# A Convenient Procedure for the Preparation of 1-(Diisopropylamino)phospholes − Application to the Synthesis of New 2,2′-Biphosphole Disulfides

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A convenient one-pot procedure for the preparation of 1-(diisopropylamino)phospholes has been developed. These phospholes have been used in a multistep procedure for synthesizing two new 2,2′-biphosphole disulfide compounds. The structures and stereochemistry of these compounds have been studied by X-ray diffraction analysis and by molecular modeling. The 1-(diisopropylamino) group, used as a bulky substituent on the phosphorus atom in combination with a phenyl group on the ring, proved to be an important factor in the stabilization of the axial chirality of 2,2′-biphosphole framework.

## Introduction

Chiral diphosphane ligands, especially the $C_2$-symmetric diphosphanes, play an important role as chiral auxiliaries in catalytic asymmetric processes.[1] Since the preparation of DIOP by Kagan in 1971,[2] numerous $C_2$-symmetric diphosphanes have been synthesized. Different sources of chirality have been exploited for the design of these diphosphanes; the centers of chirality (carbon centers as in DIOP[2] or phosphorus centers as in DIPAMP[3]), axial chirality as in BINAP,[4] and planar chirality as in Phanephos.[5] Sometimes several sources of chirality are combined within the same molecule, as in BIPNOR,[6] in which stereocenters are located on carbon and phosphorus atoms, or in TRAP,[7] with both central and planar chirality.

In 1994, we began to focus our attention on $C_2$-symmetric diphosphanes incorporating two sources of chirality. Our first studies were based on a bidentate ligand combining both central and axial chirality, the 3,3′,4,4′-tetramethyl-1,1′-diphenyl-2,2′-biphosphole (BIPHOS) first synthesized by F. Mathey.[8] We first demonstrated that this chiral diphosphane, which is an efficient ligand for transition metal ions,[9] is stereolabile in solution.[10] However, we have since been able to obtain BIPHOS complexes in stable enantiomerically pure form,[11] and this new family of complexes proved to be effective in asymmetric catalysis.

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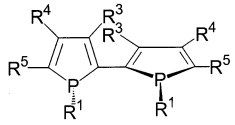
Concentrating our investigations on 2,2′-biphosphole ligands and their use in asymmetric catalysis, we were interested in the design and syntheses of new compounds possessing stable axial chirality. We decided to introduce bulky substituents such as the diisopropylamino group at position 1, and different alkyl or aryl substituents at positions 3 and 4 on the 2,2′-biphosphole framework (Scheme 1), in order to prevent free rotation around the C−C bond linking the two phosphole rings. Moreover, the diisopropylamino group, which exhibits different electronic effects with respect to the phenyl group in position 1 in BIPHOS, may also enhance the pyramidal inversion barrier of the phosphorus atom.[12]




Scheme 1. 2,2′-Biphosphole framework

For the goal of obtaining new 1,1′-bis(diisopropylamino)-2,2′-biphospholes, a simple and versatile method for syntheses of 1-(diisopropylamino)-substituted monophosphole precursors in high yields was desirable. As the available synthetic route to these compounds, restricted to 1-(diisopropylamino)-3,4-dimethylphosphole,[13] involved a rather complicated multistep procedure and proceeded in rather low yield, we attempted to develop a new method for preparing 1-(diisopropylamino)phosphole moieties.

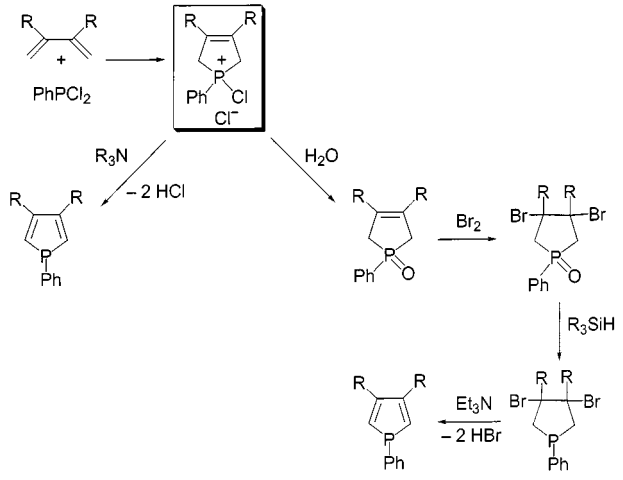
Here we report a convenient one-pot procedure for the preparation of various 1-(diisopropylamino)phospholes **2a**,**b** and their use in the synthesis of new 2,2′-biphosphole disulfides **8a**,**b** and one free 2,2′-biphosphole **10a**. The structures and stereochemistry of the disulfide compounds

have been studied by X-ray diffraction analysis and by molecular modeling.

## Results and Discussion

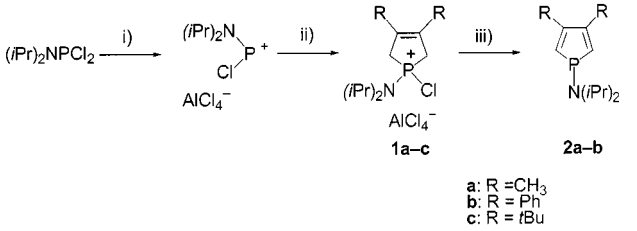
### Synthesis of 1-(Diisopropylamino)phospholes 2

The conventional synthetic routes to the phosphole rings involve the MacCormack reaction,[14] in which the five-membered ring is assembled by means of a cycloaddition reaction between a dichlorophosphane and a 1,3-diene. The resulting 3-phospholenium salt is then directly or indirectly dehydrohalogenated to give a phosphole[15] (Scheme 2). The major problem with this method is that the McCormack reaction requires several days or weeks to reach completion. Transient phosphenium ions $[(R)(Cl)P]^+$ have, in fact, been postulated as intermediates in this reaction. On the other hand, stable phosphenium moieties such as phosphenium tetrachloroaluminate ions,[16] are known to be good dienophiles and give 1,4-addition reactions with 1,3-butadienes[17] to afford 3-phospholenium tetrachloroaluminates. However, these compounds have never been used in a synthetic approach to phospholes. We thus investigated reactions between the chlorophosphenium ion $[(i\mathrm{Pr}_2\mathrm{N})(Cl)P]^+$ [18] and various dienes in order to obtain the corresponding 1-chloro-3-phospholenium cations, which might then be dehydrohalogenated to give phospholes.

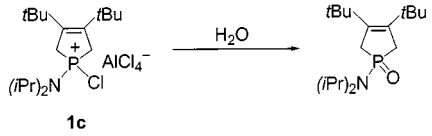



Scheme 2. General synthesis of phospholes via 3-phospholenium compounds

The chlorophosphenium ion $[(i\mathrm{Pr}_2\mathrm{N})(Cl)P]^+$, obtained by the action of $AlCl_3$ on dichloro(diisopropylamino)phosphane,[19] reacted cleanly and rapidly with 2,3-dimethyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene, and 2,3-di-*tert*-butyl-1,3-butadiene to afford quantitatively the corresponding 3-phospholenium cations **1a** ($\delta^{31}P$ = 91.30), **1b** ($\delta^{31}P$ = 88.99), and **1c** ($\delta^{31}P$ = 76.07) (Scheme 3). The dehydrohalogenation of **1** could not be accomplished with nitrogen bases (such as $Et_3N$ or some pyridine derivatives) according to Mathey's method.[20] However, the dehydrohalogenation of compounds **1a** and **1b** was readily achieved by use of an amide base such as LDA or LiHMDS, and the corresponding phospholes **2a** and **2b** were obtained in 68% and 84% yields, respectively (Scheme 3). In the case of **1c**, the dehydrohalogenation reaction was unsuccessful, possibly because the bulky substituents in **1c** might have prevented deprotonation by the amide base. The 3,4-di-*tert*-butyl-1-diisopropylamino-3-phospholene oxide probably resulted from hydrolysis of the phospholenium ion (Scheme 4) during the workup.




Scheme 3. Synthesis of phospholes **2a,b**: i) $AlCl_3$, $CH_2Cl_2$, −78 °C to room temp.; ii) diene, $CH_2Cl_2$, −20 °C to room temp.; iii) LiHMDS, THF, −78 °C to room temp.




Scheme 4. Hydrolysis of phospholenium **1c**

The phospholes **2a**,**b** were isolated and fully characterized, and the structure of **2a** was confirmed by X-ray diffraction analysis (Figure 1). As usually observed in related molecules,[15b] the phosphole ring adopts an envelope conformation. The dihedral angle between the butadiene moiety and the C(1)−P(1)−C(4) plane is 11.21° (cf. 9.6° for 1-benzylphosphole[21a] and 13.7° for 4,5-dimethyl-1,2,3-triphenylphosphole[21b]). Thus, the phosphorus atom retains its slightly pyramidal geometry: Σ(CPC angles) = 306.1°, similarly to the 1-alkoxyphosphole:[21a] Σ(CPC angles) = 309.5°. It is worth pointing out that the amino group, which is itself planar, makes a dihedral angle of 91.7° with the phosphole ring.

