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Chiral atropisomeric five-membered biheteroaromatic diphosphines: new ligands of the bibenzimidazole and biindole series

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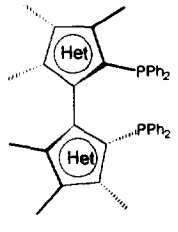
Abstract

Two new chiral atropisomeric biheteroaromatic diphosphines are described: 2,2′-bis(diphenylphosphino)-1,1′-bibenzimidazole (**3a**) and 3,3′-dimethyl-1,1′-bis(diphenylphosphino)-2,2′-biindole (**4a**). Structural characterization is given and configurational stability at room temperature demonstrated. The oxidation potential was recognized as a good tool to evaluate the electronic availability of the phosphorus atom in the series of biheteroaromatic diphosphines. Its value increases parallel to the electronic demand of the heterocyclic system and also depends on the position of the diphenylphosphino group. © 1997 Elsevier Science S.A.

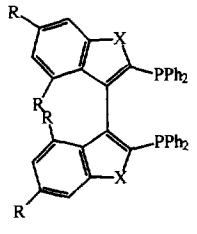
Keywords: Diphosphines; Heterocyclic phosphines; Palladium complexes; Catalysis; Crystal structure

1. Introduction

One year ago we presented a new class of chiral atropisomeric diphosphines: the class of five-membered biheteroaromatic diphosphines, schematically represented by the general structure **1** [1]. The first ligand of this series, nicknamed tetraMe-bitianp, **2a** [2], was recently joined by others, namely the unsubstituted analogous (**2b**) (bitianp), and the corresponding oxygenated compound (**2c**) (bifurp) [3].



1



2

a X = S, R = CH_3 tetraMe-bitianp
b X = S, R = H bitianp
c X = O, R = H bifurp

While the bibenzo[b]furan ligand **2c** was found configurationally lablie at room temperature, the bibenzo[b]thiophene system **2b** was perfectly stable at temperatures exceeding 100 °C and was easily obtained

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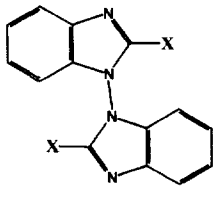
in an enantiomerically pure state. Its behaviour as a chiral ligand for Ru(II) and Rh(I) was found so outstanding in asymmetric homogeneous stereoselective catalysis, and its synthesis so smooth, that optically pure bitianp has been prepared on a kilogram scale and is gaining ground in industrial application.

Biheteroaryl ligands associate some features typical of carbocyclic biaryl systems with others peculiar to five-membered heteroaromatic rings. The advantages are as follows. (i) The nature of the heterocycle strongly influences the electronic availability of the phosphorus atoms and their electronic tuning can be brought about by changing the supporting heterocyclic system. Alternatively, electronic modulation of the diphenylphosphino groups can be effected by changing their positions on a given heterocycle. (ii) Synthetic approaches to pentatomic heterocyclic compounds are in principle easier than those available for carbocyclic aromatic systems. (iii) The effects on stereoselectivity of the geometry associated with two interconnected pentatomic rings are comparable with the data reported in the literature for known biaryl systems, all resulting from the connection of two six-membered rings.

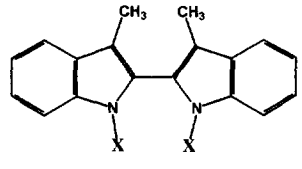
This paper deals with the syntheses and characterization of two new five-membered biheteroaromatic diphosphines: 2,2′-bis(diphenylphosphino)-1,1′-bibenzimidazole (bimip, **3a**) and 3,3′-dimethyl-1,1′-bis(diphenylphosphino)-2,2′-biindole (biscap, **4a**).



