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# The coordination chemistry of enantiopure diimines derived from 1-phosphanorbornadiene-2-carboxaldehydes

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**Abstract**

The reaction of *trans*-1,2-diaminocyclohexane with enantiopure (*R*)-2-formyl-1-phosphanorbornadiene (**1**) takes place with efficient kinetic resolution and gives an easily separable mixture of the corresponding (*S*,*S*)-bis-imine (**3**) and (*R*)-mono-imine (**4**). The absolute configuration of **3** has been established by X-ray crystal structure analysis. The coordination chemistry of enantiopure **3** with Pd(II), Rh(I), and Ru(II) has been investigated. The reaction of $[PdCl_2(cod)]$ mainly affords a binuclear complex **6** whose structure has been established by X-ray analysis. One $PdCl_3^-$ unit is coordinated to one P and one $PdCl^+$ unit is tricoordinated to the other P and the two N. The two square planar units are parallel and the Pd···Pd distance is 3.1787(5) Å. The reaction of $[RhCl(cod)]_2$ gives the very reactive tetracoordinate cationic $[Rh(P_2N_2)]^+$ species **7** which is able to activate one C–Cl bond of chloroform to give the dichloromethyl-Rh complex (**8**) whose octahedral structure has been ascertained by X-ray analysis.


*Keywords:* 1-phosphanorbornadienes; Enantiopure; P,N ligands; Kinetic resolution; Pd, Rh, Ru complexes

## 1. Introduction

The tetradentate $P_2N_2$ ligands are presently under intensive investigation because they provide very stable chelates with transition metals which can be used to build robust catalysts [1]. Among them, the bis(phosphino) derivatives of (1*S*,2*S*)-diaminocyclohexane have been used with significant success in asymmetric catalysis [2]. Their robustness is well put in evidence by the fact that their $[RuCl]^+$ complexes have been used in the enantioselective epoxidation of olefins [3]. From another standpoint, we and others have developed during the last few years the chemistry and catalytic uses of enantiopure 1-phosphanorbornadienes [4]. These systems are characterized by the presence of a chiral non-racemizable phosphorus atom situated at the bridgehead of a bicyclic system. Among them, the 1-phosphanorbornadiene-2-carboxaldehydes proved to be especially easy to prepare [5]. Combining these phosphinoaldehydes with various diamines including (1*S*,2*S*)-diaminocyclohexane in an attempt to get a synergy between the optically active carbon centers of the diamine and the phosphorus centers of the bicyclic structures appeared as an attractive idea. We report here on our work on the synthesis and coordination chemistry of such species.

## 2. Results and discussion

Our starting product has been the readily available (*R*)-2-formyl-1-phosphanorbornadiene (**1**). As a test reaction, we first studied its condensation with ethylenediamine. The reaction takes place at room temperature in the presence of an acid catalyst and a water scavenger:

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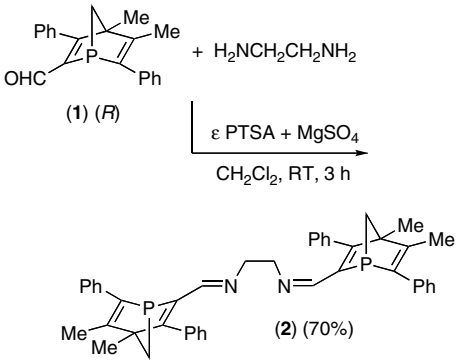
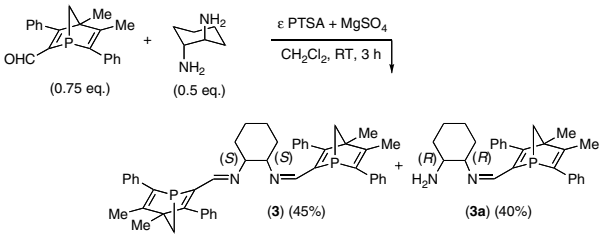


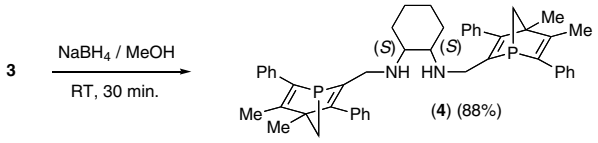

(1)

The reaction was then transposed with *trans*-1,2-diaminocyclohexane. An efficient kinetic resolution takes place. The (*S*,*S*)-diamine yields the expected diphosphine **3**, whereas the condensation of the (*R*,*R*)-diamine stops at the monophosphine:



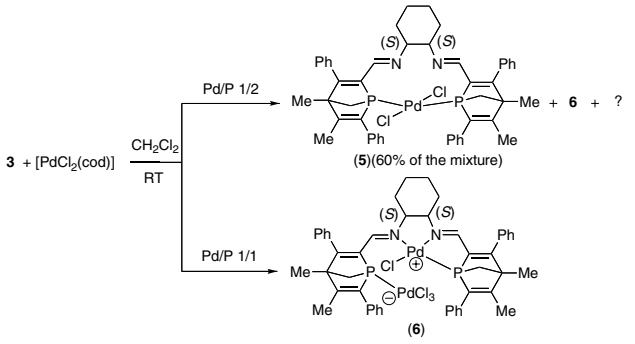

(2)