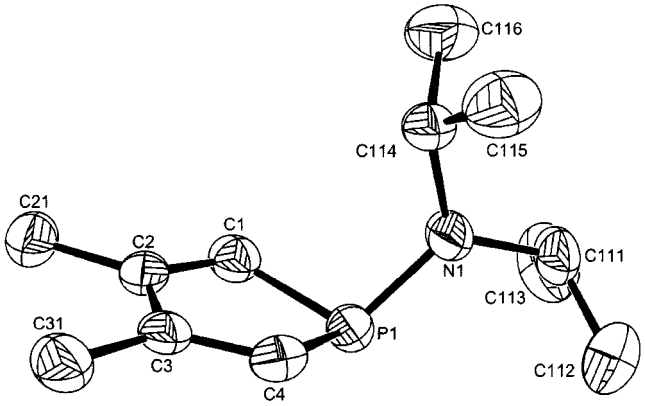
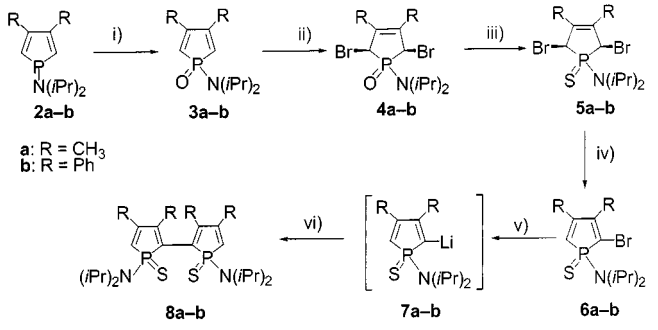



Figure 1. ORTEP view of molecule **2a** with atom labelling scheme; ellipsoids represent 50% probability; selected bond lengths [Å] and bond angles [°]: P(1)−N(1) 1.669(2), P(1)−C(1) 1.793(2), P(1)−C(4) 1.797(2); C(1)−P(1)−N(1) 108.02(8), N(1)−P(1)−C(4) 108.50(9), C(1)−P(1)−C(4) 89.55(8)

This one-pot sequence thus provides simple and quick access to 1-(diisopropylamino)phospholes in high yield with respect to $i\mathrm{Pr_2NPCl_2}$. This new procedure afforded a new 1-(diisopropylamino)phosphole **2b**, with phenyl groups in the 3 and 4 positions,[22] and constitutes an efficient alternative route to the synthesis of the 1-(diisopropylamino)-3,4-dimethylphosphole **2a**.[13] Indeed, the synthesis of the phosphole **2a** via the 3,4-dimethyl-1-phenylphosphole obtained from a classical McCormack reaction required prolonged reaction times (12 d) and gave the product in only moderate yield with respect to $\mathrm{PhPCl_2}$ (25−30%).

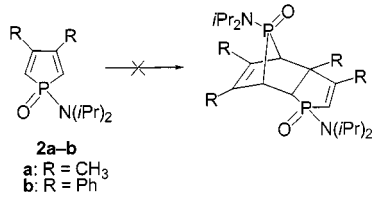
### Synthesis of 1,1′Bis(diisopropylamino)-2,2′-biphospholes 8

In 1992,[23] Mathey reported a convenient route for the preparation of 2,2′-biphosphole, involving the oxidative coupling reaction of 2-lithiophosphole. The starting point of this method required the α-functionalization of the phosphole ring. By an analogous procedure, we attempted to synthesize 2,2′-biphospholes starting from phospholes **2a**,**b**. The strategy used was based on a sequence of oxidation at the phosphorus atom, bromination and dehydrobromination of the diene system, and finally a coupling reaction via a 2-lithiophosphole intermediate (Scheme 5).




Scheme 5. Synthesis of 2,2′-biphospholes **8a**,**b**: i) *m*-CPBA, $\mathrm{CH_2Cl_2}$, −30 °C to room temp.; ii) $\mathrm{pyrH^+}$, $\mathrm{Br_3^-}$, $\mathrm{CH_2Cl_2}$, −20 °C to room temp.; iii) $\mathrm{P_4S_{10}}$, toluene, reflux; iv) KOH, $\mathrm{MeOH/CH_2Cl_2}$, room temp.; v) *n*BuLi, THF, −90 °C; vi) $\mathrm{CuCl_2}$, THF, −90 °C to room temp.

In the first step (Scheme 5), the phospholes **2a**,**b** reacted with *meta*-chloroperbenzoic acid at −30 °C to give the corresponding phosphole 1-oxides **3a**,**b** (**3a**: $\delta^{31}\mathrm{P} = 46.90$; **3b**: $\delta^{31}\mathrm{P} = 43.98$). These oxides, unlike 1-phenylphosphole 1-oxides,[24] were stable for 48 h at room temperature in dichloromethane solution and did not dimerize to give the [4 + 2] Diels−Alder cycloadducts (Scheme 6) even at 40 °C in dichloromethane solution over 24 h, or at 110 °C in toluene solution over 4 h. The lack of dimerization of the **3a**,**b** can be attributed to steric effects rather than electronic effects of the diisopropylamino group. Indeed, Quin[25] has observed dimer compounds with smaller substituted amino groups, such as 1-(dimethylamino) or 1-(diethylamino).




Scheme 6. The [4+2] Diels−Alder cycloadducts were not obtained from the oxides **3a**,**b**

In the second step, 1,4-bromo addition onto the diene systems of the phosphole rings, carried out with pyridinium tribromide, provided compounds **4a**,**b** in high yields (Scheme 5). In the case of **3a**, monitoring of the reaction mixture by $^{31}\mathrm{P}$ NMR spectroscopy indicated the quantitative conversion of **3a** into a mixture of two stereoisomers, the major stereoisomer **4a**′ ($\delta = 36.4$) and the minor stereoisomer **4a**′′ ($\delta = 38.4$), in an 80:20 ratio (Scheme 7).


Scheme 7. Stereoisomers of compounds **4a**,**b** and **5a**,**b**

The separation of these two isomers was difficult. Only a small amount of **4a**′ could be isolated in pure form by crystallization of the crude mixture from dichloromethane, but this allowed a complete characterization. This major stereoisomer **4a**′ was the result of a 1,4-bromo addition at the face opposite to that occupied by the $i\mathrm{Pr_2N}$ group. Indeed, the α-H atoms were *trans* to the P=O group (Figure 2), which was consistent with the low $^2J_{\mathrm{H\text{-}P}}$ value (2.8 Hz)[23] observed in the $^1\mathrm{H}$ NMR spectrum. The X-ray crystal structure analysis (Figure 2) clearly shows an envelope conformation for the phospholene ring with a dihedral angle of 6.23° between the C(1)−C(2)−C(3)−C(4) and C(1)−P(1)−C(4) planes, as observed in analogous compounds.[26] The nitrogen atom is nearly planar ($\Sigma = 358.3°$), the P(1)−N(1) distance is rather short [1.636 (3) Å], and the P=O bond length is typical of a double bond [1.471 (3) Å].[27] The minor stereoisomer **4a**′′ which had a high $^2J_{\mathrm{H\text{-}P}}$ value (7.2 Hz), was not isolated in pure form but probably corresponded to the other diastereoisomer, as was also observed in the case of 2,5-dibromo-2,5-dihydro-3,4-dimethyl-1-phenylphosphole 1-oxide[23] (Scheme 7).

In the case of **4b**, only one stereoisomer was isolated, in 98% yield. Complete assignment of the structure could not be made on the basis of on the $^2J_{\mathrm{P\text{-}H}}$ value (6.8 Hz), which was between 2.8 Hz and 7. 2 Hz, and an X-ray crystal structure was necessary to reveal the stereochemistry of **4b**, which proved to be the same as that of the major stereoisomer **4a**′ (cf. data deposited with the CCDC).

