ppm (*J*(RhP) = 249.5 Hz). Using an excess of ligand afforded the by-product [Rh{(*R*,*R*)-**2**}$_2$](BF_4) (δ = 167.5 ppm; *J*(RhP) = 209.4 Hz), which turned out to be inactive. As shown in Table 1, all diphosphoramidites promoted fast olefin hydrogenation. As a general trend we found that alkyl hydrazines gave higher reaction rates than those with aryl substituents. Very fast hydrogenations, comparable to those observed by Feringa and Reetz for monophosphoramidites, were observed with the *tert*-butyl derivatives **4** and **5**.[4] The alkyl hydrazines **2–5**, as well as the phenyl hydrazines **6** and **7** gave

Table 1 Rh-catalysed asymmetric hydrogenation of 2-(acetylamino)-3-(aryl)-propenoic methyl esters with ligands **2–9**

Entry	Ar	Ligand	Time/h	Ee (%)[a]	Config.
1	Ph	(*R*,*R*)-**2**	1	85	*S*
2	(4-F)-Ph	(*R*,*R*)-**2**	1	81	*S*
3	(4-Cl)-Ph	(*R*,*R*)-**2**	1	83	*S*
4	(3,4-Cl)-Ph	(*R*,*R*)-**2**	1	86	*S*
5	Ph	(*S*,*S*)-**3**	1	85	*R*
6	(4-F)-Ph	(*S*,*S*)-**3**	1	82	*R*
7	(4-Cl)-Ph	(*S*,*S*)-**3**	1	83	*R*
8	(3,4-Cl)-Ph	(*S*,*S*)-**3**	1	84	*R*
9	Ph	(*R*,*R*)-**4**	0.25	91	*S*
10	(4-F)-Ph	(*R*,*R*)-**4**	0.25	92	*S*
11[b]	(4-F)-Ph	(*R*,*R*)-**4**	0.5	92	*S*
12[c]	(4-F)-Ph	(*R*,*R*)-**4**	2	95	*S*
13[d]	(4-F)-Ph	(*R*,*R*)-**4**	4	93	*S*
14	(4-Cl)-Ph	(*R*,*R*)-**4**	0.25	92	*S*
15	(3,4-Cl)-Ph	(*R*,*R*)-**4**	0.25	92	*S*
16[c]	Ph	(*S*,*S*)-**5**	2	93	*R*
17[c]	(4-F)-Ph	(*S*,*S*)-**5**	2	94	*R*
18[c]	(4-Cl)-Ph	(*S*,*S*)-**5**	2	93	*R*
19[c]	(3,4-Cl)-Ph	(*S*,*S*)-**5**	2	93	*R*
20	Ph	(*R*,*R*)-**6**	2	86	*S*
21	(4-F)-Ph	(*R*,*R*)-**6**	2	91	*S*
22	(4-Cl)-Ph	(*R*,*R*)-**6**	2	90	*S*
23	(3,4-Cl)-Ph	(*R*,*R*)-**6**	2	89	*S*
24	Ph	(*S*,*S*)-**7**	2	84	*R*
25	(4-F)-Ph	(*S*,*S*)-**7**	2	93	*R*
26	(4-Cl)-Ph	(*S*,*S*)-**7**	2	91	*R*
27	(3,4-Cl)-Ph	(*S*,*S*)-**7**	2	88	*R*
28	Ph	(*R*,*R*)-**8**	4	60	*S*
29	(4-F)-Ph	(*R*,*R*)-**8**	4	58	*S*
30	(4-Cl)-Ph	(*R*,*R*)-**8**	4	50	*S*
31	(3,4-Cl)-Ph	(*R*,*R*)-**8**	4	57	*S*
32	Ph	(*S*,*S*)-**9**	4	59	*R*
33	(4-F)-Ph	(*S*,*S*)-**9**	4	58	*R*
34	(4-Cl)-Ph	(*S*,*S*)-**9**	4	50	*R*
35	(3,4-Cl)-Ph	(*S*,*S*)-**9**	4	56	*R*

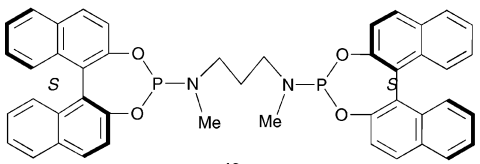
General conditions: $P(H_2) = 5$ bar; T = rt; solvent: CH_2Cl_2 [substrate : Rh : ligand = 100 : 1 : 1.1]; 100% conversion in all cases.[a] Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column. [b] Run carried out at 0 °C. [c] Run carried out at 1 bar. [d] Run carried out at 1 bar and 0 °C.