The absolute configuration of **3** was established by X-ray crystal structure analysis (Fig. 1). We completed our work on the $P_2N_2$ ligands by a study of the reduction of **3**:




(3)

We then focused our attention on the coordination chemistry of **3**. The reaction pathway of **3** with $[PdCl_2(cod)]$ depends on the Pd/P ratio. With a 1/2 ratio, the main product is the classical $[PdCl_2(P_2)]$ complex **5** whose formation appears to be instantaneous according to the monitoring of the reaction mixture by $^{31}P$ NMR spectroscopy. Its symmetrical structure is ascertained by its single $^{31}P$ resonance at 43.4 ($CDCl_3$) vs. −23.7 ppm for **3**. Complex **5** is unstable and was only characterized by $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. With a Pd/P ratio of 1/1, the reaction product is the zwitterionic dinuclear P–$N_2$P-complex **6** which is quite stable:




(4)

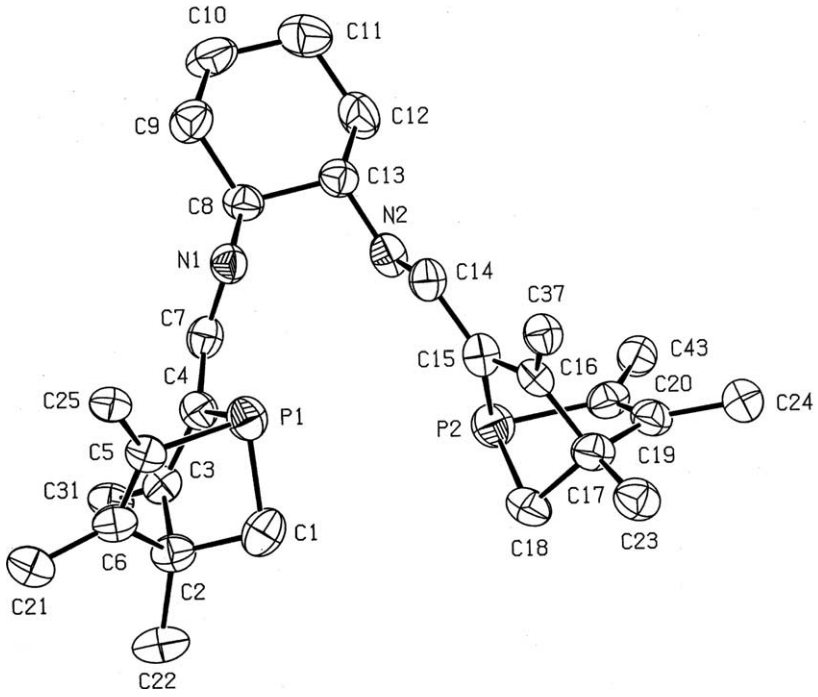
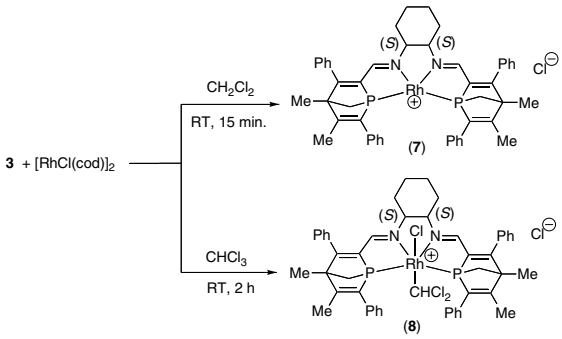



Fig. 1. ORTEP drawing of **3** showing the absolute configuration of the 1,2-diminocyclohexane unit.

Complex **6** displays two resonances on its $^{31}P$ NMR spectrum: $\delta^{31}P$ 44.7 and 55.2. Its structure was established by X-ray analysis (Fig. 2). Both palladium atoms have geometries close to square planar: the sum of the angles at $Pd_1$ is 359.95° and the sum of the angles at $Pd_2$ 359.5° The two planes are almost parallel and the two palladium atoms are located one above the other: the angles L–$Pd_1$–$Pd_2$ are in the range 84.93(3)–95.67(4)° and the angles L–$Pd_2$–$Pd_1$ in the range 87.8(1)–95.35(3)°. At 3.1787(5) Å, the distance between the two palladium atoms is too long for a genuine bond, but, obviously, a significant coulombic interaction does exist (Pd–Pd bonds as long as 2.93 Å have been recorded in the literature [6]). Quite expectedly, the longest Pd–Cl bond is *trans* to $P_1$ (2.366(1) Å), and the shortest *trans* to $N_2$ (2.292(1) Å). As far as we know, zwitterionic complexes similar to **6** have not been described in the literature previously.