In the next step, the compounds **4a**,**b** were transformed into their corresponding sulfides **5a**,**b** prior to dehydrobro-

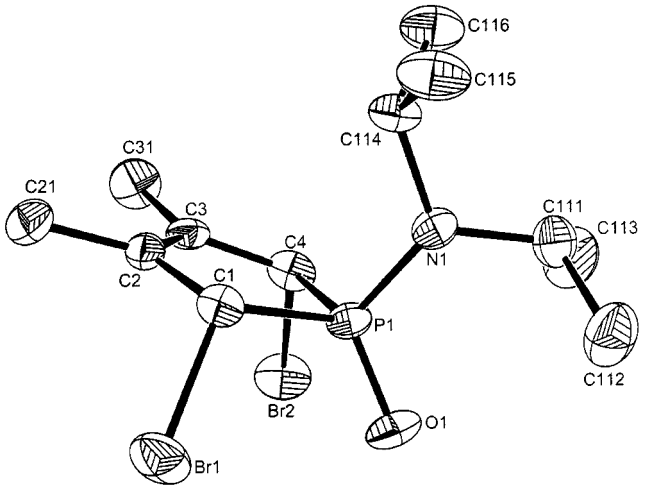



Figure 2. ORTEP view of molecule **4a′** with atom labelling scheme; ellipsoids represent 50% probability; selected bond lengths [Å] and bond angles [°]: P(1)−N(1) 1.636(3), P(1)−O(1) 1.471(3), P(1)−C(1) 1.842(4), P(1)−C(4) 1.841(4), C(1)−Br(1) 1.971(4), C(4)−Br(2) 1.981(4); N(1)−P(1)−C(1) 105.7(2), N(1)−P(1)−C(4) 109.7(2), C(1)−P(1)−C(4) 92.9(2), C(1)−P(1)−O(1) 117.0(2), C(4)−P(1)−O(1) 115.4(2), N(1)−P(1)−O(1) 114.0(2)

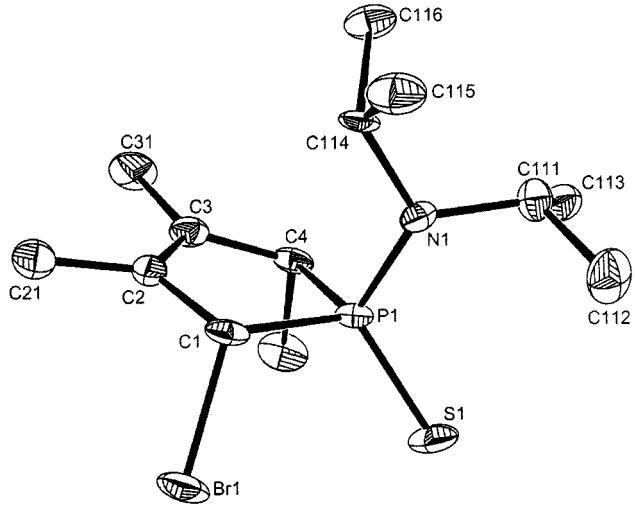
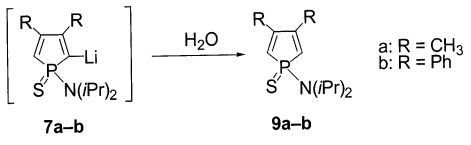



Figure 3. ORTEP view of molecule **5a′** with atom labelling scheme; ellipsoids represent 50% probability; selected bond lengths [Å] and bond angles [°]: P(1)−N(1) 1.653(3), P(1)−S(1) 1.931(2), P(1)−C(1) 1.859(4), P(1)−C(4) 1.847(4), C(1)−Br(1) 1.962(4), C(4)−Br(2) 1.979(4); N(1)−P(1)−C(1) 105.20(2), N(1)−P(1)−C(4) 107.8(2), C(1)−P(1)−C(4) 92.4(2), C(1)−P(1)−S(1) 117.4(1), C(4)−P(1)−S(1) 116.0(2), N(1)−P(1)−S(1) 115.3(1)

mination.[22] Treatment of a crude mixture of the two stereoisomers **4a′** and **4a′′** (in an 80:20 ratio) with $P_4S_{10}$ in refluxing toluene for 1 h quantitatively afforded a mixture of **5a′** and **5a′′** in the same ratio (Scheme 5). In the major isomer **5a′** (Figure 3), the α-H atoms were *trans* to the P=S group, thus demonstrating that the sulfurization had taken place with retention of the stereochemistry at the phosphorus atom. The molecular structure of **5a′** was isomorphous with **4a′**, as indicated by the unit cell parameters and space group. As the major product **5a′** was presumably produced from the major isomer **4a′**, the minor product **5a′′**, which could not be isolated, presumably originated from the minor isomer **4a′′**. Similarly, **4b** was transformed into **5b** in quantitative yield with retention of stereochemistry at the phosphorus atom. The crude compound was fully characterized and its structure, established by X-ray analysis, confirmed the retention of configuration at the phosphorus during the sulfurization reaction, as for **5a′** (cf. data deposited with the CCDC).

Dehydrobromination of **5a**,**b** was then performed with methanolic potassium hydroxide to yield **6a**,**b** in 75 and 70% yields, respectively (Scheme 5). These 2-bromophosphole sulfides **6a**,**b** were fully characterized and the structure of **6b** was confirmed by X-ray analysis (cf. data deposited with the CCDC).

We were unable to achieve the desulfurization of **6a**,**b** by classical reduction with different phosphanes.[28] We then attempted to synthesize the 2,2′-biphospholes by means of a direct coupling reaction from the 2-bromophosphole sulfides **6a**,**b**, via the 2-lithio derivatives **7a**,**b** (Scheme 5). The addition of *n*-butyllithium to a solution of **6a**,**b** in THF at −90 °C, followed by the addition of copper(II) chloride, resulted in the formation of a mixture of the 2,2′-biphosphole disulfides **8a**,**b** (Scheme 5) and, as undesired side products, the 1-(diisopropylamino)phosphole sulfides **9a**,**b**, formed by hydrolysis of the 2-lithiophosphole intermediates **7a**,**b** (Scheme 8). Compound **8a**, isolated in 45% yield as a single diastereoisomer, was characterized by $^1H$, $^{31}P$, and $^{13}C$ NMR, mass spectrometry, and X-ray analysis. In contrast, **8b** was isolated in 14% yield as a mixture of two diastereoisomers **8b′** and **8b′′** in a 51:49 ratio and we were unable to separate **8b′** and **8b′′** by conventional methods. However, whereas the diastereoisomer **8b′′** was amorphous, the diastereoisomer **8b′** crystallized and some single crystals suitable for X-ray analysis were obtained. The molecular structures of compounds **8a** and **8b′** are shown in Figures 4 and 5, respectively. In both compounds, the phosphole rings are all planar within experimental error, but they are twisted with respect to each other along the C(1)−C(1′) bond. The dihedral angles between the two phosphole rings (67.32° in **8a** and 61.29° in **8b′**) give rise to axial chirality. These values, which are much lower than those in analogous 2,2′-biphospholes disulfides,[10] may be associated with the bulky diisopropylamino substituents.




Scheme 8. Hydrolysis of 2-lithiophosphole intermediates **7a−b**

These structural determinations unambiguously established the relative configurations of both the central and the axial elements of chirality. In these two compounds, both phosphorus atoms had the same central absolute configuration ([*R*,*R*] or [*S*,*S*]), in association either with an opposite axial absolute configuration in **8a**, or with the same axial

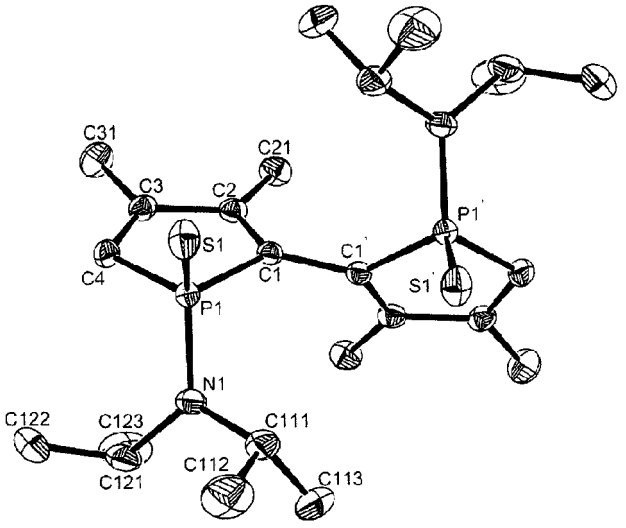



Figure 4. ORTEP view of molecule **8a** with atom labelling scheme; ellipsoids represent 50% probability; selected bond lengths [Å] and bond angles [°]: P(1)−N(1) 1.651(1), P(1)−S(1) 1.9532(4), P(1)−C(1) 1.820(1), P(1)−C(4) 1.787(1), C(1)−C(1′) 1.462(2); N(1)−P(1)−C(1) 107.85(8), N(1)−P(1)−C(4) 111.82(8), C(1)−P(1)−C(4) 92.40(5), C(1)−P(1)−S(1) 114.72(3), C(4)−P(1)−S(1) 112.26(4), N(1)−P(1)−S(1) 115.51(4)

