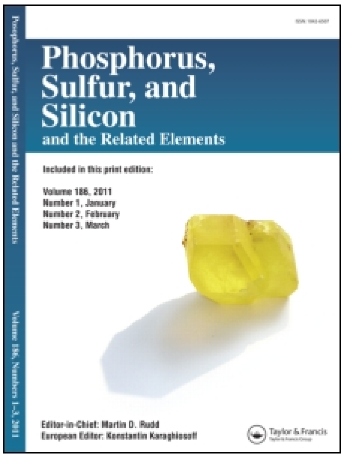

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STEREOCHEMISTRY AND STRUCTURE OF PHELLANPHOS AND NOPAPHOS, TWO CHIRAL DIPHOSPHINES FOR ASYMMETRIC HYDROGENATION

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STEREOCHEMISTRY AND STRUCTURE OF PHELLANPHOS AND NOPAPHOS, TWO CHIRAL DIPHOSPHINES FOR ASYMMETRIC HYDROGENATION

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Stereochemistry of phellanphos and nopaphos which are interesting chiral ligands for Rh(I)-catalyzed hydrogenation has been studied. The molecular structures of phellanphos disulfide **3** and nopaphos disulfide **5** which are precursors of these phosphines have been determined by single-crystal X-ray diffraction methods.

These structures are discussed in their relationship to other known compounds of similar structure and to the configurations of the chelate rings which are obtained when phellanphos and nopaphos coordinate to rhodium.

INTRODUCTION

Asymmetric hydrogenation is arriving to a mature stage thanks to synthesis of a large variety of chiral phosphines able to give efficient chiral rhodium catalysts.[1-6]

Chelating diphosphines are the most useful ligands, and amongst them 1,2-diphosphines **1** were shown by Bosnich and Fryzuck to be highly stereoselective for asymmetric synthesis of α-aminoacids.[7] Diels-Alder reaction was recently proposed as a new method to create simultaneously the two vicinal asymmetric centers of a 1,2-diphosphine.[8-11] Norphos **2** was synthesized from cyclopentadiene and *trans*(O)$PPh_2CH{=}CH{-}P(O)Ph_2$ followed by a resolution.[8,9] Phellanphos **4** and nopaphos **6** were obtained[11] through the reactions depicted in Scheme 1.

Stereochemistry of **4** and **6** was mainly deduced from interpretation based on ^{13}C nmr of the disulfides **3** and **5**. In this work we present crystal structures of **3** and **5** which confirm the proposed stereochemistry and give some light on conformation of these molecules. Some nmr data are also used to define the conformation in solution.

STRUCTURE OF PHELLANPHOS DISULFIDE 3

Crystal data are indicated in the experimental section. Final refinement gave a R-value of 0.036.

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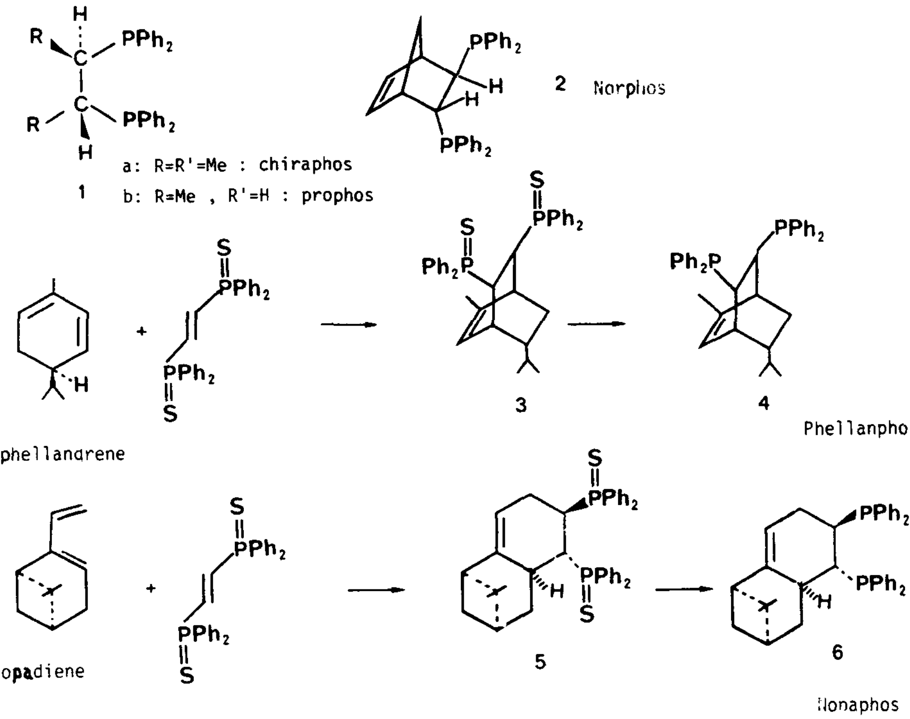


