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Synthesis of 1,3-Diphospha-2,3-dihydro-1*H*-phenalenes

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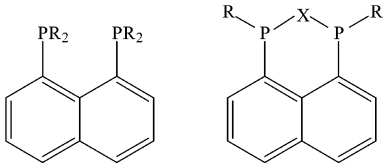
The reaction of 1,8-dilithionaphthalene (**1**) with methylenebis[(dialkylamino)chlorophosphanes] [$R_2N(Cl)PCH_2P(Cl)NR_2$; R = Me (**2a**), Et (**2b**)] leads to the formation of new heterocyclic compounds, 1,3-diphospha-2,3-dihydro-1*H*-phenalenes **3a**,**b** as a mixture of *cis* and *trans* isomers. DFT calculations indicate that the *cis* isomers are thermodynamically more stable by about 1–3 kcal/mol than the *trans* isomers. Compounds **3a**,**b** can be converted into dithio the derivatives **5a**,**b** and the borane complexes **6a**,**b**, which were characterized by NMR spectroscopy and investigated by X-ray diffraction analysis. The dialkylamino groups in **3** can be substituted by chlorine to give the chlorophosphane **7**.

Introduction

Derivatization of the naphthalene 1,8-positions has received much attention in recent decades. A large number of compounds containing different atoms and functional groups in these positions have been described.[1] Such substitution in the bay region of naphthalene leads to the proximity of substituents and causes steric strain, which is released by out-of-plane and/or in-plane distortions. This gives rise to unique stereochemistry and to the appearance of interesting chemical properties. The 1,8-naphthalenes substituted by phosphorus atoms have become one of the most investigated areas.[2] This is partially accounted for by the variety of coordination and valence states of the phosphorus atom, which increases the number of possible phosphorus functionalities. The interest in 1,8-bis(phosphanyl)-naphthalenes is also associated with their use as ligands for the synthesis of transition-metal complexes.[3]

Previous investigations of phospha-substituted naphthalenes have been mainly focused on compounds of type **A** (Figure 1). Information about derivatives **B** with the heterocyclic six-membered ring is restricted only by the species in which phosphorus atoms are bridged by oxygen or sulfur (X = O, S).[2a,4]



A **B** (X = O, S)

Figure 1. Phospha-substituted naphthalenes types **A** and **B** (with the heterocyclic six-membered ring).

We decided to complete this knowledge with the synthesis of system **B**, which has a methylene group (X = CH_2) bridging two phosphorus atoms. Such compounds can be considered as 1,3-diphospha-substituted 2,3-dihydro-1*H*-phenalenes. Depending on the position of substituents at phosphorus atoms, they can exist as *cis* and *trans* isomers. This circumstance may be of importance if such compounds find application as ligands in transition-metal complexes. For example, the optically active noncyclic methylene-bridged diphosphane *t*Bu(Me)P–CH_2–P(Me)*t*Bu has become the commercially available ligand (MiniPHOS), which is used in catalytic asymmetric synthesis.[5]

Results and Discussion

In this paper we describe the synthesis and characterization of 2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3]phosphinines **3a**,**b** with dialkylamino groups at the phosphorus atoms. The choice of these substituents for the model system is accounted for by the relative accessibility of the starting methylene diphosphanes **2a**,**b** and by the possibility of their subsequent substitution by chlorine atoms. The reaction of 1,8-dilithionaphthalene (**1**) with methylenebis[(dialkylamino)chlorophosphanes] **2a**,**b** turned out to be strongly

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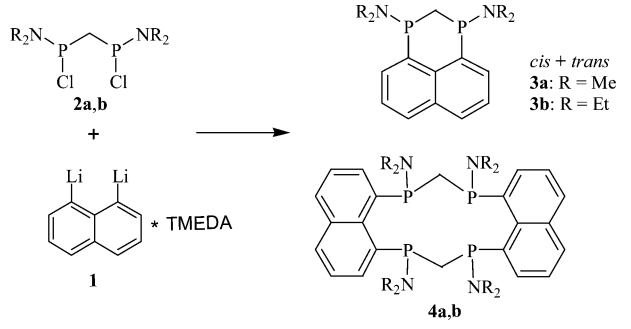
dependent on the solvent used and was successful only in hexane (Scheme 1). In more polar solvents the reaction proceeded quickly, however the ^{31}P NMR spectra of reaction mixtures displayed mainly a very broad signal in the range 30–60 ppm, probably belonging to a polymeric product as a result of intermolecular coupling. In hexane, **1** is poorly soluble, by which the intramolecular cyclization is promoted. As a result 1,3-diphosphaphenalene **3** is obtained in about 65% yield as a mixture of *cis* and *trans* isomers. In the ^{31}P NMR spectra these compounds show two singlets at δ = 46.3 and 51.9 ppm (R = Me). About 35% of the intensity belongs to the above-mentioned broad and hardly visible signal of the supposed polymer and dimeric product **4a**,**b**. The formation of the latter depends strongly on the volume of the dialkylamino substituents at phosphorus atoms and dilution of the reaction mixture. If R is methyl, the content of **4a** was ≤1%, whereas with R = Et the yield of **4b** reached 3–10%.[6]



Scheme 1.

