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Synthesis and stereochemical studies of rhodium complexes with (–)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane

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Abstract

The $[Rh((S,S)\text{-BDPP})_2]^+$ (1) cation, where BDPP (–)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane, has been synthesized and fully characterized by spectroscopy and by an X-ray diffraction study of the solvated chloride salt. The coordination about Rh is slightly distorted square planar and the six-membered chelate rings adopt skew conformation. Oxidative addition of HCl to **1** yields the *trans*-chlorohydrido derivative (**2**). In the octahedral complex the six-membered chelate rings have the chair conformation, as evidenced by ^1H, ^{13}C and ^{31}P NMR spectroscopy.

Introduction

We recently reported that Rh^I and Pt catalysts formed by the chiral chelating six-membered ring BDPP are remarkably efficient catalysts in asymmetric hydrogenation [1] and hydroformylation [2], respectively. The ring conformation has an important influence on optical yield [3], with the BDPP ligand probably adopting a chiral skew conformation. Furthermore, X-ray crystallographic studies revealed that in $[Rh((S,S)\text{-BDPP})(NBD)]^+$ the BDPP ligand is in a chair conformation, whereas in the $[Rh((S,S)\text{-BDPP})(COD)]^+$ it is in a skew conformation [3,4].

Being interested in the stereochemistry of the coordinated BDPP we extended our work to $[Rh((S,S)\text{-BDPP})_2]^+$ (**1**) and $[RhHCl((S,S)\text{-BDPP})_2]^+$ (**2**) complexes. Although there are many reports dealing with the synthesis and characterization of $[Rh(P\text{–}P)_2]^+$ systems [5–12] and their reactions with small gaseous molecules, the crystal structure of **1**, which we have now determined, represented the one gap in the series of $[Rh(Ph_2P(CH_2)_nPPh_2)_2]^+$ complexes ($n = 1\text{–}4$). Crystallographic data are now available for the ionic $[Rh(dpe)_2]^+\ ClO_4^-$ [5], $[Rh(chiraphos)_2]^+\ Cl^-$ [8], $[Rh(dppb)_2]^+\ BF_4^-$ [8] and $[Rh((S,S)\text{-BDPP})_2]^+\ Cl^-$. We also report here a detailed

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analysis of the ^1H, ^{13}C and ^{31}P NMR data of complex **2** in deriving more information about the effect of oxidative addition on the structure of the complex.

Results and discussion

In principle six-membered chelate rings may adopt chair, skew and boat ring conformations. Of these only the chair and skew isomers will be considered here, since the boat isomer can be excluded for steric reasons.

In Fig. 1 we show some of the stereoisomers of square planar (A = B = O) and *trans* octahedral complexes (A = H, B = Cl) containing (*S*,*S*)-BDPP. In these case of the chair conformation interconversion of the ring produces structures **T1**–**T3**. The least crowded **T1**, in which both rings are on the "hydride" side of the P(1)–P(4) plane, has a twofold symmetry axis which goes through the rhodium and perpendicular to the P(1)–P(4) plane. Inversion of one chelate ring would lead to **T2**, which is still not very crowded as judged from a molecular model. The main C_2 axis has been lost, however, and there is a new twofold axis in the P(1)–P(4) plane, which implies that the *cis* related P atoms are identical. Inversion of the other ring