In dichloromethane, 1,2-dichloroethane or acetone, **3** reacts rapidly with $[RhCl(cod)]_2$ to give the expected tetracoordinate cationic complex **7**. Its symmetrical structure is ascertained by its single $^{31}P$ resonance at 45.3 ($CD_2Cl_2$) with a characteristic $^1J_{Rh-P}$ coupling of 172.7 Hz. Complex **7** is highly reactive and was only characterized by $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. When running the reaction in chloroform, complex **7** activates one of the carbon–chlorine bonds of the solvent and yields the hexacoordinate dichloromethyl complex **8** in 86% yield:




(5)

The structure of **8** was established by X-ray analysis (Fig. 3). The coordination geometry of rhodium is a distorted octahedron with a widened $P_1$–Rh–$P_2$ angle of 107.82(6)° but with an almost linear $C_{21}$–Rh–$Cl_1$ subunit (178.2(2)°). The Rh–$C_{21}$ bond is rather short at 2.081(5) Å, whereas the $C_{21}$–$Cl_2$ and $C_{21}$–$Cl_3$ bonds are rather long at 1.797(6) and 1.808(5) Å, respectively (see [7] for the discussion of similar data). The activation of the C–Cl bonds of chloroform by a $[RhCl(N_3)]$ complex has already been described in the literature [7]. The same phenomenon – lengthening of the C–Cl bonds and shortening of the Rh–C bond – has been observed and explained by some contribution of the carbenic formulation $[Rh{=}C]^+Cl^-$. In our case, this contribution is certainly minimal since rhodium bears a positive charge. Anyhow, our cationic $[Rh(N_2P_2)]^+$ complex **8** is less electron-rich

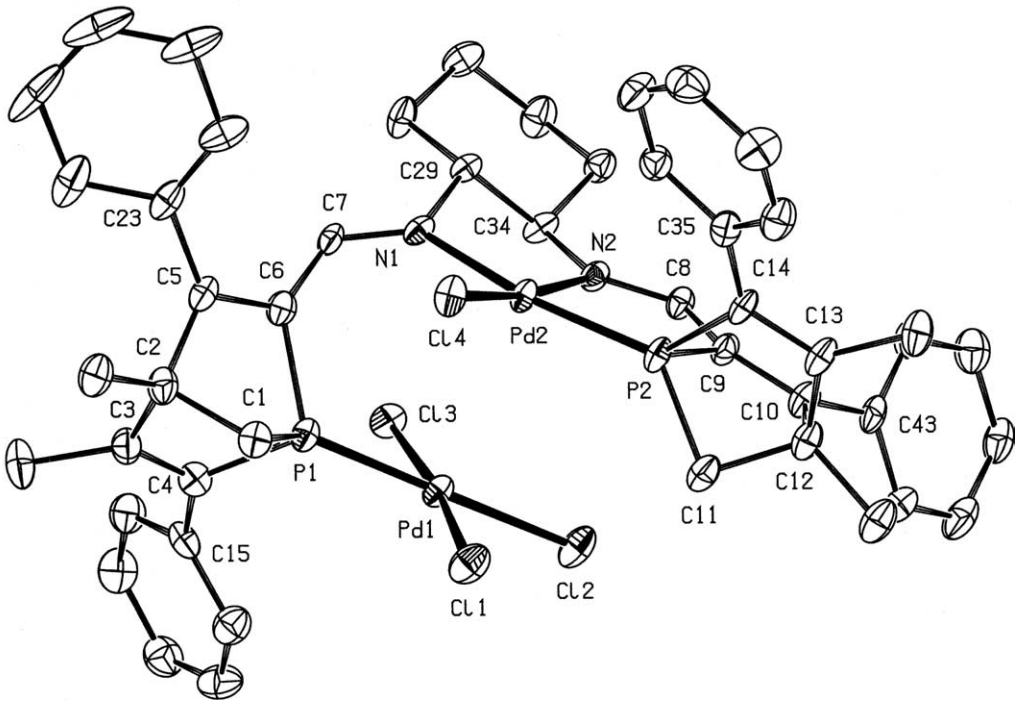



Fig. 2. ORTEP drawing of **6**. Significant bond distances (Å) and angles (°): P(1)–Pd(1) 2.189(1), Pd(1)–Cl(1) 2.316(1), Pd(1)–Cl(2) 2.366(1), Pd(1)–Cl(3) 2.300(1), Pd(1)–Pd(2) 3.1787(5), P(2)–Pd(2) 2.225(1), Pd(2)–N(1) 2.072(3), Pd(2)–N(2) 2.027(4), Pd(2)–Cl(4) 2.292(1); P(1)–Pd(1)–Cl(1) 91.03(4), P(1)–Pd(1)–Cl(3) 82.75(4), Cl(1)–Pd(1)–Cl(2) 94.28(4), Cl(3)–Pd(1)–Cl(2) 91.89(4), N(2)–Pd(2)–N(1) 81.5(1), N(2)–Pd(2)–P(2) 84.7(1), N(1)–Pd(2)–Cl(4) 97.9(1), P(2)–Pd(2)–Cl(4) 95.40(4).