remarkably high ee's, lying in the range 84–95%. For comparison, with Reetz's longer ligand **12**, the hydrogenation of methyl 2-acetamido acrylate led to ee's no higher than 50%.[9] The best ee's were obtained with ligands **4** and **5**. Their efficiency possibly results from the steric pressure exerted by each of the butyl groups on the neighbouring binaphthyl moiety, which incidentally come closer to the coordinated substrate and therefore may increase the chiral induction. Almost as high ee's were observed with the phenylhydrazines **6** and **7**. However, with the *o*-tolyl derivatives **8** and **9**, the ee's drop to 50–60%. The origin of this effect is not known, but could be due to the restricted rotation of the *o*-tolyl rings about the corresponding N–C(tolyl) bonds, which therefore may lead to two isomeric complexes in solution, with (at least) one of them giving low ee's. Further, with **8** and **9**, the hydrogenation rates decreased by a factor of 2, suggesting that the methyl groups of the tolyl rings approach the apical coordination sites, thereby decreasing the ease of forming a rhodium hydrido species.



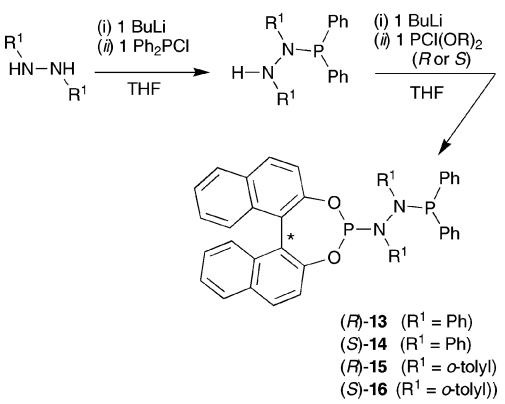
X = H, **11a**
X = F, **11b**
X = Cl,**11c**

11d



12

To confirm that phenyl substituents are preferable to *o*-tolyl ones, we also studied the mixed aminophosphine–phosphoramidite ligands **13–16**. These hybrid ligands were obtained in *ca.* 60% overall yield in two steps (Scheme 3) consisting of: (*i*) treatment of the appropriate hydrazine with 1 equiv. of *n*-BuLi and subsequent reaction with 1 equiv. of PPh_2Cl;[16] (*ii*) reaction of the resulting aminophosphine with 1 equiv. of *n*-BuLi, followed by reaction with *R*- or *S*-$PCl(OR)_2$ ([$(HOR)_2$ = BINOL). Both types of ligand led to fairly fast hydrogenation rates, although *ca.* 4 times lower than those observed with the symmetrical ligands described above. While the *o*-tolyl derivatives gave mediocre ee's (Table 2, entries 9–16), the enantioselectivities obtained with the phenyl



(*R*)-**13** (R^1 = Ph)
(*S*)-**14** (R^1 = Ph)
(*R*)-**15** (R^1 = *o*-tolyl)
(*S*)-**16** (R^1 = *o*-tolyl))

Scheme 3 Synthesis of the mixed aminophosphine–phosphoramidite ligands **13–16**.

Table 2 Rh-catalysed asymmetric hydrogenation of 2-(acetylamino)-3-(aryl)-propenoic methyl esters with ligands **13–16**

Entry	Ar	Ligand	Time/h	Ee (%)[a]	Config.
1	Ph	(*R*)-**13**	2	89	*S*
2	(4-F)-Ph	(*R*)-**13**	2	89	*S*
3	(4-Cl)-Ph	(*R*)-**13**	2	89	*S*
4	(3,4-Cl)-Ph	(*R*)-**13**	2	91	*S*
5	Ph	(*S*)-**14**	2	88	*R*
6	(4-F)-Ph	(*S*)-**14**	2	88	*R*
7	(4-Cl)-Ph	(*S*)-**14**	2	88	*R*
8	(3,4-Cl)-Ph	(*S*)-**14**	2	91	*R*
9	Ph	(*R*)-**15**	8	9	*S*
10	(4-F)-Ph	(*R*)-**15**	8	15	*S*
11	(4-Cl)-Ph	(*R*)-**15**	8	10	*S*
12	(3,4-Cl)-Ph	(*R*)-**15**	8	10	*S*
13	Ph	(*S*)-**16**	8	7	*R*
14	(4-F)-Ph	(*S*)-**16**	8	16	*R*
15	(4-Cl)-Ph	(*S*)-**16**	8	9	*R*
16	(3,4-Cl)-Ph	(*S*)-**16**	8	12	*R*

General conditions: $P(H_2) = 5$ bar; T = rt. solvent: CH_2Cl_2 [substrate : Rh : ligand = 100 : 1 : 1.1]; 100% conversion in all cases.[a] Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column.

analogues, 88–91%, were only marginally lower than with their symmetrical counterparts (Table 2, entries 1–8). These findings further corroborate recent results, which established that non C_2-symmetrical systems which combine a chiral monophosphane and an achiral one are not incompatible with high ee's.[17,18]

In summary, this study demonstrates that very short BINOL-derived diphosphoramidites can, like their longer counterparts, be used as efficient olefin hydrogenation catalysts. The activity and enantioselectivity of the hydrazine derivatives studied in this work is markedly influenced by the nature of the two N-substituents, symmetrical but bulky groups leading to the best results. Overall, this work poses the general question whether "short" diphosphoramidites bearing chiral phosphorus units other than 3,5-dioxa-4-phospha-cyclohepta-dinaphthyl groups are also suitable for efficient asymmetric catalysis.