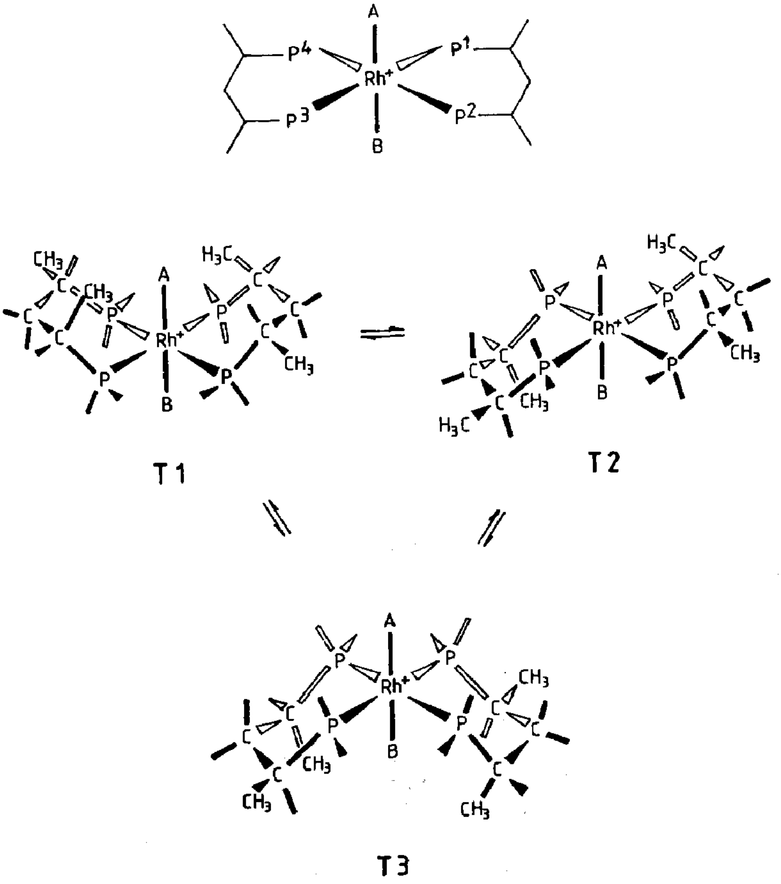

Fig. 1. Possible stereoisomers with chair conformations.

gives **T3**, which is markedly crowded, both chelate rings being on the "halogen" side. When A = B = O, **T1** is identical with **T3**.

Complexes with skew chelate ring conformations (both methyls adopt identical equatorial or axial positions) have two twofold symmetry axis, and so e.g., the P atoms are identical. Diaxially disposed methyl groups are not favoured on steric ground. In accord the ^{31}P NMR spectra of **1** (which can be considered as an A = B = O case with $X = Cl^-$ or BF_4^-) exhibits a simple doublet at ambient temperature. When the temperature is lowered the resonances broadened, but the limiting spectrum could not be reached even at −70 ° C.

The 250 MHz proton spectrum also confirms this view. The methine protons give a symmetrical sextet at 2.55 ppm and the methylenes a heptet-like multiplet at 1.25 ppm, whereas the methyl groups give a broadened signal at 0.72 ppm. These data show that the phosphorus atoms are involved in a dynamic process, but do not show whether the chelate ring is conformationally fluxional [3] or whether the solvent is coordinated to the rhodium to give rise to a stereochemically nonrigid pentagonal-bipyramidal geometry. Evidence for the existence of a five-coordinated solvate complex of $[Rh(dpp)_2]^+$ has recently been found [6].

Conductivity data for the chloro- and tetrafluoro-borate complexes of BDPP are consistent with those obtained for the ionic dpe, dpp [11], and chiraphos [8] complexes (see Experimental).

The structure of **1** was determined by X-ray diffraction. Atomic positional and thermal parameters, relevant bond lengths and angles are reported in Tables 1 and 2. A stereoview of the overall geometry of the cation, with the atom numbering scheme, is shown in Fig. 2.

The structure of **1** consists of discrete cations, anions, and CH_2Cl_2 solvate molecules. The $[Rh((S,S)\text{-BDPP})_2]^+$ cation possesses C_2 symmetry; the twofold axis runs through the rhodium atom in the P(1)–P(4) mean plane, and an approximate C_2 axis is perpendicular to the real one and passes along the C(3)–Rh line; these two axes generate a third, which is perpendicular to both of the others.

The nearest two Cl anions, which also lie on twofold axes, are 5.612(4) Å above and below the Rh atom, and the Cl...Rh...Cl angle is 170.8(1)°. The shortest interatomic distance between the included dichloromethane and the cation: Cl(2)...C(5) is 3.644(8) Å.

The coordination about Rh is symmetrically distorted square planar. Displacements of phosphorus atoms from the P(1)–P(4) mean plane are pairwise identical, because of the C_2 symmetry the P(1) atoms are 0.139(1) Å below and above the mean plane, while the P(2) atoms are 0.128(1) Å above and below it.

The Rh–P distances in **1**, 2.334(1) and 2.337(1), mean 2.336 Å, are longer than those 2.291(2), 2.308(2), mean 2.300 Å, reported for $[Rh((S,S)\text{-chiraphos})_2]^+$ [8] and slightly longer than those, 2.304(2), 2.361(2), mean 2.329 Å, observed for $[Rh(dpb)_2]^+$ [6]. We have found shorter Rh–P distances in $[Rh(COD)((S,S)\text{-BDPP})]ClO_4$ (2.302 Å) and $[Rh(NBD)((S,S)\text{-BDPP})]ClO_4$ (2.304 Å) [4]. The two chelate rings adopt the preferred δ-skew conformation with equatorially disposed methyl groups (Fig. 3, Table 3). The highly symmetrical disposition of the phenyl rings is very similar to that observed in $[Rh(chiraphos)_2]^+$ [8].