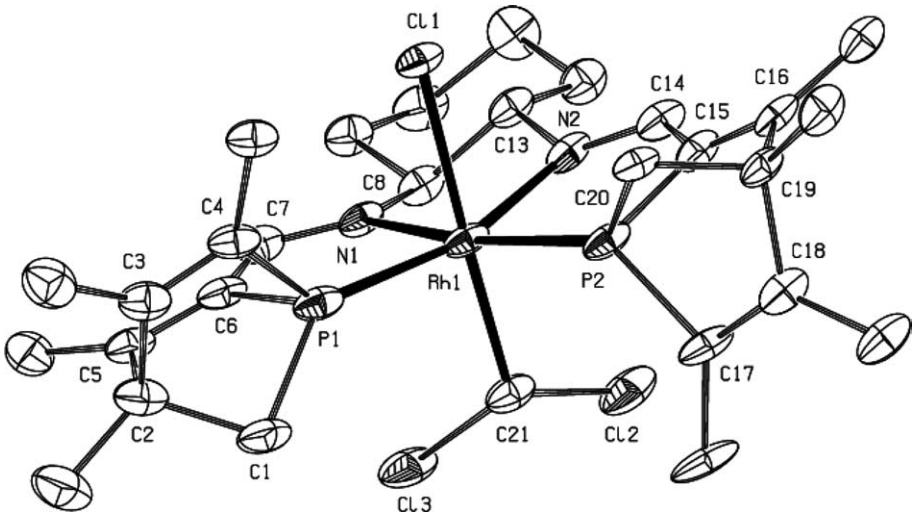



Fig. 3. ORTEP drawing of **8**. Phenyl substituents have been omitted for clarity. Significant bond distances (Å) and angles (°): Rh(1)–N(1) 2.052(4), Rh(1)–N(2) 2.066(5), Rh(1)–P(1) 2.260(2), Rh(1)–P(2) 2.255(1), Rh(1)–Cl(1) 2.421(1), Rh(1)–C(21) 2.081(5); N(1)–Rh(1)–N(2) 82.1(2), N(1)–Rh(1)–C(21) 91.5(2), N(1)–Rh(1)–N(2) 82.1(2), N(2)–Rh(1)–C(21) 96.7(2), N(2)–Rh(1)–P(2) 84.9(1), C(21)–Rh(1)–P(2) 90.3(1), N(1)–Rh(1)–P(1) 84.9(1), C(21)–Rh(1)–P(1) 93.5(2), P(2)–Rh(1)–P(1) 107.82(6), N(1)–Rh(1)–Cl(1) 89.2(1), N(2)–Rh(1)–Cl(1) 81.8(1), P(2)–Rh(1)–Cl(1) 88.68(4), P(1)–Rh(1)–Cl(1) 88.20(5).

than the [RhCl($N_3$)] complex and is unable to activate the C–Cl bonds of dichloromethane contrary to this latter species.

Our study was completed by the preparation of the more conventional hexacoordinate [$RuCl_2$(**3**)] complex **9**, which was only characterized by spectroscopy and elemental analysis and which is quite similar to a [$RuCl_2(N_2P_2)$] complex prepared by Noyori for catalytic studies [2a]. The study of the catalytic properties of this new range of enantiopure complexes will be reported later.

## 3. Experimental

### 3.1. General

All reactions were carried out under nitrogen by using standard techniques. Solvents were dried under nitrogen by standard procedures, distilled before use and stored under argon. *trans*-1,2-Diaminocyclohexane was obtained from commercial suppliers and used without further purification. $[Rh(cod)Cl]_2$ [8], [$RuCl_2$-$(DMSO)_4$] [9], [$PdCl_2$(cod)] [10] and 1-phosphanorbornadiene-2-carboxaldehyde (**1**) [5] were prepared according to the literature methods.

Elemental analyses were performed by the *Service de microanalyse du CNRS*, *Gif/Yvette*, France. NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for $^1$H, 75.47 for $^{13}$C and 121.50 MHz for $^{31}$P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane ($^1$H and $^{13}$C) and external 85% aqueous $H_3PO_4$($^{31}$P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method on a Hewlett–Packard (HP) 5989B coupled with a GC HP 5890.

### 3.2. Preparation of bis-imine ($R_P,R_P$)-(**2**)

To a solution of aldehyde **1** (1.6 g, $5\times10^{-3}$ mol), *p*-toluenesulfonic acid monohydrate (0.01 g, $0.05\times10^{-3}$ mol) and $MgSO_4$ (1.2 g, $1\times10^{-2}$ mol) in dichloromethane (15 mL) was added within 30 min a solution of ethylenediamine (0.3 g, $5\times10^{-3}$ mol) in dichloromethane (15 mL). The reaction mixture was stirred for 3 h at room temperature until no more aldehyde was detected and then filtered through celite. The solvent was removed in vacuo and the residue was redissolved in a minimum amount of hot ethanol. The solution was cooled to 0 °C to give an orange solid which was filtered and dried in vacuo. Yield: 1.5 g, 70%. $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ −24.3. $^1$H NMR ($CDCl_3$): $\delta$ 1.30 (6H, s, –C$H_3$), 1.99 (6H, s, –C$H_3$), 2.0 (4H, d × d, $J$ = 6.0 Hz and 4.0 Hz, –C$H_2$), 3.63 (4H, s, –N–C$H_2$–), 6.91–7.31 (20H, m, Ph*H*), 7.86 (2H, d, $J$ = 8.7 Hz, –N=C*H*–). $^{13}$C{$^1$H} NMR $\delta$ 16.3 (s, –*C*$H_3$), 20.7 (s, –*C*$H_3$), 62.5 (s, –*C*$H_2$–N–), 64.6 (s, –*C*$H_2$-), 72.2 (d, $J$ = 5.8 Hz, –*C*–), 173.5 (d, $J$ = 2.0 Hz, –*C*H=N–). Mass spectrum: *m/z* 663 (M + 1), 399 (M − 263). $[\alpha]_D$ = 82.0 ($c$ = 0.55, $CH_2Cl_2$).

