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Chiral bidentate aminophosphine ligands: synthesis, coordination chemistry and asymmetric catalysis

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Chiral aminophosphines $Ph_2PN(R)(CH_2)_nN(R)PPh_2$ **1–4** [$n = 2$, R = CH(CH$_3$)(Ph) **1**; $n = 3$, R = CH(CH$_2$CH$_3$)(Ph) **2**, $n = 2$, R = CH(CH$_3$)(1-naphthyl) **3**; $n = 2$, R = CH(CH$_3$)(C$_6$H$_{11}$) **4**] were synthesized by the reaction of $ClPPh_2$ with the appropriate easily accessible enantiopure amine building blocks. For compounds **1** and **2**, the corresponding selenides **5** and **6** were prepared to determine the electronic character of the phosphine moieties. By reaction of **1** with either $PdCl_2$(cod) or PdCl(CH$_3$)(cod) the *cis*-complexes **7** and **8** were obtained. The molecular structure for complex **7**, *cis*-[$PdCl_2$(**1**)], was determined by X-ray crystallography. Reaction of $PtCl_2$(cod) with **1** or **2** yielded the corresponding monomeric *cis*-isomers **9** and **10**. The rhodium derivative [RhCl(CO)(**1**)] (**11**) was obtained as a mixture of *cis* and *trans*-isomers. Preliminary results in the rhodium catalyzed hydroformylation of styrene and vinyl acetate, with ee's up to 51% and high regioselectivities, showed the potential of these chiral aminophosphines for homogeneous catalysis.

Introduction

The coordination chemistry of diphosphine ligands with a variety of transition metals is widely studied and several types of coordination modes have been established over the years.[1] Numerous families of novel (chiral) ligands have been synthesized,[2] with emphasis on *cis*-chelating properties to form monomeric metal complexes. Besides ligand design based on desired behaviour towards transition metal complexes and the catalytic activity of such systems, the approach of modular design and availability of cheap resources has gained significant importance. We have previously shown the transformation of the bulk chemical Bisphenol A into diphosphine ligands, suited for complexation with transition metals.[3] Especially in asymmetric catalysis such a modular approach is highly desirable, since full understanding of the factors governing the enantioselectivity during the catalytic cycle is often lacking and the availability of tunable ligand families would greatly enhance the generation of data leading to new insight. We have therefore set out to explore new and hitherto neglected chiral auxiliaries such as chiral amines as functional groups.

The synthesis and limited use of heteroatom substituted phosphines (Fig. 1) and their transition metal complexes has received quite some attention again lately,[4–6] due to the search for new structural diversity and catalytic activities. However, little has appeared on the use of *chiral* amines as backbone structures for phosphorus ligands, although some reports described their application in the asymmetric *hydrogenation* of various substrates.[7–10] Wills *et al.* have described the synthesis and application of the so-called ESPHOS ligand system (Fig. 1) in the rhodium catalyzed asymmetric hydroformylation of vinyl acetate, with high enantioselectivities.[11] Chiral amines are widely available nowadays due to heavy industrial investments in commercially viable synthetic intermediates and specialty chemicals. We were therefore interested to investigate their applicability for the synthesis of novel aminophosphine ligands.

Here we report on the synthesis of the chiral bidentate aminophosphine ligands **1–4** (Fig. 2) together with a study of their coordination chemistry towards the transition metals palladium, platinum and rhodium and preliminary results in rhodium catalyzed asymmetric hydroformylation.

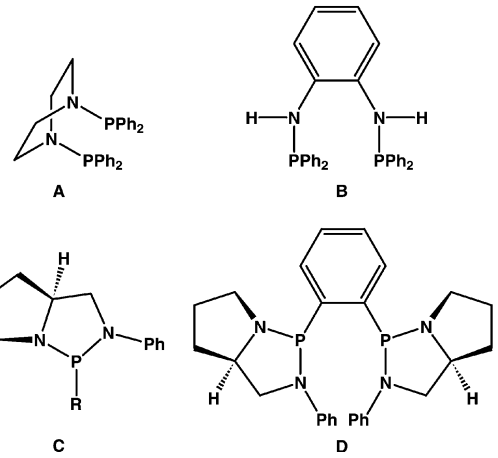
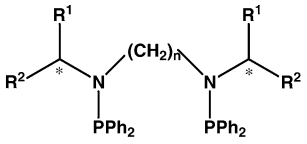


Fig. 1 Representation of ligand systems based on substituted heteroatoms: piperazine (**A**) and 1,2-diaminobenzene (**B**), developed by the group of Woollins[4] and the SEMI-ESPHOS (**C**) and ESPHOS compounds (**D**) reported by Wills *et al.*[11]



ligand	n	R^1	R^2
1	2	Me	Ph
2	3	Et	Ph
3	2	Me	Np
4	2	Me	Cy

Fig. 2 Bis(aminophosphine) ligands; Np = 1-naphthyl; Cy = cyclohexyl.

Results and discussion

Preparation of diphosphines 1–4

Compounds **1–3** were made in a two-step procedure starting from the primary amine and a dihaloalkane (Scheme 1). The first step involved nucleophilic S_N2 substitution on the dihaloalkane to form two secondary amines. By reaction with $ClPPh_2$ in the presence of NEt_3, the corresponding diphosphines were obtained in good overall yields. Compounds **1–3** were fully