The skew conformations of the chelate ring with a small bite angle (88.2 ° (1)), the long Rh–P distances, and the alternating displacements of phosphorus atoms are presumably due to repulsion between the phenyl groups.

Table 1

Atomic positional and thermal parameters with estimated standard deviations in paranthesis

Atom	x/a	y/b	z/c	B_{eq} [a]
Rh	0.65959(1)	−0.65959	0.0	2.57(1) Mult = 0.5
Cl	0.1381(3)	−0.1381	0.5	8.3(1) Mult = 0.5
P(1)	0.54231(7)	−0.62295(7)	0.09716(8)	3.17(7)
P(2)	0.68798(7)	−0.78525(7)	0.08971(7)	2.79(7)
C(1)	0.4973(4)	−0.6328(4)	0.2775(3)	6.4(5)
C(2)	0.5549(3)	−0.6725(3)	0.2071(3)	4.0(3)
C(3)	0.5529(3)	−0.7655(3)	0.2223(3)	4.7(3)
C(4)	0.5913(3)	−0.8197(3)	0.1555(3)	3.7(3)
C(5)	0.5992(3)	−0.9122(3)	0.1973(4)	4.9(4)
C(11)	0.5209(3)	−0.5122(3)	0.1102(3)	3.8(3)
C(12)	0.5817(4)	−0.4818(3)	0.1378(4)	5.6(4)
C(13)	0.5697(4)	−0.4002(4)	0.1529(5)	6.8(6)
C(14)	0.4960(4)	−0.3476(4)	0.1354(6)	7.9(6)
C(15)	0.4386(5)	−0.3765(4)	0.1102(5)	7.5(6)
C(16)	0.4484(3)	−0.4584(3)	0.0966(4)	5.2(4)
C(21)	0.4445(3)	−0.6519(2)	0.0854(3)	3.6(3)
C(22)	0.3686(3)	−0.6292(3)	0.1352(4)	5.0(3)
C(23)	0.2968(3)	−0.6618(4)	0.1257(5)	6.9(6)
C(24)	0.3025(4)	−0.7174(4)	0.0738(4)	6.0(5)
C(25)	0.3760(4)	−0.7393(4)	0.0249(4)	5.3(4)
C(26)	0.4473(3)	−0.7065(3)	0.0300(3)	4.6(4)
C(31)	0.7285(3)	−0.8776(2)	0.0386(2)	3.4(3)
C(32)	0.6773(3)	−0.8971(3)	−0.0116(3)	4.0(3)
C(33)	0.7015(4)	−0.9672(3)	−0.0515(4)	5.0(4)
C(34)	0.7757(5)	−1.0190(3)	−0.0404(3)	5.7(5)
C(35)	0.8273(4)	−0.9991(3)	0.0091(4)	5.5(4)
C(36)	0.8040(3)	−0.9291(4)	0.0488(3)	3.8(3)
C(41)	0.7553(3)	−0.7868(3)	0.1664(3)	3.4(3)
C(42)	0.7837(3)	−0.8581(3)	0.2207(3)	3.9(3)
C(43)	0.8284(3)	−0.8517(3)	0.2818(3)	4.5(4)
C(44)	0.8459(4)	−0.7754(4)	0.2887(3)	5.4(5)
C(45)	0.8177(3)	−0.7040(3)	0.2361(3)	4.7(4)
C(46)	0.7749(3)	−0.7102(3)	0.1766(3)	3.9(3)
Cl(2)	0.9976(2)	−0.8745(2)	0.4442(2)	11.7(3) Mult = 0.5
C(a)	0.980(2)	−0.980	0.5	5.3(7) Mult = 0.125
C(b)	0.897(4)	−0.897	0.5	5.9(8) Mult = 0.125

[a] B(eq) is defined as $B_{eq} = \frac{4}{3}$ trace $(B \times G)$ where B is the thermal motion tensor and G is the direct metric tensor.

Reaction of **1** with anhydrous or aqueous hydrogen chloride yields the *trans*-chlorohydrido derivative.

In octahedral transition-metal complexes with two bidentate phosphine ligands the two positions not occupied by P atoms can be *cis* or *trans* related. The $^{31}P\{^1H\}$ spectrum of $[RhHCl((S,S)BDPP)_2]^+$ (**2**) shows an A_2B_2X splitting pattern (two sharp doublet of triplets) at room temperature (see Fig. 4). The small ^2J(P–P) value (34 Hz) suggests that members of the identical P atom pairs must be *trans* related (P(1) = P(3) and P(2) = P(4)), and so structure **T2** can be excluded from further consideration.