SCHEME 1

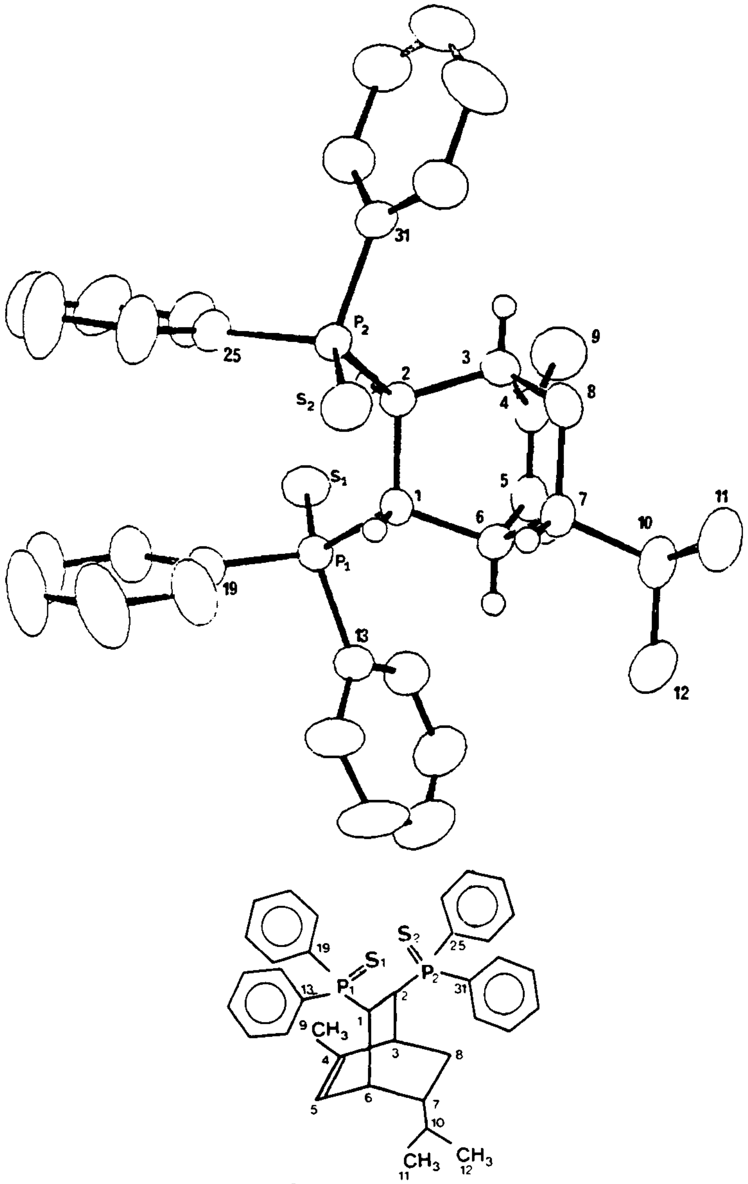
The description of the molecule is in Figure 1 which shows also the absolute configuration, as deduced from the fact that **3** was prepared from (R)-(−)-α-phellandrene. Main bond lengths and angle values are indicated in Table I. The results fully support the relative stereochemistry previously proposed.[11] The antiperiplanar arrangements $P_1C_1C_6C_7$ and $P_2C_2C_3C_4$ postulated on the basis of large $^3J_{P-C}$ values are nicely confirmed by the values of torsion angles (167.5° and 173.1°, respectively). The alternate stereochemistry fixing P_1 syn to C_7 and P_2 syn to C_4 is then completely excluded. The anti disposition of the isopropyl group with respect to the C_1C_2 bridge is also confirmed by the value of the $C_1C_6C_7C_{10}$ dihedral angle (169.6°).