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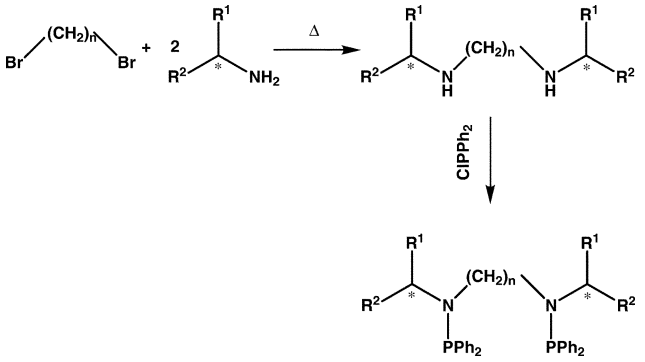
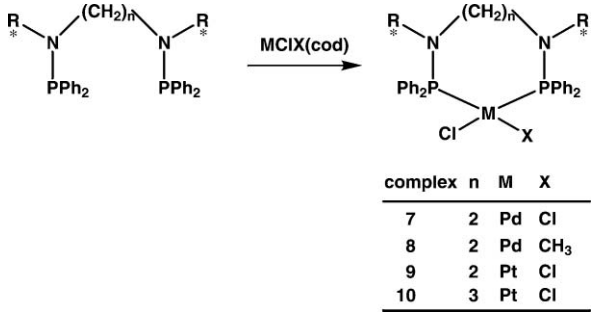


Scheme 1 Generic synthetic route, illustrative for compounds **1–3**.



complex	n	M	X
7	2	Pd	Cl
8	2	Pd	CH_3
9	2	Pt	Cl
10	3	Pt	Cl

Scheme 2 Preparation of Pd and Pt complexes **7–10**.

characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as well as by elemental analysis, see the Experimental section for details.

For compound **4** an alternative synthetic methodology was devised, to avoid tedious destillation of unreacted amine starting material during purification of the desired product. Condensation of glyoxal with two equivalents of the appropriate chiral amine gave the corresponding diimine in high yield. Reduction of the imine with $LiAlH_4$ and subsequent reaction of the amino-functionalities with $ClPPh_2$ in the presence of NEt_3 gave the aminophosphine **4** in good yield. Washing with acetonitrile afforded the pure compound without the need for further purification. Also this new compound was fully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as well as by elemental analysis.

The ^{31}P NMR spectra of all compounds **1–4** showed one singlet with a chemical shift of around δ 50 ppm, significantly downfield from a triarylphosphine such as PPh_3. In the ^{1}H NMR spectra a distinctive pattern, including P–H coupling, was present for the chiral carbon moiety adjacent to the nitrogen atoms. In the ^{13}C NMR spectra through-space P–C coupling was observed. In short, the geometry around the nitrogen atoms was trigonal planar, implying that the nitrogen atoms are sp^2 hybridized, which indicates a significant degree of P–N π-bonding.[5] This is currently being further investigated by theoretical calculations, combined with experimental data, including the molecular structure of **4**.[12]

A simple and efficient method to evaluate the σ-donor character and hence the basicity of a phosphine moiety is to measure the magnitude of the coupling constant $^{1}J_{Se-P}$ in the ^{31}P NMR spectrum of the ^{77}Se isotopomer of the corresponding diphenylphosphine selenide.[13,14] An increase in the coupling constant is indicative of increasing s-character of the phosphorus lone-pair and hence of lower basicity. Compounds **1** and **2** were reacted with elemental selenium for 30 min in toluene at 70 °C. In the ^{31}P NMR spectrum of the corresponding selenides **5** and **6** in CH_2Cl_2, a singlet was found at δ 70.3 ppm and 69.1 ppm, respectively. Both signals were flanked by two ^{77}Se-satellites, and the coupling constants J_{Se-P} were 752 Hz and 750 Hz, respectively, showing that both ligands are essentially identical in their electronic character of the phosphorus moieties. These values are in agreement with the few available literature data on aminophosphines.[4a,5] The J_{Se-P} values are higher than for corresponding diarylphosphines, which implies lower basicity of the phosphine moiety, due to higher electronegativity of the adjacent nitrogen atom.[15]

The coordination behaviour of these chiral amine-based diphosphine ligands was studied with the representative ligand **1** towards palladium, platinum and rhodium precursors.

Preparation of palladium(II) complexes 7 and 8

Reaction of $[PdCl_2(cod)]$ with **1** for 2 h at room temperature resulted in a yellow solid compound, complex (**7**) (Scheme 2), for which the ^{31}P NMR spectrum showed a singlet at δ 87.3 ppm. Little structural information can be deduced from this chemical shift however. The ligand backbone skeleton (*viz.* size, flexibility) is analogous to the well studied ligand dppb, for which only the *cis*-isomer is reported.[16]

To further elucidate the structure of complex **7**, ligand **1** was reacted with $[PdCl(CH_3)(cod)]$ (Scheme 2) to give complex **8** as a micro-crystalline yellow solid. Characterization of this species in solution by ^{31}P NMR spectroscopy showed an AB system with two doublets at δ 91.3 and 81.0 ppm with coupling constants J_{P-P} of 28 Hz, while in the ^{1}H NMR spectrum a doublet of doublets was present at δ 0.47 ppm for the methyl ligand at palladium. Both observations clearly indicate the sole formation of *cis*-$[PdCl(CH_3)(\mathbf{1})]$,[17] with the downfield doublet at δ 91.3 ppm corresponding to the phosphine *trans* to chloride and the upfield doublet at δ 81.0 ppm to the phosphine *trans* to the methyl ligand. Furthermore, in the ^{1}H NMR spectrum two triplets at δ 4.26 and 4.41 ppm were found for the inequivalent CH_2-groups in the backbone. Both complexes **7** and **8** were surprisingly very soluble in acetonitrile, but we could obtain single crystals by slow diffusion of hexane into a CH_2Cl_2 solution of complex **7**. The molecular structure of this compound was unequivocally determined by X-ray crystallography. Fig. 3 shows the structure of **7** together with data on selected bond lengths and angles. The asymmetric unit cell contained two independent molecules that differed mainly in the orientation of the phenyl rings on