The ^{13}C spectrum confirms that the chelate ring does not have a symmetry axis, the methine carbon signals (at 29.0 and 33.0 ppm) appearing as pseudo-multiplets

Table 2

Selected bond lengths (Å) and bond angles (° C) with e.s.d.'s in parantheses

Bond lengths					
Rh–P(1)	2.334(2)	P(1)–C(21)	1.817(7)	C(1)–C(2)	1.522(10)
Rh–P(2)	2.337(1)	P(2)–C(4)	1.873(7)	C(2)–C(3)	1.512(9)
P(1)–C(2)	1.877(6)	P(2)–C(31)	1.835(6)	C(3)–C(4)	1.520(8)
P(1)–C(11)	1.839(6)	P(2)–C(41)	1.825(6)	C(4)–C(5)	1.548(9)

Bond angles			
P(1)–Rh–P(2)	88.2(1)	Rh–P(2)–C(4)	112.6(4)
P(1)–Rh–P(1★) [a]	92.1(1)	Rh–P(2)–C(31)	115.5(3)
P(1)–Rh–P(2★)	173.4(1)	Rh–P(2)–C(41)	117.0(4)
P(2)–Rh–P(2★)	92.1(1)	C(4)–P(2)–C(31)	99.5(5)
Rh–P(1)–C(2)	112.8(4)	C(4)–P(2)–C(41)	103.2(5)
Rh–P(1)–C(11)	115.1(4)	C(31)–P(2)–C(41)	106.9(5)
Rh–P(1)–C(21)	117.2(4)	P(1)–C(2)–C(1)	117.3(9)
C(2)–P(1)–C(11	99.7(5)	P(1)–C(2)–C(3)	112.6(8)
C(2)–P(1)–C(21)	102.7(5)	C(1)–C(2)–C(3)	109.4(10)
C(11)–P(1)–C(21)	107.3(5)	C(2)–C(3)–C(4)	121.7(10)
		P(2)–C(4)–C(3)	112.9(8)
		P(2)–C(4)–C(5)	116.4(8)
		C(3)–C(4)–C(5)	108.3(9)

[a] ★ atom at [$-y$, $-x$, $-z$].

(due to the virtual coupling to the other P atom) and the methyl (17.5 and 21.0 ppm) and methylene (37.5 ppm) carbon signals as singulets. These data are consistent with a chair form in which the methyl groups take axial and equatorial positions.

The 250 MHz ^{1}H NMR data support this view. There is a symmetrical multiplet at −16.1 ppm from the hydride (Fig. 5) (spin-simulation of the A_2B_2XY system gave following coupling constants: ^1J(H–Rh) 13.5 Hz, ^2J(H–P) 17.5 and 7.4 Hz), two pseudo-quartets for the methyl (at 0.12 and 1.08 ppm), two multiplets at 2.28 and 4.5 ppm for the methine, and a broad multiplet between 1.2 and 1.5 ppm for the

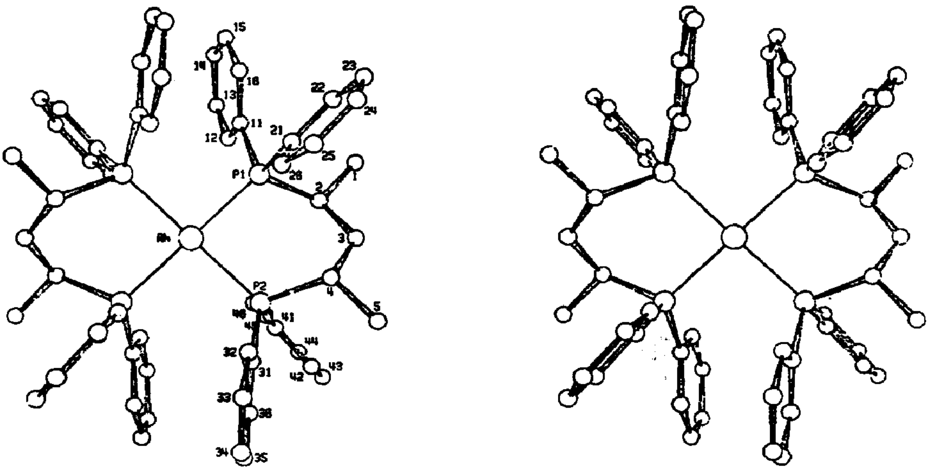

Fig. 2. Stereoview of the [Rh((*S,S*)-BDPP)$_2$]$^+$ cation with the atom numbering scheme.