One of the isomers is obviously preferable under kinetic reaction control. After completion of the reaction the *trans*/*cis* ratio is 30:20. However, the minor isomer seems to be thermodynamically more stable; its content slowly grows, reaching equilibrium at the ratio 95:5. One could suppose that the mutual repulsion of the Alk_2N groups in the *cis* isomer would lead to its transformation into the *trans* isomer. However, the situation turned out to be just the opposite and the final product was characterized as the *cis* isomer.

Indeed, quantum chemistry calculations for the dimethylamino derivative **3a** confirmed the *cis* isomer to be more stable (by 3.7 and 1.7 kcal/mol at the DFT and MP2 level of theory, respectively). These values did not substantially change if the solvent effects were taken into account using the COSMO procedure (see Exp. Section, Details of Calculations). The total energy differences between *cis* and *trans* forms calculated for heptane, chloroform and THF were 3.4–3.5 and 1.5 kcal/mol at the DFT and MP2 levels of theory, respectively. In the equilibrium conformation the dimethylamino groups occupy the equatorial position (Figure 2) for more details see Supporting Information). Two minima are separated by the transition state (**3a**-*ts*), corresponding to the process of inversion at one of the phosphorus atoms. One of the dimethylamino groups possesses an equatorial position and the other one is axial. They can easily exchange their positions: the activation energy for the **3a**-*trans* **3a**-*trans′* cycle inversion corresponding to the C_2-symmetrical transition-state **3a**-*trans(ts)* is only 6.0 kcal/mol.

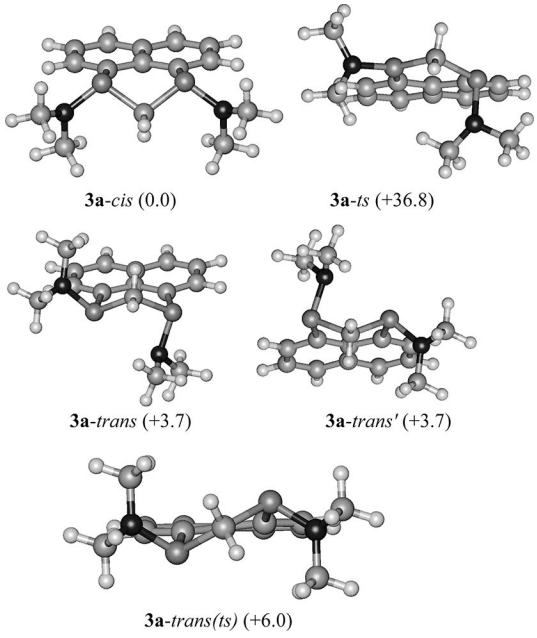


Figure 2. VMD presentation of the calculated (B3LYP/6-311++G**) structures and relative energies (kcal/mol) corresponding to the dynamic isomerizations of **3a**.

Even for compound **3b**, containing the more sterically demanding Et_2N groups, the DFT and MP2 calculations predicted a slightly higher stability for the *cis* configuration **3b**-*cis* (ΔE = 1.3 and 1.0 kcal/mol, respectively).

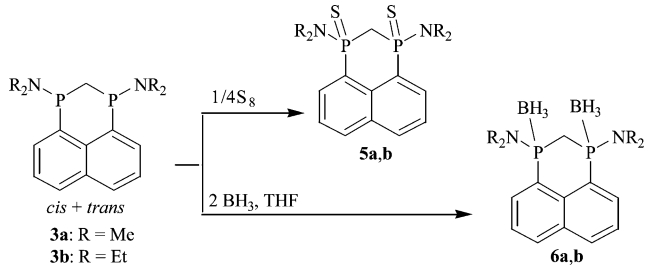
The activation energy barrier for the intramolecular *trans*–*cis* isomerization is rather high (36.8 kcal/mol; B3LYP/6-311++G**), which does not agree with the transformation observed at room temperature. Additionally, the rate of this process depends on the solvent used: it proceeds very slowly in hexane and is accelerated in THF or chloroform. Thus, the mechanism of the isomerization can probably be accounted for by the intermolecular exchange of diethylamino groups.

According to the calculations both the **3a**-*trans* and **3a**-*cis* isomers (Figure 2) possess the envelope conformations. All atoms of the six-membered heterocycle except the bridging methylene group are coplanar, which makes the CH_2 protons in both isomers inequivalent. In **3a**-*cis* and **3b**-*cis* these protons showed two doublets of triplets in the ^1H NMR spectra. Interestingly, the same protons of the disappearing *trans* isomers of **3a** and **3b**, instead of the expected triplets, display a complex multiplet, which can probably be referred to the AA′-part of the AA′XX′ spin system. The activation energy barrier for the envelope inversion is very low and in solution it should undergo fast flip-flop movement. For this reason the magnetic unequivalence of CH_2 protons in the *trans* isomers can probably be accounted for

by the different distances between phosphorus atoms and axially oriented protons (2.50 and 2.40 Å), which cause different $^2J_{PH}$ values.

Despite the presence of rather bulky dialkylamino groups, the naphthalene framework and the two phosphorus atoms in 1,8-positions lie in the same plane, which is in line with the configuration of sulfur- and oxygen-bridged cyclic compounds.[2a,4] Among noncyclic phosphorus-substituted 1,8-naphthalenes, only the smallest PH_2 derivative displays only in-plane deviations.[2k] All the others are nonplanar, because of strong out-of-plane distortions.