Experimental

General procedures

All manipulations involving diphosphoramidites and aminophosphine–phosphoramidites were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded with Bruker FT Instruments (AC-200 and AC-300). ^1H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. Some compounds appear as a mixture of two isomers. The corresponding peak listings take into account both isomers. Mass spectra were recorded on a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2 as solvent. Specific rotations (units: deg cm^2 g^{-1})

were measured on a Perkin-Elmer 341 digital polarimeter with a 1 dm cell. The complex $[PtCl_2(PhCN)_2]$ was prepared according to a literature procedure.[19] The cationic complex $[Rh(COD)_2]BF_4$ was obtained by treatment of $[RhCl(COD)]_2$[20] with $AgBF_4$ in CH_2Cl_2–acetone, followed by reaction with 1,5-cyclooctadiene.

General procedure for the synthesis of diphosphoramidites 2–5

To a solution of the appropriate dialkylhydrazine hydrochloride in THF (50 cm^3) were added 3 equiv. of diisopropylethylamine and 2 equiv. of chloro-(*R* or *S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite in toluene (50 cm^3). The mixture was stirred overnight at room temperature before being filtered over flashed Al_2O_3. The solvent was removed *in vacuo* to afford the product as a white solid.

(*R*,*R*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-dimethylhydrazine (*R*,*R*)-2. (*R*,*R*)-**2** was obtained as described above from *N*,*N*′-dimethylhydrazine hydrochloride (0.435 g, 3.270 mmol) using N^iPr_2Et (1.269 g, 9.810 mmol, *ca.* 1.71 cm^3) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (2.294 g, 6.540 mmol). Yield: 0.820 g, 36%, mp 105–106 °C. Owing to the presence of two isomers (ratio 1 : 2), two sets of signals appear in the NMR spectra. In the following, all the peaks are listed in the order in which they appear. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.07$–7.91, 7.67–7.62 and 7.51–7.29 (3 m, 24 H, arom. H), 2.74 and 2.49 (two s, 6 H, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 149.38–130.95 (quat. C), 130.57–124.82 (arom. CH), 124.10–122.97 (quat. C), 122.30–121.35 (arom. CH), 35.14 (s, NCH_3 of major isomer), 34.93 (s, NCH_3 of minor isomer). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 146.5 (s, minor isomer), 142.2 (s, major isomer). $[\alpha]_D^{20} = -49.1$ (*c* 0.95 in toluene); *m*/*z* (EI) 688.23 (19%, M^+ requires 688.17). Found C 73.22, H 4.28, N 3.95. $C_{42}H_{30}N_2O_4P_2$ (688.65) requires C 73.25, H 4.39, N 4.07%.

(*S*,*S*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-dimethylhydrazine (*S*,*S*)-3. (*S*,*S*)-**3** was prepared according to the above procedure from *N*,*N*′-dimethylhydrazine hydrochloride (0.290 g, 2.180 mmol), using N^iPr_2Et (0.846 g, 6.540 mmol, *ca.* 1.14 cm^3) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.529 g, 4.360 mmol). Yield: 0.500 g, 33%, mp 105–106 °C. NMR as for (*R*,*R*)-**2**. $[\alpha]_D^{20}$ = + 50.2 (*c* 0.95 in toluene); *m*/*z* (EI) 688.30 (12%, M^+ requires 688.17). Found C 73.18, H 4.42, N 4.01. $C_{42}H_{30}N_2O_4P_2$ (688.65) requires C 73.25, H 4.39, N 4.07%.