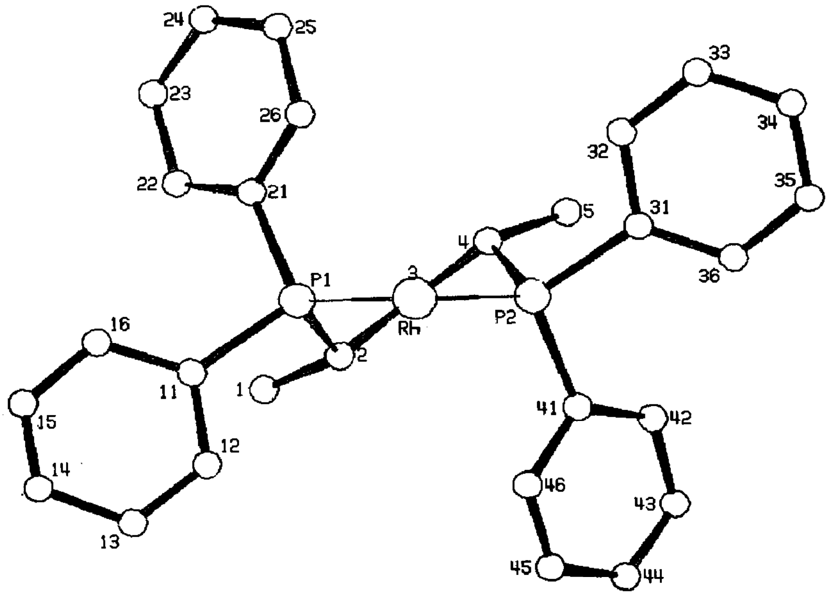

Fig. 3. Perspective view of [Rh((*S*,*S*)-BDPP)$_2$]$^+$ along the bisector of the P–Rh–P bond, omitting one BDPP ligand.

Table 3

Endocyclic torsion angles (deg) with standard deviations in parantheses for the chelate ring.

Atoms	Value (deg)
Rh–P(1)–C(2)–C(3)	−71.3(7)
P(1)–C(2)–C(3)–C(4)	36.5(7)
C(2)–C(3)–C(4)–P(2)	35.1(7)
C(3)–C(4)–P(2)–Rh	−71.0(6)
C(4)–P(2)–Rh–P(1)	28.5(3)
P(2)–Rh–P(1)–C(2)	28.2(3)

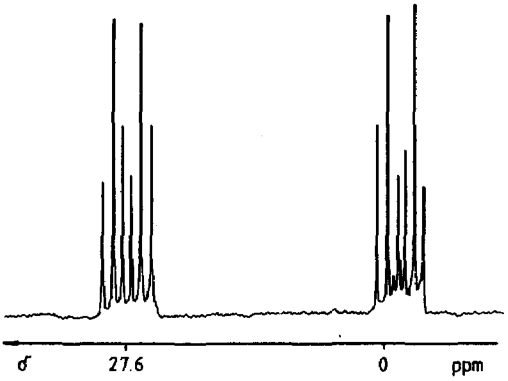

Fig. 4. ^{31}P NMR spectra of [RhHCl(S,S)-BDPP)$_2$]$^+$ recorded in CDCl$_3$ at 309 K.

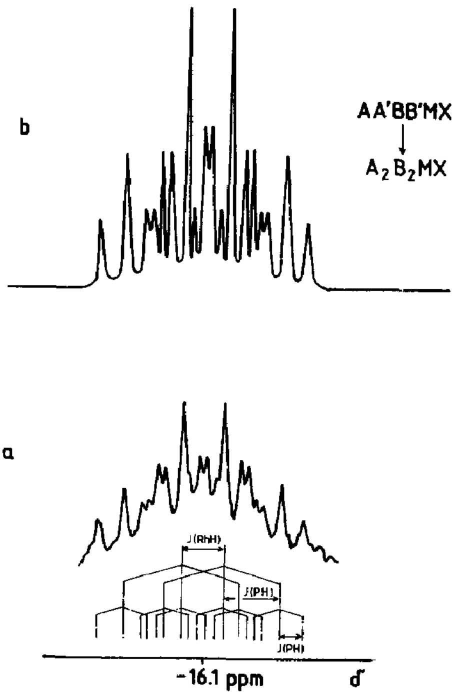

Fig. 5. ^{1}H NMR spectra of $[RhHCl((S,S)\text{-}BDPP)_2]^+$ recorded in $CDCl_3$ at 309 K [a]; simulated [b]. A,A′ = P(1), P(3); B,B′ = P(2), P(4); M = Rh, X = H.

methylene protons. Selective irradiations proved that the low-field methines belong to the low-field methyls whereas the high-field ones belong to the high-field methyls. The axial methyl groups are thought to absorb at higher field.