### 3.3. Preparation of bis-imine ($R_P,R_P,S_C,S_C$)-(**3**)

To a solution of aldehyde **1** (2.4 g, $7.5\times10^{-3}$ mol), *p*-toluenesulfonic acid monohydrate (0.01 g, $0.05\times10^{-3}$ mol) and $MgSO_4$ (1.2 g, $1\times10^{-2}$ mol) in dichloromethane

(15 mL) was added within 30 min a solution of *trans*-1,2-diaminocyclohexane (0.57 g, $5 \times 10^{-3}$ mol) in dichloromethane (15 mL). The reaction mixture was stirred for 3 h at room temperature until no more aldehyde was detected, and then filtered through celite. The solvent was removed in vacuo and the residue was redissolved in a minimum amount of hot ethanol. The solution was cooled to 0 °C to give white crystals which were filtered and dried in vacuo. Yield: 1.6 g, 45%; m.p. = 221 °C. Crystals suitable for a X-ray crystal structure analysis were obtained from absolute ethanol at room temperature. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −23.7. $^1H$ NMR ($CDCl_3$): $\delta$ 1.26 (2H, m, –C$H_2$–), 1.33 (6H, s, –C$H_3$), 1.61 (4H, m, –C$H_2$–), 1.64 (2H, m, –C$H_2$–), 1.99 (4H, s, –C$H_2$–), 2.03 (6H, s, –C$H_3$), 3.06 (2H, m, =N–C$H$–), 6.93–7.31 (20H, m, Ph$H$), 7.82 (2H, d, $J$ = 8.7 Hz, –N=C$H$–). $^{13}C\{^1H\}$ NMR $\delta$ 16.4 (s, –C$H_3$), 20.8 (s, –C$H_3$), 24.8 (s, –C$H_2$–), 32.8 (s, –C$H_2$–), 64.1 (s, –C$H_2$), 72.2 (d, $J$ = 5.6 Hz, –C–), 74.0 (s, –C$H$–N=), 172.6 (d, $J$ = 1.3 Hz, –C$H$=N–). Mass spectrum: $m/z$ 716 (M + 1), 399 (M − 316). $[\alpha]_D = -250$ ($c$ = 1.1, $CH_2Cl_2$).

### 3.4. Preparation of mono-imine ($R_P,R_C,R_C$)-(**3a**)

This compound was obtained as a crude product from the mother liquor of the crystallization of **3**. Yield: 40% (from integration of $^{31}P$ NMR spectra). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$−23.5. $^1H$ NMR ($CDCl_3$): $\delta$ 1.09 (2H, m, –C$H_2$–), 1.26 (2H, m, –C$H_2$–), 1.38 (3H, s, –C$H_3$), 1.57 (2H, m, –C$H_2$–), 1.70 (2H, m, –C$H_2$–), 2.06 (2H, d, $J$ = 16.0 Hz, –C$H_2$–), 2.08 (3H, s, –C$H_3$), 2.51(1H, m, $NH_2$–C$H$–), 2.93 (1H, m, =N–C$H$–), 7.01–7.46 (10H, m, Ph$H$), 8.0 (1H, d, $J$ = 8.6 Hz, –N=C$H$–). $^{13}C\{^1H\}$ NMR $\delta$ 15.9 (s, –C$H_3$), 20.2 (s, –C$H_3$), 24.9 (d, $J$ = 19.0 Hz, –C$H_2$–), 33.2 (d, $J$ = 24.3 Hz, –C$H_2$–), 54.5 (s, $NH_2$–C$H$), 63.5 (s, –C$H_2$–) 71.9 (d, $J$ = 5.8 Hz, –C–), 78.0 (s, –C$H$–N=), 172.8 (d, $J$ = 1.8 Hz, –C$H$=N–). Mass spectrum: $m/z$ 415 (M + 1).