3

a X = Ph_2P bimip

b X = Ph_2PO bimipo



4

a X = Ph_2P biscap

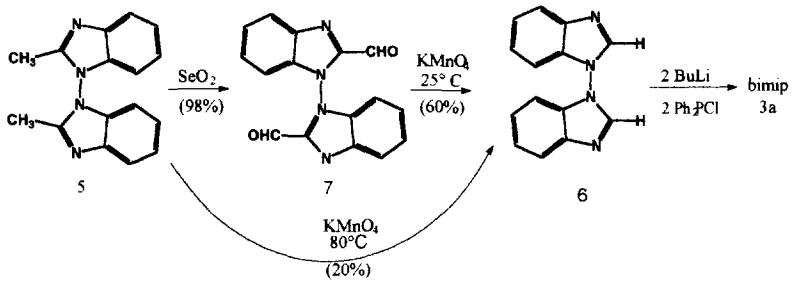
b X = Ph_2PO biscapo

There are several reasons for this choice. Both these ligands exhibit structural peculiarities: bimip is the first atropisomeric diphosphine with hindered rotation around a nitrogen–nitrogen bond; biscap is the first atropisomeric diphosphine with the phosphino group bonded to an aromatic nitrogen atom. There is also the need to enlarge the family of the diphenylphosphino biheteroaryls, since only a large series of geometrically homogeneous ligands allows a correct comparison of the different electronic availability of their phosphino groups and a weighting of its influence on the catalytic properties of their metal complexes. Brown and coworkers [4] have recently reported the synthesis and resolution of 2,2′-bis(diphenylphosphino)-3,3′-biindole, differing from **4a** in the position of the phosphino groups on the indole ring and in the location of the interanular bond. This precedent would allow a useful comparison of two indole ligands, structurally quite similar, but probably very different in the electronic endowment of the phosphorus atoms. Within this framework, we made an effort to find some experimental, quantitative evidence of the claimed different electronic availability of all the heterocyclic diphosphines reported by us till now, namely **2a** (tetraMe-bitianp), **2b** (bitianp), **2c** (bifurp), **3a** (bimip) and **4a** (biscap), using binap as a reference.

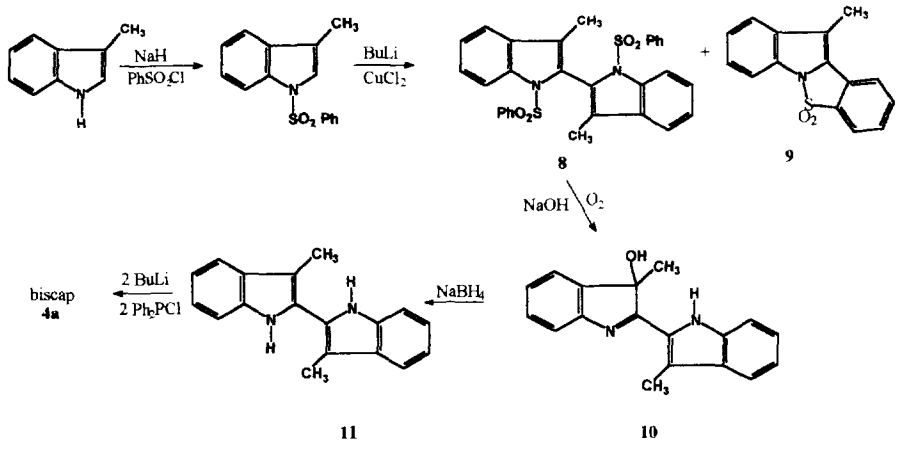
2. Results and discussion

2.1. Synthesis of the ligands

The synthesis of 2,2′-bis(diphenylphosphino)-1,1′-bibenzimidazole (**3a**) begins from known 3,3′-dimethyl-1,1′-bibenzimidazole (**5**), easily prepared from *ortho*-phenylendiamine through a rather simple four-step scheme [5]. Potassium permanganate oxidation of **5** in neutral aqueous medium at 90 °C directly afforded 1,1′-bibenzimidazole (**6**), though in low yields (20%). In order to improve the yields, this transformation was divided into two steps: selenium dioxide oxidation of **5** in refluxing dioxane solution gave dialdehyde **7**, which was further oxidized with potassium permanganate at room temperature to give **6** in a 55% overall yield. Double lithiation of **6**, followed by the addition of two equivalents of diphenylchlorophosphine, gave bimip (**3a**) with satisfactory yields.



The synthesis of 3,3′-dimethyl-1,1′-bis(diphenylphosphino)-2,2′-biindole (**4a**) begins with inexpensive, commercially available scatole. Protection of the nitrogen atom and lithiation, followed by the addition of an excess of cupric chloride, produced 3,3′-dimethyl-1,1′-dibenzenesulphonyl-2,2′-biindole (**8**) with satisfactory yields. Some 1H-indole[1,2-b]benzo[d]isothiazole-5,5′-dioxide (**9**) was also formed as a by-product of this reaction. It results from intramolecular oxidative coupling of the dianion produced by basic removal of the indolic hydrogen atom and the hydrogen atom in *ortho* position to the benzenesulphonyl group. Alkaline deprotection was performed while oxygen was introduced into the reaction mixture; the hydroxyindoline derivative **10** formed under these conditions is highly insoluble and can easily be purified by crystallization. Instead, 3,3′-dimethyl-2,2′-biindole **11**, known in the literature [6] but prepared through rather complex procedures, is very soluble and difficult to purify. The latter, however, can easily be obtained by sodium borohydride reduction of the hydroxy derivative **10**. Joining of the diphenylphosphino groups to **11** is a very easy process, and biscap (**4a**) was obtained with excellent yields.



An interesting feature of both these ligands is the scarce oxidizability of the phosphino groups in air.