Although the *cis* isomers of **3a** and **3b** are thermally rather stable, our attempts to crystallize them were unsuccessful. However, these compounds can be used in further reactions without purification. For example, addition of sulfur or borane (BH_3·THF) to a mixture of isomers of **3a** or **3b** led quantitatively to the appropriate thio (**5a**,**b**) or borane derivatives **6a**,**b** with the same distribution of isomers (Scheme 2). Unlike starting trivalent compounds, these isomers do not interconvert and were separated from each other by column chromatography and crystallization.



Scheme 2.

It is interesting that the reaction of **3a**,**b** with BH_3 differs from the analogous reaction of noncyclic 1,8-bis(diphenylphosphanyl)naphthalene reported recently. In that case even with excess of BH_3 only one phosphorus atom of two formed a complex with borane, which after treatment with acids unexpectedly gave a bridged $[P–BH_2–P]^+$ charged system.[7]

Similarly to the trivalent precursors, the ^{1}H NMR spectra of the *cis* isomers **5a**,**b** and **6a**,**b** show two doublets of triplets of the inequivalent CH_2 protons. The X-ray diffraction study of **6b**-*cis* revealed a rather unexpected disposition of the phosphorus atoms and naphthalene frame (Figure 3). One of the phosphorus atoms is almost ideally coplanar with the naphthalene fragment (the dihedral angle ∠P1–C1–C2–C3 179.47°) and displays considerable in-plane deviation (∠C10–C1–P1 127.45°). The other one is substantially deviated out of the naphthalene plane (∠C7–C8–C9–P2 171.12°).

One more feature of this molecule deserves attention. The phosphorus atoms are unusually strongly oppositely deviated from each other. The P1–C11–P2 angle (118.70°) is extremely large for the sp^3-hybridized carbon. On the other hand, the angles C2–C1–P1 (113.08°) and C8–C9–P2 (115.10°), as well as the angles C1–P1–C11 (104.21°) and C9–P2–C11 (104.54°), are substantially smaller than 120° and 109°, respectively.

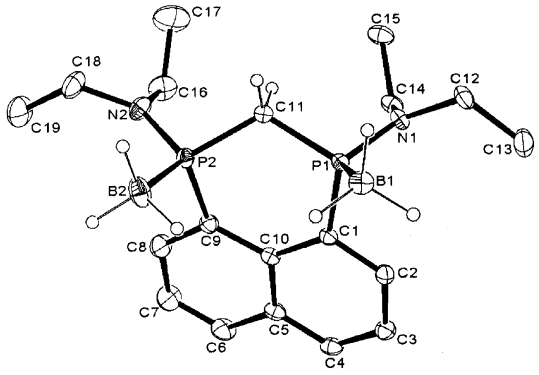


Figure 3. ORTEP drawing of the molecular structure of **6b**-*cis*. Thermal ellipsoids shown at 30% probability and all naphthalene and ethyl H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 3.126, P1–B1 1.9068(16), P2–B2 1.8980(17), P1–N1 1.6501(11), P2–N2 1.6514(12), P1–C11 1.8211(12), C11–P2 1.8121(13), P1–C1 1.8211(12), C9–P2 1.8111(14), C1–C10 1.4342(17), C4–C5 1.413(2), N1–C12 1.4687(16), C12–C13 1.515(2); C10–C1–P1 127.45(10), P2–C11–P1 118.70(7), C1–C10–C9 125.47(11), P1–C1–C2–C3 179.47(11), C7–C8–C9–P2 –171.12(15), P1–C1–C10–C5 178.40(9), P2–C9–C10–C5 168.54(10), C11–P1–C1–C2 170.18(10), C3–C4–C5–C6 179.72(14).

For the X-ray investigations of the *trans* configuration the sulfuration product **5a**-*trans* was chosen (Figure 4). Its structure does not differ substantially from that calculated for the trivalent precursor. The heterocycle possesses an envelope conformation, with the C15 atom deviating from the plane. The phosphorus atoms are almost coplanar with the naphthalene plane. Although the P–C–P angle (115.36°) is not as strained as in the *cis* isomer, it is still substantially wider than the normal tetrahedral angle. Unlike starting trivalent compounds, the CH_2 bridging protons are equivalent in the sulfurated *trans*-**5a**,**b** and hydroborated *trans*-**6a**,**b** derivatives and display "normal" triplets in the ^{1}H NMR spectra.

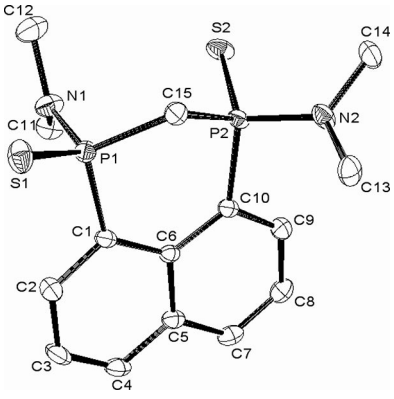
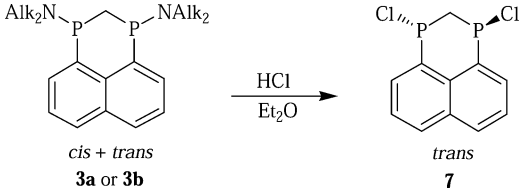