Formation of the **T3** is much less likely than that of **T1** because the coordination of the relatively bulky chlorine atom is hindered on the crowded side of the P(1)–P(4) plane (see Fig. 1).

James et al. [8] carried out a detailed study of the analogous compound, $[RhHCl((S,S)\text{-chiraphos})_2]^+$, and produced sound evidence to support a *trans* structure. The relatively high value of 2150 cm^{-1} ν(Rh–H), the ^{1}H and ^{13}C NMR virtual coupling data, the small J(P–P) value (34 Hz), the relatively small ^1J(Rh–P) (89.1 and 93.3 Hz) and J(PH) values (17.5 and 7.4 Hz) for **2** are consistent with the *trans* structure, and the data are similar to those obtained by James et al. [8].

The CD spectra of **1** and **2** provided further evidence for the conformations of the chelate rings (Fig. 6). The maximum magnitude of the first positive CE is about twelve times larger for **1** than for **2**, and furthermore the maximum magnitude of the first negative CE is about four times larger for **1** than for **2**. Complexes of chiral 1,3-diamine [13,14] and 1,3-diphosphines [3] show a stronger Cotton effect, the chelate ring being predominantly in the skew conformation. The observed strong CE's in **1** and the weak CE's in **2** can be assumed to be related to skew and chair conformations of the chelate rings, respectively.

Slack et al. reported [7] that $[RhHCl(Ph_2P(CH_2)_2PPh_2)_2]BF_4$, an achiral analogue of complex **2** shows dynamic behaviour at ambient temperature (whereas the BDPP complex does not). Except for the chemical shift values, the low temperature (203 K) ^{31}P NMR data are similar to those observed for $[RhHCl(chiraphos)_2]Cl$ [8]

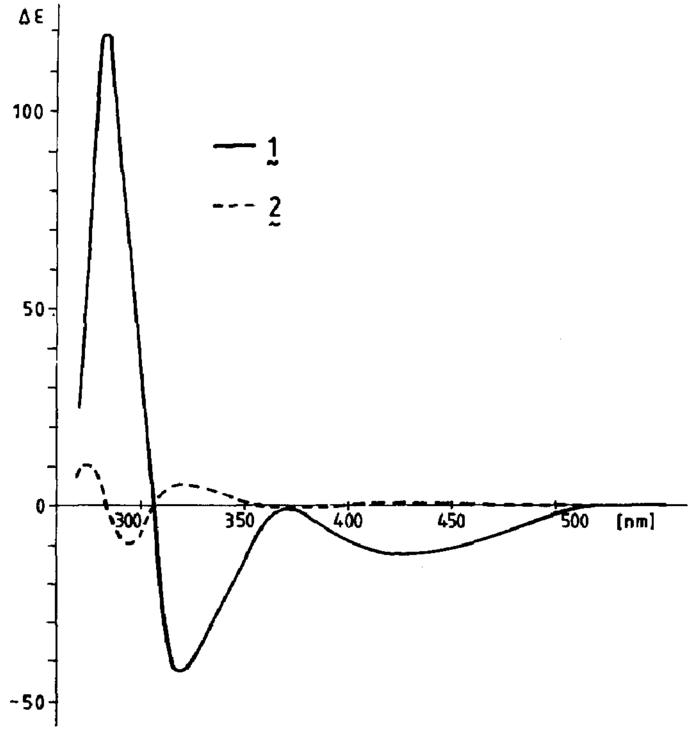

Fig. 6. CD spectra of **1** and **2** in CH_2Cl_2.

and [RhHCl((*S*,*S*)-BDPP)$_2$]Cl. However, at room temperature the spectrum showed a doublet. No explanation the origin of this fluxional behaviour was given. The ^1H NMR spectrum exhibited a sextet at −15 ppm with a line separation of 13.5 Hz (J(P–H) = J(Rh–P) = 13.5 Hz was assumed).

Unfortunately low temperature ^1H spectrum has not been reported. Although Slack et al. also noticed the unexpected identity of the chemical shift of phosphorus atoms *trans* to chlorine and hydride, finally they proposed *cis* geometry for the complex, arguing that there is still an exchange at low temperature between the hydride and chloride coordination side. However, even if we assume a fast exchange of the chloride and hydrogen atoms, the latter will always be trans to a P atoms, and so a much larger J(P–H) value would be expected.

The proposed *cis–trans* isomerisation [7] is not the only alternative, fluxionality can also be related to the conformation of the chelate rings, since the probability of the energetically favoured face-edge arrangement of the phenyl groups (in this chiral conformation the P atoms differ pairwise) also depends on it. For the dpp complex the interconversion barrier of the chelate ring must be small (there is no substituent on the ring), whereas for the analogous complexes of chiraphos or BDPP it must be significantly higher (owing to the steric interaction of the phenyl rings increased by the equatorially disposed methyl groups).