(*R*,*R*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-di-*tert*-butylhydrazine (*R*,*R*)-4. (*R*,*R*)-**4** was obtained as described above from *N*,*N*′-di-*tert*-butylhydrazine hydrochloride (0.201 g, 1.111 mmol), using N^iPr_2Et (0.431 g, 3.333 mmol, *ca.* 0.59 cm^3) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.780 g, 2.222 mmol). Yield: 0.327 g, 38%, mp 121–122 °C. Owing to the presence of two isomers (ratio 1 : 5), two sets of signals appear in the NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.01$–7.86 and 7.71–7.58 (two m, 24 H, arom. H), 2.37 and 1.12 (two s, 18 H, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 152.88$–131.41 (quat. C), 130.99–124.60 (arom. CH), 123.83–122.23 (quat. C), 122.01–121.81 (arom. CH), 57.90 (s, *C*CH_3), 26.89 (s, C*C*H_3 of minor isomer), 24.06 (s, C*C*H_3 of major isomer). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 147.9 (s, minor isomer), 136.6 (s, major isomer). $[\alpha]_D^{20} = -70.3$ (*c* 1.05 in toluene); *m*/*z* (EI) 772.20 (39%, M^+ requires 772.26). Found C 74.72, H 5.41, N 3.52. $C_{48}H_{42}N_2O_4P_2$ (772.81) requires C 74.60, H 5.48, N 3.62%.

(*S*,*S*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-di-*tert*-butylhydrazine (*S*,*S*)-5. (*S*,*S*)-**5** was prepared as above using *N*,*N*′-di-*tert*-butylhydrazine hydrochloride (0.182 g, 1.007 mmol), N^iPr_2Et (0.390 g, 3.021 mmol, *ca.* 0.53 cm^3) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.706 g, 2.014 mmol). Yield: 0.160 g, 21%, mp 121–122 °C. NMR as for (*R*,*R*)-**4**. $[\alpha]_D^{20}$ = +69.2 (*c* 1.05 in toluene); *m*/*z* (EI) 772.35 (31%, M^+ requires 772.26). Found C 74.72, H 5.51, N 3.69. $C_{48}H_{42}N_2O_4P_2$ (772.81) requires C 74.60 H, 5.48, N 3.62%.

General procedure for the synthesis of diphosphoramidites 6–9

To a solution of 1 equiv. of the appropriate azoalkane in THF (50 cm^3) was added an excess of sodium cut into small pieces. After stirring for 72 h, the unreacted sodium was removed mechanically. The solution of the resulting disodium salt was then added *via* cannula over 1 h to a stirred THF solution of 2 equiv. of the chlorophosphite maintained at −78 °C. After 72 h, the solution was filtered through Al_2O_3. Evaporation of the solvent under reduced pressure gave a residue which was washed with *n*-heptane (100 cm^3). Drying *in vacuo* afforded a white solid.

(*R*,*R*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-diphenylhydrazine (*R*,*R*)-6. (*R*,*R*)-**6** was obtained as described above using azobenzene (1.152 g, 6.872 mmol), Na (0.632 g, 27.492 mmol) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (2.410 g, 6.872 mmol). Yield: 4.820 g, 52%, mp 134–136 °C. Owing to the presence of two isomers (ratio 1 : 5), two sets of signals appear in the NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.05–7.79, 7.67–7.64, 7.46–7.20 and 7.06–6.74 (4 m, 34 H, arom. H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 150.52–130.86 (quat. C), 130.75–124.81 (arom. CH), 124.48–124.41 (quat. C), 123.89–112.43 (arom. CH). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 142.8 (s, minor isomer), 140.1 (s, major isomer). $[\alpha]_D^{20}$ = −304.1 (*c* 5.4 in toluene); *m*/*z* (EI) 812.31 (29%, M^+ requires 812.20). Found C 76.85, H 4.23, N 3.45. $C_{52}H_{34}N_2O_4P_2$ (812.78) requires C 76.84, H 4.22, N 3.45%.

(*S*,*S*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-diphenylhydrazine (*S*,*S*)-7. (*S*,*S*)-**7** was obtained as described above from azobenzene (3.131 g, 17.180 mmol), Na (1.580 g, 68.730 mmol) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (12.051 g, 34.360 mmol). Yield: 7.401 g, 53%, mp 135–137 °C. NMR as for (*R*,*R*)-**6**. $[\alpha]_D^{20}$ = +305.9 (*c* 5.4 in toluene); *m*/*z* (EI) 812.17 (36%, M^+ requires 812.20). Found C 76.80, H 4.38, N 3.31. $C_{52}H_{34}N_2O_4P_2$ (812.78) requires C 76.84, H 4.22, N 3.45%.

(*R*,*R*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-(di-*o*-tolyl)hydrazine (*R*,*R*)-8. (*R*,*R*)-**8** was obtained as described above using azo(*o*-tolyl)benzene[21] (0.530 g, 2.520 mmol), Na (0.580 g, 25.206 mmol) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.768 g, 5.041 mmol). Yield: 1.039 g, 49%, mp 151–153 °C. Owing to the presence of two isomers (ratio 1 : 10), two sets of signals appear in the NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.00–7.92, 7.83–7.81, 7.56–7.07,

6.96–6.87 and 6.73–6.68 (5 m, 32 H, arom. H), 1.30 and 1.07 (two s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.70–111.98 (quat. C and arom. CH), 15.83 (s, Ar-*C*H$_3$). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 144.6 (s, minor isomer), 138.7 (s, major isomer). $[\alpha]_D^{20}$ = −370.6 (*c* 1.13 in toluene); *m*/*z* (EI) 840.33 (29%, M$^+$ requires 840.23). Found C 77.07, H 4.58, N 3.44. $C_{54}H_{38}N_2O_4P_2$ (840.84) requires C 77.13, H 4.56, N 3.33%.