Figure 4. ORTEP drawing of the molecular structure of **5a**-*trans*. Thermal ellipsoids shown at 30% probability and all H atoms omitted. Selected bond lengths [Å] and angles [°]: P1–P2 3.057, P1–S1 1.9520(10), P2–S2 1.9333(10), P1–N1 1.653(3), P2–N2 1.663(2), P1–C1 1.804(3), P2–C10 1.814(2), P1–C15 1.810(3), C15–P2 1.807(3), C1–C6 1.434(4), C4–C5 1.420(4), N1–C12 1.462(4); C6–C1–P1 124.70(19), P2–C15–P1 115.37(16), C10–C6–C1 125.8(2), P1–C1–C2–C3 176.80, P2–C10–C9–C8 179.81, P1–C1–C6–C5 –176.37, P2–C10–C6–C5 –179.26, C3–C4–C5–C7 178.97.

The dialkylamino groups in compounds **3** can easily be substituted by chlorine to give compound **7** (Scheme 3). This reaction proceeds readily and quantitatively after addition of HCl or PCl_3 to the mixture of isomers **3a**,**b**.



Scheme 3.

DFT calculations of **7** predict the *trans* isomer to be thermodynamically more stable (by 2.8 and 3.8 kcal/mol at the DFT and MP2 levels of theory, respectively) than the *cis* isomer (see Supporting Information). Similarly to **3a**-*trans*, the C_2 symmetrical structure **7**-*trans(ts)* is a transition state corresponding to the inversion in the six-membered cycle (Figure 5). The low calculated activation energy for this process (3.1 kcal/mol) provides the high rate for such isomerization and, thus, the pseudo-C_2 symmetry for **7** observed in the NMR experiment.

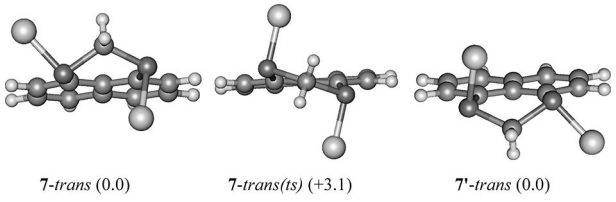


Figure 5. VMD presentation of the calculated (B3LYP/6-311++G**) structures and relative energies (kcal/mol) corresponding to the dynamic isomerizations of **7**-*trans*.

Indeed, the NMR spectra of compound **7** confirmed the formation of only the *trans* isomer. This compound could be interesting as a synthone for different transformations. However, unexpectedly, this compound turned out to be stable only in reaction solution (hexane, ether) for several hours at room temperature. As soon as the solvent is removed, chlorophosphane **7** decomposes to give a complicated mixture of compounds displayed in the ^{31}P NMR spectrum as several broad signals at –40 and +20 to 40 ppm. Nevertheless, taking into account that the content of **7** in the reaction solution reaches 60%, it can be used without isolation.

Experimental Section

General: All operations were performed under nitrogen in a drybox. Solvents were dried and purified according to common procedures. Methylene-bis(dialkylaminochlorophosphanes) [**2a** (R = Me), **2b** (R = Et)] were prepared from methylenebis(dichlorophosphane)[8] and *N*,*N*-dimethyl- or *N*,*N*-diethyl-(trimethylsilyl)amine in petroleum ether at 0 °C and isolated in 60% yield by distillation in vacuo at 0.04 Torr [b.p. 77–78 °C (**2a**), 108–110 °C (**2b**)]. The ^1H, ^{13}C and ^{11}B NMR spectra were recorded with Varian Gemini 400 MHz and the ^{31}P NMR spectra with JEOL FX-90Q spectrometers. The δ = ^1H and δ = ^{13}C chemical shifts are referenced to tetramethylsilane (TMS), the δ = ^{31}P to 85% aqueous H_3PO_4 and the δ = ^{11}B chemical shifts are given relative to $BF_3{\cdot}O(C_2H_5)_2$. TLC was performed by using alumina plates coated with silica (Fluka Kieselgel F_{254}). The plates were visualized by ultraviolet fluorescence or in an iodine chamber. Preparative separations were performed by silica gel flash column chromatography (Fluka Kieselgel 40, 230–400 mesh).

1,8-Dilithionaphthalene–TMEDA Complex (1): The lithiation of naphthalene was conducted according to the literature procedure.[9] The reaction suspension in hexane was then cooled to –25 °C. The yellow-brown precipitate of **1** formed overnight was separated, washed three times with cold hexane and immediately used.

***cis*- and *trans*-*N*,*N*,*N*′,*N*′-Tetraalkyl-2,3-dihydro-1*H*-naphtho[1,8-*de*]-[1,3]diphosphinine-1,3-diamine (3a,b):** Methylenebis[(dialkylamino)-chlorophosphane] **2a** or **2b** (0.546 mmol) in hexane (4 mL) was added at –25 °C to 1,8-dilithionaphthalene–TMEDA complex (**1**) (140 mg, 0.546 mmol) in hexane (2 mL) and the reaction suspension was stirred at room temperature for 2 h. The solvent was evaporated in vacuo from the separated liquid phase to give yellow (**3a**) or red (**3b**) oil containing about 60–65% of the product, which was used in further reactions without purification.