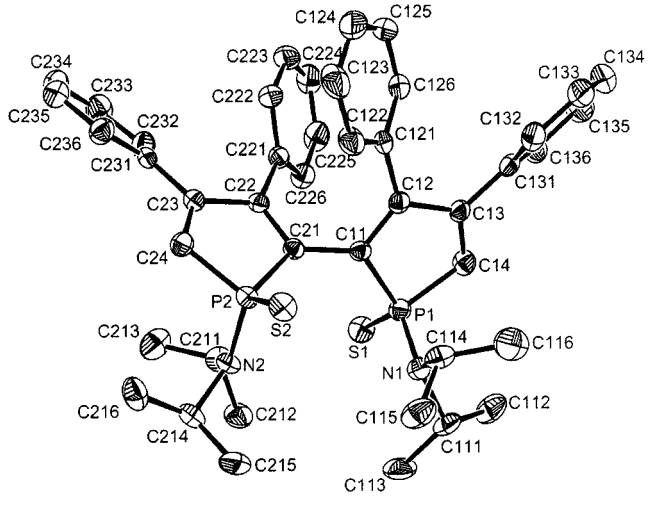



Figure 5. ORTEP view of molecule **8b′** with atom labelling scheme; ellipsoids represent 50% probability; selected bond lengths [Å] and bond angles [°]: P(1)−N(11) 1.666(3) [1.665(3)], P(1)−S(1) 1.947(1) [1.944(1)], P(1)−C(11) 1.842(3) [1.829(3)], P(1)−C(14) 1.794(4) [1.785(3)]; N(1)−P(1)−C(11) 110.1(1) [109.4(1)], N(1)−P(1)−C(14) 107.6(2) [108.7(2)], C(11)−P(1)−C(14) 91.6(2) [91.7(2)], C(11)−P(1)−S(1) 113.7(2) [114.1(1)], C(14)−P(1)−S(1) 115.0(1) [114.4(1)], N(1)−P(1)−S(1) 116.2(1) [115.9(1)]

absolute configuration in **8b′**. The different possibilities of combining axial and central chiralities in 2,2′-biphosphole are depicted in Figure 6, in Newman projections along the C−C axis of the bond linking the two phosphole rings. This stereochemical analysis shows the occurrence of six stereoisomers corresponding to three pairs of enantiomers. The first diastereoisomer, (*S*[*RR*], *R*[*SS*]), is obtained for **8a** and the second diastereoisomer, (*S*[*SS*], *R*[*RR*]), is obtained for one of the two diastereoisomers of **8b′**. For the other diastereoisomer **8b′′**, two possibilities arise; this isomer could correspond either to the third diastereoisomer, (*R*[*SR*], *S*[*RS*]), or to the first diastereoisomer, (*S*[*RR*], *R*[*SS*]). However, as the diastereoisomer (*R*[*SR*], *S*[*RS*]) was not observed in the case of the less hindered **8a**, we assume that **8b′′** corresponds to the diastereoisomer (*S*[*RR*], *R*[*SS*]), as observed in the case of **8a**.

These results were supported by molecular mechanics calculations performed on 2,2′-biphosphole disulfides **8** with the different phosphorus configurations, [*R*,*R*] ([*S*,*S*]) and [*R*,*S*] ([*S*,*R*]). Systematic conformational analysis of the rotation process around the C−C bond linking the two phosphole rings was carried out. For **8b**, the calculations showed that the [*R*,*S*] ([*S*,*R*]) isomer was energetically less favored than the [*R*,*R*] ([*S*,*S*]) isomer, although the difference in energy was small (3 kcal·mol$^{-1}$). For the [*R*,*R*] ([*S*,*S*]) isomer, two minima, corresponding to two stable conformers, were located at the same energy level on the potential energy surface, in agreement with our experimental results. The estimated energy barrier between these two conformers was 16 kcal·mol$^{-1}$. Experimentally, no interconversion between **8b′** and **8b′′** occurred even at +90 °C in toluene, according to NMR studies. These two conformers are shown in Figure 7. In the first conformer, the torsion angle[29] of +53.5° is close to the torsion angle observed from X-ray analysis for **8b′** (torsion angle = 46°). In the second conformer, the torsion angle of −35.5° is indicative of an axial absolute configuration opposite to that in the first conformer. These results, which are consistent with the existence of the two diastereoisomers, (*S*[*SS*], *R*[*RR*]) and (*S*[*RR*], *R*[*SS*]), in the case of **8b** thus support our hypothesis that **8b′** corresponds to the (*S*[*RR*], *R*[*SS*]) diastereoisomer. Similar calculations performed on **8a** showed that the [*R*,*R*] ([*S*,*S*]) and [*R*,S] ([*S*,*R*]) isomers had the same energy. However, only the [*R*,*R*] ([*S*,*S*]) forms were isolated and characterized experimentally. For this isomer, calculations showed the existence of many conformers for which the differences in energy were small (2−4 kcal·mol$^{-1}$). The geometry of the most stable conformer (Figure 8), which predicted a torsion angle of 43.6°, was close to that established by X-ray analysis for **8a** (torsion angle = 58°). The observation of only one isomer in solution in the case of **8a** is probably attributable to free rotation around the C−C bond. Indeed, according to the calculations, **8a** had a lower free enthalpy of activation than **8b** for the rotation barrier around the C−C bond (5 kcal·mol$^{-1}$). In the solid state, isomer **8a** crystallized to give the most stable form, which corresponds to the (*S*[*RR*], *R*[*SS*]) diastereoisomer.78

The last stage in our synthesis was the reduction of **8a**,**b** to free 2,2′-biphosphole **10a**,**b**. Unfortunately, under Mathey's[28] conditions to obtain BIPHOS,[23] treatment of disulfides **8a**,**b** either with trimethylphosphane or with tris(2-cyanoethyl)phosphane did not afford the corresponding 2,2′-biphospholes **10a**,**b** but resulted in the formation of unidentified products. By using Mikolajczyk's procedure,[30] we were able to observe the formation of 2,2′-biphosphole **10a**, starting from the disulfide **8a** (Scheme 9), by $^{31}$P NMR and mass spectrometry. As the procedure gave rather low

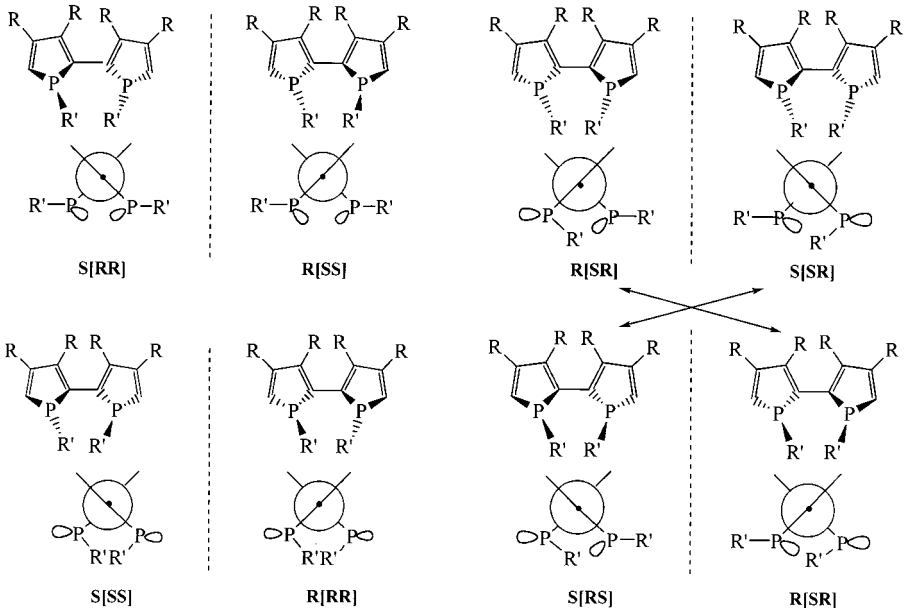



Figure 6. The $2^3$ stereoisomers of 2,2′-biphospholes possessing 2 chiral centers and 1 chiral axis; among these eight stereoisomers, six are truly inequivalent; axial chirality is given first and central chirality is between square brackets

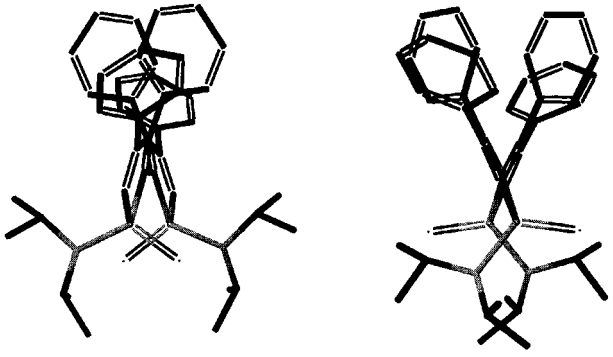


Figure 7. The two stable conformers of compound **8b**

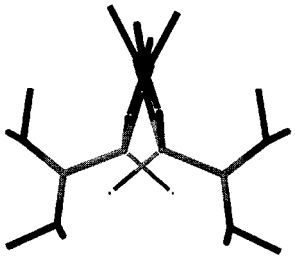
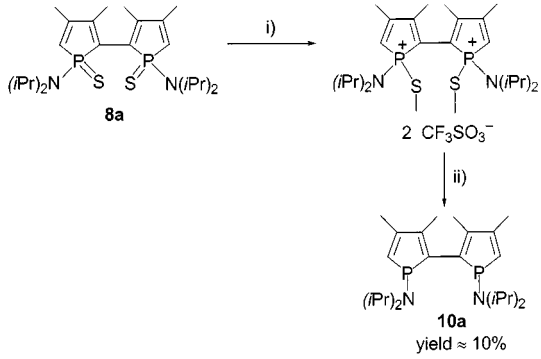


Figure 8. The stable conformer of compound **8a**

yields of **10a**, however, the compound could not be isolated in a pure form. We are currently investigating new methods for the desulfurization of these 1,1′-bis(diisopropyl)-2,2′-biphosphole disulfides, in order to continue our study of the influence of the diisopropylamino group on the 2,2′-biphosphole framework.




