Rhodium(I), Palladium(II) and Platinum(II) Coordination Chemistry of the Short-Bite Chiral Ligands (S_c)-*N*,*N*-Bis(diphenylphosphanyl)-*sec*-butylamine, (R_a,R_a)-*N*,*N*-Bis(binaphthylphosphonito)phenylamine and (R_a,S_c)-*N*-(Diphenylphosphanyl)-*N*-(binaphthylphosphonito)-*sec*-butylamine

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The new short-bite chiral ligands (S_c)-*N*,*N*-bis(diphenylphosphanyl)-*sec*-butylamine [(S_c)-**1**], (R_a,R_a)-*N*,*N*-bis(binaphthylphosphonito)phenylamine [(R_a,R_a)-**2**] and (R_a,S_c)-*N*-(diphenylphosphanyl)-*N*-(binaphthylphosphonito)-*sec*-butylamine [(R_a,S_c)-**3**] have been treated with rhodium(I), palladium(II) and platinum(II) substrates. The (S_c)-**1** ligand reacts with [Pd(C_6H_5CN)$_2$Cl$_2$], [Pt(COD)Cl$_2$] and [Rh(COD)(THF)$_2$]PF$_6$ to afford the products [Pd(S_c-**1**)Cl$_2$] (**4**), [Pt(S_c-**1**)Cl$_2$] (**5**) and [Rh(COD)(S_c-**1**)]PF$_6$ (**6**), respectively, in high yields. By bubbling CO to a CH_2Cl_2 solution of **6**, we formed the dicarbonyl species [Rh(CO)$_2$(S_c-**1**)]PF$_6$ (**7**), which is stable only in solution under CO. Compounds **4** and **5** were characterized additionally by X-ray diffraction studies. The ligand (R_a,R_a)-**2** reacts with [Pd(C_6H_5CN)$_2$Cl$_2$] and [Pt(COD)I$_2$] to give [Pd(R_a,R_a-**2**)Cl$_2$] (**8**) and [Pt(R_a,R_a-**2**)I$_2$] (**9**), respectively; the reaction with [Rh(CO)$_2$Cl]$_2$ or [Rh(COD)(THF)$_2$]PF$_6$ affords a mixture of mono- and binuclear compounds, in which the ligand is oxidized to the corresponding phosphonate or is partially hydrolysed. The compounds [Pd(R_a,S_c-**3**)Cl$_2$] (**10**) and [Pt(R_a,S_c-**3**)I$_2$] (**11**) were obtained in the analogous reactions using the asymmetric (R_a,S_c)-**3** ligand. This ligand reacted with [Rh(CO)$_2$Cl]$_2$ in a 2:1 molar ratio in hexane to give a mixture of products in almost equal amounts. The $^{31}P\{^1H\}$ NMR spectrum recorded in $CDCl_3$ allowed us to identify the chelate [Rh(R_a,S_c-**3**)(CO)Cl] (**12**); the nature of the accompanying dinuclear species **13** is not clear. The catalytic systems formed by [Rh(acac)(CO)$_2$] and the ligands (R_a,R_a)-**2** and (R_a,S_c)-**3**, at ligand/metal ratios of 1:1 and 1:2, were unstable under the experimental conditions used (CO/H_2 pressure of 50 atm and temperature of 40 °C) for the hydroformylation of styrene; instead, metallic rhodium was afforded together with unidentified decomposition products.

Introduction

The design and synthesis of new chiral ligands remains a significant research subject for the development of transition metal-catalysed asymmetric syntheses. Satisfactory enantioselectivities have been obtained when many families of ligands, with very different features, have been prepared and applied in asymmetric catalytic reactions.[1] Among these ligands, the widest range of applications have been found for those containing atropisomeric C_2-symmetric moieties.[2]

Recently, we began[3] synthesising chiral short-bite ligands that resemble the well-known bis(diphenylphosphanyl)methane (dppm), phenylpyrophosphite, and phenylaminobis(diphenylphosphane) (dpppa), but contain atropisomeric C_2-symmetric binaphthyl moieties bonded to the phosphorus donor atoms rather than the phenyl groups. We have also reported[3] the application of these ligands in palladium−allyl-catalysed reaction of 1,3-diphenylallyl acetate with dimethylmalonate. Owing to their favourable structural features, short-bite ligands have been widely used in organometallic chemistry.[4] These bidentate ligands have their donor-atoms separated by one spacer atom; their coordination to a metal centre can produce either chelated mononuclear or bridged dinuclear complexes. In the mononuclear complexes, the short-bite ligand forms a strained four-membered ring with a very narrow bite angle; in the dinuclear complexes, two metal centres are held in close proximity by the features of the bridging short-bite ligand and can cooperate to activate a substrate. This property of the dinuclear complexes has been found to operate during homogeneous catalysis.[5]

When using short-bite chiral ligands, both coordination modes (chelated mononuclear or bridged dinuclear complexes) can, in principle, produce beneficial effects during

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catalytic enantioselective processes. In fact, the reduced number and rigidity of the conformational isomers formed by a strained four-membered metallacycle can induce a minor number of processes having different activation energies. For the bridged dinuclear complexes, novel modes of reactivity can be achieved for the activation of a substrate as a consequence of cooperative interactions between the metal centres.