### 3.5. Preparation of bis-amine ($R_P,R_P,S_C,S_C$)-(**4**)

To a solution of bis-imine (**3**) (0.57 g, $0.8 \times 10^{-3}$ mol) in dichloromethane (10 mL) was added solid $NaBH_4$ (0.90 g, $2 \times 10^{-3}$ mol) in one portion. Then acetic acid (0.4 mL, $6 \times 10^{-3}$ mol) was added and the mixture stirred at room temperature for 2 h. After hydrolysis with 3 N HCl, neutralization with 20% KOH, three extractions of the aqueous phase with $CH_2Cl_2$, the organic phase was dried over $MgSO_4$. The organic residue in $CH_2Cl_2$ (20 mL) was treated with DABCO (0.27 g, $2.4 \times 10^{-3}$ mol) for 12 h at RT. After evaporation, the organic residue was purified by chromatography on silica gel with $CH_2Cl_2$/AcOEt 80/20. Yield 0.80 g, 88%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ −17.6. $^1H$ NMR ($CDCl_3$): $\delta$ 0.63 (2H, m, –C$H_2$–), 0.87 (2H, m, –C$H_2$–), 1.22 (6H, s, –C$H_3$), 1.38 (2H, m, –C$H_2$–), 1.66 (2H, m, –C$H_2$–), 1.95 (6H, m, –C$H_2$– and –N–C$H$–), 1.97 (6H, s, –C$H_3$), 3.24 (4H, m, –N–C$H_2$–), 6.86–7.31 (20H, m, Ph$H$). $^{13}C\{^1H\}$ NMR $\delta$ 14.7 (s, –C$H_3$), 19.7 (s, –C$H_3$), 23.5 (s, –C$H_2$–), 30.0 (s, –C$H_2$–), 45.3 (d, $J$ = 10.5 Hz, –C$H_2$–N), 59.3 (s, –C$H$–N–), 65.3 (s, –C$H_2$–), 69.9 (d, $J$ = 4.4 Hz, –C–). Mass spectrum $m/z$ 721 (M + 2). $[\alpha]_D = 113$ ($c$ = 1.2, $CDCl_3$).

### 3.6. Preparation of [$PdCl_2$(3)] (**5**)

A suspension of $PdCl_2$(cod) (14.0 mg, $0.05 \times 10^{-3}$ mol) in $CDCl_3$ (1 mL) was added to a solution of bis-imine (**3**) (36 mg, $0.05 \times 10^{-3}$ mol) in $CDCl_3$ (1 mL). The $^{31}P$ NMR spectrum of the mixture was immediately recorded showing the formation of complex **5** (purity ca. 90%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 43.4. $^1H$ NMR ($CDCl_3$): $\delta$ 1.21 (4H, m, –C$H_2$–), 1.50 (6H, s, –C$H_3$), 1.68 (2H, m, –C$H_2$–), 2.20 (6H, s, –C$H_3$), 2.62 (2H, m, –C$H_2$–), 2.73 (2H, d, $J$ = 10.2 Hz, –C$H_2$–), 3.29 (2H, d, $J$ = 9.9 Hz, –C$H_2$–), 4.79 (2H, m, =N–C$H$–), 7.13–7.74 (20H, m, Ph$H$), 8.17 (pseudo t, –N=C$H$–). $^{13}C\{^1H\}$ NMR $\delta$ 15.2 (s, –C$H_3$), 18.6 (s, –C$H_3$), 23.3 (s, –C$H_2$–), 27.7(s, –C$H_2$–), 65.4 (s, –C–), 70.2 (d, $J$ = 16.8 Hz, –C$H_2$–), 73.5 (s, –C$H$–N=), 176.5 (s, –C$H$=N–).

### 3.7. Preparation of [$Pd_2Cl_4$(3)] (**6**)

A suspension of $PdCl_2$(cod) (58.0 mg, $0.2 \times 10^{-3}$ mol) in $CH_2Cl_2$ (5 mL) was added to a solution of bis-imine (**3**) (72 mg, $0.1 \times 10^{-3}$ mol) in $CH_2Cl_2$ (2 mL). A yellow solution of complex **6** was immediately formed. The solution was concentrated under reduced pressure. Ethanol was slowly added to the $CH_2Cl_2$ solution until it turned cloudy. Pale yellow crystals were filtered and dried in vacuo. Yield 80 mg, 80%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 55.2 and 44.7. $^1H$ NMR ($CDCl_3$): $\delta$ 1.20 (2H, m, –C$H_2$–), 1.44 (3H, s, –C$H_3$), 1.57 (3H, s, –C$H_3$), 1.68 (2H, m, –C$H_2$–), 1.87 (2H, m, –C$H_2$–), 2.19 (3H, s, –C$H_3$), 2.27 (3H, s, –C$H_3$), 2.60 (1H, m, –C$H_2$–), 2.73 (1H, d, $J$ = 10.0 Hz, –C$H_2$–), 2.80 (1H, m, –C$H_2$–), 3.08 (1H, d, $J$ = 10.7 Hz, –C$H_2$–), 3.75 (1H, d × d, $J$ = 10.0 Hz and 4.0 Hz, –C$H_2$–), 4.13 (1H, m, =N–C$H$–), 4.31 (1H, d × d, $J$ = 10.4 Hz and 4.0 Hz, –C$H_2$–), 4.67 (1H, m, =N–C$H$–), 7.22–7.80 (20H, m, Ph$H$), 7.78 (1H, d, $J$ = 8.8 Hz, –N=C$H$–), 7.84 (1H, d, $J$ = 8.4 Hz, –N=C$H$–). $^{13}C\{^1H\}$ NMR $\delta$ 15.4 (d, $J$ = 8.4 Hz, –C$H_3$), 16.0 (d, $J$ = 8.4Hz, –C$H_3$), 20.0 (d, $J$ = 3.7 Hz, –C$H_3$), 20.2 (d, $J$ = 4.3 Hz, –C$H_3$), 24.2 (s, –C$H_2$–), 24.5 (s, –C$H_2$–), 31.5 (s, –C$H_2$–), 31.6 (s, –C$H_2$–), 63.3 (d, $J$ = 4.7 Hz, –C–), 66.0 (d, $J$ = 3.3 Hz, –C–), 68.6 (s, –C$H$–N=), 68.7 (d, $J$ = 44.3 Hz, –C$H_2$–), 72.5 (d, $J$ = 35.7 Hz, –C$H_2$–), 77.7 (s, –C$H$–N=), 177.6 (d, $J$ = 6.2 Hz, –C$H$=N–),176.0 (d, $J$ = 1.4 Hz, –C$H$=N–). $[\alpha]_D = 16.8$ ($c$ = 0.5, $CH_2Cl_2$).