Scheme 9. Reduction of disulfide **8a**: i) $CF_3SO_3Me$, $CH_2Cl_2$, room temp.; ii) *t*BuSLi, $Et_2O/CH_2Cl_2$, −78 °C to room temp.

## Conclusions

We have developed a convenient one-pot procedure to prepare two 1-(diisopropylamino)phospholes. These phosphole moieties have been used for the synthesis of two new 2,2′-biphospholes derivatives, 1,1′-bis(diisopropylamino)-3,3′,4,4′-tetramethyl-2,2′-biphosphole 1,1′-disulfide (**8a**) and 1,1′-bis(diisopropylamino)-3,3′,4,4′-tetraphenyl-2,2′-biphosphole 1,1′-disulfide (**8b**). Compound **8b** exists as two stable diastereoisomers, unlike compound **8a**, according to both experimental and theoretical studies. Thus, these results show that a combination of bulky substituents in positions 1 ($iPr_2N$) and 3 (Ph) is an important factor in the

stabilization of axial chirality. We are currently studying methods for the reduction of these 1,1′-bis(diisopropylamino)-2,2′-biphosphole disulfides to the 1,1′-bis(diisopropylamino)-2,2′-biphospholes in order to study the configurational stability of their phosphorus centers, their coordination chemistry, and potential applications in asymmetric catalysis.

## Experimental Section

**General:** All reactions were carried out under dry argon by use of Schlenk glassware and vacuum-line techniques. Solvents were freshly distilled from standard drying agents. Flash chromatography was carried out under argon on Merck silica gel (230−400 mesh). Melting points (uncorrected) were determined with a Stuart Scientific SMP1 apparatus. $^1$H, $^{31}$P{$^1$H}, and $^{13}$C{$^1$H, $^{31}$P} NMR spectra were recorded with a Bruker AM 250 instrument operating at 250, 101, and 63 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to $Me_4Si$ ($^1$H and $^{13}$C) or 85% $H_3PO_4$ ($^{31}$P). Mass spectra were obtained with a Mermag R10−10 instrument. Elemental analyses were performed by the "Service d'Analyse du Laboratoire de Chimie de Coordination" at Toulouse. *P,P*-Dichloro(diisopropylamino)phosphane was prepared as described in the literature.[19]

**1-(Diisopropylamin)o-3,4-dimethylphosphole (2a):** ($i$Pr)$_2$NPCl$_2$ (2.1 g, 10.3 mmol) was added dropwise at −78 °C to a stirred suspension of $AlCl_3$ (1.34 g, 10 mmol) in dichloromethane (30 mL). After 15 min, the mixture was allowed to warm to room temp. and the stirring was continued for 1 h to afford a colorless solution of the corresponding phosphenium compound. This solution was cooled again to −78 °C, and 2,3-dimethyl-1,3-butadiene (0.83 g, 10.1 mmol) was added dropwise to give an orange solution. This mixture was stirred for 15 min at −78 °C and for 3 h at room temperature, and the solvent was then evaporated under reduced pressure to give the crude phospholenium compound **1a**. Compound **1a** was then dissolved in THF (25 mL) and cooled to −78 °C, and LiHMDS (1 M, 20 mmol) was added dropwise. The mixture was stirred for 15 min at −78 °C and for 1 h at room temp. and then concentrated to dryness. The resulting residue was extracted with small portions of pentane. The combined pentane phases were washed twice with water and dried with $MgSO_4$, and the solvents were evaporated to give **2a** as a white-yellow solid (1.83 g, 68%). $^{31}$P NMR ($CDCl_3$): δ = 28.40. $^1$H NMR ($CDCl_3$): δ =1.04 [d, $J_{H,H}$ = 6.6 Hz, 12 H, (C$H_3$)$_2$CH], 1.99 (d, $J_{H,P}$ = 5.3 Hz, 6 H, $CH_3$), 2.85 [m, 2 H, ($CH_3$)$_2$C$H$], 6.04 (d, $J_{H,P}$ = 36 Hz, 2 H, CHP). $^{13}$C NMR ($CDCl_3$): δ = 17.4 (d, $J_{C,P}$ = 6.7 Hz,$CH_3$), 23.6 [d, $J_{C,P}$ = 6 Hz, ($C$H$_3$)$_2$CH], 48.7 [d, $J_{C,P}$ = 7.2 Hz, ($CH_3$)$_2$$C$H], 129.6 (s, CHP), 145.1 (d, $J_{C,P}$ = 15.2 Hz, $CH_3C$). MS (DCI, $CH_4$): $m/z$ (%) = 212 (100%) [MH]$^+$. Crystals suitable for X-ray analysis were obtained by slow concentration of a pentane solution.

**1-(Diisopropylamino)-3,4-diphenylphosphole (2b):** The experimental procedure was the same as above. Compound **2b** was obtained as an orange oil (84%). $^{31}$P NMR ($CDCl_3$): δ = 35.19. $^1$H NMR ($CDCl_3$): δ = 1.24 [d, $J_{H,H}$ = 7.2 Hz, 12 H, (C$H_3$)$_2$CH], 3.15 [m, 2 H, ($CH_3$)$_2$C$H$], 6.70 (d, $J_{H,P}$ = 33 Hz, 2 H, CHP), 7.0−7.5 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$): δ = 23.9 [d, $J_{C,P}$ = 5.5 Hz, ($C$H$_3$)$_2$CH], 50.4 [d, $J_{C,P}$ = 8.5 Hz, ($CH_3$)$_2$$C$H], 126.9−128.6 (s, Ph), 134.5 (s, CHP), 138.9 (d, $J_{C,P}$ = 4 Hz, $C_{ipso}$), 147.4 (d, $J_{C,P}$ = 16 Hz, Ph$C$). MS (DCI, $CH_4$): $m/z$ (%) = 336 (100) [M + H]$^+$. $C_{22}H_{26}NP$ (335.43): C 78.8, H 7.81, N 4.18; found C 78.97, H 7.50, N 4.03.

**1-(Diisopropylamino)-3,4-dimethylphosphole 1-Oxide (3a):** A solution of dry *meta*-chloroperbenzoic acid (1.207 g, 7.46 mmol) in dichloromethane (8 mL) was added dropwise at −30 °C to a dichloromethane solution (10 mL) of **2a** (1.431 g, 6.70 mmol). The mixture was allowed to stir at 0 °C for 1 h and then concentrated to dryness. The crude **3a** was only characterized by $^{31}$P and $^1$H NMR and used without further purification. $^{31}$P NMR ($CDCl_3$): δ = 46.9. $^1$H NMR ($CDCl_3$): δ =1.24 [d, $J_{H,H}$ = 6.75 Hz, 12 H, (C$H_3$)$_2$CH], 1.98 (s, 6 H, C$H_3$), 3.54 [m, 2 H, ($CH_3$)$_2$C$H$N], 5.84 (d, $J_{HP}$ 24.88 Hz, 2 H, CHP).

**1-(Diisopropylamino)-3,4-diphenylphosphole 1-Oxide (3b):** The experimental procedure was the same as above. Compound **3b** was obtained as a yellow oil (680 mg, 87%). $^{31}$P NMR ($CDCl_3$): δ = 42.98. $^1$H NMR ($CDCl_3$): δ =1.30 [d, $J_{H,H}$ = 6.75 Hz, 12 H, (C$H_3$)$_2$CHN], 3.67 [m, 4 H, ($CH_3$)$_2$$CH$N], 6.12 (d, $J_{H,P}$ = 23.3 Hz, 2 H, CHP), 6.98−7.7 (m, 20 H, Ph). $^{13}$C NMR ($CDCl_3$): δ = 23.5 [s, ($C$H$_3$)$_2$CH], 46.8 [s, ($CH_3$)$_2$$C$H], 124.21 (d, $J_{C,P}$ = 116 Hz, CHP), 127.9−128.5 (m, Ph), 135.95 (d, $J_{C,P}$ = 19.9 Hz, $C_{ipso}$), 153.27 (d, $J_{C,P}$ = 24.4 Hz, Ph$C$). MS (DCI, $CH_4$): $m/z$ (%) = 352 (100) [M + H]$^+$.