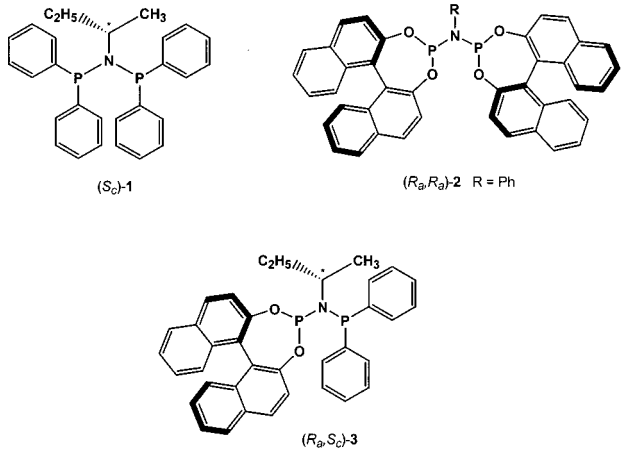
As far as we know, only a few chiral, optically pure, short-bite ligands have been reported; of these ligands, only the diphosphane MiniPHOS has been explored as a catalyst precursor in asymmetric synthesis and it affords excellent enantioselectivities in representative carbon−carbon bond-formation reactions.[6]

Prior to studying catalytic systems formed from a metal substrate and a chiral P−N−P short-bite ligand in conventional metal-catalysed asymmetric carbon−carbon bond formation, we explored the coordinating properties of the synthesized (S_c)-*N*,*N*-bis(diphenylphosphanyl)-*sec*-butylamine, (R_a,R_a)-*N*,*N*-bis(binaphthylphosphonito)phenylamine and (R_a,S_c)-*N*-(diphenylphosphanyl)-*N*-(binaphthylphosphonito)-*sec*-butylamine.

Results and Discussion

Ligands

Scheme 1 presents the new short-bite chiral P−N−P ligands used in the reactions with rhodium(I), palladium(II) and platinum(II) substrates.



Scheme 1

These ligands were designed so that we could verify the effects that the position, nature, absolute configuration and number of stereogenic centres have on the enantioselective catalysis. The ligands were synthesized[3] by reacting the corresponding primary amine RNH_2 [R = Ph, (S_c)-(+)-*sec*-$C_2H_5CHCH_3$] with the chlorodiphenylphosphane or the phosphorochloridite derived from (R_a)-binaphthol in a 1:2 molar ratio in toluene at 0 °C in the presence of an excess of NEt_3. Ligands similar to (S_c)-**1** have been reported previously,[7] but their coordination chemistry has not been explored extensively. The ligands (S_c)-**1**, (R_a,R_a)-**2** and (R_a,S_c)-**3** should behave, in principle, either as chelating, originating, four-membered metallacycles or as bridging ligands giving dimetalllic species. Literature reports indicate that the presence of an alkyl or aryl group on the nitrogen atom favours the formation of a four-membered strained ring when the ligand coordinates to a metal centre.[8]

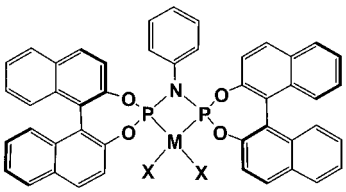
Reactions with Rhodium(I), Palladium(II) and Platinum(II) Substrates

The reaction of $[Pd(C_6H_5CN)_2Cl_2]$ with (S_c)-**1** in a 1:1 molar ratio in CH_2Cl_2 afforded $[Pd(S_c\text{-}\mathbf{1})Cl_2]$ (**4**) in high yield as a yellow orange solid that is stable to air and moisture for a long period of time. This complex was characterized by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectra; an X-ray diffractometric study established its nature as a mononuclear complex, with (S_c)-**1** chelating to the palladium(II) centre. The $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ displays a singlet at δ = 29.6 ppm; in the ^1H NMR spectrum, the chiral moiety provides the signals at δ = 0.43 (t, $^3J_{H,H}$ = 7 Hz, CH_3), 0.79 (d, $^3J_{H,H}$ = 7 Hz, CH_3), 1.29 and 0.95 (m, diastereotopic CH_2) and 3.28 (m, CH) ppm.

Similarly to $[Pd(C_6H_5CN)_2Cl_2]$, $[Pt(COD)Cl_2]$ reacted with an equimolar amount of (S_c)-**1** in toluene to give $[Pt(S_c\text{-}\mathbf{1})Cl_2]$ (**5**) as a white microcrystalline solid that is stable to air for a long time in the solid state and in solution. An X-ray diffractometric study indicated that **5** is isostructural with **4**. In its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$, the phosphorus atom resonance of **5** appears as a singlet at δ = 15.5 ppm having ^{195}Pt satellites ($^1J_{Pt,P}$ 3285 Hz); in the ^1H NMR spectrum, the pattern of the chiral moiety CHMeEt is the same as that obtained for **4**, except that it shows additional peaks due to ^{195}Pt satellites.

The addition of a THF solution of (S_c)-**1** to an equimolar solution of $[Rh(COD)(THF)_2]PF_6$, obtained in situ from $[Rh(COD)Cl]_2$ and NH_4PF_6, in THF, readily gave $[Rh(COD)(S_c\text{-}\mathbf{1})]PF_6$ (**6**) as an orange solid. Analytical and conductivity data, together with CO reactivity and NMR spectroscopic data, support this formulation. In fact, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ displays a doublet at δ = 50.1 ppm ($^1J_{RhP}$ = 134 Hz). Upon bubbling CO into a CH_2Cl_2 solution of **6**, displacement of COD occurs readily with formation of the dicarbonyl species $[Rh(CO)_2(S_c\text{-}\mathbf{1})]PF_6$ (**7**) [$\tilde{\nu}_{CO}$ (CH_2Cl_2) = 2059 and 2098 cm^{-1}] together with small amount of another carbonyl compound, which is very likely to be the five-coordinate species $[Rh(CO)_3(S_c\text{-}\mathbf{1})]PF_6$; compound **7** requires a CO atmosphere and can be handled only in solution.