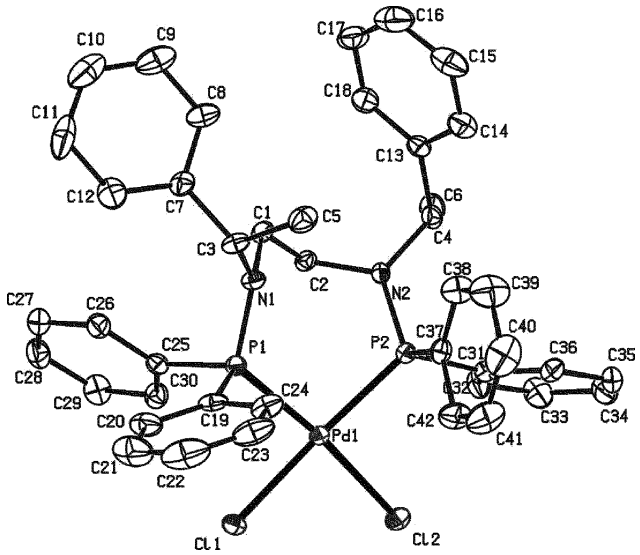


Fig. 3 ORTEP representation of the first of two independent molecules of complex **7**, *cis*-$[PdCl_2(\mathbf{1})]$. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd_1–P_1 2.2681(6), Pd_1–P_2 2.2549(5), Pd_1–Cl_1 2.3507(5), Pd_1–Cl_2 2.3489(6), N_1–P_1 1.6811(18), N_2–P_2 1.6591(19), N_1–C_1 1.460(3), N_2–C_2 1.470(3), N_1–C_3 1.499(3), N_2–C_4 1.504(3), C_1–C_2 1.506(3), N_1–N_2 3.089(2), P_1–P_2 3.3808(8); P_1–Pd_1–P_2 96.74(2), Cl_1–Pd_1–Cl_2 90.19(2), P_1–Pd_1–Cl_1 83.36(2), P_1–Pd_1–Cl_2 173.41(2), P_2–Pd_1–Cl_1 173.66(2), Pd_1–P_1–N_1 120.84(7), Pd_1–P_2–N_2 115.31(6), P_1–N_1–C_1 116.56(14), P_2–N_2–C_2 119.39(14), P_1–N_1–C_3 125.83(14), P_2–N_2–C_4 123.21(14), C1–N_1–C_3 113.91(17), C_2–N_2–C_4 116.04(17), C_1–C_2–N_2 113.90(18), C_2–C_1–N_1 115.35(18).

the phosphorus atoms. For clarity only one residue molecule is shown.

The geometry around the palladium atom in complex **7**, *cis*-[$PdCl_2$(**1**)], is slightly distorted square planar, with the aminophosphine moieties coordinated in a mutual *cis*-fashion, in agreement with the spectroscopic data. The distortion is evident from the bite angle P_1–Pd_1–P_2 of 96.74(2)°, which led to P_1–Pd_1–Cl_1 and P_1–Pd_1–Cl_2 angles of 83.36(2)° and 173.41(2)°, respectively. The Flack parameter refined to 0.01(9) for the absolute structure shown in Fig. 3, consistent with the (*S*) configuration of the amine starting material. The seven-membered chelate ring has a boat or open-envelope conformation. Values found for the Pd–P, Pd–Cl and P–N bond lengths were within the ranges reported for similar aminophosphine complexes.[4,18–20] The two P–N bond lengths were 1.6591(19) Å for P_2–N_2 and 1.6811(18) Å for P_1–N_1. The ethane backbone is severely twisted with a torsion angle N_1–C_1–C_2–N_2 of −66.1(2)°. Notably, the geometry around the nitrogen atoms N_1 and N_2 is trigonal planar, with bond angles of between 116.04(17) and 125.83(14)°, and N_1 and N_2 displaced by 0.1722(17) and 0.1041(18) Å respectively from the C–C–P mean planes. This is again a clear indication of considerable double-bond character (*via* a π-interaction) between the P and N atoms. The intramolecular P_1–P_2 distance was 3.3808(8) Å while the N_1–N_2 distance was 3.089(2) Å.

Preparation of dichloroplatinum(II) complexes 9 and 10

Reaction of [$PtCl_2$(cod)] with ligand **1** yielded the straightforward formation of a white solid compound, complex **9** (Scheme 2). Characterization of the species present in solution by ^{31}P NMR spectroscopy showed a single peak at δ 62.1 ppm, flanked by ^{195}Pt satellites and a coupling constant J_{Pt-P} of 4151 Hz. This latter value is a clear indication of *cis*-coordination of the diphosphine to the platinum center, yielding *cis*-[$PtCl_2$(**1**)].[21] The chemical shift is remarkably high for a diphosphine-based *cis*-platinum complex and reflects the electronic influence of the amino-groups. It is virtually similar to a silsesquioxane-based diphosphinite Pt-complex developed previously in our group.[22] When the same reaction was performed with ligand **2** an off-white solid was obtained, complex **10**, for which the ^{31}P NMR spectrum a singlet at 60.5 ppm, together with ^{195}Pt satellites and a coupling constant J_{Pt-P} of 4285 Hz, suggesting formation of *cis*-[$PtCl_2$(**2**)].

Preparation of chlorocarbonylrhodium(I) complex 11

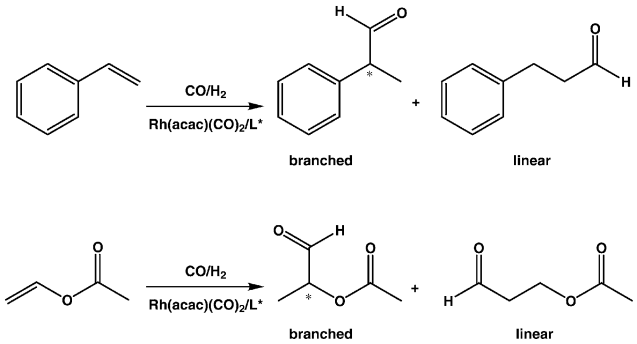
Grimblot *et al.* have previously reported X-ray photoelectron and IR spectroscopy studies on RhCl(CO)-complexes with various phosphine ligands, including aminophosphines, and their correlation with the results obtained in rhodium catalyzed hydroformylation of 1-hexene.[23] Their initial studies on the influence of the (amino)phosphine ligand on the CO stretching frequency in the corresponding Rh-complex led to the conclusion that all tested ligands led to *trans*-complexes except for dppe.