The classical quasi boat conformation of the 6-membered rings $C_1C_2C_3C_4C_5C_6$ and $C_1C_2C_3C_8C_7C_6$ is in agreement with the ring dihedral angles (Table I).

The [2.2.2] bicyclooctene skeleton of **3** has no symmetry plane coinciding with the C_1C_2 bridge because of the distortion introduced by the double bond. The two sulfur atoms are far away from each other, probably to escape interactions.

The dihedral angle $P_1C_1C_2P_2$ is 102.8°, lower than the value deduced from molecular models.[11b] With this value and a non-bonded $P_1 \ldots P_2$ distance of 4.01 Å there is no major difficulties for chelation on rhodium.

Phellanphos should be a bidentate ligand, in agreement with the high values of enantiomeric excess obtained in asymmetric synthesis of some α-aminoacids[11b] and $^2J_{P-P}$ value in the rhodium complex.[11b] Nevertheless it could be suspected that the



3

FIGURE 1 An ORTEP diagram of phellanphos sulfide.

chelation ring must be distorted to some extent with respect to the chiraphos–rhodium complex because of the geometry of the phellanphos skeleton. This will be made clearer by comparing some structural parameters. X-ray data[12] on (Rh chiraphos COD)$^+$ and on (Rh chiraphos MAC)$^+$ established that the dihedral angle PCCP is close to 50° (50.5° and 49.0° respectively). A similar value (49.5°) was also found in the (Rh diphos MAC)$^+$ complex[12c] and can be taken as characteristic of the

TABLE 1

Selected structure data of phellanphos disulfide 3

Bond distances and non bonded distances (Å) with standard deviations in parentheses

C_1C_2: 1.559(5)
C_1C_6: 1.558(5)
C_2C_3: 1.565(5)
C_3C_4: 1.519(6)
C_3C_8: 1.535(6)
C_4C_9: 1.493(7)
C_4C_5: 1.324(6)

C_5C_6: 1.496(7)
C_6C_7: 1.548(6)
C_7C_8: 1.548(6)
C_7C_{10}: 1.545(6)
$C_{10}C_{11}$: 1.507(7)
$C_{10}C_{12}$: 1.524(8)

P_1S_1: 1.954(1)
P_2S_2: 1.959(1)
P_1C_{19}: 1.827(5)
P_1C_{13}: 1.818(4)
P_2C_{25}: 1.824(4)
P_2C_{31}: 1.827(4)

P_1C_1: 1.868(4)
P_2C_2: 1.845(4)
$S_1 \ldots S_2$: 6.106(2)
$P_1 \ldots P_2$: 4.012(1)

Torsion angles (deg)

$P_1C_1C_2P_2$: 102.8
$P_1C_1C_2C_3$: -131.0
$P_2C_2C_1C_6$: -132.2
$C_1C_2C_3C_4$: 60.8
$C_2C_1C_6C_5$: -51.6
$C_2C_1C_6C_7$: 67.3
$P_1C_1C_6C_5$: 73.7
$P_1C_1C_6C_7$: -167.5
$P_2C_2C_3C_4$: -173.1

$P_2C_2C_3C_8$: 70.1
$C_1C_6C_7C_{10}$: 169.6
$C_5C_6C_7C_{10}$: -71.9
$C_3C_8C_7C_{10}$: 129.0
$C_1C_2P_2S_2$: 37.7
$C_2C_1P_1S_1$: 34.6
$C_3C_4C_5C_6$: 0.7
$C_4C_5C_6C_7$: -58.7
$C_5C_6C_7C_8$ 52.9