**2,5-Dibromo-2,5-dihydro-1-(diisopropylamino)-3,4-dimethylphosphole 1-Oxide (4a):** Pyridinium tribromide (2.50, 7.8 mmol) was added rapidly at −20 °C to a dichloromethane solution of crude **3a** previously obtained. The mixture was allowed to stir for 20 min at 0 °C and 2 h at room temp. and was then treated with aqueous sodium sulfite. The aqueous layer was washed 3 times with dichloromethane; the organic extracts were washed until neutral with water, dried with $MgSO_4$, and filtered. After removal of the solvent, the major isomer **3a′** was recrystallized from dichloromethane at −18 °C to give white crystals (1.76 g, 84%). m.p. 145 °C (decomp). $^{31}$P NMR ($CDCl_3$): δ = 36.34. $^1$H NMR ($CDCl_3$): δ = 1.25 [d, $J_{H,H}$ = 6.78 Hz, 12 H, (C$H_3$)$_2$CH], 1.91 (s, 6 H, C$H_3$), 3.21 [m, 2 H, ($CH_3$)$_2$$CH$], 4.36 (d, $J_{H,P}$ = 2.7 Hz, 2 H, C$H$Br). $^{13}$C NMR ($CDCl_3$): δ = 15.7 (d, $J_{C,P}$ = 10 Hz, $CH_3$), 23.0 [s, ($CH_3$)$_2$CH], 46.4 (d, $J_{C,P}$ = 86 Hz, CHP), 47.1 [s, ($CH_3$)$_2$$C$H], 135.9 (d, $J_{C,P}$ = 14 Hz, $CH_3C$). MS (DCI, $CH_4$): $m/z$ (%) = 388 (8) [M + H]$^+$, 308 (17) [M + H − Br]$^+$, 228 (100) [M + H − 2 Br]$^+$. $C_{12}H_{22}Br_2NOP$ (387.10): C 37.23, H 5.73, N 3.62; found C 36.46, H 4.94, N: 2.67.

**2,5-Dibromo-2,5-dihydro-1-(diisopropylamino)-3,4-diphenylphosphole 1-Oxide (4b):** The synthesis of **4b** was accomplished by the same procedure as described above for **4a**. Compound **4b**, obtained as yellow solid (98%), was used without further purification. $^{31}$P NMR ($CDCl_3$): δ = 35.48. $^1$H NMR ($CDCl_3$): δ = 1.33 [d, $J_{H,H}$ = 6.8 Hz, 12 H, (C$H_3$)$_2$CH], 3.45 [m, 2 H, ($CH_3$)$_2$C$H$], 4.88 (d, $J_{H,P}$ = 6.6 Hz, 2 H, CHP), 7.32 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$): δ = 23.17 [s, ($C$H$_3$)$_2$CH], 44.6 (d, $J_{C,P}$ = 88 Hz, CHP), 48.13 [s, ($CH_3$)$_2$$C$H], 128.57−128.88 (m, Ph), 135.3 (d, $J_{C,P}$ = 11.2 Hz, $C_{ipso}$), 141.3 (d, $J_{C,P}$ = 13.5 Hz, Ph$C$). MS (DCI, $CH_4$): $m/z$ (%) = 512 (51) [M + H]$^+$, 432 (76) [M + H − Br]$^+$, 352 (100) [M + H − 2 Br]$^+$. $C_{22}H_{26}Br_2NOP$ (511.25): C 51.6, H 5.13, N 2.74; found C 52.97, H 4.09, N: 2.46. Crystals suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution from the crude product before treatment; these crystals contained an equimolar mixture of **4b** and *m*-chlorobenzoic acid.

**2,5-Dibromo-2,5-dihydro-1-(diisopropylamino)-3,4-dimethylphosphole 1-Sulfide (5a):** A mixture of crude **4a** (1.70 g, 4.39 mmol) and $P_4S_{10}$ (1.1 g, 2.63 mmol) was refluxed in toluene (10 mL) for 30 min. After removal of the solvent, the major isomer **5a′** was isolated by flash chromatography on silica gel (dichloromethane/pentane, 50:50) and purified by recrystallization from dichloromethane. Compound **5a′** was obtained as a yellow solid (807 mg, 53%

for the two steps). $^{31}$P NMR ($CDCl_3$): δ = 80.45. $^1$H NMR ($CDCl_3$): δ = 1.27 [d, $J_{H,H}$ = 7.0 Hz, 12 H, $(CH_3)_2CH$], 1.92 (s, 6 H, $CH_3$), 3.45 [m, 2 H, $(CH_3)_2CH$,], 4.78 (d, $J_{H,P}$ = 1.2 Hz, 2 H, CHBr). $^{13}$C NMR ($CDCl_3$): δ = 16.3 (d, $J_{C,P}$ = 8 Hz, $CH_3$), 22.9 [s, $(CH_3)_2CH$], 48.9 [s, $(CH_3)_2CH$], 52.9 (d, $J_{C,P}$ 66 Hz, CHP), 135.4 (d, $J_{C,P}$ = 10 Hz, $CCH_3$). MS (DCI, $CH_4$): *m/z* (%) = 404 (85) [M + H]$^+$, 324 (100) [M + H − Br]$^+$. $C_{12}H_{22}Br_2NPS$ (403.2): C 35.75, H 5.50, N 3.47; found C 35.86; H 4.60; N 4.73.

**2,5-Dibromo-2,5-dihydro-1-(diisopropylamino)-3,4-diphenylphosphole 1-Sulfide (5b):** The synthesis of **5b** was accomplished by the same procedure as described above for **5a**, from **4b** (6.75 g) and $P_4S_{10}$ (3.54 g). Crude **5b** was obtained in quantitative yield as an orange solid (6.90 g, 99%) and was used without further purification. $^{31}$P NMR ($CDCl_3$): δ = 78.70. $^1$H NMR ($CDCl_3$): δ = 1.34 [d, $J_{H,H}$ = 3.2 Hz, 12 H, $(CH_3)_2CH$], 3.67 [m, 2 H, $(CH_3)_2CH$], 5.20 (d, $J_{H,P}$ = 5 Hz, 2 H, CH), 7.14−7.30 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$): δ = 23.18 [s, $(CH_3)_2CH$], 49.44 [s, $(CH_3)_2CH$], 51.90 (d, $J_{C,P}$ = 65.8 Hz, CHP), 128.50−128.99 (m, Ph), 135.61 (d, $J_{C,P}$ = 9.3 Hz, $C_{ipso}$), 141.38 (d, $J_{C,P}$ 9.7 Hz, Ph*C*). MS (DCI, $CH_4$): *m/z* (%) = 528 (35) [M + H]$^+$, 448 (40) [M + H − Br]$^+$, 368 (100) [M + H − 2 Br]$^+$. $C_{22}H_{26}Br_2NPS$ (527.3): C 50.11, H 4.97, N 2.66; found C 50.12, H 4.74, N 2.47. Crystals suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution.

**2-Bromo-1-diisopropylamino-3,4-dimethylphosphole 1-Sulfide (6a):** A solution of KOH (80 mg, 1.44 mmol) in methanol (2 mL) was added dropwise to a solution of **5a′** (290 mg, 0.72 mmol) in dichloromethane (4 mL). The resulting mixture was allowed to stir at room temperature for 2 h 30 and was then diluted with dichloromethane (20 mL). The mixture was washed three times with water and the combined aqueous layers were re-extracted with dichloromethane. The organic layers were combined, dried with $MgSO_4$, and filtered, and the solvents were evaporated to dryness to afford crude **6a** as a brown solid (243 mg, 75%). $^{31}$P NMR ($CDCl_3$): δ = 62.98. $^1$H NMR ($CDCl_3$): δ = 1.25 [d, $J_{H,H}$ = 7.2 Hz, 12 H, $(CH_3)_2CH$], 1.93 (d, $J_{H,P}$ = 3 Hz, 3 H, $CH_3$), 2.,03 (d, $J_{H,P}$ = 3 Hz, 3 H, $CH_3$), 3.50 [m, 2 H, $(CH_3)_2CH$], 5.87 (d, $J_{H,P}$ = 28 Hz, 1 H, CHP). $^{13}$C NMR ($CDCl_3$): δ = 15.2 (d, $J_{C,P}$ = 12 Hz, $CH_3$), 18.3 (d, $J_{C,P}$ = 18 Hz, $CH_3$), 23.3 [d, $J_{C,P}$ = 14 Hz, $(CH_3)_2CH$], 47.4 [d, $J_{C,P}$ = 6 Hz, $(CH_3)_2CH$], 121.5 (d, $J_{C,P}$ = 100 Hz, CBrP), 122.3 (d, $J_{C,P}$ = 100 Hz, CHP), 143.,4 (d, $J_{C,P}$ = 15 Hz, $CH_3C$), 150.0 (d, $J_{C,P}$ = 15 Hz, $CH_3C$). MS (DCI, $CH_4$): *m/z* (%) = 324 (100) [M + 2 H]$^+$; 322 (97) [M]$^+$. $C_{12}H_{21}BrNPS$ (322.25): C 44.73, H 6.57, N 4.35; found C 44.91, H 6.63, N 4.15. Crystals suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution.