3a-*cis*: ^1H NMR ($CDCl_3$): δ = 2.17 [A part of the ABX_2 system, dt, $^2J_{H,H}$ = 9.96, $^2J_{H,P}$ = 2.49 Hz, 1 H, PC*H*$_2$P], 2.74 (pseudo t, $^3J_{H,P}$ = 4.98 Hz, 12 H, C*H*$_3$), 2.88 (B part of ABX_2 system, dt, $^2J_{H,H}$ = 9.96, $^2J_{H,P}$ = 1.87 Hz, 1 H, PC*H*$_2$P), 7.39–7.90 (6 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (THF): δ = 51.56 (s) ppm.

3a-*trans*: ^1H NMR ($CDCl_3$): δ = 2.36 [m (see Figure 3), 2 H, PC*H*$_2$P], 2.67 [d, $^3J_{H,P}$ = 9.77 Hz, 12 H, N(C*H*$_3$)], 7.39–7.90 (6 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (THF): δ = 45.22 (s) ppm.

3b-*cis*: ^1H NMR ($CDCl_3$): δ = 1.10 (t, $^3J_{H,H}$ = 6.84 Hz, 12 H, CH_2CH_3), 2.25 (A part of the ABX_2 system, dt, $^2J_{H,H}$ = 9.96, $^2J_{H,P}$ = 2.80 Hz, 1 H, PC*H*$_2$P), 3.00 (B part of ABX_2 system, dt, $^2J_{H,H}$ = 9.96, $^2J_{H,P}$ = 1.87 Hz, 1 H, PC*H*$_2$P), 3.10 (m, 8 H, NC*H*$_2$CH$_3$), 7.51 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 7.85 (m, 4 H, H-2, H-7, H-4, H-5, Ar) ppm. $^{31}P\{^1H\}$ NMR (THF): δ = 50.21 (s) ppm.

3b-*trans*: ^1H NMR ($CDCl_3$): δ = 1.17 (br. t, $^3J_{H,H}$ = 6.84 Hz, 12 H, CH_2CH_3), 2.42 [m (see Figure 3), 2 H, PC*H*$_2$P], 3.10 (m, 8 H, NC*H*$_2$CH$_3$), 7.39 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 7.62 (m, 2 H, H-2, H-7, Ar), 7.67 (d, $^3J_{H,H}$ = 8.79 Hz, 2 H, H-4, H-5, Ar) ppm. $^{31}P\{^1H\}$ NMR (THF): δ = 44.07 (s) ppm.

***N*,*N*,*N*′,*N*′-Tetraalkyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3]diphosphinine-1,3-diamine 1,3-Disulfide (5a,b):** Sulfur (20 mg, 0.63 mmol, 5% excess) was added at room temperature to a solution of **3a** or **3b** (ca. 0.3 mmol) in benzene (2 mL). In 10 min the solvent was evaporated under reduced pressure and the isomers were separated by column chromatography on silica gel.

5a-*cis*: R_f = 0.28 (CH_2Cl_2/EtOAc, 250:1); yield 24 mg (23%), white crystals, m.p. 209–210 °C. ^1H NMR ($CDCl_3$): δ = 2.54 (d, $^3J_{H,P}$ = 12.7 Hz, 12 H, NC*H*$_3$), 3.25 (A part of ABX_2 system, dt, $^2J_{H,H}$ = 15.63, $^2J_{H,P}$ = 9.77 Hz, 1 H, PC*H*$_2$P), 3.91 (B part of ABX_2 system, m, 1 H, PC*H*$_2$P), 7.72 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 8.14 (d, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-4, H-5, Ar), 8.66 (dd, $^3J_{H,P}$ = 9.78, $^3J_{H,H}$ = 7.32 Hz, 2 H, H-2, H-7, Ar) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 37.43 (s, N*C*H$_3$), 38.79 (t, $^1J_{C,P}$ = 49.59 Hz, P*C*H$_2$P), 125.45 (t, $^3J_{C,P}$ = 7.25 Hz, C-3, C-6, Ar), 126.6 (dd, $^1J_{C,P}$ = 103, $^3J_{C,P}$ = 3.82 Hz, C-1, C-8, Ar), 130.78 (t, *J* = 8.77 Hz, C-4a or C-8a), 133.19 (t, *J* = 9.54 Hz, C-4a or C-8a, Ar), 133.93 (s, C-4, C-5, Ar), 135.76 (t, $^2J_{C,P}$ = 5.34 Hz, C-2, C-7, Ar) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 57.97 (s) ppm. $C_{15}H_{20}N_2P_2S_2$ (354.41): calcd. C 50.83, H 5.69; found C 50.96, H 5.70.

5a-*trans*: R_f = 0.49 (CH_2Cl_2/EtOAc, 250:1); yield 20 mg (19%), white crystals, m.p. 164–165 °C (after recrystallization from tolu-

ene). ^{1}H NMR ($CDCl_3$): δ = 2.48 (d, $^3J_{H,P}$ = 12.7 Hz, 12 H, NCH_3), 3.42 (t, $^2J_{H,P}$ = 14.65 Hz, 2 H, PCH_2P), 7.71 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 8.12 (d, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-4, H-5, Ar), 8.53 (dd, $^3J_{H,P}$ = 9.77, $^3J_{H,H}$ = 7.84 Hz, 2 H, H-2, H-7, Ar) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 35.57 (t, $^1J_{C,P}$ = 50.35 Hz, PCH_2P), 37.04 (s, NCH_3), 125.58 (t, $^3J_{C,P}$ = 7.25 Hz, C-3, C-6, Ar), 127.7 (d, $^1J_{C,P}$ = 99.18 Hz, C-1, C-8, Ar), 131.16 (t, J = 9.16 Hz, C-4a or C-8a, Ar), 132.87 (t, J = 9.54 Hz, C-4a or C-8a, Ar), 133.52 (s, C-4, C-5, Ar), 134.18 (t, $^2J_{C,P}$ = 4.58 Hz, C-2, C-7, Ar) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 57.63 (s) ppm. $C_{15}H_{20}N_2P_2S_2$ (354.41): calcd. C 50.83, H 5.69; found C 50.91, H 5.75.