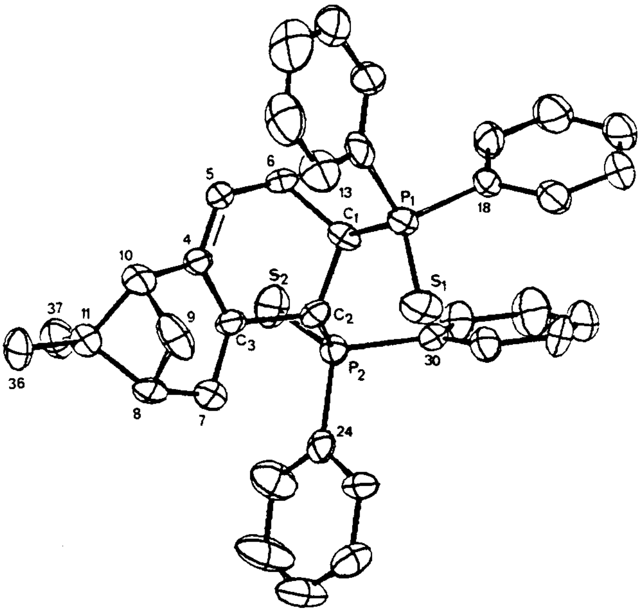
$C_7C_8C_3C_4$: -58.0
$C_8C_3C_4C_5$: 58.1
$C_1C_2C_3C_8$: -56.0
$C_1C_6C_7C_8$: -65.6
$C_2C_3C_8C_7$: 57.9
$C_1C_2C_3C_8$: -56.0
$C_3C_2C_1C_6$: -6.0
$C_2C_3C_4C_5$: -60.9
$C_4C_5C_6C_1$: 58.0

Bond angles (deg.) with standard deviations in parentheses

$P_1C_1C_2$: 112.7(3)
$P_1C_1C_6$: 112.2(3)
$P_2C_2C_1$: 113.0(3)
$P_2C_2C_3$: 113.2(3)
$C_2C_1C_6$: 108.6(3)
$C_1C_2C_3$: 108.2(3)

$C_3C_4C_5$: 113.0(4)
$C_3C_4C_9$: 120.42(5)
$C_5C_4C_9$: 126.54(5)
$C_1C_6C_5$: 109.43(3)
$C_1C_6C_7$: 106.55(3)
$C_5C_6C_7$: 109.97(4)

$C_6C_7C_8$: 107.4(4)
$C_6C_7C_{10}$: 113.2(4)
$C_3C_8C_7$: 110.5(3)
$C_4C_3C_8$: 107.8(4)
$C_4C_5C_6$: 114.6(4)



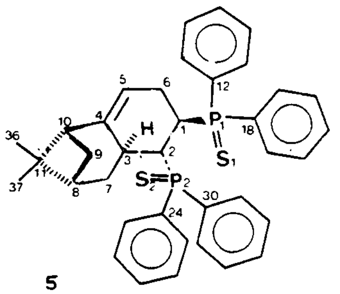


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FIGURE 2 An ORTEP diagram of nopaphos sulfide.