**2-Bromo-1-(diisopropylamino)-3,4-diphenylphosphole 1-Sulfide (6b):** The synthesis of **6b** was accomplished by the same procedure as described above for **6a**, from **5b** (6.90 g) and KOH (1.47 g). Crude **6b**, obtained as an orange solid (4.01 g, 70%), was used without further purification. $^{31}$P NMR ($CDCl_3$): δ = 63.57. $^1$H NMR ($CDCl_3$): δ = 1.32 [d, $J_{H,H}$ = 6.8 Hz, 6 H, $(CH_3)_2CH$], 1.36 [d, $J_{H,H}$ = 6.8 Hz, 6 H, $(CH_3)_2CH$], 3.80 [m, 2 H, $(CH_3)_2CH$], 6.29 (d, $J_{H,P}$ = 28 Hz, 1 H, CHP), 6.91−7.29 (m, 10 H, Ph). $^{13}$C NMR ($CDCl_3$): δ = 23.5 [d, $J_{C,P}$ = 11 Hz, $(CH_3)_2CH$], 47.5[d, $J_{C,P}$ = 4.3 Hz, $(CH_3)_2CH$], 124.9 (d, $J_{C,P}$ = 96.7 Hz, CHP), 127.7 (d, $J_{C,P}$ = 100 Hz, CBrP), 127.9−129.1 (m, Ph), 133.9 (d, $J_{C,P}$ = 13.5 Hz, $C_{ipso}$), 135.5 (d, $J_{C,P}$ = 18 Hz, $C_{ipso}$), 145.2 (d, $J_{C,P}$ = 31.2 Hz, Ph*C*), 152.5 (d, $J_{C,P}$ 16.6 Hz, Ph*C*). MS (DCI, $CH_4$): *m/z* (%) = 448 (100) [M + 2 H]$^+$; 447 (39) [M + H]$^+$; 446 (95) [M]$^+$. $C_{22}H_{25}BrNPS$ (446.4): C 59.20, H 5.65, N 3.14; found C 59.60, H 5.82, N 3.42. Crystals suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution.

**1,1′-Bis(diisopropylamino)-3,3′,4,4′-tetramethyl-2,2′-biphosphole 1,1′-Disulfide (8a):** *n*-Butyllithium (510 μL, 0.82 mmol) was added dropwise at −90 °C to a solution of phosphole sulfide **6a** (240mg; 0.74 mmol) in THF (10 mL). After 30 min of stirring, solid $CuCl_2$ (148 mg, 1.12 mmol) was added. The resulting mixture was stirred at −80 °C for 2 h and was then allowed to warm at room temperature. After filtration, the filtrate was diluted with dichloromethane (20 mL) and was washed with aqueous $NH_3$ (14%) until the blue color of the aqueous layer disappeared. The organic phase was then washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The crude residue was then dissolved in a small amount of dichloromethane and precipitated with a large excess of pentane. After filtration, **8a** was obtained as yellow solid (161 mg, 45%), m.p. 258 °C (decomp.). $^{31}$P NMR ($CDCl_3$): δ =68.2. $^1$H NMR ($CDCl_3$): δ = 1.11 [d, $J_{H,H}$ = 7 Hz, 12 H, $(CH_3)_2CH$], 1.22 [d, $J_{H,H}$ = 7 Hz, 12 H, $(CH_3)_2CH$], 1.70 (AB system, $^3J_{H,P}$ = $^4J_{H,P}$ = 2.0 Hz, 6 H, $CH_3$), 2.00 (b, 6 H, $CH_3$), 3.89 [m, 4 H, $(CH_3)_2CH$], 5.92 (d, $J_{H,P}$ = 30 Hz, 2 H, CHP). $^{13}$C NMR ($CDCl_3$): δ = 15.7 (d, $J_{C,P}$ = 15 Hz, $CH_3$), 17.7 (d, $J_{C,P}$ = 18 Hz, $CH_3$), 23.7 [s, $(CH_3)_2CH$], 47.3 [s, $(CH_3)_2CH$], 126.0 (d, $J_{C,P}$ = 95 Hz, CHP), 135.1 (d, $J_{C,P}$ = 98 Hz, C−C), 144.0 (d, $J_{C,P}$ = 31 Hz, $CH_3C$), 146.3 (d, $J_{C,P}$ = 18.8 Hz, $CH_3C$). MS (DCI, $CH_4$): *m/z* (%) = 485 (100) [M + H]$^+$. $C_{24}H_{42}N_2P_2S_2$ (484.7): C 59.48, H 8.73, N 5.78, S:13.23; found C 59.73, H 8.67, N 5.69, S 12.93. Crystals suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution.

**1,1′-Bis(diisopropylamino)-3,3′,4,4′-tetraphenyl-2,2′-biphosphole 1,1′-Disulfide (8b):** The synthesis of **8b** was accomplished by the same procedure as described above for **8a**, from **6b** (4.01 g), *n*-butyllithium (1.6 M, 6.2 mL), and $CuCl_2$ (1.81 g), to afford 454 mg of **8b** as a mixture of two diastereoisomers (14%) in a 51:49 ratio. MS (DCI, $CH_4$): *m/z* (%) = 733 (100) [M + H]$^+$, 632 (99) [M + H − N(*i*Pr)$_2$]$^+$. $C_{44}H_{50}N_2P_2S_2$ (732.95): C 72.10, H 6.88, N 3.82; found C 71.89, H 6.77, N 3.92. *Major isomer:* $^{31}$P NMR ($CDCl_3$): δ = 75.76. $^1$H NMR ($CDCl_3$): δ = 1.31 [d, $J_{H,H}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$], 1.52 [d, $J_{H,H}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$], 4.29 [m, 4 H, $(CH_3)_2CH$], 6.36 (d, $J_{H,P}$ = 29.1 Hz, 2 H, CHP), 6.78−6.90 (m, 8 H, Ph), 7.01−7.17 (m, 12 H, Ph). Crystals of the major isomer suitable for X-ray analysis were obtained by slow concentration of a dichloromethane solution. *Minor isomer:* $^{31}$P NMR ($CDCl_3$): δ = 69.36. $^1$H NMR ($CDCl_3$): δ = 1.40 [d, $J_{H,H}$ = 6.7 Hz, 12 H, $(CH_3)_2CH$], 1.63 [d, $J_{H,H}$ = 6.7 Hz, 12 H, $(CH_3)_2CH$], 4.67 [m, 4 H, $(CH_3)_2CH$], 6.38 (d, $J_{H,P}$ = 29.1 Hz, 2 H, CHP), 6.62−6.71 (m, 8 H, Ph), 6.93−7.00 (m, 12 H, Ph).

Compounds **9a** and **9b**, obtained as undesired side products in the syntheses of **8a** and **8b**, respectively, were isolated in the filtrate and purified by flash chromatography on silica gel (dichloromethane/pentane, 30:70)

**1-(Diisopropylamino)-3,4-dimethylphosphole 1-Sulfide (9a):** Yellow solid (50%). $^{31}$P NMR ($CDCl_3$): δ = 65.5. $^1$H NMR ($CDCl_3$): δ = 1.21 [d, $J_{H,H}$ = 6.5 Hz, 12 H, $(CH_3)_2CH$], 1.98 (d, $J_{H,P}$ = 1.0 Hz, 6 H, $CH_3$), 3.62 [m, 2 H, $(CH_3)_2CH$], 5.88 (d, 2 H, $J_{H,P}$ = 28.8 Hz, CHP). $^{13}$C NMR ($CDCl_3$): δ = 17.01 (d, $J_{C,P}$ = 19.5 Hz, $CH_3$), 23.22 [s, $(CH_3)_2CH$], 47.68 [s, $(CH_3)_2CH$], 132.41 (s, CHP), 148.44 (d, $J_{C,P}$ 21.8 Hz, $CH_3C$). MS (DCI,$CH_4$): *m/z* (%) = 244 (100) [MH]$^+$, 143 (11) [M − 100]$^+$.