2.2. Structural characterization of the ligands 3a and 4a

The structure of bimip **3a** and that of its palladium dichloride complex **3a**-$PdCl_2$ were fully elucidated by single crystal X-ray diffraction (Figs. 1 and 2). Selected geometrical parameters of **3a** and **3a**-$PdCl_2$ are compared in Table 1. An inspection of the conformation of the diphosphine core P(1)–C(50)–N(51)–N(61)–C(60)–P(2) shows that there is no dramatic difference in the values of the torsion angles between the coordinated ligand and the uncoordinated one. The phosphorus atom is almost coplanar with the heteroaromatic ring and the torsion around the interanular N(51)–N(61) bond differs by about 17° on passing from the coordinated molecule to the free one. Apart from the phenyl rings, it therefore seems that intramolecular interactions might play a major role in determining the conformational arrangement of the diphosphine core, thus providing a good configurational stability to the ligand. While no substantial variation in bond distances is observed upon coordination (only an expected contraction of the P–C distances is observed in the complex, small compared with the limit of significance), significant changes involving some of the bond angles are detected. For

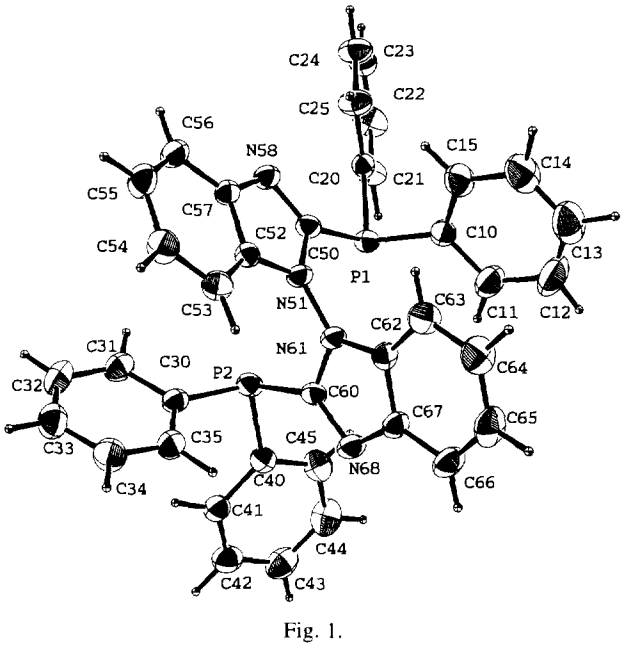


Fig. 1.

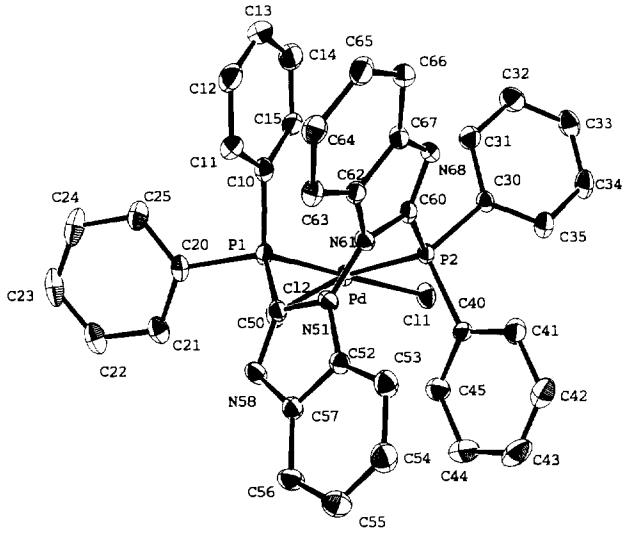


Fig. 2.

instance, in **3a** the C–P–C angles are on average smaller (101.4°) than in the complex (104.7°), in agreement with the greater hindrance of the phosphorus lone pair with respect to the Pd–P bond electron density.

As also observed in the case of analogous palladium complexes of tetraMe-bitianp **2a** and bitianp **2b**, a quasi-C_2 symmetry is present in **3a**-$PdCl_2$. This is known to be a useful feature to observe good stereoselectivity levels in many asymmetric transformations catalyzed by transition metal complexes in solution.

Configurational stability of bimip was experimentally supported by the easy analytical resolution of bimip by HPLC on a chiral column (Daicel Chiracel OD), showing fully separated equivalent peaks. A further demonstration was given by the ^{31}P NMR spectra of the diastereomeric complexes resulting from the reaction of bimip **3a** with a chiral enantiomerically pure palladium reagent: di-μ-chloro-bis[(R)-dimethyl(α-methylbenzyl)aminato-2-C,N]dipalladium(II). Complexation can be carried out directly in the NMR tube, according to a known procedure [7]. A 1:1 diastereomeric mixture is expected in the case of configurationally stable ligands, while an unbalanced thermodynamic mixture is given by configurationally labile phosphines. In the case of bimip, the integrals of the signals related to the two diastereomeric complexes are identical (Fig. 3).