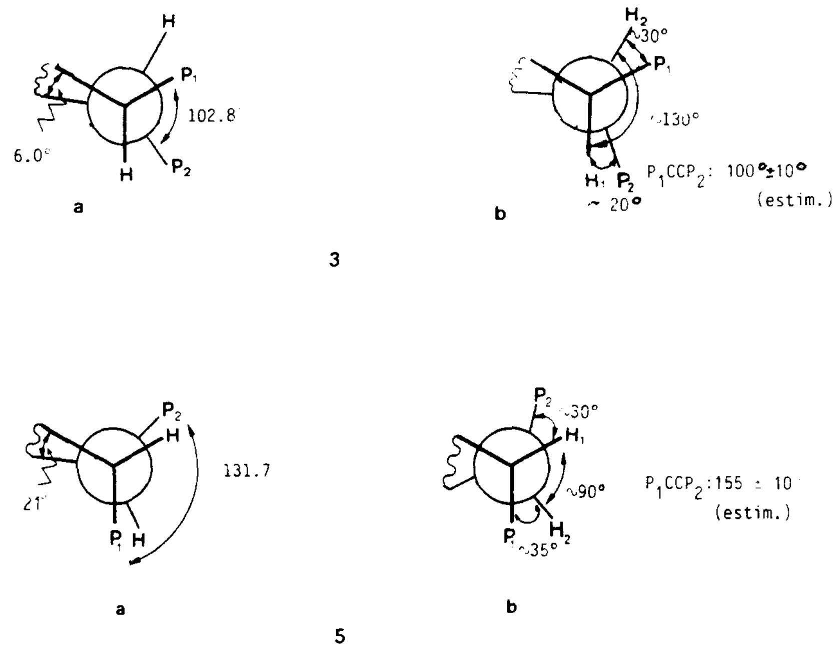


FIGURE 3 Dihedral angles measured along the C_1C_2 bond of 3 and 5: (a) in the X-ray crystal structure; (b) in solution, by ^1H nmr spectroscopy.

geometry of an unperturbed pentagonal chelated ring when 1,2-diphosphines are compared together. The bite angle P-Rh-P is another parameter for discussing the structure of five-membered chelate ring, it is equal to 83.8°, 83.1° and 83° respectively in the chiraphos and diphos complexes.[12]

Recently, the crystal structure of $[\text{Rh norphos NBD}]^+ \text{ClO}_4^-$ was described.[13] The dihedral angle P—C—C—P which should be in the range of 120° for the free ligand was found to be closed to 63.6° in the rhodium complex, at the expense of various structural adjustments in the carbon skeleton. Even then, the chelate ring remains distorted with respect to that in the chiraphos complex with an increase in the P—Rh—P angle (86.4°) and in the Rh—P bond lengths (5% increase). The P...P distance (3.176 Å) is also longer than in two chiraphos complexes[12a,12b] (3.033 Å and 2.998 Å). The P...P distance in rhodium complexes is an interesting value to consider since it is directly related to both the bite angle Ph—Rh—P and the Rh—P bond distances. This distance is also correlated to the dihedral angle P—C—C—P and must be consistent with geometrical constraints of the ligand skeleton. Since the [2.2.1] bicycloheptene framework of norphos 2 could accommodate distortions for closing the dihedral angle P—C—C—P from 120° to 64°[13] it is quite likely that the [2.2.1] bicyclooctene skeleton or phellanphos will accommodate a P—C—C—P dihedral angle of 60°. Another but unlikely possibility would be to retain the dihedral angle P—C—C—P of phellanphos, because of its rigidity, close to the "natural" value (> 100°) and to get a severely distorted chelate ring. A dihedral angle of 104° will impose a P...P bond of 4.0 Å. With such a large distance it is necessary to have both a large bite angle (~ 100°)[13] and Rh—P bonds longer than usual.

Since the value of the dihedral angle P—C—C—P is certainly crucial for the asymmetric induction given by the catalyst we also investigated the conformation of the phellanphos disulfide **3** in solution. It was possible to fully analyze the spectrum obtained by ^{1}H nmr at 400 MHz. Particularly informative were the coupling constants: $^3J_{H_1H_2}$, $^3J_{P_1H_2}$ and $^3J_{P_2H_1}$. The standard Karplus relation $^3J_{HH}$ and a modified Karplus type relation $^3J_{PH}$[17,18] gave the dihedral angles H_1—C—C—H_2 (≃ 130°), P_1—C—C—H_2 (≃ 10°) from which is deduced an average value at 130° ± 10° for P—C—C—P (see Figure 3). It is clear that the conformation of **3** is approximately the same in solution and in the crystal.

STRUCTURE OF NOPAPHOS DISULFIDE 5

The structure of nopaphos disulfide has been proposed as **5** after a careful examination of the various conformations compatible with the $^3J_{C-P}$ values observed in the ^{13}C nmr spectrum.[11b] An unexpected finding was that the cyclohexene ring is not in half-chair conformation but in a 1,3-diplanar conformation[19] where the phosphorus

TABLE II

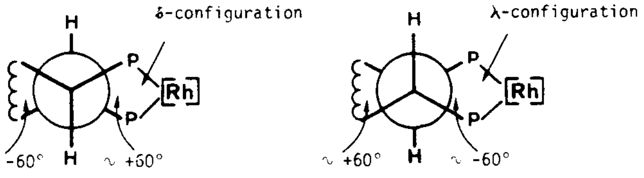
Selected structure data of nopaphos disulfide **5**