Upon addition of ligand **1** to a CH_2Cl_2-solution of [$RhCl(CO)_2]_2$, the solution immediately turned yellow. After 2 h of reaction at room temperature, removal of volatiles left a clear yellow microcrystalline solid, complex **11**.

The ^{31}P NMR spectrum for this complex showed a mixture of the *cis*- and *trans*-isomers in a ratio of 34:66 in favour of the *trans*-isomer. This latter species was characterized by a doublet at δ 81.0 ppm, and a coupling constant of J_{Rh-P} 133 Hz, which is a typical value for diphenylphosphine ligands. The *cis*-complex appeared as a set of two doublets of doublets at δ 99.6 ppm and δ 75.3 ppm. The respective coupling constants J_{Rh-P} were 180 Hz for the P *trans* to the Cl ligand and 133 Hz for the P *trans* to the CO ligand, while the J_{P-P} was 33 Hz. The related FT-IR-spectrum showed an absorption band in the carbonyl region at ν_{CO} 1968 cm^{-1}, which is in the range found for complexes with σ-donor ligands at the Rh center.[24–27]

Asymmetric hydroformylation of styrene and vinyl acetate

In order to evaluate the catalytic properties of chiral aminophosphines and encouraged by reports on their usefulness in rhodium catalyzed asymmetric hydrogenation of alkenes,[7–10] we chose to apply these ligands in the rhodium-catalyzed asymmetric hydroformylation of styrene and vinyl acetate (Scheme 3). $Rh(acac)(CO)_2$ was used as a standard rhodium precursor and before introduction of the substrate, the catalytic system was activated for 1 h with 20 bar syngas at 60 °C to generate the catalytic resting state Rh(H)$(CO)_2$(P^P). Standard reaction conditions for the catalytic runs were a temperature of 60 °C and 20 bar of syngas (CO : H_2 = 1 : 1), with a reaction time of 15 h in case of styrene. The substrate to rhodium ratio and ligand to rhodium ratio were 1500 and 2 : 1, respectively. For vinyl acetate 20 h reaction time and a substrate to rhodium ratio of 1250 : 1 were used.



Scheme 3 General reaction-scheme for the Rh-catalyzed hydroformylation of styrene (top) and vinyl acetate (bottom).

In the hydroformylation of styrene the chemoselectivity to aldehyde products was typically >99%, with regioselectivities (b/l ratio) of up to 12 for ligand **3**. Turnover frequencies of up to 78 h^{-1} were obtained, which is comparable to activities found for benchmark systems. The enantioselectivity was low with a maximum of only 12% with ligand **4**. Since it is known that the outcome of the hydroformylation with a given catalytic system can be highly dependent on the substrate,[11,28] we were interested to see if the asymmetric hydroformylation of vinyl acetate would render different results. The substrate vinyl acetate differs from styrene in two important aspects, *viz.* (a) vinyl acetate cannot form η^3-complexes and (b) the carbonyl oxygen can participate in bonding to the metal.

With ligand **3** we were able to reach an enantiomeric excess of 34% at 60 °C, which is significantly higher than the best result obtained for styrene. The regioselectivity was extremely high with a b/l ratio exceeding 17. Even more encouragingly, the enantiomeric excess increased to 51% upon decreasing the reaction temperature to 40 °C. Although these results do not outperform other chiral diphosphine ligands, further improvements should be feasible by adjustment of the various tunable fragments in our aminophosphine scaffold. Research is ongoing to determine optimal ligand design.

Conclusions

We have shown the successful synthesis of aminophosphine compounds **1–4**, based on chiral primary amines as well as the selenide derivatives **5** and **6**. The coordination behaviour of ligand **1** and ligand **2** towards Pd, Pt and Rh is described. The ligands show clear tendencies to coordinate in a *cis*-fashion to these transition metals, as indicated by ^{31}P NMR spectroscopy. For the complex *cis*-[$PdCl_2$(**1**)] the molecular structure is determined, showing a relatively small bite angle of 96.74° for ligand **1**.

We have demonstrated the successful application of these chiral aminophosphine ligands in the asymmetric hydroformylation of both styrene and vinyl acetate, with enantioselectivities of up to 51%. We are currently expanding on the theme of chiral amine-based phosphorus ligands, together with a theoretical study aimed at underpinning the electronic character of these ligands.

Experimental

General

All manipulations were carried out under argon using standard Schlenk techniques. Chemicals were purchased from VWR, Acros, Lancaster or Aldrich and solvents were either taken HPLC-grade from an argon-flushed column, packed with aluminium oxide, or distilled under argon prior to use over an appropriate drying agent. NMR spectra were recorded at room temperature on a Varian Mercury 400 MHz spectrometer. Chemical shifts are given in ppm and spectra are referenced to $CDCl_3$ (^1H, $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). FT-IR spectra were taken on an AVATAR E.S.P. 360 FTIR spectrometer. $PdCl_2$(cod),[29] $PdCl(CH_3)$(cod)[30] and $PtCl_2$(cod)[31] were prepared according to literature procedures.