We were not able to get crystals of **4a**, or of its metal complex, suitable for X-ray diffraction analysis. Structural assignment was however unequivocally demonstrated by analytical and spectral data. Also in this case, chiral HPLC showed two well-resolved peaks, suggesting that biscap is configurationally stable at room temperature. The same conclusion was suggested by the analysis of the ^{31}P NMR spectrum of the mixture of

Table 1
Selected interatomic distances (Å), angles (°) and torsion angles (°)

Compound	**3**	**3**-$PdCl_2$
Pd–Cl(1)		2.343(1)
Pd–Cl(2)		2.325(1)
Pd–P(1)		2.260(1)
Pd–P(2)		2.274(1)
P(1)–C(10)	1.833(2)	1.809(5)
P(1)–C(20)	1.832(3)	1.828(5)
P(1)–C(50)	1.825(3)	1.821(5)
P(2)–C(30)	1.825(2)	1.806(5)
P(2)–C(40)	1.824(6)	1.823(5)
P(2)–C(60)	1.827(3)	1.827(5)
N(51)–N(61)	1.375(2)	1.377(5)
N(51)–C(50)	1.400(3)	1.386(6)
N(51)–C(52)	1.381(3)	1.386(6)
C(52)–C(57)	1.396(4)	1.399(6)
N(58)–C(50)	1.307(4)	1.315(6)
N(58)–C(57)	1.401(4)	1.403(6)
N(61)–C(60)	1.387(4)	1.386(6)
N(61)–C(62)	1.387(3)	1.390(6)
C(62)–C(67)	1.389(4)	1.391(6)
N(68)–C(60)	1.309(4)	1.311(6)
N(68)–C(67)	1.400(3)	1.394(6)
Cl(1)–Pd–Cl(2)		91.34(5)
Cl(1)–Pd–P(1)		177.52(5)
Cl(1)–Pd–P(2)		82.52(5)
Cl(2)–Pd–P(1)		91.14(5)
Cl(2)–Pd–P(2)		170.18(5)
P(1)–Pd–P(2)		95.02(5)
Pd–P(1)–C(10)		113.1(2)
Pd–P(1)–C(20)		123.0(2)
Pd–P(1)–C(50)		104.0(2)
Pd–P(2)–C(30)		115.3(2)
Pd–P(2)–C(40)		109.1(2)
Pd–P(2)–C(60)		119.0(2)
C(10)–P(1)–C(20)	103.1(1)	104.0(2)
C(10)–P(1)–C(50)	98.8(1)	108.3(2)
C(20)–P(1)–C(50)	102.3(1)	103.3(2)
C(30)–P(2)–C(40)	104.3(1)	110.3(2)
C(30)–P(2)–C(60)	100.3(1)	101.2(2)
C(40)–P(2)–C(60)	99.3(2)	100.9(2)
N(61)–N(51)–C(50)	126.3(2)	126.4(4)
N(61)–N(51)–C(52)	125.0(2)	125.1(4)
C(50)–N(51)–C(52)	108.6(2)	108.5(4)
C(50)–N(58)–C(57)	106.4(2)	106.1(4)
N(51)–N(61)–C(60)	124.9(2)	126.4(4)
N(51)–N(61)–C(62)	126.1(2)	125.2(4)
C(60)–N(61)–C(62)	108.5(2)	108.1(4)
C(60)–N(68)–C(67)	105.6(2)	105.6(4)
P(1)–C(50)–N(51)	119.4(2)	123.0(3)
P(1)–C(50)–N(58)	130.1(2)	123.7(4)
N(51)–C(50)–N(58)	110.4(2)	110.9(4)
N(58)–C(57)–C(52)	110.5(2)	110.1(4)
P(2)–C(60)–N(61)	118.2(2)	121.7(4)
P(2)–C(60)–N(68)	130.1(2)	126.9(4)
N(61)–C(60)–N(68)	111.0(2)	111.3(4)
N(61)–C(62)–C(67)	103.7(3)	103.9(4)
N(68)–C(67)–C(62)	111.1(2)	111.1(4)
P(1)–C(50)–N(51)–N(61)	−0.3(3)	14.6(6)
C(50)–N(51)–N(61)–C(60)	−84.2(3)	−67.3(6)
N(51)–N(61)–C(60)–P(2)	8.2(3)	−2.9(6)

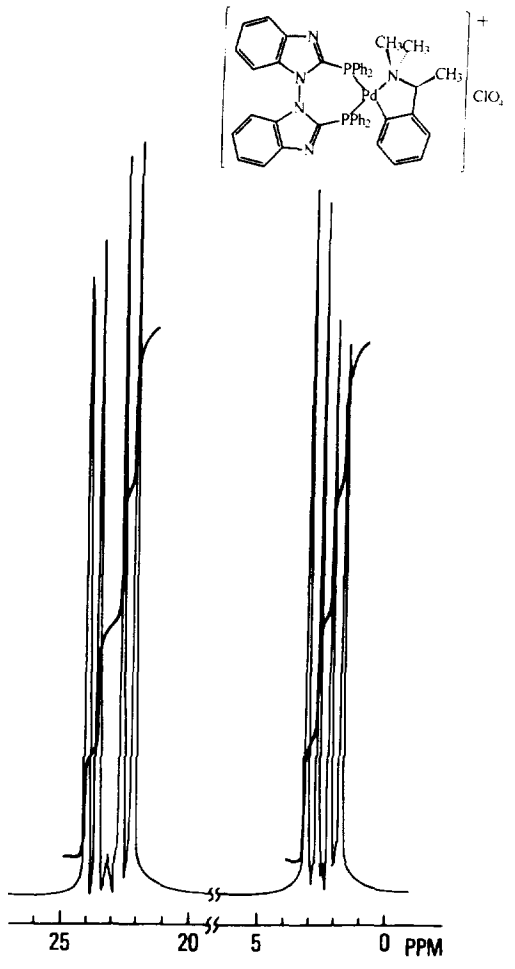


Fig. 3.