The ligand (R_a,R_a)-**2** reacts in solution with $[Pd(C_6H_5CN)_2Cl_2]$ and $[Pt(COD)I_2]$ to give $[Pd(R_a,R_a\text{-}\mathbf{2})Cl_2]$ (**8**) and $[Pt(R_a,R_a\text{-}\mathbf{2})I_2]$ (**9**), respectively, as yellow-orange solids (Scheme 2).



Scheme 2

These formulations are based on analytical and NMR spectroscopic data. The resonances of the phosphorus atoms appear in the $^{31}P\{^1H\}$ NMR spectra, recorded in $CDCl_3$, as singlets at higher fields than the free ligand, at δ = 82.1 and 94.5 ppm ($^1J_{Pt,P}$ = 5296 Hz) for **8** and **9**, respectively. Both **8** and **9** are moderately stable to air and moisture.

The reaction of (R_a,R_a)-**2** with $[Rh(CO)_2Cl]_2$ or $[Rh(COD)(THF)_2]PF_6$ leads to the formation of a mixture of compounds in which the ligand is oxidized to the corresponding phosphonate or is partially hydrolysed. We were not able to obtain fully characterized products from these mixtures.

The asymmetric (R_a,S_c)-**3** ligand reacts in CH_2Cl_2 with $[Pd(C_6H_5CN)_2Cl_2]$ in a 1:1 molar ratio to afford [Pd(R_a,S_c-**3**)Cl_2] (**10**) together with small trace amounts of **4**. The formation of **4** by $N-P_{Phosphonite}$ bond cleavage of **10** in the presence of trace amounts of H_2O[9] is very unlikely; most probably the formation of **4** is due to the presence of trace amounts of (S_c)-**1** as an impurity in the sample of the (R_a,S_c)-**3** ligand we used. Compound **10** is a yellow solid that is moderately stable in the presence of air or moisture; it was isolated in low yield after column chromatography. Its formulation is supported by the presence of two doublets in the $^{31}P\{^1H\}$ NMR spectrum recorded in $CDCl_3$ at δ = 81.8 and 39.9 ppm, with $^2J_{P,P}$ = 17 Hz, which correspond to the phosphonito and phosphino phosphorus atoms, respectively.

Similarly to $[Pd(C_6H_5CN)_2Cl_2]$, $[Pt(COD)I_2]$ reacted with (R_a,S_c)-**3** in a 1:1 molar ratio in toluene to give the product [Pt(R_a,S_c-**3**)I_2] (**11**) as a white microcrystalline solid that is moderately stable to air in the solid state and in solution. Its formulation is supported by the presence of resonances in the $^{31}P\{^1H\}$ NMR spectrum, recorded in $CDCl_3$, that correspond to phosphonito and phosphino phosphorus atoms, together with peaks due to ^{195}Pt satellites.

The reaction of (R_a,S_c)-**3** with $[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio in hexane led to a mixture of products in almost equal amounts. The $^{31}P\{^1H\}$ NMR spectrum of the crude product, recorded in $CDCl_3$ (see a in Figure 1), allows us to identify the chelate [Rh(R_a,S_c-**3**)(CO)Cl] (**12**) and a dinuclear species **13**, the nature of which we are not able to fully explain.

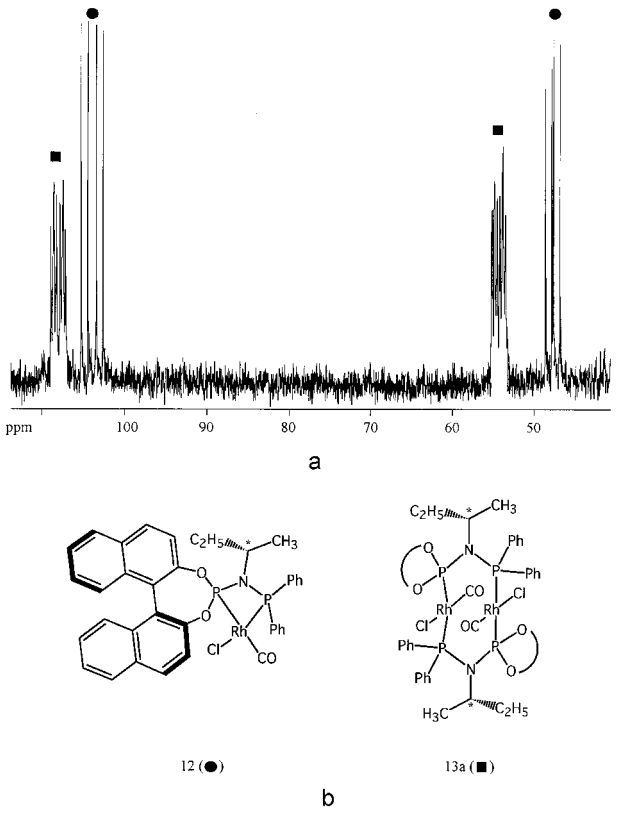


Figure 1. $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at 298 K: filled black square: compound **13**, filled black circle: compound **12**