Bond distances and non bonded distances (Å) with standard deviations in parentheses			
C_1C_2: 1.548(10)	C_7C_8: 1.533(13)	P_1C_1: 1.900(8)	$P_1 \ldots P_2$: 4.275(3)
C_1C_6: 1.542(11)	C_8C_9: 1.501(13)	P_1C_{12}: 1.823(10)	$S_1 \ldots S_2$: 5.344(3)
	C_8C_{11}: 1.549(11)	P_1C_{18}: 1.822(9)	$H_3 \ldots C_{11}$: 3.078
C_2C_3: 1.564(10)	$C_{10}C_9$: 1.551(14)	P_1S_1: 1.950(3)	$H_3 \ldots C_9$: 3.700
C_3C_4: 1.515(10)	$C_{10}C_{11}$: 1.553(11)	P_2C_2: 1.852(8)	$H_3 \ldots P_2$: 2.675
C_3C_7: 1.539(12)	$C_{11}C_{36}$: 1.544(13)	P_2C_{24}: 1.823(9)	$H_3 \ldots C_{36}$: 4.607
C_4C_5: 1.328(10)	$C_{11}C_{37}$: 1.474(14)	P_2S_2: 1.960(3)	$H_3 \ldots C_{37}$: 2.746
C_5C_6: 1.495(12)		P_2C_{30}: 1.314(8)	
Torsion angles (deg.)			
$P_1C_1C_2P_2$: −131.7	$C_5C_4C_3C_2$: 38.4		
$C_2C_1P_1S_1$: 5.6	$C_7C_3C_4C_{10}$: −13.1		
$C_1C_2P_2S_2$: −69.9	$C_3C_4C_{10}C_9$: 55.0		
$C_3C_2P_2S_2$: 55.0	$C_4C_{10}C_9C_8$: −85.3		
$C_6C_1P_1S_1$: 133.3	$C_{10}C_9C_8C_7$: 85.4		
$C_4C_3C_2C_1$: −22.3	$C_9C_8C_7C_3$: −53.1		
$C_3C_2C_1C_6$: −21.1	$C_8C_7C_3C_4$: 10.7		
$C_2C_1C_6C_5$: 52.3	$C_4C_{10}C_{11}C_8$: 79.7		
$C_1C_6C_5C_4$: −40.6	$C_{10}C_{11}C_8C_7$: −82.4		
$C_6C_5C_4C_3$: −5.5	$C_{11}C_8C_7C_3$: 43.3		
Bond angles (deg.) with standard deviations in parentheses			
$P_1C_1C_2$: 110.8(6)	$C_2C_1C_6$: 112.7(7)	$C_4C_5C_6$: 121.0(9)	$C_9C_{10}C_{11}$: 87.2(8)
$P_1C_1C_6$: 113.3(7)	$C_1C_2C_3$: 114.4(7)	$C_1C_6C_5$: 110.5(8)	$C_9C_8C_{11}$: 89.1(8)
$P_2C_2C_1$: 108.4(6)	$C_2C_3C_4$: 114.1(7)	$C_3C_4C_{10}$: 117.1(7)	$C_8C_{11}C_{10}$: 84.6(7)
$P_2C_2C_3$: 108.6(6)	$C_3C_4C_5$: 119.2(8)	$C_8C_9C_{10}$: 86.3(8)	$C_7C_8C_9$: 108.3(9)

atoms are in pseudo-axial positions. The stereochemistry given by X-ray analysis confirms formula **5** and is represented in Figure 2. The structural data are in Table II. The trans stereochemistry between P_1 and P_2 is seen in Figure 2. The crucial stereochemistry at C_3 as indicated in **5** was confirmed by comparison between the distances H_3—C_{11} (3.078 Å) and H_3—C_9 (3.700 Å). H_3 is clearly cis with respect to C_{11}. The conformation of the unsaturated ring in **5** in the solid state (dihedral angles 0, −40, +52, −21, −22, +38) can be compared to the more stable conformations of cyclohexene.[19] The conformation is definitely not a half-chair conformation and cannot be described as a diplanar conformation (which needs two zero dihedral angles). However, it can be approximated to some extent to a 1,4-diplanar or half-boat conformation (dihedral angles[19]: 0, −39, +37, 0, −37, +39). The dihedral angle $P_1C_1C_2P_2$ is 131.7°, lower than the value of 170° obtained by ^{13}C nmr.[11b]