Syntheses

***N*,*N*′-Bis[*S*(−)-α-methylbenzyl]-*N*,*N*′-bis(diphenylphosphino)-ethane-1,2-diamine (1).** *N*,*N*′-Bis[*S*(−)-α-methylbenzyl]ethane-1,2-diamine was prepared by following a procedure by Mimoun *et al.*[32] To a flask containing 4 equivalents of *S*(−)-α-methylbenzylamine (46.7 g, 385 mmol) at 130 °C was added dropwise 1,2-dibromoethane (17.0 g, 91 mmol). After 1 h at elevated temperature the mixture was cooled to 80 °C and a 4 M aqueous solution of KOH (28.4 g, 506 mmol) was added. After extraction of the mixture with ethyl acetate and concentration, the mixture was fractionally distilled at 2.5 mbar, the diamine (18.3 g, 68 mmol) was obtained at 155 °C as a colorless oil in 75% yield. Spectral properties were similar as described before.

Compound **1** was prepared by adding the diamine (2.51 g, 9.45 mmol) dropwise to a mixture of triethylamine (2.5 g, 25 mmol) and chlorodiphenylphosphine (4.22 g, 19.1 mmol) in diethyl ether. The produced ammonium salts are removed from the suspension by filtration and the mixture concentrated, forming a white solid. After stripping with hexanes and recrystallization from hot acetonitrile the analytically pure compound **1** (4.21 g, 6.61 mmol) was obtained as a white semi-crystalline solid in 70% yield. Spectral properties were similar as described before.

***N*,*N*′-Bis[*R*(−)-α-ethylbenzyl]-*N*,*N*′-bis(diphenylphosphino)-propane-1,3-diamine (2).** The procedure described for **1** was followed, starting from *R*(−)-α-ethylbenzylamine (49.07 g, 363 mmol) and 1,3-dibromopropane (17.35 g, 86 mmol). Distillation at 1.5 mbar at 165 °C afforded *N*,*N*′-bis[*R*(−)-α-ethylbenzyl]propane-1,3-diamine (16.33 g, 53 mmol) in 61% yield.

^1H NMR ($CDCl_3$) δ 7.2–7.4 (10H, Ph), 3.43 (t, 2H, C*H*CH$_2$CH$_3$, $^3J_{H-H}$ = 6.2 Hz), 2.49 (m, 4H, C*H*$_2$NH), 1.55–1.80 (m, 8H, CH$_2$C*H*$_2$CH$_2$; CHC*H*$_2$CH$_3$; N*H*), 0.79 (t, 6H, CHCH$_2$C*H*$_3$, $^3J_{H-H}$ = 7.3 Hz).

^{13}C NMR ($CDCl_3$) δ 144.4, 128.5, 127.5, 127.1 (4s, Ph), 65.5 (*C*HCH$_2$CH$_3$), 46.8 (*C*H$_2$NH), 31.2 (CH*C*H$_2$CH$_3$), 30.4 (*C*H$_2$CH$_2$NH), 11.1 (CHCH$_2$*C*H$_3$).

Starting from *N*,*N*′-bis[*R*(−)-α-ethylbenzyl]propane-1,3-diamine (2.64 g, 8.5 mmol), chlorodiphenylphosphine (3.83 g, 17.4 mmol) and triethylamine (2.4 g, 24 mmol), compound **2** (5.14 g, 7.57 mmol) was obtained as a white solid in 89% yield.

^1H NMR ($CDCl_3$) δ 7.40–7.34 (m, 10H, Ph), 7.28–7.14 (m, 16H, Ph), 6.91–6.85 (m, 4H, Ph), 3.43 (dt, 2H, C*H*CH$_2$CH$_3$, $^3J_{P-H}$ = 16.1 Hz,$^3J_{H-H}$ = 6.2 Hz), 2.40 (m, 4H, C*H*$_2$N), 2.20 (m, 4H, CHC*H*$_2$CH$_3$), 0.81 (t, 6H, CHCH$_2$C*H*$_3$, $^3J_{H-H}$ = 7.7 Hz), 0.72 (m, 2H, CH$_2$C*H*$_2$CH$_2$).

^{13}C NMR ($CDCl_3$) δ 143.4 (s, Ph), 140.1, 139.9 (2d, Ph, $^1J_{P-C}$ = 67 Hz), 132.6, 131.5 (2d, Ph, $^2J_{P-C}$ = 21 Hz), 128.3, 128.0, 128.0, 127.7, 127.6, 127.5, 126.8 (7s, Ph), 66.3 (d, *C*HCH$_2$CH$_3$, $^2J_{P-C}$ = 26 Hz), 47.2 (d, *C*H$_2$N, $^2J_{P-C}$ = 11 Hz), 28.5 (CH*C*H$_2$CH$_3$), 28.2 (CH$_2$*C*H$_2$CH$_2$), 11.8 (CHCH$_2$*C*H$_3$).

^{31}P NMR ($CDCl_3$) δ 45.8.

Anal. Calc. for $C_{45}H_{48}N_2P_2$: C, 79.62; H, 7.13; N, 4.13. Found: C, 79.30; H, 7.09; N, 4.03%.

***N*,*N*′-Bis[*S*(−)-(1-(1-naphthyl)ethyl)]-*N*,*N*′-bis(diphenylphosphino)-ethane-1,2-diamine (3).** *N*,*N*′-Bis[*S*(−)-(1-(1-naphthyl)-ethyl)]ethane-1,2-diamine was prepared following the procedure for **1**, starting from *S*(−)-(1-(1-naphthyl))ethylamine (15.1 g, 88 mmol) and 1,2-dibromoethane (8.3 g, 44 mmol). After removal of the access of amine the diamine was obtained in 95% yield as a brownish syrup (15.47 g, 42 mmol) which solidified upon standing.