The formulation of compound **12** as a chelated mononuclear species is supported by the pattern of the phosphorous atom resonances in the $^{31}P\{^1H\}$ NMR spectrum and the $^1J_{RhP}$ values. As expected for the proposed structure, compound **12** exhibits two doublets of doublets in the $^{31}P\{^1H\}$ NMR spectrum, recorded in $CDCl_3$, centred at δ = 103.9 ppm (dd, $^1J_{RhP}$ = 222, $^2J_{P,P}$ = 98 Hz) and at δ = 47.7 ppm (dd, $^1J_{RhP}$ = 122, $^2J_{P,P}$ = 98 Hz) for the phosphonito and phosphino phoshorus atoms, respectively; the value of $\tilde{\nu}_{CO}$ at 1990 cm^{-1} (nujol mull) in the IR spectrum supports a structure in which the carbonyl unit is in a trans position to the higher-trans-influence phosphonito group. As shown in Figure 1 (a), the NMR spectrum of the crude product also indicates, in the region of the phosphonito and phosphanyl phoshorus atom resonances, well-resolved signals at δ = 108.0 (ddd, $^1J_{RhP}$ = 133, $^2J_{P,P}$ = 46, $^2J_{P,P}$ = 35 Hz) and 54.4 ppm (ddd, $^1J_{RhP}$ = 124, $^2J_{P,P}$ = 46, $^2J_{P,P}$ = 35 Hz) arising from AA′BB′XX′ systems. These spectroscopic data allow us to assign a dinuclear structure to **13**, but they are not sufficient to fully characterize it. On the basis the $^{31}P\{^1H\}$ NMR spectroscopic data, we tentatively propose for **13** the dinuclear head-to-tail structure, **13a** (see b in Figure 1).[10] The large decrease in the value of $^1J_{RhP}$ on proceeding from **12** to **13** can also suggest an oxidation process from Rh^I to Rh^{II} and propose an $Rh^{II}-Rh^{II}$ undefined dimer formulation.[11,12] We have ascertained that **12** and **13** do not interconvert; the bulkiness of the binaphthyl

moiety probably prevents the exchange reaction between **12** and **13**.

Crystal and Molecular Structure of [Pd(S_c-**1**)Cl_2] (**4**) and [Pt(S_c-**1**)Cl_2] (**5**)

Compounds **4** and **5** are isostructural. In the crystals of **4** (and of **5**), two crystallographically independent, but very similar, complexes of [Pd(S_c-**1**)Cl_2] (and of [Pt(S_c-**1**)Cl_2]) are present. ORTEP views of one of the two molecules of the complexes **4** and **5** are shown in Figure 2 and 3, respectively.

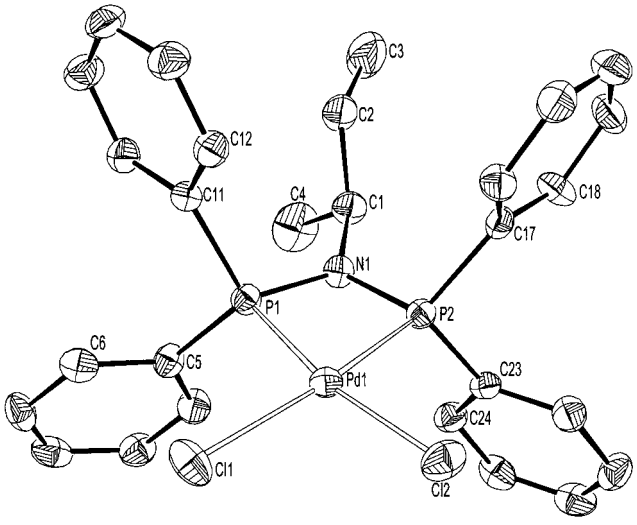


Figure 2. View of one of the two independent molecules of **4**, together with the atomic numbering system. Thermal ellipsoids are drawn at the 30% probability level

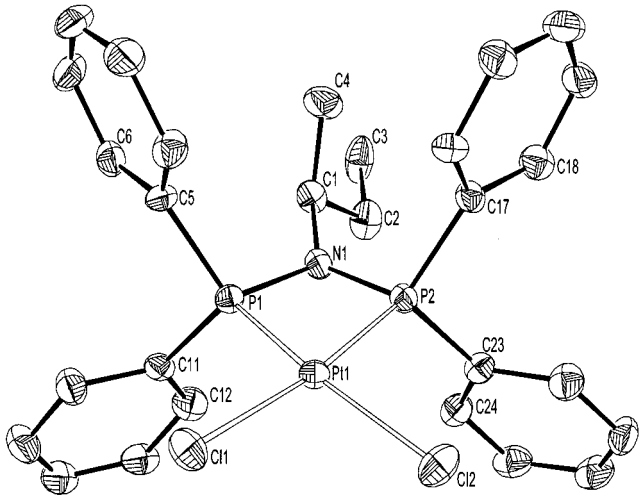


Figure 3. View of one of the two independent molecules of **5**, together with the atomic numbering system. Thermal ellipsoids are drawn at the 30% probability level

Lists of selected bond lengths and angles of **4** and **5** are given in Table 1 and 2, respectively.