### 3.8. Preparation of [Rh(3)]$^+$Cl$^-$ (7)

A solution of [Rh(cod)Cl]$_2$ (12.5 mg, $0.025 \times 10^{-3}$ mol) in $CD_2Cl_2$ (1 mL) was added to a solution of bis-imine (**3**) (36 mg, $0.05 \times 10^{-3}$ mol) in $CD_2Cl_2$ (1 mL). The red solution was stirred for 15 min. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 45.3 (d, $J = 172.7$ Hz). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.2 (4H, m, –C*H*$_2$–), 1.44 (6H, s, –C*H*$_3$), 1.82 (2H, m, –C*H*$_2$–), 2.10 (6H, s, –C*H*$_3$), 2.28 (2H, d, $J = 10.0$ Hz, –C*H*$_2$), 2.40 (2H, d, $J = 10.0$ Hz, –C*H*$_2$–), 3.71 (2H, m, =N–C*H*–), 7.12–7.43 (20H, m, Ph*H*), 8.04 (2H, pseudo t, $J = 14.8$ Hz, –N=C*H*–). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 14.6 (s, –*C*H$_3$), 19.2 (d, $J = 3.5$ Hz, –*C*H$_3$), 23.6 (s, –*C*H$_2$–), 27.2 (s, –*C*H$_2$–), 67.6 (s, –*C*H$_2$–), 67.6 (d, $J = 16.0$ Hz, –*C*–), 72.4 (s, –*C*H–N=), 172.3 (s, –*C*H=N–).

### 3.9. Preparation of [RhCl(3)(CHCl$_2$)]$^+$Cl$^-$ (8)

A solution of [Rh(cod)Cl]$_2$ (12.5 mg, $0.025 \times 10^{-3}$ mol) in $CHCl_3$ (1 mL) was added to a solution of bis-imine (**3**) (36 mg, $0.05 \times 10^{-3}$ mol) in $CHCl_3$ (1 mL). The red solution was allowed to stand for two hours at room temperature. The new pale orange solution was concentrated under reduced pressure. Diethyl ether was added to $CHCl_3$ solution slowly until it turned cloudy. Pale orange crystals are filtered and dried in vacuo. Yield 43 mg, 86%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 44.95 (d × d, $J_{AX} = 180.6$, $J_{AA'} = 30.0$ Hz), 46.0 (d × d, $J_{A'X} = 180.6, J_{AA'} = 30.0$ Hz). $^1H$ NMR ($CDCl_3$): $\delta$ 1.20–1.60 (4H, m, –C*H*$_2$–), 1.63 (6H, s, –C*H*$_3$), 1.94 (2H, m, –C*H*$_2$–), 2.18 (3H, d, $J = 2.3$ Hz, –C*H*$_3$), 2.19 (3H, d, $J = 2.1$ Hz, –C*H*$_3$), 2.52 (2H, m, –C*H*$_2$–), 2.83–3.21 (4H, m, –CH$_2$–), 3.96 (1H, m, =N–C*H*–), 4.16 (1H, m, =N–C*H*–), 5.79 (1H, virtual t, –C*H*Cl$_2$), 7.06–7.54 (20H, m, Ph*H*), 8.06 (1H, d × d, $J = 30.0$ Hz and 13.2 Hz, –N=C*H*–). 8.08 (1H, d × d, $J = 30.0$ Hz and 13.2 Hz, –N=C*H*–). $^{13}C\{^1H\}$ NMR $\delta$ 15.2 (d, $J = 7.6$ Hz, –*C*H$_3$), 15.6 (d, $J = 8.4$ Hz, –*C*H$_3$), 20.4 (s, –*C*H$_3$), 20.6 (s, –*C*H$_3$), 24.4 (s, –*C*H$_2$-), 24.7 (s, –*C*H$_2$–), 29.5 (s, –*C*H$_2$–), 29.8 (s, –*C*H$_2$–), 66.6 (d, $J = 3.9$ Hz, –*C*–), 67.1 (d, $J = 3.3$ Hz, –*C*–), 71.0 (s, –*C*H$_2$–), 71.5 (s, –*C*H$_2$–), 71.6 (s, –*C*H–N=), 72.7 (s, –*C*H–N=), 177.0 (d, $J = 2.3$ Hz, –*C*H=N–),177.9 (d, $J = 2.3$ Hz, –*C*H=N–). $[\alpha]_D = 287$ ($c = 1.5$, $CH_2Cl_2$).