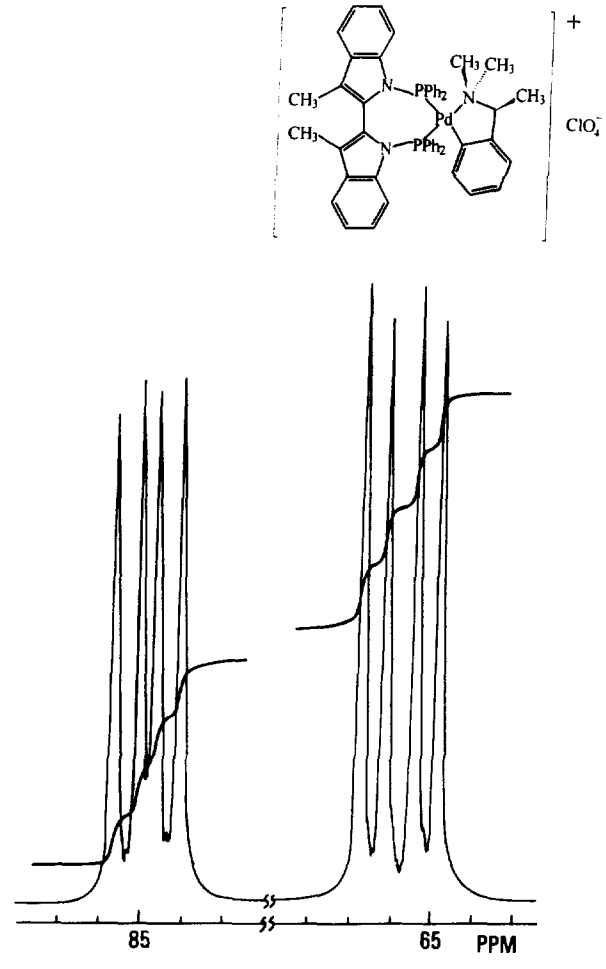


Fig. 4.

diastereomeric complexes, obtained by the reaction of biscap with the chiral palladium reagent mentioned above. The two expected diastereoisomers are formed in a 1:1 ratio (Fig. 4).

2.3. Evaluation of electronic availability of the phosphorus atoms of biheteroaromatic diphosphines

The general assumption that electronic availability of phosphorus atoms of biheteroaromatic diphosphines is strongly dependent on the nature of the supporting heterocyclic system had to be quantitatively substantiated. We considered oxidation potential as a highly indicative parameter of the electronic endowment of the phosphino groups. Experimental determinations were performed in an approximately 0.5×10^{-3} M acetonitrile solution, on a platinum anode, in the presence of 0.1 M tetraethylammonium perchlorate as the supporting electrolyte, under nitrogen at 25 °C. All the cyclic voltammograms (0.1 V s^{-1}) showed a single irreversible process, except for biscap **4a**, which displayed two peaks; the first corresponding to indole ring oxidation [8], the second to oxidation of the phosphine group. The electrochemical data, including the value for binap, are reported in Table 2.

The values are in good agreement with the electronic endowment of the heterocycle, with the electron donating effect of the methyl group and with the type of atom (carbon or nitrogen) bonded to the phosphino group.

2.4. Attempts at resolution of racemic 3a and 4a

We have performed preliminary attempts to get bimip and biscap in an enantiomerically pure state, following

Table 2
Oxidative potentials E_p of biheteroaromatic diphosphines

Substrate	E_p (V) [a]
binap	0.63
tetraMe-bitianp **2a**	0.76
bitianp **2b**	0.83
biscap **4a**	0.90 (0.78) [b]
bifurp **2c**	1.03
bimip **3a**	1.15

[a] vs. silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs. SCE).
[b] Oxidation peak of the indole nucleus.

the two most popular resolution procedures for acceding to enantiopure phosphines: (1) fractional crystallization of the diastereomeric adducts of the corresponding racemic phosphinoxide with an optically pure chiral acid, followed by alkaline decomposition of the diastereomerically pure adducts and reduction of the phosphinyl group to a phosphino group with trichlorosilane or lithium aluminium hydride [9]; (2) fractional crystallization of the diastereomeric mixture obtained by reacting equimolar amounts of racemic phosphine and an optically pure chiral palladium complex [10].