Table 1. Selected bond lengths [Å] and angles [deg] for Molecule A in **4**

Pd(1A)−P(2A) 2.217(3)	Pd(1B)−P(1B) 2.212(3)
Pd(1A)−P(1A) 2.210(3)	Pd(1B)−P(2B) 2.225(3)
Pd(1A)−Cl(1A) 2.365(3)	Pd(1B)−Cl(2B) 2.351(3)
Pd(1A)−Cl(2A) 2.353(3)	Pd(1B)−Cl(1B) 2.348(3)
P(1A)−N(1A) 1.712(7)	P(1B)−N(1B) 1.727(8)
P(1A)−C(5A) 1.818(9)	P(1B)−C(5B) 1.794(11)
P(1A)−C(11A) 1.811(9)	P(1B)−C(11B) 1.801(10)
P(1A)−P(2A) 2.596(4)	P(1B)−P(2B) 2.598(3)
P(2A)−N(1A) 1.695(7)	P(2B)−N(1B) 1.682(8)
P(2A)−C(23A) 1.802(11)	P(2B)−C(17B) 1.812(9)
P(2A)−C(17A) 1.800(10)	P(2B)−C(23B) 1.809(10)
N(1A)−C(1A) 1.498(9)	N(1B)−C(1B) 1.498(8)
C(1A)−C(2A) 1.508(11)	C(1B)−C(4B) 1.480(12)
C(1A)−C(4A) 1.543(13)	C(1B)−C(2B) 1.566(14)
C(2A)−C(3A) 1.562(9)	C(2B)−C(3B) 1.447(10)
P(2A)−Pd(1A)−P(1A) 71.78(9)	P(1B)−Pd(1B)−P(2B) 71.70(9)
P(2A)−Pd(1A)−Cl(1A) 169.25(10)	P(1B)−Pd(1B)−Cl(2B) 169.49(11)
P(1A)−Pd(1A)−Cl(1A) 97.98(10)	P(2B)−Pd(1B)−Cl(2B) 98.71(11)
P(2A)−Pd(1A)−Cl(2A) 95.57(10)	P(1B)−Pd(1B)−Cl(1B) 95.86(11)
P(1A)−Pd(1A)−Cl(2A) 165.45(10)	P(2B)−Pd(1B)−Cl(1B) 165.18(11)
Cl(1A)−Pd(1A)−Cl(2A) 94.99(10)	Cl(2B)−Pd(1B)−Cl(1B) 94.23(11)
N(1A)−P(1A)−Pd(1A) 94.1(3)	N(1B)−P(1B)−Pd(1B) 93.9(3)
N(1A)−P(2A)−Pd(1A) 94.3(2)	N(1B)−P(2B)−Pd(1B) 94.7(3)
C(1A)−N(1A)−P(2A) 132.2(6)	C(1B)−N(1B)−P(2B) 126.8(7)
C(1A)−N(1A)−P(1A) 124.2(6)	C(1B)−N(1B)−P(1B) 131.0(7)
P(2A)−N(1A)−P(1A) 99.3(3)	P(2B)−N(1B)−P(1B) 99.3(3)
N(1A)−C(1A)−C(2A) 111.0(7)	N(1B)−C(1B)−C(4B) 113.0(8)
N(1A)−C(1A)−C(4A) 113.1(7)	N(1B)−C(1B)−C(2B) 109.0(7)
C(2A)−C(1A)−C(4A) 115.0(7)	C(4B)−C(1B)−C(2B) 115.6(8)
C(1A)−C(2A)−C(3A) 111.4(8)	C(3B)−C(2B)−C(1B) 110.4(9)

The metal center is in a slightly distorted square-planar environment, being coordinated by two chlorine atoms and two phosphorous atoms of the chelating (S_c)-**1** ligand. The chelating ligand forms a four-membered ring with the N1 atom deviating by ca. 0.15 Å from the plane formed by the P1, P2 and Pd1 (or Pt1) atoms. The P1−Pd1−P2 and P1−Pt−P2 bite angles are 71.7 and 72.0° in **4** and **5**, respectively. The absolute configuration of the chiral carbon atom C1 is confirmed to be *S*.

Catalysis

We used the catalytic systems formed by [Rh(acac)$(CO)_2$] and ligands (R_a,R_a)-**2** and (R_a,S_c)-**3**, at ligand-to-metal ratios of 1:1 and 1:2, in the hydroformylation of styrene. The catalytic runs were carried out in benzene solutions using an equimolar mixture of hydrogen and carbon monoxide gases. The catalytic systems so formed were unstable under the experimental conditions (using a CO/H_2 pressure of 50 atm and a temperature of 40 °C) and afforded metallic rhodium together with unidentified decomposition products. Thus, the ligands (R_a,R_a)-**2** and (R_a,S_c)-**3** are unsuitable for the enantioselective rhodium-catalysed hydroformylation of styrene.