(*S*,*S*)-*N*,*N*′-Bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-(di-*o*-tolyl)hydrazine (*S*,*S*)-9. (*S*,*S*)-**9** was prepared as above using azo(*o*-tolyl)benzene[21] (0.424 g, 2.016 mmol), Na (0.424 g, 20.165 mmol) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.414 g, 4.033 mmol). Yield: 0.848 g, 50%, mp 149–151 °C. NMR as for (*R*,*R*)-**8**. $[\alpha]_D^{20}$ = +372.0 (*c* 1.13 in toluene); *m*/*z* (EI) 840.28 (26%, M$^+$ requires 840.23). Found C 77.14, H 4.69, N 3.43. $C_{54}H_{38}N_2O_4P_2$ (840.84) requires C 77.13, H 4.56, N 3.33%.

Synthesis of the complexes

***cis*-Dichloro-{(*R*,*R*)-*N*,*N*′-bis(dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*,*N*′-dimethylhydrazine}platinum(II) (*S*,*S*)-10.** A solution of diphosphoramidite (*S*,*S*)-**3** (0.124 g, 0.180 mmol) in CH_2Cl_2 (8 cm^3) was added to a solution of $[PtCl_2(PhCN)_2]$ (0.085 g, 0.180 mmol) in CH_2Cl_2 (10 cm^3). The solution was stirred at room temperature for 24 h. The solution was then concentrated to *ca.* 5 cm^3, upon which *n*-pentane was added (30 cm^3). Cooling this solution down to −10 °C precipitated (*S*,*S*)-**10** as a white solid. Yield: 0.168 g, 98%, mp >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.07–7.95 (m, 6 H, arom. H), 7.82–7.65 (m, 6 H, arom. H), 7.61–7.16 (m, 12 H, arom. H), 2.74 (t, 6 H, NC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) (J_{CP} values were obtained from a decoupling experiment): δ = 147.58–147.33 (quat. C′s), 135.34 (d, J_{CP} = 18.6 Hz, arom. CH), 133.62 (d, J_{CP} = 5.6 Hz, arom. CH), 132.59 (s, quat. C), 132.43 (s, quat. C), 132.16 (s, arom. CH), 132.06 (s, quat. C), 131.88 (s, quat. C), 131.70 (s, quat. C), 131.15 (s, quat. C), 129.52 (s, arom. CH), 128.67 (s, arom. CH), 127.15 (d, J_{CP} = 14.3 Hz, arom. CH), 127.14 (s, arom. CH), 126.92 (s, arom. CH), 126.65 (s, arom. CH), 126.30 (d, J_{CP} = 13.0 Hz, arom. CH), 122.46 (s, arom. CH), 120.50 (s, arom. CH), 35.60 (s, N*C*H$_3$). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 108.8 (s with Pt satellites, $^1J_{PPt}$ = 5621.2 Hz). *m*/*z* (ESI-TOF) 918.07 (76%, (M − Cl)$^+$ requires 918.10). Found C 52.82, H 3.20, N 2.94. $C_{42}H_{30}Cl_2N_2O_4P_2Pt$ (954.63) requires C 52.84, H 3.17, N 2.93%.

[Rh(COD){(*R*,*R*)-2}]BF$_4$. A solution of (*R*,*R*)-**2** (0.040 g, 0.060 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a solution of $[Rh(COD)_2]BF_4$ (0.024 g, 0.060 mmol) in CH_2Cl_2 (5 cm^3). After stirring for 1 h, the mixture was filtered over Celite. Evaporation of the solvent under reduced pressure afforded [Rh(COD){(*R*,*R*)-**2**}]BF_4. Yield: 0.090 g, 97%, mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.14 (d, ^3J = 8.9 Hz, 2 H, arom. H), 8.04–7.95 (m, 6 H, arom. H), 7.74 (d, ^3J = 8.8 Hz, 2 H, arom. H), 7.57–7.49 (m, 4 H, arom. H), 7.40–7.28 (m, 10 H, arom. H), 5.89 (br s, 2 H, H of COD), 5.60 (br s, 2 H, H of COD), 2.76 (t, 6 H, NC*H*$_3$), 2.60–2.27 (m, 8 H, H of COD). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 155.8 (d, $^1J_{PRh}$ = 249.4 Hz). Found C 60.92, H 4.29, N 2.83. $C_{50}H_{42}BF_4N_2O_4P_2Rh$ (986.54) requires C 60.87, H 4.29, N 2.84%.