Racemic phosphinoxides **3b** (bimipo) and **4b** (biscapo) were easily prepared, in quantitative yields, by hydrogen peroxide oxidation of **3a** and **4a**, in dichlorometane solution at room temperature. Both these compounds did not give adducts with optically pure dibenzoyltartaric acid, camphor-10-sulphonic acid or with equimolar mixtures of the latter and acetic acid. The poor basicity of the oxygen atom of the phosphinyl groups in **3b** and **4b** is responsible for the complexation failure, ascribed to the rather high electronic demand of the positions of the benzimidazole and indole ring carrying these groups. We have verified that acidic complexation of phosphinoxides does not occur whenever the corresponding phosphines exhibit an oxidative potential E_p higher than 0.9 V.

We also tried to fractionally crystallize the complexes resulting from the reaction of **3a** and **4a** with enantiomerically pure di-μ-chloro-bis[(R)-dimethyl(α-methylbenzyl)aminato-2-C,N]dipalladium(II). Some decomposition of the complexes was observed during crystallization from dichloromethane–methanol solutions; research is in progress to investigate whether degradation is diastereoselective.

Preparative chiral HPLC seems to be the most efficient resolution system available at the moment for obtaining enantiopure samples of bimip and biscap.

3. Conclusions

A five-membered biheteroaromatic system is a very functional backbone for chiral atropisomeric diphosphines. Synthetic approaches to structures having general formula **1** are much more flexible and easier than those available for carbocyclic biaryl diterphosphines. The family of pentatomic biheteroaromatic ligands, presented one year ago, is rapidly growing and now includes the 3,3′-bithianaphthene, 3,3′-bibenzofuran, 2,2′- and 3,3′-biindole and 1,1′-bibenzimidazole systems.

When obtained in an enantiomerically pure state, these ligands exhibit outstanding stereoselection ability, comparable with that reported in the literature for the most popular chiral atropisomeric ligands, like binap.

One of the most attractive features of these chelating systems is the possibility they offer to modulate the electronic availability of the phosphino groups, which is a crucial parameter for the catalytic activity of complexes with transition metals.

The oxidation potential appears to be a very meaningful, easily achieved parameter which will prove to be correlated, in the near future, to the kinetics and stereoselectivity of asymmetric syntheses catalyzed by transition metal complexes in solution.

4. Experimental part

^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ solution, unless stated otherwise, on a Varian XL-300 or Gemini Broad Band spectrometer. Mass spectra were recorded on a VG 7070 EQ-HF spectrometer. Melting points were determined on a Buchi apparatus and are uncorrected. Electrochemical experiments were performed in a three-electrode cell at 25 °C under nitrogen. The working electrode was a platinum microelectrode (0.003 cm^2); the counter electrode was platinum; the reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs. SCE). The voltammetric apparatus (Amel, Italy) included a 551 potentiostat modulated by a 568 programmable function generator.

4.1. Reagents

Chlorodiphenylphosphine was distilled in vacuo, under nitrogen, immediately before use and stored under argon in a refrigerator. Acetonitrile for voltammetric measurements was distilled twice over phosphorus pentoxide and once over calcium hydride. Tetraethylammonium perchlorate was dried at 70 °C before use. All other chemicals were reagent grade and were used with no further purification.

4.2. 1,1′-Bibenzimidazolyl-2,2′-dicarboxaldehyde (7)

Selenium dioxide (11 g) was added to a solution of 2,2′-dimethyl-1,1′-bibenzimidazole (**5**) (6 g) in dry dioxane (55 ml). The mixture was heated to 80 °C, under stirring, for 5 h. After removal of the selenium, the solvent was distilled under reduced pressure to give **7** (98%) as a pale yellow solid; m.p. 233 °C. ^1H NMR: δ 7.02 (2H, d), 7.50 (4H, m), 8.08 (2H, d), 10.00 (2H, s).

4.3. 1,1′-Bibenzimidazole (6)

A solution of potassium permanganate (1.6 g) in water (200 ml) was dropped into a mixture of dialdehyde **7** (3 g), water (200 ml), benzene (70 ml) and sodium carbonate (1.12 g). The reaction mixture was stirred at room temperature for 10 h. Sodium metabisulphite was added until the manganese dioxide disappeared, then the solution was treated with a 10% hydrochloric acid

solution. The organic layer was exhaustively extracted with methylene dichloride; the combined extracts were dried over sodium sulphate, then the solvent removed under reduced pressure to give a solid which was triturated with diisopropyl ether to afford **6** as a colourless solid (62%); m.p. 188 °C. ^{1}H NMR: δ 7.02 (2H, d), 7.40 (4H, m), 7.92 (2H, d), 8.17 (2H, s). ^{31}P NMR: δ 28.3. MS *m/z* 234 (M^+), 208, 118.