The $P_1 \cdots P_2$ distance is 4.275 Å, too large for allowing chelation. It is reasonable to assume a conformational change towards a half-chair when **6** coordinates to rhodium by virtue of the flexibility of the cyclohexene ring.[20]

In order to establish the ability of nopaphos to conformational changes for chelation on rhodium it was interesting to see if the conformation of **5** can vary from solution to solid state as often observed.[22] The best probe is to consider the dihedral angle P_1CCP_2. For that purpose nopaphos disulfide **5** was studied in $CDCl_3$ solution by ^1H nmr at 400 MHz. The main assignments for characteristic signals are in the experimental section. In nopaphos disulfide **5** $^3J_{H_1H_2} = 0$, meaning that the dihedral angle H_1CCH_2 is close to 90° by applying the classical Karplus equation. This is confirmed by considering the Karplus relation $^3J_{H-P}$.[17] It gives for dihedral angles H_1CCP_2 and H_2CCP_1 a value of 20–30°, from which can be deduced a value of 90° for the dihedral angle H_1CCH_2 and 155° ± 10° for dihedral angle P_1CCP_2. The latter is not very far from the result previously obtained[11b] (~ 170°) by the interpretation of $^3J_{C-P}$ couplings, and is definitely larger than the dihedral angle measured on the crystal (131.7°). Some absolute values of dihedral angles in the unsaturated ring of **5** can also be estimated thanks to $^3J_{HP}$ couplings. These are: $C_1C_2C_3C_4 \sim C_5C_6C_1C_2 \sim C_6C_1C_2C_3 \sim 30°$. These angles are in agreement with previous findings,[11b] and are different from those in the solid state (22°, 52°, 21° respectively). The flexibility of the cyclohexene system in **5** seems then well established, the diphosphine must not have any difficulty to chelate on a rhodium atom. This is confirmed by ^{31}P nmr of $[Rh\ nopaphos\ COD]^+PF_6^-$ in $CDCl_3$ solution which rules out phosphorus in trans position.[11b] We can safely predict that once



4 **6**

FIGURE 4 Partial structure and absolute configuration of chelate ring in rhodium complexes deriving from (a) phellanphos **4**; (b) nopaphos **6**.

coordinated on rhodium the chelate ring will be rigidified by its trans fusion with the polycyclic skeleton of the ligand. In addition, molecular models of (R,R)-nopaphos unambiguously establish that the chelate five-membered ring is allowed to take only one of the two enantiomeric conformations of a half-chair, namely the one with λ-configuration (Figure 4). For the same reasons (S,S)-phellanphos must coordinate to rhodium to give exclusively the chelate ring with the opposite absolute configuration (δ-configuration, Figure 4).

These predictions are in good agreement with the fact that opposite absolute configurations were obtained in asymmetric reduction of various prochiral substrates when nopaphos and phellanphos were used as ligand.[11b] We are currently trying to grow crystals of cationic complexes of nopaphos or phellanphos of good qualities to determine the crystal structures. It would be of particular interest to know the details of the shape of the chelate rings which certainly are distorted with respect to chiraphos. These deformations generally do not change the absolute configuration of the products obtained in asymmetric hydrogenation but could explain differences in optical yields when nopaphos and phellanphos are compared to chiraphos.[11b]

KARPLUS RELATIONSHIP $^3J_{P-P}$ FOR 1,2-DIPHOSPHINES DISULFIDES

An attempt was recently made to correlate $^3J_{P-P}$ values with the dihedral angles on a set of 1,2-diphosphine disulfides.[24] The dihedral angles were taken from X-ray data[25] or deduced for **3** and **5** from the molecular models and ^{13}C nmr. The present ^1H nmr study on **3** and **5** gives more secure values for the PCCP angles (100° and 155° respectively) since these were computed from the standard Karplus relation for protons. Nevertheless a general Karplus type relation $^3J_{P-P}$ remains to be established by using additional data from studies in solution of other 1,2-diphosphines. If these compounds are very rigid, the dihedral angle PCCP can be measured in the crystal, otherwise it has to be deduced from studies on the solution for avoiding the conformational changes introduced by the packing in the crystal lattice.