^1H NMR ($CDCl_3$) δ 8.15 (m, 2H, Ph), 7.84 (m, 2H, Ph), 7.78 (d, 2H, $^3J_{H-H}$ = 8.1 Hz), 7.67 (d, 2H, Ph, $^3J_{H-H}$ = 7.5 Hz), 7.45–7.55 (m, 8H, Ph), 4.53 (q, 2H, C*H*CH$_3$, $^3J_{H-H}$ = 6.6 Hz), 2.68 (s, 4H, C*H*$_2$C*H*$_2$), 2.02 (br s, 2H, N*H*), 1.53 (d, 6H, CHC*H*$_3$, $^3J_{H-H}$ = 6.6 Hz).

^{13}C NMR ($CDCl_3$) δ 141.5, 134.0, 131.6, 129.2, 127.4, 126.0, 125.9, 125.6, 124.0, 123.2 (10s, Ph), 53.9 (*C*HCH$_3$), 47.7 (*C*H$_2$NH), 24.0 (CH*C*H$_3$).

Following the (modified) procedure for **1**, starting from *N*,*N*′-bis[*S*(−)-(1-(1-naphthyl)ethyl)]ethane-1,2-diamine (1.95 g, 5.3 mmol) in 20 mL toluene, chlorodiphenylphosphine (2.38 g, 10.8 mmol) and 2 mL triethylamine (1.45 g, 14.3 mmol) in 30 mL toluene and a reaction overnight at 80 °C, **3** was obtained as a white powder (2.33 g, 3.2 mmol) in 60% yield.

^1H NMR ($CDCl_3$) δ 7.85 (m, 4H, Ph), 7.65 (m, 2H, Ph), 7.47 (m, 2H, Ph), 7.36 (m, 2H, Ph), 7.08–7.30 (m, 20 H, Ph), 6.96 (m, 4H, Ph), 4.72 (dq, 2H, C*H*CH$_3$, $^3J_{P-H}$ = 13 Hz; ^3J = 6.6 Hz), 2.69 (s, 4H, C*H*$_2$C*H*$_2$), 1.42 (d, 6H, CHC*H*$_3$, ^3J = 6.6 Hz).

^{13}C NMR ($CDCl_3$) δ 140.4 (s, Ph), 140.4, 139.6 (2d, Ph, $^1J_{P-C}$ = 85 Hz), 134.1, 132.4 (2s, Ph), 132.4 (d, Ph, $^2J_{P-C}$ = 40 Hz), 131.6, 128.9, 128.4 (3s, Ph), 128.1, 128.0 (2d, Ph, $^3J_{P-C}$ = 6 Hz), 127.8, 125.8, 125.5, 125.3, 124.6, 56.6 (d, *C*HCH$_3$, $^2J_{P-C}$ = 31 Hz), 49.9 (d, *C*H$_2$N,$^2J_{P-C}$ = 9 Hz), 21.0 (d, CH*C*H$_3$, $^3J_{P-C}$ = 10 Hz).

^{31}P NMR ($CDCl_3$) δ 55.9.

***N*, *N*′-Bis[*S*(−)-(1-cyclohexylethyl)]-*N*,*N*′-bis(diphenylphosphino)ethane-1,2-diamine (4).** Following a procedure of Weber *et al.* [33] a solution of *S*(−)-(1-cyclohexyl)ethylamine (12.1 g, 95 mmol) in 50 mL hexanes was added to a 40 wt% aqueous solution of glyoxal (47 mmol). After 30 min of reaction the phases were separated and the water layer was extracted with hexanes. After drying over $MgSO_4$, concentration *in vacuo* afforded the corresponding diimine as a white powder (12.3 g, 44 mmol, 95%) with similar spectral properties as described in literature and which was used without any purification.

To a solution of the diimine (1.79 g, 6.5 mmol) in 25 mL diethyl ether was added in portions $LiAlH_4$ (1.05 g, 27.7 mmol). After one hour the excess of $LiAlH_4$ was neutralized by carefully adding water. After drying over $MgSO_4$, extraction with diethyl ether and concentration the corresponding diamine was obtained in quantitative yield as a colorless mobile oil (1.82 g, 6.5 mmol).

^1H NMR ($CDCl_3$) δ 2.83 (dq, 2H, C*H*CH$_3$, ^3J = 5.4 Hz), 2.64 (m, 2H, C*H*$_2$NH), 2.46 (m, 2H, C*H*$_2$NH), 2.04 (br s, 2H, N*H*), 1.73 (m, 10H, Cy), 1.20 (m, 12H, Cy), 1.06 (d, 6H, CHC*H*$_3$, ^3J = 5.4 Hz).

^{13}C NMR ($CDCl_3$) δ 58.0 (*C*HCH$_3$), 47.1 (C*H*$_2$NH), 42.8, 29.9, 28.2, 26.8, 26.6, 26.5 (6s, Cy), 16.9 (CHC*H*$_3$).

Following the procedure described for **1** starting from *N*,*N*′-bis[*S*(−)-(1-cyclohexylethyl)]ethane-1,2-diamine (1.03 g, 3.67 mmol), chlorodiphenylphosphine (1.65 g, 7.48 mmol) and triethylamine (1.5 mL, 10.7 mmol) the analytically pure

compound (**4**) (1.98 g, 3.05 mmol) was obtained as a white semi-crystalline solid in 83% yield.

^{1}H NMR ($CDCl_3$) δ 7.12–7.22 (10H, PPh_2), 2.64 (dm, 4H, CH_2N, $^3J_{P-H}$ = 36.2 Hz), 2.23 (m, 2H, $CHCH_3$), 1.89 (m, 2H, Cy), 1.68 (m, 8H, Cy), 1.50 (m, 2H, Cy), 1.17 (m, 6H, Cy), 1.06 (d, 6H, $CHCH_3$, ^3J = 6.3 Hz), 0.75 (m, 4H, Cy).