Table 2. Selected bond lengths [Å] and angles [deg] for molecule A in **5**

Pt(1A)−P(1A)	2.200(2)	Pt(1B)−P(1B)	2.201(2)
Pt(1A)−P(2A)	2.2014(19)	Pt(1B)−P(2B)	2.207(2)
Pt(1A)−Cl(2A)	2.357(2)	Pt(1B)−Cl(2B)	2.346(2)
Pt(1A)−Cl(1A)	2.360(2)	Pt(1B)−Cl(1B)	2.355(2)
P(1A)−N(1A)	1.702(6)	P(1B)−N(1B)	1.722(6)
P(1A)−C(5A)	1.795(8)	P(1B)−C(5B)	1.787(8)
P(1A)−C(11A)	1.807(8)	P(1B)−C(11B)	1.810(8)
P(1A)−P(2A)	2.590(3)	P(1B)−P(2B)	2.590(3)
P(2A)−N(1A)	1.689(6)	P(2B)−N(1B)	1.683(6)
P(2A)−C(23A)	1.795(9)	P(2B)−C(17B)	1.811(8)
P(2A)−C(17A)	1.816(8)	P(2B)−C(23B)	1.819(8)
N(1A)−C(1A)	1.503(8)	N(1B)−C(1B)	1.487(8)
C(1A)−C(2A)	1.512(10)	C(1B)−C(4B)	1.542(11)
C(1A)−C(4A)	1.523(10)	C(1B)−C(2B)	1.546(12)
C(2A)−C(3A)	1.522(10)	C(2B)−C(3B)	1.451(11)
P(1A)−Pt(1A)−P(2A)	72.11(8)	P(1B)−Pt(1B)−P(2B)	71.97(7)
P(1A)−Pt(1A)−Cl(2A)	167.57(8)	P(1B)−Pt(1B)−Cl(2B)	171.23(8)
P(2A)−Pt(1A)−Cl(2A)	97.15(8)	P(2B)−Pt(1B)−Cl(2B)	99.77(9)
P(1A)−Pt(1A)−Cl(1A)	99.35(8)	P(1B)−Pt(1B)−Cl(1B)	97.22(9)
P(2A)−Pt(1A)−Cl(1A)	171.28(8)	P(2B)−Pt(1B)−Cl(1B)	167.01(9)
Cl(2A)−Pt(1A)−Cl(1A)	91.53(8)	Cl(2B)−Pt(1B)−Cl(1B)	91.34(10)
N(1A)−P(1A)−Pt(1A)	93.7(2)	N(1B)−P(1B)−Pt(1B)	93.8(2)
N(1A)−P(2A)−Pt(1A)	94.0(2)	N(1B)−P(2B)−Pt(1B)	94.7(2)
C(1A)−N(1A)−P(2A)	133.0(5)	C(1B)−N(1B)−P(2B)	125.3(5)
C(1A)−N(1A)−P(1A)	123.4(5)	C(1B)−N(1B)−P(1B)	131.9(6)
P(2A)−N(1A)−P(1A)	99.6(3)	P(2B)−N(1B)−P(1B)	99.0(3)
N(1A)−C(1A)−C(2A)	111.8(6)	N(1B)−C(1B)−C(4B)	109.8(7)
N(1A)−C(1A)−C(4A)	112.3(6)	N(1B)−C(1B)−C(2B)	112.4(6)
C(2A)−C(1A)−C(4A)	113.8(7)	C(4B)−C(1B)−C(2B)	113.2(7)
C(1A)−C(2A)−C(3A)	113.6(7)	C(3B)−C(2B)−C(1B)	113.4(9)

Experimental Section

The ligands (S_c)-**1**, (R_a,R_a)-**2** and (R_a,S_c)-**3** were prepared as reported in the literature.[3] All other reagents were purchased from Sigma−Aldrich and Strem and used as supplied. All reactions were performed under dry nitrogen in a vacuum system or in Schlenk apparatus. All solvents were purified by conventional procedures and freshly distilled prior to use. For column chromatography, we used silica gel 60 (220−440 mesh) purchased from Fluka. IR spectra were obtained from Nujol mulls on KBr plates using a Perkin−Elmer FTIR 1720 spectrometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AMX R300 instrument. ^{1}H NMR spectra were referenced to internal tetramethylsilane and ^{31}P{^{1}H} spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei are at relatively higher frequencies. Elemental analyses were performed by Redox s.n.c., Monza, Milano.

[Pd(S_c-1)Cl$_2$] (4): Solid (S_c)-**1** (0.46 g, 1.04 mmol) was added to a solution of [Pd(PhCN)$_2$Cl$_2$] (0.40 g, 1.04 mmol) in CH_2Cl_2 (30 mL).The mixture was stirred at room temperature for about 30 min. During this time, the solution became turbid and its colour switched from dark- to bright-orange. After filtration, evaporation of the solvent under reduced pressure yielded a solid that was washed twice with hexane and crystallized from CH_2Cl_2/petroleum ether (3:1, 15 mL) to obtain an orange-yellow crystalline solid. Yield: 73% (0.470 g, 0.76 mmol). ^{1}H NMR ($CDCl_3$): δ = 8.02−7.55 (m, 20 H, Ar−H), 3.28 (m, 1 H, CH), 1.29 (m, 1 H, CH_2), 0.95 (m, 1 H, CH_2), 0.79 (d, ^3J = 7 Hz, 3 H, CH_3), 0.43 (t, ^3J = 7 Hz, 3 H, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 29.6 (s) ppm. $C_{28}H_{29}Cl_2NP_2Pd$ (618.80): calcd. C 54.35, H 4.72, Cl 11.46, N 2.26; found C 54.26, H 4.68, Cl 11.70, N 2.14.

[Pt(S_c-1)Cl$_2$] (5): Following the same procedure used for the synthesis of **4**, compound **5** was obtained as a white crystalline solid by reacting [Pt(COD)Cl$_2$] (0.50 g, 1.33 mmol) and (S_c)-**1** (0.59 g, 1.33 mmol). Yield: 82% (0.777 g, 1.09 mmol). ^{1}H NMR ($CDCl_3$): δ = 8.00 (m, 10 H, Ar−H), δ = 7.50 (m, 10 H, Ar−H), 3.20 (m, 1 H, C*H), 1.02 (m, 1 H, CH_2), 0.87 (m, 1 H, CH_2), 0.77 (d, ^3J = 7 Hz, 3 H, CH_3), 0.41 (t, ^3J = 7 Hz, 3 H, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 15.5 (t, $^1J_{Pt,P}$ = 3285 Hz) ppm. $C_{28}H_{29}Cl_2NP_2Pt$ (707.49): calcd. C 47.54, H 4.13, Cl 10.02, N 1.98; found C 47.50, H 3.98, Cl 9.94, N 1.89.