EXPERIMENTAL

Apparatus. Intensities were measured on a Enraf-Nonius CAD-4 diffractometer at the Laboratory of Crystallography in Rennes, France. All calculations were made on PDP 11/60 using the Library of SDP crystallographic programs.[26] The coordinates of all the atoms (including hydrogen) were determined.

*Crystal structure of **3**.* **3** was prepared as previously described[11] and recrystallized from CH_2Cl_2/ether mp > 300°C, $(\alpha)_D = +137°$ (c = 1, $CHCl_3$). Crystal data: $S_2P_2C_{36}H_{37} = 595.77$. Space group $P2_1$. Monoclinic, $\beta = 94.69°$. a = 9.069 (0.05) Å, b = 9.439 (0.003) Å, c = 19.248 (0.01) Å, V = 1642.2 (2.35) $Å^3$. $d_{calc.} = 1.205$ g · cm^{-3}, Z = 2. $\lambda MoK_\alpha = 0.71069$ Å, $\mu = 2.803$ cm^{-1}. A total of 5173 reflections were scanned of which 2819 were used in the final refinement. Unweighted factor $R = 0.036 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, weighted factor $R_\omega = 0.042 = \Sigma\omega||F_0| - |F_c||^2/\Sigma\omega|F_0|^2$. Criteria used to define the final reflections: $I > 1 \cdot \sigma_I$.

*^1H nmr of **3** at 400 MHz.* Spectrum was measured in $CDCl_3$ with TMS as internal standard on an experimental apparatus set up by Dr. Kan, Laboratoire d'Electronique Fondamentale, Orsay. Selected decoupling experiments allowed to assign all the signals. Some representative chemical shifts in ppm and coupling constants (Hz) are reported here: H_1: $\delta = 4.10$; H_2: $\delta = 4.10$; H_5: $\delta = 5.50$; H_6: $\delta = 2.40$; H_3: $\delta = 2.20$; $^3J_{H_1H_2} = 5.5$; $^3J_{P_1H_2} = 22$; $^3J_{P_2H_1} = 21$.

*Crystal structure of **5**.* **5** was prepared as described[11] and recrystallized from CH_2Cl_2/ether. mp = 245°C, $(\alpha)_D = -313°$ (c = 1; $CHCl_3$). Crystal data: $S_2P_2C_{37}H_{38} = 608.79$. Space group $P2_12_12_1$. Orthorhombic. a = 9.036 (0) Å, b = 20.052 (0) Å, c = 18.052 (0) Å, V = 3270.9 (0.025) $Å^3$. $d_{calc.} = 1.236$ $g \cdot cm^{-3}$, Z = 4. $\lambda MoK_\alpha = 0.71069$ Å, $\mu = 2.831$ cm^{-1}. A total of 6101 reflections were scanned of which 2154 were used in the final refinement. R = 0.061, $R_\omega = 0.042$.

*^1H nmr of **5** at 400 MHz.* H_1: $\delta = 3.29$; H_2: $\delta = 4.94$; H_5: $\delta = 4.06$; H_3: $\delta = 3.40$; H_6 (cis by respect to P_1): $\delta = 2.87$; H_6 (trans by respect to P_1): $\delta = 2.15$. Couplings (Hz): $^3J_{H_1H_2} = 0$; $^3J_{P_1H_2} = 25$; $^3J_{P_2H_1} = 15$.

Supplementary Material Available. Tables of atom positional and equivalent isotropic thermal parameters, general temperatures factors expressions, weighted least-square planes and calculated and observed structure factor amplitude are available from Cambridge Crystallographic Data Center.

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Å). This is additional example of a major conformational change for a flexible 1,2-diphosphine through chelation.
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