Addition of 2.2 equiv. of (*R*,*R*)-**2** to $[Rh(COD)_2]BF_4$ afforded a mixture of [Rh(COD){(*R*,*R*)-**2**}]BF_4 and [Rh{(*R*,*R*)-**2**}$_2$]BF_4 in a ratio of *ca.* 1 : 9. The latter complex is characterized by a doublet at 167.5 ppm ($^1J_{RhP}$ = 209.4 Hz).

***N*-Diphenylphosphino-*N*,*N*′-diphenylhydrazine.** This compound was prepared according to a procedure reported in the literature.[22] *m*/*z* (ESI-TOF) 369.27 (82%, (M + H)$^+$ requires 369.15). Found C 78.18, H 5.80, N 7.59. $C_{24}H_{21}N_2P$ (368.41) requires C 78.24 H 5.75, N 7.60%.

***N*-Diphenylphosphino-*N*,*N*′-di(*o*-tolyl)hydrazine.** A hexane solution of *n*-BuLi (1.6 M, 2.10 cm^3) was added to a stirred solution of 1,2-di(*o*-tolyl)hydrazine[21] (1.070 g, 5.040 mmol) in toluene (15 cm^3) at 0 °C. After stirring for 10 min, a solution of Ph_2PCl (1.112 g, 5.040 mmol, *ca.* 0.90 cm^3) in toluene (10 cm^3) was added dropwise. The reaction mixture, which turned orange was stirred for a further 30 min at room temperature. It was then washed with water to remove LiCl. The solution was dried over $MgSO_4$, then concentrated to *ca.* 20%. Addition of EtOH (20 cm^3) produced colorless crystals after 2 h. Yield: 1.000 g, 50%, mp 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.54–7.51 (m, 4 H, arom. H), 7.50–7.35 (m, 6 H, arom. H), 7.26–7.22 (m, 2 H, arom. H), 7.02–6.96 (m, 2 H, arom. H), 6.91 (d, ^3J = 1 Hz, arom. H), 6.73 (d, ^3J = 1 Hz, arom. H), 6.67–6.59 (m, 2 H, arom. H), 5.40 (br s, 1 H, NH), 2.61 (s, 3 H, ArC*H*$_3$), 1.84 (s, 3 H, ArC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 147.75–112.14 (quat. C and arom. CH), 19.48 (d, $^4J_{CP}$ = 12.4 Hz, Ar*C*H$_3$), 16.93 (s, Ar*C*H$_3$). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 66.2 (s). *m*/*z* (ESI-TOF) 397.17 (69%, (M + H)$^+$ requires 397.18). Found C 78.57, H 6.51, N 6.96. $C_{26}H_{25}N_2P$ (396.46) requires C 78.77, H 6.36, N 7.07%.

General procedure for the synthesis of mixed phosphoramidite–aminophosphines 13–16

To a solution of 1 equiv. of the appropriate *N*-diphenylphosphino-*N*,*N*′-diarylhydrazine in THF (50 cm^3) at −78 °C was added 0.95 equiv. of *n*-BuLi (solution in hexane). After stirring for 20 min, this dark blue mixture was added slowly *via* cannula to a stirred solution of 1 equiv. of chlorophosphite. The mixture was stirred overnight at room temperature before being filtered over flashed Al_2O_3. The solvent was removed *in vacuo* to afford the product as a white solid.

(*R*)-*N*-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*′-diphenylphosphino-*N*,*N*′-diphenylhydrazine (*R*)-13. (*R*)-**13** was obtained as described above using *N*-diphenylphosphino-*N*,*N*′-diphenylhydrazine (0.685 g, 1.859 mmol), *n*-BuLi (1.6 M, 1.16 cm^3) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.652 g, 1.859 mmol). Yield: 0.444 g, 35%, mp 108–110 °C. Owing to the presence of two isomers (ratio 1 : 1), two sets of signals appear in the NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.18–7.83 (m, 4 H, arom. H), 7.67–7.05 (m, 22 H, arom. H), 6.98–6.53 (m, 6 H, arom. H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.84–135.41 (quat. C), 134.91–116.89 (quat. C and arom. CH). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 141.6 (d, $^3J_{PP}$ = 7.4 Hz, isomer 1), 138.7 (d, $^3J_{PP}$ = 14.8 Hz, isomer 2), 68.8 (d, $^3J_{PP}$ = 14.8 Hz, isomer 2), 64.8 (d, $^3J_{PP}$ = 7.4 Hz, isomer 1). $[\alpha]_D^{20}$ = −486.4 (*c* 0.79 in toluene); *m*/*z* (EI) 682.32 (25%, M$^+$ requires

682.19). Found C 77.66, H 4.98, N 4.25. $C_{44}H_{32}N_2O_2P_2$ (682.68) requires C 77.41, H 4.72, N 4.10%.