^{13}C NMR ($CDCl_3$) δ 140.7, 140.5 (2d, Ph, $^1J_{P-C}$ = 48 Hz), 132.4, 132.0 (2d, Ph, $^2J_{P-C}$ = 21 Hz), 128.0 (d, Ph, $^4J_{P-C}$ = 4 Hz), 127.9 (d, Ph, $^3J_{P-C}$ = 6 Hz), 61.8 (d, $CHCH_3$, $^2J_{P-C}$ = 26 Hz), 49.3 (d, CH_2N,$^2J_{P-C}$ = 26 Hz), 42.8 (d, $CHCHCH_3$, $^3J_{P-C}$ = 10 Hz), 31.2, 30.0, 26.4, 26.2, 26.0 (5s, Cy), 19.2 (d, $CHCH_3$, $^3J_{P-C}$ = 11 Hz).

^{31}P NMR ($CDCl_3$) δ 46.0.

Anal. Calc. for $C_{42}H_{54}N_2P_2$: C, 77.75; H, 8.39; N, 4.32. Found: C, 77.53; H, 8.53; N, 4.24%.

***N*,*N*′-Bis[*S*(−)-α-methylbenzyl]-*N*,*N*′-bis(diphenylphosphino)-ethane-1,2-diamine selenide (5).** **1** (85.9 mg, 134.9 μmol) was dissolved in 5 mL toluene and excess black selenium was added. The reaction mixture was stirred for 30 min at 70 °C. Filtration to remove unreacted selenium by cannula was followed by evaporation of the filtrate to dryness, leaving **5** as a white solid. Yield: 95% (101.8 mg, 128.2 μmol).

^{31}P NMR ($CDCl_3$) δ 70.3 (s, J_{Se-P} = 752 Hz).

Anal. Calc. for $C_{42}H_{42}N_2P_2Se_2$: C, 63.48; H, 5.33; P, 3.53. Found: C, 63.55; H, 5.41; P, 3.58%.

***N*,*N*′-Bis[*R*(−)-α-ethylbenzyl]-*N*,*N*′-bis(diphenylphosphino)-propane-1,3-diamine selenide (6).** Following the same procedure as for compound **4**, ligand **2** (92.1 mg, 135.7 μmol) was converted to selenide **6** in a yield of 98% (111.3 mg, 133.0 μmol).

^{31}P NMR ($CDCl_3$) δ 69.1 (s, J_{Se-P} = 750 Hz).

Anal. Calc. for $C_{45}H_{48}N_2P_2Se_2$: C, 64.59; H, 5.78; P, 3.35. Found: C, 64.74; H, 5.82; P, 3.38%.

***cis*-[PdCl$_2$(1)] (complex 7).** $PdCl_2$(cod) (32.9 mg, 115.2 μmol) and **1** (73.4 mg, 115.3 μmol) were dissolved in 5 mL CH_2Cl_2 and stirred for 12 h at r.t. Solvents were then evaporated *in vacuo*. After that the remaining traces of solvent were removed by stripping twice with 5 mL CH_2Cl_2 to leave complex **7** as a pure yellow solid. Yield: 96% (90.1 mg, 110.6 μmol). Layering with CH_2Cl_2/CH_3CN under slight argon flow gave yellow rectangular single crystals, suitable for X-ray analysis.

^{1}H NMR ($CDCl_3$) δ 7.99 (dd, 2H, ArH, J_1 = 4.0 Hz, J_2 = 11.2 Hz), 7.70 (dd, 2H, ArH, J_1 = 4.0 Hz, J_2 = 11.2 Hz), 7.55 (t, 1H, ArH, J_1 = 6.8 Hz), 7.49 (d, 1H, ArH, J_1 = 5.6 Hz), 7.41 (t, 6H, ArH, J_1 = 7.2 Hz), 7.30 (d, 6H, ArH, J_1 = 7.6 Hz), 6.99 (t, 4H, ArH, J_1 = 7.2 Hz), 6.90 (dd, 4H, ArH, J_1 = 7.6 Hz, J_1 = 1.2 Hz), 4.27 (m, 2H, CH), 3.59 (dd, 2H, CH_2, J_1 = 6.8 Hz, J_2 = 11.2 Hz), 3.05 (dd, 2H, CH_2, J_1 = 4.0 Hz, J_2 = 11.2 Hz), 0.82 (d, 6H, CH_3, J_1 = 6.8 Hz).

^{31}P NMR ($CDCl_3$) δ 87.3 (s).

Anal. Calc. for $C_{42}H_{42}Cl_2N_2P_2Pd$: C, 61.97; H, 5.20; N, 3.44. Found: C, 62.03; H, 5.24; N, 3.48%.

***cis*-[PdCl(CH$_3$)(1)] (complex 8).** Following the same procedure as for complex **7**, but starting from $PdCl(CH_3)$(cod) (10.5 mg, 39.6 μmol) and **1** (27.2 mg, 42.7 μmol), complex **8** was obtained as a pure yellow solid. Yield: 94% (29.6 mg, 37.2 μmol).

^{1}H NMR ($CDCl_3$) δ 7.87 (dt, 2H, ArH, J_1 = 8.8 Hz, J_2 = 1.6 Hz), 7.83 (m, 2H, ArH), 7.63 (ddd, 2H, ArH, J_1 = 11.2 Hz, J_1 = 1.2 Hz), 7.54 (ddd, 2H, ArH, J_1 = 11.2 Hz, J_1 = 1.2 Hz), 7.45 (d, 5H, ArH, J_1 = 2.0 Hz), 7.35 (d, 5H, ArH, J_1 = 7.6 Hz), 7.7.32 (m, 2H, ArH), 7.28 (m, 2H, ArH), 7.22 (dd, 4H, ArH, J_1 = 9.2 Hz, J_1 = 2.0 Hz), 7.16 (dd, 2H, ArH, J_1 = 7.2 Hz, J_1 = 2.8 Hz), 6.73 (dd, 2H, ArH, J_1 = 8.0 Hz, J_1 = 1.6 Hz), 4.41 (t, 2H, CH_2), 4.26 (t, 2H, CH_2), 3.35 (m, 2H, CH), 1.01 (d, 3H, CH_3, J_1 = 7.6 Hz), 0.73 (d, 3H, CH_3, J_1 = 6.8 Hz), 0.47 (dd, 3H, Pd(CH_3), J_1 = 7.6 Hz, J_1 = 4.4 Hz).