4.4. 2,2'-Bis(diphenylphosphino)-1,1'-bibenzimidazole (bimip) (3a)

A 1.6 M solution of butyllithium in hexane (9.5 ml) was dropped into a solution of 1,1'-bibenzimidazole (1.5 g), N,N,N',N'-tetramethylethylenediamine (2.25 ml) and dry THF (70 ml) at −60 °C, under a nitrogen atmosphere. The temperature was allowed to warm up to 0 °C, then diphenylchlorophosphine (2.78 ml) was added dropwise. After 2 h stirring at room temperature, the solvent was removed in vacuo; then water and methylene dichloride were added. The organic layer, dried over sodium sulphate, was evaporated under reduced pressure to give **3a**, which was crystallized from ethyl acetate (78%); m.p. 227 °C. ^{1}H NMR: δ 6.3 (2H, d), 6.93 (2H, t), 7.25 (20H, m), 7.55 (2H, m), 7.88 (2H, d). ^{31}P NMR: δ −28.3. MS *m/z* 525 (M^+), 417, 262.

4.5. 2,2'-Bis(diphenylphosphinyl)-1,1'-bibenzimidazole (bimipo) (3b)

A solution of racemic **3a** (1 g) in methylene dichloride (10 ml) was treated with aqueous H_2O_2 (35% w/w, 2 ml) and then stirred for 1 h. The reaction mixture was dried over sodium sulphate and the solvent evaporated under reduced pressure to give **3b**, which was triturated with diisopropyl ether (90%); m.p. 245 °C. ^{1}H NMR: δ 6.5 (2H, d), 7.08 (2H, t), 7.35 (10H, m), 7.5 (4H, m), 7.71 (4H, m), 7.92 (6H, m). ^{31}P NMR: δ +18.03.

4.6. 3-Methyl-1-phenylsulphonylindole

Sodium hydride (60% dispersion in mineral oil) (1.3 g) was added portionwise to a solution of 3-methylindole (4 g) in DMF (50 ml), keeping the temperature below 30 °C. After stirring for 15 min at room temperature, a solution of phenylsulphonyl chloride (4.7 ml) in DMF (20 ml) was added dropwise. The mixture was stirred at room temperature for 2 h, then the solvent evaporated in vacuo. The residue was treated with water and extracted exhaustively over methylene dichloride. The combined organic layer was dried over sodium sulphate, then the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column, using a methylene dichloride/hexane (1:1) mixture as eluant, to give 1-(phenylsulphonyl)-3-methylindole in a pure state (86%); m.p. 116–120 °C. ^{1}H NMR: δ 2.55 (3H, s), 7.31 (1H, s), 7.38 (6H, m), 7.85 (1H, d), 7.86 (1H, d), 7.99 (1H, d) [11].

4.7. 3,3'-Dimethyl-1,1'-diphenylsulphonyl-2,2'-biindole (8)

A 1.6 M solution of butyllithium in hexane (60 ml) was dropped into a solution of 3-methyl-1-phenylsulphonylindole (30 g) in N,N,N',N'-tetramethylethylendiamine (100 ml) and THF (10 ml) at −30 °C. After 30 min stirring, cupric chloride (13 g) was added and the temperature was allowed to rise to room temperature. After 1 h stirring, the solvent was removed in vacuo, then water and methylene dichloride were added. The organic layer was dried over sodium sulphate, then the solvent was distilled under reduced pressure. The crude residue was chromatographed on a silica gel column, using a methylene dichloride/hexane (1:1) mixture as eluant. Some unreacted starting material was eluted first (7 g, 23%), then 1H-indole[1,2-b]benzo[d]isothiazole-10-methyl-5,5'-dioxide (**9**) was eluted (7%); m.p. 170–173 °C. ^{1}H NMR: δ 7.82 (1H, d), 7.79 (1H, d), 7.69 (1H, d), 7.65 (1, d), 7.55 (1H, d), 7.46 (1H, t), 7.38 (1H, t), 7.26 (1H, d), 2.53 (3H, s). MS *m/z*: 269 (M^+), 204. Finally, 1,1'-diphenylsulfonyl-3,3'-dimethyl-2,2'-biindole (**8**) (35%) was recovered; m.p. 234 °C. ^{1}H NMR: δ 1.62 (6H, s), 7.3 (6H, m), 7.48 (10H, m), 8.35 (2H, d). MS: *m/z* 540 (M^+), 399, 258, 130.

4.8. 3-Hydroxy-3-methyl-2-[2-(3-methyl)indolyl]-Δ^1-indoline (10)

A solution of 3,3'-dimethyl-1,1'-diphenylsulfonyl-2,2'-biindole (**8**) (10 g) and potassium hydroxide (8.3 g) in dioxane (80 ml) and ethanol (300 ml) was refluxed for 5 h, then concentrated under reduced pressure. The mixture was treated with water and extracted with methylene dichloride. The organic layer was dried over sodium sulphate. Air was introduced into the solution, under stirring, for 24 h at room temperature. The precipitated solid was filtered to give a first crop of 3-hydroxy-3-methyl-2-[2-(3-methyl)indolyl]-Δ^1-indoline (**10**) (2 g). Mother liquors were concentrated and the residue was chromatographed on a silica gel column, using a methylene dichloride/ethyl acetate (10:0.1) mixture as eluant to give **10** (54%); m.p. 94 °C. ^{1}H NMR: δ 1.52 (3H, s), 2.6 (3H, s), 4.15 (1H, s), 7.00 (SH, m), 7.14 (1H, t), 7.29 (1H, d), 7.52 (1H, d), 9 (1H, s).