5b-*cis*: R_f = 0.17 (CH_2Cl_2); yield 26 mg (21%). ^{1}H NMR ($CDCl_3$): δ = 1.14 (t, $^3J_{H,H}$ = 6.84 Hz, 12 H, NCH$_2$CH_3), 2.99 (A part of the ABX_2 system, dt, $^2J_{H,H}$ = 18.07, $^2J_{H,P}$ = 13.67 Hz, 1 H, PCH_2P), 3.23 (m, 8 H, NCH_2CH$_3$), 3.58 (B part of the ABX_2 system, m, $^2J_{H,H}$ = $^2J_{H,P}$ = 13.67 Hz, 1 H, PCH_2P), 7.63 (t, $^3J_{H,H}$ = 7.32 Hz, 2 H, H-3, H-6, Ar), 8.03 (dd, $^3J_{H,H}$ = 6.81, $^4J_{H,H}$ ≈ 2 Hz, 2 H, H-4, H-5, Ar), 8.16 (dd, $^3J_{H,P}$ = 16.11, $^3J_{H,H}$ = 7.32 Hz, 2 H, H-2, H-7, Ar) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.63 (s, NCH$_2$CH_3), 38.29 (t, $^1J_{C,P}$ = 46.54 Hz, PCH_2P), 39.59 (s, NCH_2CH$_3$), 125.98 (m, C-3, C-6, Ar), 131.25 (t, $^1J_{C,P}$ = 100 Hz, C-1, C-8, Ar), 131.75 (t, $J_{C,P}$ = 12.21 Hz, C-4a or C-8a, Ar), 132.17 (t, $^2J_{C,P}$ = 3 Hz, C-2, C-7, Ar), 133.51 (s, C-4, C-5, Ar), 133.90 (t, $J_{C,P}$ = 10.68 Hz, C-4a or C-8a, Ar) ppm. ^{31}P{^{1}H} NMR (hexane): δ = 54.91 (s) ppm. MS (EI): *m*/*z* (%) = 410 (19.1) [M$^+$], 306 (53.2), 235 (14.2), 221 (7.1), 189 (34.8), 170 (8.9), 72 (100).

5b-*trans*: R_f = 0.54 (CH_2Cl_2); yield 37 mg (30%), white crystals, m.p. 152–153 °C (after recrystallization from toluene). ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, $^3J_{H,H}$ = 7.32 Hz, 12 H, NCH$_2$CH_3), 3.02 (m, 8 H, NCH_2CH$_3$), 3.44 (t, $^2J_{H,P}$ = 14.65 Hz, 2 H, PCH_2P), 7.69 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 8.10 (dd, $^3J_{H,H}$ = 7.81, $^4J_{H,H}$ ≈ 2 Hz, 2 H, H-4, H-5, Ar), 8.54 (dd, $^3J_{H,P}$ = 16.60, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-2, H-7, Ar) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.40 (s, CH_3), 40.71 (s, CH$_2$CH$_3$), 41.19 (t, $^1J_{C,P}$ = 47.30 Hz, PCH_2P), 125.93 (t, $^3J_{C,P}$ = 7.25 Hz, C-3, C-6, Ar), 129.30 (ps t, $^1J_{C,P}$ = 50.35 Hz, C-1, C-8, Ar), 132.28 (t, J = 9.54 Hz, C-4a or C-8a, Ar), 133.25 (t, J = 9.92 Hz, C-4a or C-8a), 133.87 (s, C-4, C-5, Ar), 134.61 (t, $^2J_{C,P}$ = 4.58 Hz, C-2, C-7, Ar) ppm. ^{31}P{^{1}H} NMR (hexane): δ = 54.78 (s) ppm. MS (EI): *m*/*z* (%) = 410 (65.9) [M$^+$], 338 (6.8), 306 (100), 267 (12.8), 235 (20), 221 (12.9), 204 (57.1), 189 (64.3), 170 (15), 157 (5.4), 72 (57.9), 44 (7.1).

***N*,*N*,*N*′,*N*′-Tetraalkyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3]diphosphinine-1,3-diamine–1,3-Diborane Complex (6a,b):** BH_3/THF (twofold excess) was added at 0 °C to a solution of a mixture of isomers of **3a** (ca. 0.3 mmol) or **3b** (ca. 0.67 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 30 min and then washed twice with water (1 mL). The organic layer was separated and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel.