(*S*)-*N*-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*′-diphenylphosphino-*N*,*N*′-diphenylhydrazine (*S*)-14. (*S*)-**14** was prepared according to the above procedure using *N*-diphenylphosphino-*N*,*N*′-diphenylhydrazine (1.310 g, 3.556 mmol), *n*-BuLi (1.6 M, 2.1 cm^3) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (1.247 g, 3.556 mmol). Yield: 0.700 g, 29%, mp 108–110 °C. NMR as for (*R*)-**13**. $[\alpha]_D^{20} = +485.7$ (*c* 0.79 in toluene); *m*/*z* (ESI-TOF) 683.01 (19%, $(M + H)^+$ requires 683.20). Found C 77.66, H 4.98, N 4.25. $C_{44}H_{32}N_2O_2P_2$ (682.68) requires C 77.41, H 4.72, N 4.10%.

(*R*)-*N*-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*′-diphenylphosphino-*N*,*N*′-di(*o*-tolyl)hydrazine (*R*)-15. (*R*)-**15** was obtained as described above using *N*-diphenylphosphino-*N*,*N*′-di(*o*-tolyl)hydrazine (0.310 g, 0.782 mmol), *n*-BuLi (1.6 M, 0.46 cm^3) and chloro-(*R*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.274 g, 0.782 mmol). Yield: 0.211 g, 40%, mp 119–121 °C. Owing to the presence of two isomers (ratio 1 : 3), two sets of signals appear in the NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01–7.74, 7.66–7.02, 6.94–6.86 and 6.72–6.54 (4 m, 30 H, arom. H), 2.71 and 1.05 (two s, $ArCH_3$, isomer 1), 2.57 and 1.68 (two s, $ArCH_3$, isomer 2). ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 144.56 and 66.50 (two s, major conformer), 138.72 and 67.16 (two s, minor conformer). $[\alpha]_D^{20} = -517.8$ (*c* 0.86 in toluene); *m*/*z* (EI) 710.13 (33%, M^+ requires 710.23). Found C 77.69, H 5.09, N 4.08. $C_{46}H_{36}N_2O_2P_2$ (710.74) requires C 77.74, H 5.11, N 3.94%.

(*S*)-*N*-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yl)-*N*′-diphenylphosphino-*N*,*N*′-di(*o*-tolyl)hydrazine (*S*)-16. (*S*)-**16** was prepared according to the above procedure using *N*-diphenylphosphino-*N*,*N*′-di(*o*-tolyl)hydrazine (0.530 g, 1.337 mmol), *n*-BuLi (1.6 M, 0.48 cm^3) and chloro-(*S*)-2,2′-*O*,*O*′-(1,1′-binaphthyl)phosphite (0.469 g, 1.337 mmol). Yield: 0.334 g, 37%, mp 120–122 °C. NMR as for (*R*)-**15**. $[\alpha]_D^{20} = +519.2$ (*c* 0.86 in toluene); *m*/*z* (EI) 710.26 (27%, M^+ requires 710.23). Found C 77.72, H 5.13, N 4.03. $C_{46}H_{36}N_2O_2P_2$ (710.74) requires C 77.74, H 5.11, N 3.94%.

General procedure for asymmetric hydrogenation and determination of enantiomeric excesses

To a solution of $[Rh(COD)_2]BF_4$ (1 equiv.) in CH_2Cl_2 (10 mL) was added a solution of the ligand (1.1 equiv.) in CH_2Cl_2 (10 mL), and the resulting mixture was stirred for 30 min. before being used in the catalytic run. The solution was introduced with a syringe into a 100 mL glass-lined, stainless steel autoclave containing a magnetic stirring bar and the substrate (2.5 mmol). Hydrogen pressure (1 or 5 bar) was then applied. The runs were carried out at room temperature or 0 °C. At the end of the catalytic run, the autoclave was depressurized and the mixture was passed through a short silica column to remove the catalyst. Conversions were monitored by ^{1}H NMR. Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column.