4.9. 3,3'-Dimethyl-2,2'-biindole (11)

A solution of sodium borohydride (0.51 g) in water (3 ml) was added to a solution of **10** (2.5 g) in ethanol (150 ml) degassed with nitrogen. The mixture was stirred for 2 h, then the pH was adjusted to 6 with a 10%

hydrochloric acid solution. The solution was stirred for 12 h. The precipitated solid was filtered under nitrogen to give 3,3'-dimethyl-2,2'-biindole (90%). ^{1}H NMR: δ 2.40 (6H, s), 7.18 (2H, t), 7.25 (2H, t), 7.39 (2H, d), 7.63 (2H, d), 8.00 (2H, s). MS m/z: 260 (M^+).

4.10. 1,1'-Bis(diphenylphosphino)-3,3'-dimethylbiindole (4a)

A 1.6 M solution of butyllithium in hexane (1.2 ml) was dropped into a solution of 3,3'-dimethyl-2,2'-biindole (**11**) (0.24 g) in dry and degassed THF (5 ml) at −20 °C. A solution of diphenylphosphino chloride (0.4 g) in THF (5 ml) was added after 2 min. The mixture was stirred for 12 h, then evaporated under reduced pressure and the residue treated with water and methylene dichloride. The organic layer was dried over sodium sulphate and the solvent removed by distillation. The residue was chromatographed on a silica gel column, with a hexane/methylene chloride (8:2) mixture as eluant, to give 1,1'-bis(diphenylphosphino)-3,3'-dimethyl-biindole (**4a**) (90%). ^{1}H NMR: δ 2.05 (6H, s), 6.70 (2H, d), 6.85 (2H, t), 7.1 (8H, m), 7.30 (14H, m), 7.59 (2H, d). ^{31}P NMR: δ 37. MS m/z 628 (M^+), 551, 444, 366, 289.

4.11. N,N'-Bis(diphenylphosphinyl)-3,3'-dimethyl-2,2'-biindole (biscapo) (4b)

A solution of racemic **4a** (1.1 g) in methylene dichloride (50 ml) was treated at 30 °C with aqueous H_2O_2 (35% w/w, 1.75 ml). The solution was stirred at −30 °C for 1 h and then at room temperature for 2 h. The reaction mixture was dried over sodium sulphate and the solvent evaporated under reduced pressure to give a residue which was chromatographed on a silica gel column using an ethyl acetate/methylene dichloride (3:7) mixture as eluant. The final fractions were collected and evaporated to dryness to give **4b** (70%); m.p. 267–271 °C. ^{1}H NMR: δ 1.85 (6H, s), 7.00 (10H, m), 7.25 (10H, m), 7.40 (4H, m), 7.6 (4H, m). ^{31}P NMR: δ 24.12. MS m/z 660 (M^+).

4.12. Preparation of Pd(II) dichloride complexes of bimip

A mixture of bimip (0.052 g, 0.1 mmol) and $(C_6H_5CN)_2PdCl_2$ (0.038 g, 0.1 mmol) in dichloromethane (5 ml) was stirred at room temperature for 18 h; the solvent was removed under reduced pressure to leave the palladium dichloride complex **3a** as a yellow solid, in quantitative yield. Crystallization of the crude product by slow diffusion of diethyl ether into a dichloromethane saturated solution afforded crystals suitable for X-ray structure analysis.

4.13. X-ray structure determination of 3a and 3a-$PdCl_2$

Details of the data collection and refinement of the structures are reported in Table 3; atomic coordinates, displacement parameters, interatomic distances and angles of **3a** and **3a**-$PdCl_2$ have been deposited at the Cambridge Crystallographic Data Centre. Crystals of **3a** and **3a**-$PdCl_2$ were mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with graphite monochromated Mo Kα radiation (0.71073 Å) on an Enraf–Nonius CAD4 computer controlled kappa axis diffractometer for **3a** and on a Siemens P4 diffractometer for **3a**-$PdCl_2$ respectively. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections, measured by the computer controlled diagonal slit method of centring. The data were collected at room temperature using a variable scan rate. The scan range (°) was determined as a function of θ to correct for the separation of the Kα doublet. As a check on crystal and electronic stability, three representative reflections were measured every 3 h and showed no decay of the scattering power of the crystals during the data collection. Lorentz and polarization corrections were applied, whereas a series of psi-scans performed on selected reflections revealed that no absorption correction was necessary. The structures were solved by direct methods and refined in full-matrix least-squares minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors were taken from Cromer and Waber [11]. Anomalous dispersion effects were included in F_c; the values for δf and $\delta f'$ were those of Cromer [12]. All calculations were performed on a 80486/33 computer using Personal SDP software [13].

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