### 3.10. Preparation of [RuCl$_2$(3)] (9)

A solution of *trans*-RuCl$_2$(DMSO)$_4$ (60.0 mg, $0.12 \times 10^{-3}$ mol) and bis-imine (**3**) (72 mg, $0.1 \times 10^{-3}$ mol) in THF (5 mL) was refluxed for 4 h. A purple solution was obtained. The solvent was removed in vacuo to give an oily residue which was chromatographed on a silica gel column. A purple band was eluted first with $CH_2Cl_2$/AcOEt 90/10. Yield 27 mg, 30%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 56.2. $^1H$ NMR ($CDCl_3$): $\delta$ 1.18 (4H, m, –C*H*$_2$–), 1.45 (6H, s, –C*H*$_3$), 1.68 (2H, m, –C*H*$_2$–), 2.10 (6H, s, –C*H*$_3$), 2.34 (2H, s, –C*H*$_2$–), 2.53 (2H, d, $J = 9.5$ Hz, –C*H*$_2$–), 2.70 (2H, d, $J = 9.5$ Hz, –C*H*$_2$–), 3.61 (2H, d, $J = 7.0$ Hz, =N–C*H*–), 7.09–7.54 (20H, m, Ph*H*), 8.17 (virtual t, –N=C*H*–). $^{13}C\{^1H\}$ NMR $\delta$ 13.3 (s, –*C*H$_3$), 19.6 (s, –*C*H$_3$), 24.4 (s, –*C*H$_2$–), 27.7 (s, –*C*H$_2$–), 28.7 (s, –*C*H$_2$–), 66.1 (s, –*C*H$_2$), 66.9 (d, $J = 11.8$ Hz, –*C*–), 70.1 (s, –*C*H–N=), 168.4 (s, –*C*H==N–). Mass spectrum: *m*/*z* 888 (M + 1), 816 (M − 2Cl). Anal. Calc. for $C_{48}H_{48}N_2P_2Cl_2Ru$: C, 65.0; H, 5.45; N, 3.16. Found: C, 65.11; H, 5.95; N, 2.81%.

### 3.11. X-ray structure data

Nonius Kappa CCD diffractometer, *f* and *w* scans, Mo K$\alpha$ radiation ($I = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97 [11], refinement against $F^2$ in SHELXL97 [12] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

### 3.12. Data collection for 3

Colorless plate, $0.24 \times 0.12 \times 0.03$ mm; orthorhombic, $P2_12_12_1$, $a = 11.884(5)$, $b = 9.604(5)$, $c = 35.450(5)$ Å, $V = 4046(3)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.173$ g cm$^{-3}$, $\mu = 0.142$ cm$^{-1}$, $F(0\,0\,0) = 1520$, $\theta_{max} = 22.46°$, HKL ranges: −12 12; −10 9; −38 38, 8086 data collected, 5057 unique data ($R_{int} = 0.0395$), 3730 data with $I > 2\sigma(I)$, 473 parameters refined, GOF($F^2$) = 0.0506, final *R* indices ($R_1 = \sum|F_o| - |F_c|/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$): $R_1 = 0.1053$, $wR_2 = 1.000$, max/min residual electron density. 229 (0.039)/−0.170 (0.039) e A$^{-3}$.

### 3.13. Data collection for 6

Orange plate, $0.18 \times 0.18 \times 0.05$ mm; monoclinic, $P2_1$, $a = 12.8520(10)$, $b = 16.9590(10)$, $c = 12.9940(10)$ Å, $\beta = 104.5700(10)°$, $V = 2741.1(3)$ Å$^3$, $Z = 2$, $\rho_{calc} = 1.589$ g cm$^{-3}$, $\mu = 1.144$ cm$^{-1}$, $F(0\,0\,0) = 1332$, $\theta_{max} = 27.48°$, HKL ranges: −10 16; −22 18; −16 16, 15,072 data collected, 11392 unique data ($R_{int} = 0.0221$), 10,421 data with $I > 2\sigma(I)$, 554 parameters refined, GOF($F^2$) = 0.0381, final *R* indices: $R_1 = 0.1054$, $wR_2 = 1.067$, max/min residual electron density 1.560 (0.095)/−1.097 (0.095) e A$^{-3}$.

### 3.14. Data collection for 8

Colorless plate, $0.20 \times 0.20 \times 0.04$ mm; orthorhombic, $P2_12_12_1$, $a = 12.4430(10)$, $b = 15.0200(10)$, $c = 33.4170(10)$ Å, $V = 6245.4(7)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.542$ g cm$^{-3}$, $\mu = 1.047$ cm$^{-1}$, $F(0\,0\,0) = 2928$, $\theta_{max} = 27.41°$, HKL ranges: −16 11; −13 18; −42 43, 35,405 data

collected, 13,362 unique data ($R_{int} = 0.0290$), 10,482 data with $I > 2\sigma(I)$, 671 parameters refined, GOF($F^2$) = 0.0551, final $R$ indices: $R_1 = 0.1595$, $wR_2 = 1.062$, max/min residual electron density 1.465 (0.100)/−1.135 (0.100) e $A^{-3}$.1

## 4. Supporting information available

X-ray crystal structure analyses of ligand **3** and complexes **6** and **8**. This material is available free of charge.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 252160–162. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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