Experimental

Elemental analyses were performed with a Perkin–Elmer 240 apparatus. Infrared spectra (IR) were recorded on a Carl Zeiss Specord 75 spectrophotometer. Proton magnetic resonance spectra (^{1}H NMR) were recorded on TESLA BS 487C and Bruker W250 instruments. ^{13}C and ^{31}P NMR spectra were recorded on a Varian-CFT-20 instrument at 20.1 and 32.1 MHz, respectively. Chemical shifts are given as parts per million (ppm) relative to Me_4Si for ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from 85% H_3PO_4 are reported as negative for the ^{31}P NMR spectra. All of the reactions, manipulations, and purification steps involving solvents and solutions were performed under a dry nitrogen or argon by standard Schlenk techniques. Hydrated rhodium(III) chloride was purchased from W.C. HEREAUS GMBH. (*S*,*S*)-BDPP was prepared as previously described [1].

Synthesis of compounds

[Rh((S,S)-BDPP)$_2$]$^+$Cl$^-$ · $\frac{1}{2}$C$_6$H$_6$. A solution of (*S*,*S*)-BDPP (193.6 mg, 0.44 mmol) in benzene (5 ml) was added to a stirred solution of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) [15] (49.3 mg, 0.1 mmol) in benzene (3 ml). The resulting orange red solution was stirred for 1 h during which a yellow solid separated. This was filtered off and washed with benzene (5 ml). The yield was 165 mg (81%). Anal. Found: C, 69.7; H, 6.0. $RhC_{61}H_{63}P_4Cl$ calcd.: C, 69.25; H, 5.95%.

[Rh((S,S)-BDPP)$_2$]$^+$Cl$^-$ · $\frac{1}{2}$CH$_2$Cl$_2$. Bright yellow crystals suitable for the X-ray study were obtained by introducing a layer hexane on top of a CH_2Cl_2 solution. Anal. Found: C, 66.1; H, 5.9. $RhC_{58}H_{60}P_4Cl \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 69.25, H, 5.59%. ^{1}H NMR($CDCl_3$): δ 0.72 (br.s, 12H, 4 × CH_3), 1.25 (hept. like m, 4H, 2 × CH_2), 2.55 (sext., 4H, 4 × CH), 7.08–7.39 ppm (m, 40H, 8 × Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.9 (pt, ^1J(P–C) + ^3J(P–C) 22.1 Hz, CH), 37.3 (s, CH_2), 18.5 (s, CH_3), 134.7 (s, br, C_{ipso}), 128.35 (d, ^2J(P–C) 2 Hz, CH_{ortho}), 132.4 (s, br, CH_{meta}), 130.0 ppm (d, ^4J(P–C) 2 Hz, CH_{para}). Λ_M: 83.4 in MeOH and 63 $ohm^{-1}\,cm^2\,mol^{-1}$ in CH_2Cl_2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 28.2 ppm(d, ^1J(Rh–P) 133 Hz).

[Rh((S,S)-BDPP$_2$]$^+$ BF$_4$$^-$ · $\frac{1}{2}$CH$_2$Cl$_2$. A mixture of $[RhCl(COD)]_2$ (147.9 mg, 0.3 mmol) BDPP (580.8 g, 1.32 mmol), and 70 ml of methanol was stirred for 20 min. Upon slow addition of $NaBF_4$ (1.5 g, 13.7 mmol) in 150 ml of deoxygenated water a yellow precipitate formed. The slurry was stirred for 1 h and the solid then filtered off. [Rh((*S*,*S*)-BDPP)$_2$]BF$_4$ was recrystallized from a dichloromethane/diethyl ether mixture. The perchlorate salt was prepared similarly. Anal. Found: C, 63.2; H, 5.4. $RhC_{58}H_{60}P_4BF_4 \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 63.26; H, 5.31%. Λ_M: 99 in MeOH and 63 $ohm^{-1}\,cm^2\,mol^{-1}$ in CH_2Cl_2.

X-ray structure determination of [Rh((S,S)-BDPP)$_2$]$^+$Cl$^-$ · $\frac{1}{2}$CH$_2$Cl$_2$

A crystal size of 0.15 × 0.20 × 0.30 mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator using Cu-K_α (λ 1.54184 Å) radiation. Cell parameters were obtained by least-squares fit for 25 reflections in the range $5 \leq \theta \leq 26°$. Total of measured intensities $N_{tot} = 5987$ ($-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $0 \leq l \leq 20$). Averaging of the symmetry-related reflections gave 4544 unique observations (N_{ave}), an agreement factor on intensity was 0.022; 3910 reflections with $I \geq 3\sigma(I)$ were used in the least-square analysis. Three standard reflections were measured every hour, but no intensity variation was detected.