6a-*cis*: R_f = 0.3 (CH_2Cl_2/hexane; 3:1); yield 24 mg (25%), colourless, m.p. 179–180 °C. ^{1}H NMR ($CDCl_3$): δ = 0.4–1.5 (br. m, BH_3), 2.66 (d, $^3J_{H,P}$ = 10.7 Hz, 12 H, CH_3), 2.69 (A part of ABX_2 system, m, 1 H, PCH_2P), 2.91 (B part of ABX_2 system, m, $^2J_{H,H}$ = $^2J_{H,P}$ = 14.65 Hz, 1 H, PCH_2P), 7.61 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 7.95 (dd, $^3J_{H,P}$ = 14.65, $^3J_{H,H}$ = 6.84 Hz, 2 H, H-2, H-7, Ar), 8.12 (d, $^3J_{H,H}$ = 8.01 Hz, 2 H, H-4, H-5, Ar) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.90 (t, $^1J_{C,P}$ = 22.13 Hz, PCH_2P), 37.87 (d, $^2J_{C,P}$ = 2.29 Hz, NCH_3), 124.79 (dd, $^1J_{C,P}$ = 61.04, $^3J_{C,P}$ = 2.67 Hz, C-1, C-8, Ar), 125.42 (d, $^3J_{C,P}$ = 12.21 Hz, C-3, C-6, Ar), 132.55 (d, $^2J_{C,P}$ = 11.44 Hz, C-2, C-7, Ar), 132.80 (d, $^4J_{C,P}$ = 1.53 Hz, C-4, C-5, Ar), 133.23 (t, $J_{C,P}$ = 6.10 Hz, C-4a or C-8a, Ar), 133.50 (t, $J_{C,P}$ = 6.49 Hz, C-4a or C-8a, Ar) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 63.2 (br. m) ppm. $C_{15}H_{26}B_2N_2P_2$ (317.95): calcd. C 56.66, H 8.24; found C 56.42, H 8.15.

6a-*trans* could not be completely purified by column chromatography: R_f = 0.66. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 56 (br. m) ppm.

6b-*cis*: R_f = 0.32 (CH_2Cl_2/hexane; 3:1); yield 21 mg (8.4%, after recrystallization from hexane), light green, m.p. 134–136 °C. ^{1}H NMR ($CDCl_3$): δ = 0.5–1.4 (br. m, BH3), 1.10 (t, $^3J_{H,H}$ = 6.84 Hz, 12 H, NCH$_2$CH_3), 2.73 (A part of ABX_2 system, dt, $^2J_{H,H}$ = 14, $^2J_{H,P}$ = 9 Hz, 1 H, PCH_2P), 2.89 (A part of ABX_2 system, m, $^2J_{H,H}$ = $^2J_{H,P}$ = 14 Hz, 1 H, PCH_2P), 3.12 (m, 8 H, NCH_2CH$_3$), 7.57 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 7.99 (m, 4 H, H-2, H-4, H-5, H-7, Ar) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = –60.23 (br) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.75 (d, $^3J_{C,P}$ = 1.53 Hz, NCH$_2$CH_3), 23.03 (t, $^1J_{C,P}$ = 19.45 Hz, PCH_2P), 40.98 (d, $^2J_{C,P}$ = 2.29 Hz, NCH_2CH$_3$), 125.68 (d, $^3J_{C,P}$ = 12.21 Hz, C-3, C-6, Ar), 126.62 (d, $^1J_{C,P}$ = 62.56 Hz, C-1, C-8, Ar), 132.82 (d, $^2J_{C,P}$ = 10.68 Hz, C-2, C-7, Ar), 133.04 (d, $^4J_{C,P}$ = 1.53 Hz, C-4, C-5, Ar), 134.07 (t, $J_{C,P}$ = 7.25 Hz, C-4a or C-8a, Ar), 134.27 (t, $J_{C,P}$ = 6.87 Hz, C-4a or C-8a, Ar) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 64.47 (br) ppm.

6b-*trans*: R_f = 0.75 (CH_2Cl_2/hexane; 3:1); yield 31 mg (12% after recrystallization from toluene), white crystals, m.p. 194–195 °C. ^{1}H NMR ($CDCl_3$): δ = 0.4–1.4 (br., BH3), 0.99 (t, $^3J_{H,H}$ = 7.32 Hz, 12 H, NCH$_2$CH_3), 2.84 (t, $^2J_{H,P}$ = 9.77 Hz, 2 H, PCH_2P), 3.07 (m, 8 H, NCH_2CH$_3$), 7.67 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 8.08 (d, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-4, H-5, Ar), 8.22 (dd, $^3J_{H,P}$ = 13.67, $^3J_{H,H}$ = 6.84 Hz, 2 H, H-2, H-7, Ar) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = –4.52 (d, $^1J_{P,B}$ = 61.04 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 14.65 (s, NCH$_2$CH_3), 26.42 (t, $^1J_{C,P}$ = 20.60 Hz, PCH_2P), 41.84 (s, NCH_2CH$_3$), 125.35 (d, $^1J_{C,P}$ = 69.42 Hz, C-1, C-8, Ar), 125.76 (d, $^3J_{C,P}$ = 12.97 Hz, C-3, C-6, Ar), 133.47 (s, C-4, C-5, Ar), 133.58–133.71 (m, C-4a, C-8a, Ar), 134.53 (d, $^2J_{C,P}$ = 13.73 Hz, C-2, C-7, Ar) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 54.53 (br. m) ppm.