^{31}P NMR ($CDCl_3$) δ 91.3 (d, J_{P-P} = 28 Hz, P *trans* to Cl), 81.0 (d, J_{P-P} = 28 Hz, P *trans* to CH_3).

***cis*-[PtCl$_2$(1)] (complex 9).** $PtCl_2$(cod) (36.3 mg, 97.0 μmol) and **1** (66.3 mg, 104.1 μmol) were dissolved in 5 mL CH_2Cl_2 and stirred for 2 h at r.t. Then the solvent was removed *in vacuo.* After that the remaining traces of solvent were removed by stripping 2 times with 5 mL hexanes to leave complex **9** as a white powder. Yield: 92% (80.6 mg, 89.3 μmol).

^{1}H NMR ($CDCl_3$) δ 7.99 (dd, 4H, J_1 = 8.0 Hz), 7.73 (dd, 4H, J_1 = 8.0 Hz), 7.49 (m, 4H), 7.40 (s, 6H), 7.42 (t, 8H, J_1 = 6.8 Hz), 7.32 (t, 6H, J_1 = 6.8 Hz), 6.90 (dd, 4H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 4.29 (t, 2H, CH, J_1 = 7.2 Hz), 3.60 (dt, 4H, CH_2, J_1 = 14.4 Hz, J_2 = 2.8 Hz), 3.01 (t, 4H, CH_2, J_1 = 13.6 Hz), 0.80 (d, 6H, CH_3, J_1 = 6.8 Hz).

^{31}P NMR ($CDCl_3$) δ 62.1 (s, J_{Pt-P} = 4151 Hz).

***cis*-PtCl$_2$(2) (complex 10).** Following the same procedure as for complex **9**, but using ligand **2** (75.0 mg, 110.5 μmol) and $PtCl_2$(cod) (35.3 mg, 94.3 μmol) complex **10** was obtained in a yield of 95% (84.7 mg, 89.6 μmol).

^{1}H NMR ($CDCl_3$) δ 8.24 (dd, 4H, J_1 = 4.4 Hz, J_2 = 6.8 Hz), 7.96 (dd, 4H, J_1 = 4.4 Hz, J_2 = 6.8 Hz), 7.51 (t, 14H, J_1 = 7.2 Hz), 7.26 (t, 4H, J_1 = 2.4 Hz), 6.99 (t, 4H, J_1 = 3.6 Hz), 3.83 (t, 2H, NCH, J_1 = 8.4 Hz), 3.00 (m, NCH_2), 2.67 (m, 2H, NCH_2), 1.76 (m, 2H, $CH_2CH_2CH_2$), 1.35 (m, 4H, CH_2CH_3), 0.30 (t, 6H, CH_3, J_1 = 7.6 Hz).

^{31}P NMR ($CDCl_3$) δ 60.5 (s, J_{Pt-P} = 4285 Hz).

[Rh(Cl)(CO)(1)] (complex 11). $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (56.9 mg, 146.3 μmol) and **1** (186.4 mg, 292.7 μmol) were stirred in 10 mL of CH_2Cl_2 for 16 h, giving a light yellow solution. After removal of the solvent *in vacuo*, **11** was obtained as a bright-yellow microcrystalline solid.

^{31}P NMR ($CDCl_3$) δ 99.6 (dd, *cis*, P *trans* to Cl, J_{Rh-P} = 180 Hz, J_{P-P} = 33 Hz), 81.0 (d, *trans*, J_{Rh-P} = 133 Hz), 75.3 (dd, *cis*, P *trans* to CO, J_{Rh-P} = 133 Hz, J_{P-P} = 33 Hz).

FTIR (ATR mode, solid, cm^{-1}): ν 1967.5 (Rh(CO)).

Anal. Calc. for $C_{43}H_{42}ClN_2OP_2Rh$: C, 64.31; H, 5.27; P, 3.49. Found: C, 64.13; H, 5.37; P, 3.55%.

Crystal structure determination of 7

Intensity data for the complex **7** were collected using graphite-monochromated Mo-Kα radiation, on a Nonius KappaCCD diffractometer. A semi-empirical absorption correction based on multiple measurements was applied using SADABS.[34a] The structure was solved by automated Patterson methods using DIRDIF,[34b] and refined on F^2 using SHELXL97.[34c] One of the six phenyl rings in the structure is disordered over two conformations and was refined with a disorder model. All hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The Flack parameter refined to −0.01(9) for the absolute structure shown in Fig. 3. Structure validation and molecular graphics preparation were performed with the PLATON package.[35] Formula $C_{42}H_{42}Cl_2N_2P_2Pd$; molecular weight 814.02 g mol^{-1}; monoclinic; space group $P2_1$ (no. 4); unit cell dimensions: a = 11.3330(10), b = 26.0777(10), c = 12.6339(10) Å, β = 92.7710(10)°; V = 3279.4(5) Å^3; T = 150 K; Z = 4; μ(Mo-Kα) = 0.760 mm^{-1}; total reflections = 52367; unique reflections (R_{int}) = 14632 (0.026); $wR_2(F^2)$ (all data) = 0.0444; $R_1(F)$ = 0.0219.

CCDC reference number 250561.

See http://www.rsc.org/suppdata/dt/b4/b414668a/ for crystallographic data in CIF or other electronic format.

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