[Rh(COD)(S_c-1)]PF$_6$ (6): NH_4PF_6 (0.260 g, 1.6 mmol) was added to a solution of [Rh(COD)Cl]$_2$ (0.400 g, 0.8 mmol) in THF (25 mL). The bright-yellow solution was stirred at room temperature for 30 min. Upon adding the solid ligand (S_c)-**1** (0.706 g, 1.6 mmol), an instantaneous change of colour occurred from yellow to orange, together with formation of an orange precipitate. The solvent was evaporated under reduced pressure and the residual solid was washed three times with hexane to afford the pure title complex **6** as an orange powder. Yield: 65% (0.830 g, 1.04 mmol). ^{1}H NMR ($CDCl_3$): δ = 7.80−7.40 (m, 32 H, Ar−H), 3.06 (m, 1 H, C*H), 0.82 (m, 1 H, CH_2), 0.71 (m, 1 H, CH_2), 0.64 (d, ^3J = 7 Hz, 3 H, CH_3), 0.34 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 50.1 (d, $^1J_{RhP}$ = 134 Hz), −143.9 (PF_6) ppm. $C_{36}H_{41}F_6NP_3Rh$ (797.55): calcd. C 54.22, H 5.18, F 14.29, N 1.76; found C 53.92, H 5.22, F 14.15, N 1.73.

[Pd(R_a,R_a-2)Cl$_2$] (8): A solution of (R_a,R_a)-**2** (0.563 g, 0.78 mmol) in toluene (10 mL) was added dropwise to a solution of [Pd(PhCN)$_2$Cl$_2$] (0.300 g, 0.78 mmol) in the same solvent (20 mL) that was cooled in an ice bath. The reaction mixture was stirred for 30 min; during this time, precipitation of an orange solid occurred. The solid was separated by filtration, washed a few times with petroleum ether and then dried under reduced pressure to give the product **8** as an orange solid. Yield: 74% (0.519 g, 0.58 mmol). ^{1}H NMR ($CDCl_3$): δ = 8.33−7.28 (m, 29 H, Ar−H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 82.1 (s) ppm. $C_{46}H_{29}Cl_2NO_4P_2Pd$ (899.0): calcd. C 61.46, H 3.25, Cl 7.89, N 1.56; found C 61.36, H 3.15, Cl 8.02, N 1.50.

[Pt(R_a,R_a-2)I$_2$] (9): A solution of ligand (R_a,R_a)-**2** (0.130 g, 0.18 mmol) in toluene (10 mL) was added dropwise at room temperature to a solution of [Pt(COD)I$_2$] (0.100 g, 0.18 mmol) in the same solvent (20 mL). After 1 h, the bright-yellow solution was concentrated under reduced pressure until the volume was ca. 5 mL; after the addition of pentane (30 mL), a deep-yellow solid precipitated. This solid was crystallized from CH_2Cl_2/pentane (3:1, 10 mL) to obtain the pure complex **9** as a yellow powder. Yield: 79% (0.166 g, 0.14 mmol). ^{1}H NMR ($CDCl_3$): δ = 8.49 (m, 6 H, Ar−H), 8.04−7.95 (m, 11 H, Ar−H), 7.51−7.31 (m, 4 H, Ar−H), 6.89 (m, 4 H, Ar−H), 6.80−6.75 (m, 4 H, Ar−H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 94.5 ($^1J_{Pt,P}$ = 5296 Hz) ppm. $C_{46}H_{29}I_2NO_4P_2Pt$ (1170.59): calcd. C 47.20, H 2.50, I 21.68, N 1.20; found C 46.98, H 2.58, I 21.48, N 1.26.

[Pd(R_a,S_c-3)Cl$_2$] (10): A solution of ligand (R_a,S_c)-**3** (0.108 g, 0.189 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [Pd(PhCN)$_2$Cl$_2$] (0.073 g, 0.189 mmol) in the same solvent (25 mL). The reaction mixture was stirred for 30 min at room temperature. The solution was concentrated under reduced pressure until the volume was ca. 5 mL; after the addition of pentane (30 mL), a yellow solid precipitated. This solid was crystallized from CH_2Cl_2/pentane (3:1, 10 mL), washed twice with petroleum ether and then dried under vacuum to give compound **10**. Yield: 68% (0.101 g, 0.13 mmol). ^{1}H NMR ($CDCl_3$): δ = 8.04−7.95 (m, 22 H, Ar−H),

Table 3. Crystal data and structural refinement for compounds **4** and **5** ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_c^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$)

Compound	**4**	**5**
Formula	$C_{28}H_{29}Cl_2NP_2Pd$	$C_{28}H_{29}Cl_2NP_2Pt$
Formula mass	618.76	707.45
Wavelength (Å)	0.71073 (Mo-*Kα*)	0.71073 (Mo-*Kα*)
Crystal system	orthorhombic	orthorhombic
Space group	$P\ 2_12_12_1$	$P\ 2_12_12_1$
Unit cell dimensions (Å)	$a = 14.931(3)$	$a = 14.951(3)$
$b = 16.891(3)$	$b = 16.966(3)$	
$c = 21.089(5)$	$c = 21.053(5)$	
V (Å^3)	5319(2)	5340(2)
Z, density (calcd.) (Mg/m^3)	8, 1.545	8, 1.760
Abs. coefficient (cm^{-1})	10.37	55.93
F(000)	2512	2768
Crystal size (mm)	0.18 × 0.32 × 0.37	0.22 × 0.21 × 0.22
θ range (°)	1.54−28.22	1.54−27.98
Reflection collected, independent reflections	31872, 11746 [$R_{(int)} = 0.0788$]	31436, 11395 [$R_{(int)} = 0.0590$]
Obsd. reflections [$I > 2\sigma(I)$]	5209	8705
Data/restraints/parameters	11746/0/621	11395/0/621
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0433$, $wR_2 = 0.0467$	$R_1 = 0.0406$, $wR_2 = 0.0916$
R indices (all data)	$R_1 = 0.1310$, $wR_2 = 0.0602$	$R_1 = 0.0608$, $wR_2 = 0.0991$

3.15 (m, 1 H, CH), 1.18 (m, 1 H, CH_2), 0.82 (m, 1 H, CH_2), 0.73 (d, ^3J = 7 Hz, 3 H, CH_3), 0.41 (t, ^3J = 7 Hz, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 81.8 (d, $^2J_{P,P}$ = 17 Hz), 39.9 (d, $^2J_{P,P}$ = 17 Hz) ppm. $C_{36}H_{31}Cl_2NO_2P_2Pd$ (784.91): calcd. C 57.74, H 4.17, Cl 9.47, N 1.87; found C 57.84, H 4.21, Cl 9.62, N 1.77.