***trans*-1,3-Dichloro-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3]diphosphinine (7):** HCl in Et_2O (1.69 mmol) was added under cooling (–25 °C) to a $CDCl_3$ solution (2 mL) of a mixture of *cis* and *trans* isomers of **3b** obtained as described above (starting from 102 mg, 0.353 mmol of **2b**). The reaction solution after separation from diethylammonium chloride formed and concentration to a volume of about 0.6 mL showed the following NMR spectroscopic data for compound **7**. ^{1}H NMR ($CDCl_3$): δ = 2.89 (t, $^2J_{H,P}$ = 10.74 Hz, 2 H, PCH_2P), 7.69 (t, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-3, H-6, Ar), 8.10 (d, $^3J_{H,H}$ = 7.81 Hz, 2 H, H-4, H-5, Ar), 8.54 (dd, $^3J_{H,P}$ = 11.72, $^3J_{H,H}$ = 6.84 Hz, 2 H, H-2, H-7, Ar) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.07 (t, $^1J_{C,P}$ = 40.74 Hz, PCH_2P), 125–135 (Ar) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 83.17 (s) ppm.

X-ray Crystallographic Study: Data were collected on a Bruker Smart Apex II (**5a-*trans***) and Siemens P4 (**6b-*cis***) diffractometer using graphite-monochromated Mo-K_α radiation (71.073 pm). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program.[10] All non-hydrogen atoms were refined anisotropically and the position of the hydrogen atoms was calculated as a riding model.

5a-*trans* ($C_{15}H_{20}N_2P_2S_2$): M_w = 354.39, orthorhombic, space group *Fdd*2, a = 19.5269(11), b = 47.461(3), c = 7.4201(4) Å, α = β = γ = 90.00°, V = 6876.7(7) Å^3, T = 173(1) K, Z = 16, μ(Mo-K_α) = 0.491 mm^{-1}; 6065 reflections measured, 265 parameters refined using 3109 unique reflections (R_{int} = 0.051) to final indices R_1 [$I > 2\delta(I)$] = 0.0325 and wR_2 (all data) = 0.0760 {$w = 1/[\delta^2(F_o^2) + (0.0364P)^2 + 9.7206P]$ where $P = (F_o^2 + 2F_c^2)/3$}. The final residual

Fourier positive and negative peaks were equal to 0.478 and –0.206 e/Å^3.

6b-*cis* ($C_{19}H_{34}B_2N_2P_2$): M_w = 374.04, monoclinic, space group $P2_1/c$, a = 12.0200(10), b = 15.5860(10), c = 13.0050(10) Å, $\alpha = \gamma$ = 90.00°, β = 115.620(10)°, V = 2196.9(3) Å^3, T = 173(2) K, Z = 4, μ(Mo-K_α) = 0.202 mm^{-1}; 11335 reflections measured, 237 parameters refined using 5014 unique reflections (R_{int} = 0.044) to final indices R_1 [$I > 2\delta(I)$] = 0.0338 and wR_2 (all data) = 0.0906 {$w = 1/[\delta^2(F_o^2) + (0.0416P)^2 + 0.7741P]$ where $P = (F_o^2 + 2F_c^2)/3$}. The final residual Fourier positive and negative peaks were equal to 0.431 and –0.278 e/Å^3.

CCDC-723044 (for **5a**-*trans*) and -723851 (for **6b**-*cis*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Details of Calculations: The structures of the studied compounds were fully optimized with the GAUSSIAN-03 set of programs[11] using the DFT (B3LYP[12]) level of approximation using 6-311++G** basis sets. As default within the GAUSSIAN packet the mentioned basis sets are defined as the proper 6-311G Pople basis sets[13] for hydrogen and the second period atoms (C, N, O, F) and the (12s,9p) McLean–Chandler basis set[14] for phosphorus and sulfur, expanded with the appropriate polarization and diffuse Gaussian functions. A three-parameter hybrid functional was used including correlated functionals of Becke,[12] Lee, Yang and Parr B3LYP[15] and VWN-III.[16] In order to check if the structures are local minima in energy the vibration frequency was determined computationally for the optimized geometries calculating the first and second derivatives analytically. For energy considerations, single-point MP2 energy calculations were performed for optimized structures. The CPCM (COSMO)[17] procedure was used for modelling the solvent effects.

Optimized structures were pictured using the VMD program.[18]

Supporting Information (see footnote on the first page of this article): Total energies calculated for **3a**, **3b** and **7** at the DFT (B3LYP/6-311++G**) and MP2 (MP2/6-311++G**//B3LYP/6-311++G**) levels of approximations, zero-point energy correction values (ZPE), ZPE-corrected energies and relative energies (ΔE), and lowest vibration frequencies (ν). Cartesian coordinates and VMD plots for the optimized (B3LYP/6-311++G**) structures.

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[6] Because of different disposition of the diethylamino groups, **4b** consists of a mixture of isomers and displays several signals of different intensities in the ^{31}P NMR spectrum at 38.00, 38.95, 39.89, 42.45 ppm (THF). After complete sulfuration of the reaction mixture its mass spectrum (EI) contained, in addition to the molecular peaks of **5b**(*cis*,*trans*), the molecular peak of the sulfurated dimeric product M($C_{38}H_{56}N_4P_4S_4$) = 820. Because of very low yield, **4a** was only detected in the ^{31}P NMR spectrum of the reaction mixture by the most intensive peaks at 42.25, 42.72, 43.13 ppm (THF).

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