X-Ray crystallography

Crystal data for complex (*S*,*S*)-10. Crystals of (*S*,*S*)-**10** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. $PtC_{42}H_{30}Cl_2N_2O_4P_2 \cdot 2H_2O$, M = 990.64, orthorhombic, $P2_12_12_1$, a = 11.1024(4), b = 13.8168(5), c = 26.9261(9) Å, V = 4130.5(3) $Å^3$, $Z = 4$, $D_x = 1.593$ Mg m^{-3}, λ(Mo-Kα) = 0.71073 Å, $\mu = 36.52$ cm^{-1}, $F(000) = 1960$, $T = 295(1)$ K. The sample (0.25 × 0.22 × 0.22 mm) was studied on a Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo-Kα radiation. Data collection was carried out using CrysAlis.[23] 30171 Reflections were collected ($1.76 < \theta < 27.54°$), of which 7755 had $I > 2.0\ \sigma(I)$. The structure was solved with SIR-97[24] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms could be localized on a Fourier difference map. The whole structure was refined with SHELXL-97.[25] Hydrogen atoms were included and refined using a riding mode in SHELX-97. The compound crystallizes with two molecules of water. Final results: $R_1 = 0.042$, $wR_2 = 0.114$, goodness of fit 1.067, 496 parameters, residual electron density: min./max. = −1.15/2.35. Flack parameter: −0.005(7).†

Acknowledgements

Genzyme Pharmaceuticals is gratefully acknowledged for financial support. We thank Johnson Matthey for a generous loan of rhodium and platinum salts.

References

1 M. Van Den Berg, A. J. Minnaard, E. P. Schudde, J. van Esch, A. H. M. de Vries, J. G. de Vries and B. L. Feringa, *J. Am. Chem. Soc.*, 2000, **122**, 11539.
2 M. Van Den Berg, R. M. Haak, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries and B. L. Feringa, *Adv. Synth. Catal.*, 2002, **344**, 1003.
3 M. Van Den Berg, A. J. Minnaard, R. M. Haak, M. Leeman, E. P. Schudde, A. Meetsma, B. L. Feringa, A. H. M. de Vries, C. E. P. Maljaars, C. E. Willans, D. Hyett, J. A. F. Boogers, H. J. W. Henderickx and J. G. de Vries, *Adv. Synth. Catal.*, 2003, **345**, 308.
4 H. Bernsmann, M. Van Den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. de Vries and B. L. Feringa, *J. Org. Chem.*, 2005, **70**, 943.
5 D. J. Ager, A. H. M. de Vries and J. G. de Vries, *Platinum Met. Rev.*, 2006, **50**, 54.
6 R. Hoen, T. Tiemersma-Wegman, B. Procuranti, L. Lefort, J. G. de Vries, A. J. Minnaard and B. L. Feringa, *Org. Biomol. Chem.*, 2007, **5**, 267.
7 R. Hulst, N. K. de Vries and B. L. Feringa, *Tetrahedron: Asymmetry*, 1994, **5**, 699.
8 M. T. Reetz, J.-A. Ma and R. Goddard, *Angew. Chem., Int. Ed.*, 2005, **44**, 412.
9 M. T. Reetz, G. Mehler and O. Bondarev, *Chem. Commun.*, 2006, 2292.
10 M. L. Clarke, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 2003, **22**, 19.
11 L. Eberhardt, D. Armspach, D. Matt, L. Toupet and B. Oswald, *Eur. J. Inorg. Chem.*, 2007, 4153.
12 L. Eberhardt, D. Armspach, D. Matt, L. Toupet and B. Oswald, *Eur. J. Org. Chem.*, 2007, DOI: 10.1002/ejoc.200700533.
13 A. M. Z. Slawin, M. Wainwright and J. D. Woolins, *J. Chem. Soc., Dalton Trans.*, 2002, 513.
14 G. Francio, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi and A. Tiripicchio, *Eur. J. Inorg. Chem.*, 1999, 1219.
15 I. S. Mikhel, G. Bernadinelli and A. Alexakis, *Inorg. Chim. Acta*, 2006, **359**, 1826.

16 Y. V. Fedotova, A. N. Kornev, V. V. Sushev, Y. A. Kursky, T. G. Mushtina, N. P. Makarenko, G. K. Fukin, G. A. Abakumov, L. N. Zakharov and A. L. Rheingold, *J. Organomet. Chem.*, 2004, **689**, 3060.
17 E. Cesarotti, S. Araneo, I. Rimoldi and S. Tassi, *J. Mol. Catal. A: Chem.*, 2003, **204–205**, 211.
18 M. T. Reetz, G. Mehler and A. Meiswinkel, *Tetrahedron: Asymmetry*, 2004, **15**, 2165.
19 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, 1973.
20 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
21 J. M. Khurana and S. Singh, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1893.
22 Y. V. Fedotova, A. N. Kornev, V. V. Sushev, Y. A. Kursky, T. G. Mushtina, N. P. Makarenko, G. K. Fukin, G. A. Abakumov, L. N. Zakharov and A. L. Rheingold, *J. Organomet. Chem.*, 2004, **689**, 3060.
23 O. D. L. CrysAlis, *RED software, version 1.171.29.9*.
24 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1998, **31**, 74.
25 G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, Univ. of Göttingen, Germany, 1997.