The structure was solved by direct methods [16] in space group R3 in a hexagonal system, and the system was then transformed into a rhombohedral one. Full-matrix least-squares refinement indicated that the whole molecule possessed a C_2 symmetry and the correct space group was $R32$. A crystal density determination confirmed that there is included dichloromethane with half occupancy, and its carbon atom is on the twofold axis in a statistically disordered structure, so that the multiplicity of the Cl atom is 0.5 and that of the C atoms is 0.125, respectively. At the end of isotropic refinement an empirical absorption correction was performed [17]; the relative transmission coefficients ranged from 0.733 to 1.406 (mean value 0.971). Positions of H atoms were generated from assumed geometries and included in the structure factor calculations, but not refined. The $\Sigma(\Delta F^2)$ function was minimized, and 316 parameters were refined, with anisotropic temperature factors assigned to all non-hydrogen atoms. Final $R = 0.043$, $R_w = 0.062$, $R_{tot} = 0.044$, $S = [\Sigma w(|F_0| - |F_c|)^2/(NO - NV)]^{1/2} = 2.24$ $(\Delta/\sigma)_{max} = 0.51$. The highest peak in the final difference map was 1.29(9) e/Å^3.

Programs used were: Enraf–Nonius SDP [18], PLUTO [19] and local programs run on a PDP 11/34 minicomputer (128 kW). Tables of anisotropic thermal parameters, H atom coordinates, and lists of calculated and observed structure factors may be obtained from the authors.

Crystal data: $C_{58}H_{60}ClP_4Rh \cdot \frac{1}{2}CH_2Cl_2$, $M = 1061.85$, rhombohedral R32 (no. 155), a 16.485(1) Å, α 79.33(1)°, V 4272.7(4) Å^3, $Z = 3$, $F(000)$ 1659, D_c 1.24 g cm^{-3}, D_m 1.25 g cm^{-3}, μ(Cu-K_α) 47.0 cm^{-1}.

Reaction of [Rh((S,S)-BDPP)$_2$]$^+$ Cl$^-$ with hydrogen chloride

A. $RhCl_3 \cdot 3H_2O$ (0.25 g, 0.95 mmol) was refluxed for 3 h in 50 cm^3 of ethanol that had been refluxed under CO for 0.5 h [20]. After addition of (S,S)-BDPP (0.84 g, 1.9 mmol) refluxing was continued for 10 min, and $NaB(C_6H_5)_4$ (0.4 g, 1.25 mmol) was then added. The solvent was drawn off, the residue treated with acetone, and resulting solution was filtered to remove NaCl. Removal of the acetone gave yellow crystals. The yield was 1.18 g (88%). Anal. Found: C, 70,9; H, 5.9. $RhC_{58}H_{61}ClB(C_6H_5)_4$ calcd.: C, 73.55, H, 6.05%. Attempts to obtain single crystals suitable for an X-ray study were unsuccessfull.

^{1}H NMR (CDCl$_3$): δ −16.10 (18 lines, ^1J(Rh–H) 13.5 Hz, ^3J(H–P(1)) 17.5 Hz, ^3J(H–P(2)) 7.4 Hz, 1H, Rh–H), 0.13 (virtual q, ^3J(H–H) 7.5 Hz, 6H, 2 × CH$_3$), 1.07 (virtual q, ^3J(H–H) 7.5 Hz, 6H, 2 × CH$_3$), 1.2–1.5 (br.m., 2H, CH$_2$), 2.28 (m, 2H, 2 × CH), 4.5 (m, 2H, 2 × CH), 6.8–8.0 ppm (m, 60H, Ph). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.5 (s, CH_3^{ax}), 21.0 (s, CH_3^{eq}), 29.0 (virtual m, CH^{ax}), 33.0 (virtual m, CH^{eq}), 37.5 (s, CH$_2$), 122–138 ppm (aromatic carbon atoms). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −1.9 (dt, J(P(1)–Rh) = 89.1 Hz, J(P(1)–P(2)) 34 Hz, 2P), 27.6 ppm (dt, J(P(2)–Rh) 93.3 Hz, J(P(2)–P(1)) 34 Hz, 2P). Infrared ν(CO)(KBr): 2150 cm^{-1}.

B. Identical spectroscopic data were obtained when the addition was carried out in situ by treating a solution of Rh((S,S)-BDPP)Cl with a concentrated aqueous hydrochloric acid.

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