**1-(Diisopropylamino)-3,4-diphenylphosphole 1-Sulfide (9b):** Yellow solid (80%), m.p. 133−135 °C. $^{31}$P NMR ($CDCl_3$): δ = 64.50. $^1$H NMR ($CDCl_3$): δ = 1.31 [d, $J_{H,H}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$], 3.83

[m, 2 H, $(CH_3)_2CH$], 6.32 (d, $J_{H,P}$ = 27.3 Hz, 2 H, CHP), 6.99−7.08 (m, 4 H, Ph), 7.17−7.30 (m, 6 H, Ph). $^{13}C$ NMR ($CDCl_3$): δ = 23.3 [s, $(CH_3)_2CH$], 47.7 [d, $J_{C,P}$ = 3.7 Hz, $(CH_3)_2CH$], 127.9 (m, Ph), 128.1 (d, $J_{C,P}$ = 94 Hz, CHP), 128.3−128.5 (m, Ph), 135.7 (d, $J_{C,P}$ = 19.4 Hz, $C_{ipso}$), 150.4 (d, $J_{C,P}$ = 21.2 Hz, Ph*C*). MS (DCI, $CH_4$): *m*/*z* (%) = 368 (100) [M + H]$^+$. $C_{22}H_{26}NPS$ (367.50): C 71.90, H 7.13, N 3.81; S 8.72; found C 70.27, H 7.35, N 3.42, S 7.57.

**1,1′-Bis(diisopropylamino)-3,3′,4,4′-tetramethyl-2,2′-biphosphole (10a):** $CF_3SO_3Me$ (0.300 mL, 2.48 mmol) was added dropwise to a solution of **8a** (0.602 mg, 1.24 mmol) in dichloromethane (20 mL).

Table 1. Crystal data

| | **2a** | **4a′** | **4b** | **5a′** |
|---|---|---|---|---|
| Empirical formula | $C_{12}H_{22}NP$ | $C_{12}H_{22}NOPBr_2$ | $C_{29}H_{31}Br_2ClNO_3P$ | $C_{12}H_{22}NSPBr_2$ |
| Formula mass | 211.3 | 387.1 | 667.81 | 403.16 |
| Temperature [K] | 180(2) | 180(2) | 150(2) | 180 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/a$ | $C2/c$ | $P2_1/a$ |
| *a* [Å] | 7.4043(10) | 11.4016(15) | 11.3735(10) | 12.112(2) |
| *b* [Å] | 7.6092(10) | 7.7488(10) | 12.9365(9) | 7.7547(7) |
| *c* [Å] | 12.6715(16) | 18.0964(22) | 39.017(3) | 17.643(3) |
| α [°] | 90.91(2) | 90.0 | 90.0 | 90.0 |
| β [°] | 98.62(2) | 103.15(2) | 94.51(1) | 104.73(2) |
| γ [°] | 110.01(2) | 90.0 | 90.0 | 90.0 |
| *V* [Å$^3$] | 661.5(2) | 1556.8(3) | 5722.9(8) | 1602.6(6) |
| *Z* | 2 | 4 | 8 | 4 |
| ρ(calcd) [gcm$^{-3}$] | 1.061 | 1.651 | 1.550 | 1.671 |
| μ(Mo-$K_\alpha$) [cm$^{-1}$] | 1.757 | 52.450 | 30.135 | 52.155 |
| θ range [°] | 2.86 < θ < 25.97 | 2.86 < θ < 26.20 | 2.39 < 2θ < 24.09 | 2.39 < θ < 26.11 |
| Reflections measured | 6376 | 15210 | 13831 | 10274 |
| Independent reflections ($R_{int}$) | 2366 (0.0476) | 3061 (0.0540) | 4460 (0.0428) | 3145 (0.0597) |
| Reflections used [$I > 2\sigma(I)$] | 1726 | 2155 | 3658 | 2259 |
| *R* | 0.0396 | 0.0426 | 0.0295 | 0.0450 |
| $R_w$ | 0.0480 | 0.0446 | 0.0313 | 0.0486 |
| $(\Delta/\sigma)_{max}$ | 0.052 | 0.017 | 0.021 | 0.045 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ | −0.22/0.23 | −0.62/0.72 | −0.36/0.50 | −1.11/0.76 |
| GOF | 1.026 | 1.0534 | 0.965 | 0.944 |
| Variable parameters | 128 | 155 | 339 | 155 |

Table 2. Crystal data *(Continued)*

| | **5b** | **6b** | **8a** | **8b′** |
|---|---|---|---|---|
| Empirical formula | $C_{22}H_{26}Br_2NPS$ | $C_{22}H_{25}$ BrNPS | $C_{24}H_{42}N_2P_2S_2$ | $C_{44}H_{50}$ $N_2P_2S_2$ |
| Formula mass | 527.30 | 446.39 | 484.68 | 732.96 |
| Temperature [K] | 160(2) | 160(2) | 160(2) | 180(2) |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1$ | $C2/c$ | $P2_1/c$ |
| *a* [Å] | 7.8928(21) | 11.846(3) | 24.225(4) | 8.7740(8) |
| *b* [Å] | 10.0827(25) | 12.928 (2) | 8.1372(9) | 23.391(3) |
| *c* [Å] | 14.817(4) | 15.033(4) | 18.142(3) | 19.3229(16) |
| α [°] | 73.68(3) | 90.0 | 90.0 | 90.0 |
| β [°] | 82.23(3) | 110.39(3) | 129.34(1) | 97.74(1) |
| γ [°] | 80.38(3) | 90.0 | 90.0 | 90.0 |
| *V* [Å$^3$] | 1110.9(5) | 2158.1(9) | 2766.3(11) | 3929.6(7) |
| *Z* | 2 | 4 | 4 | 4 |
| ρ(calcd) [gcm$^{-3}$] | 1.576 | 1.374 | 1.164 | 1.239 |
| μ(Mo-$K_\alpha$) [cm$^{-1}$] | 37.818 | 20.816 | 3.115 | 2.504 |
| θ range [°] | 2.23 < θ < 26.03 | 2.14 < θ < 26.15 | 2.27 < θ < 26.11 | 2.04 < θ < 24.21 |
| Reflections measured | 11031 | 21540 | 11676 | 25321 |
| Independent reflections ($R_{int}$) | 4047 (0.0430) | 8418 (0.0833) | 2671 (0.0413) | 6019 (0.0974) |
| reflections used [$I > 2\sigma(I)$] | 3298 | 6496 | 2299 | 2534 |
| *R* | 0.0392 | 0.0537 | 0.0310 | 0.0317 |
| $R_w$ | 0.0412 | 0.0559 | 0.0346 | 0.0311 |
| $(\Delta/\sigma)_{max}$ | 0.032 | 0.020 | 0.082 | 0.043 |
| $\Delta\rho_{min}/\Delta\rho_{max}$ | −1.17/1.12 | −0.83/1.06 | −0.21/0.34 | −0.22/0.24 |
| GOF | 0.999 | 1.01 | 0.9947 | 1.0876 |
| Variable parameters | 245 | 476 | 137 | 452 |

After 24 h of stirring, the resulting suspension was concentrated to ca. 10 mL and cooled to −78 °C. Then, a solution of *t*BuSLi, obtained by treatment of 2-methyl-2-propanethiol (0.300 mL, 2.48 mmol) in ether (4 mL) with *n*-butyllithium (2.48 mmol, 1.55 mL, 2.5 M in hexane) at −40 °C, was added dropwise. The resulting solution was stirred for 15 min at −78 °C and for 2 h at room temp. and then concentrated to dryness. The resulting residue was extracted with small portions of pentane. The combined pentane phases were washed with water and dried with $MgSO_4$, and the solvents were evaporated to give crude compound **10a** (52 mg, 10%). $^{31}P$ NMR ($CDCl_3$): δ = 44.90. MS (DCI, $CH_4$): *m*/*z* (%) = 421 (100) $[M + H]^+$.

**X-ray Crystallographic Study:** All data were collected with a Stoe IPDS (Imaging Plate Diffraction System) diffractometer equipped with an Oxford Cryosystem cooler device. The final unit cell parameters were obtained by least-squares refinement of 5000 (or 8000) reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. The eight structures were solved by direct methods (SIR92 or SIR97)[31] and refined by least-squares procedures on *F*. H atoms were located on difference Fourier maps, but they were introduced by calculation into idealized positions [*d*(CH)= 0.96 Å] and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon atom to which they were attached. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $F_o$ and $F_c$ are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]^2$ where $w' = 1/\Sigma_1^n A_r T_r(x)$ with 3 coefficients $A_r$ for the Chebyshev polynomial $A_r T_r(x)$ where $x$ was $F_c/F_c(\max)$.[32] Models reached convergence with $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, with the values listed in Tables 1 and 2. The criteria for a satisfactory complete analysis were ratios of rms shift to standard deviation of less than 0.1 and no significant features in final difference maps. The calculations were carried out with the CRYSTALS package[33] running on a PC. The molecular view was obtained with the aid of ORTEP32.[34] Fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and atomic coordinates for H atoms have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165119−165126. Copies of the data can be obtained free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 IE2, UK.

**Computational Details:** The molecular mechanics calculations were carried out with the CAChe program, using the MM2 force field. The molecular geometries were fully optimized until the energy change was less than $10^{-5}$ kcal/mole or until the molecule had been updated 3000 times. 721 points were optimized to generate the potential energy surface.

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