[Pt(R_a,S_c-3)I$_2$] (11): Following the same procedure used for the synthesis of **10**, compound **11** was obtained as a white solid after reacting [Pt(COD)I_2] (0.094 g, 0.168 mmol) and solid (R_a,S_c)-**3** (0.096 g, 0.168 mmol) in CH_2Cl_2. Yield: 67% (0.115 g, 0.11 mmol). ^1H NMR ($CDCl_3$): δ = 8.04−7.95 (m, 22 H, Ar−H), 3.08 (m, 1 H, CH), 1.14 (m, 1 H, CH_2), 0.75 (m, 1 H, CH_2), 0.61 (d, ^3J = 7 Hz, 3 H, CH_3), 0.35 (t, ^3J = 7 Hz, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 98.3 (d, $^2J_{P,P}$ = 19, $^1J_{Pt,P}$ 4876 Hz), 45.8 (d, $^2J_{P,P}$ = 19, $^1J_{Pt,P}$ 3218 Hz) ppm. $C_{36}H_{31}Cl_2NO_2P_2Pt$ (1020.50): calcd. C 42.37, H 3.06, I 24.87, N 1.37; found C 42.34, H 3.01, I 24.69, N 1.31.

Reaction of [RhCO)$_2$Cl]$_2$ with (R_a,S_c)-3: Solid (R_a,S_c)-**3** (0.320 g, 0.56 mmol) was added at room temperature to a stirred solution of [Rh(CO)$_2$Cl]$_2$ (0.112 g, 0.288 mmol) in hexane (30 mL). After the addition, precipitation of a yellow compound was observed. The mixture was stirred for 30 min at room temperature, and then the solvent was evaporated under reduced pressure. The solid was washed with hexane (3 × 10 mL) until the filtered solution was colourless, i.e., indicating that the excess of [Rh(CO)$_2$Cl]$_2$ had been separated. The $^{31}P\{^1H\}$ NMR spectrum of the crude product (Figure 1), recorded in $CDCl_3$, indicated the presence of both [Rh(R_a,S_c-**3**)(CO)Cl] (**12**) and [Rh(μ-R_a,S_c-**3**)(CO)Cl]$_2$ (**13**) together with other species at very low concentrations. We failed to obtain compounds **12** and **13** as analytically pure solids, either by using column chromatographic methods or differences in their solubilities. The reaction of [RhCO)$_2$Cl]$_2$ with (R_a,S_c)-**3** in a 1:2 molar ratio also afforded a mixture of **12** and **13**. **Compound [Rh(R_a,S_c-3)(CO)Cl] (12):** IR (KBr, Nujol): $\tilde{\nu}_{CO}$ = 1990 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.04−6.95 (m, 22 H, Ar−H), 2.66 (m, 1 H, CH), 1.23 (m, 1 H, CH_2), 0.81 (m, 1 H, CH_2), 0.49 (d, ^3J = 6 Hz, 1 H, CH_3), 0.23 (t, ^3J = 7 Hz, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 103.9 (dd, $^1J_{RhP}$ = 222, $^2J_{P,P}$ = 98 Hz), 47.7 (dd, $^1J_{RhP}$ = 122, $^2J_{P,P}$ = 98 Hz) ppm. **Compound [Rh(μ-R_a,S_c-3)(CO)Cl]$_2$ (13):** ^1H NMR ($CDCl_3$): δ = 8.04−6.95 (m, 44 H, Ar−H), 2.90 (m, 2 H, CH), 1.18 (m, 2 H, CH_2), 0.72 (m, 2 H, CH_2), 0.78 (d, ^3J = 7 Hz, 6 H, CH_3), 0.43 (d, ^3J = 7 Hz, 6 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 108.0 (ddd, $^1J_{RhP}$ = 133, $^2J_{P,P}$ = 46, $^2J_{P,P}$ = 35 Hz), 54.4 (ddd, $^1J_{RhP}$ = 124, $^2J_{P,P}$ = 46, $^2J_{P,P}$ = 35 Hz) ppm.

X-ray Data Collection, Structural Solution and Refinement for Compounds 4 and 5: The intensity data of compound **4** and **5** were collected at room temperature on a Bruker Smart 1000 single-crystal diffractometer. Crystallographic and experimental details for the structures are summarized in Table 3.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2)[13] with anisotropic thermal parameters used in the last cycles of refinement for all the non-hydrogen atoms.

The hydrogen atoms were introduced into geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement, we used a weighting scheme: $w = 1/[\sigma^2F_o^2 + (0.0069\ P)^2]$ (**4**, **Pd**), $w = 1/[\sigma^2F_o^2 + (0.0454\ P)^2]$ (**5**, **Pt**), where $P = (F_o^2 + 2\ F_c^2)/3$.

CCDC-215879 (for **4**) and -215878 (for **5 Pt**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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