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Transformations of Benzothiadiphosphole System: General One-Pot Synthesis of 1,2,5-Dithiaphosphepines and Their Precursor Phosphanethiols

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ABSTRACT: *Treatment, at room temperature, of benzothiadiphosphole* **1** *with* $BrMg(CH_2)_5MgBr$ *gives intermediate* **A**, *which was allowed to stand for about 3 h at room temperature. The subsequent addition of RMgX to the reaction mixture and the final treatment with an excess of* S_8 *and water affords the dithiaphosphepine sulfide* **8** *in good yields. The structure of this new heterocyclic system, containing both an S—S unit and a P═S group, is confirmed by an single crystal X-ray structure determination. If the reaction is carried out without final treatment with sulfur we obtain, using PhMgBr as mono-Grignard reagent, the corresponding ring-opened product* **11b**, *which can be easily transformed into the corresponding ring-opened sulfide* **12b** *by simple treatment with elemental sulfur. Further addition of sulfur to* **12b** *gives quantitatively the cyclic dithiaphosphepine sulfide* **8b**. *The two phosphanethiols* **11b** *and* **12b** *are of considerable interest. In fact, recently, attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine groups, also known as S—P—S pincer ligands.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:339–345, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20099

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INTRODUCTION

The facile synthesis of heterocyclic systems containing phosphorus is of considerable current interest, principally because they play a central role in coordination chemistry and homogeneous catalysis [1]. In addition, cyclic systems containing both phosphorus and sulfur should be particularly interesting as bidentate or polydentate ligands but this type of compounds has received much less attention. Recently, in a communication we reported [2] a simple synthesis of the first examples of a new heterocyclic system, namely 11*H*-dibenzo[c,f][1,2,5]dithiaphosphepine, containing in a seven-membered ring an S—S unit and a P═S group. Now, in this paper, we report further details of this new procedure to obtain new derivatives of this heterocyclic system and an X-ray crystallographic study confirming the structure

previously proposed. In addition we found that it is possible to obtain in a similar manner in one-pot synthesis also PhP(p-MeC$_6$H$_3$-SH-2)$_2$, (**11b**) and its sulfide PhPS(p-MeC$_6$H$_3$-SH-2)$_2$ (**12b)**, which are the ring-opened precursors of the above heterocyclic system containing the S—S unit. Compounds **11** and **12** are of considerable interest because recently attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine donor sites, as their combination is likely to confer unusual structures and reactivities on their metal complexes [3].

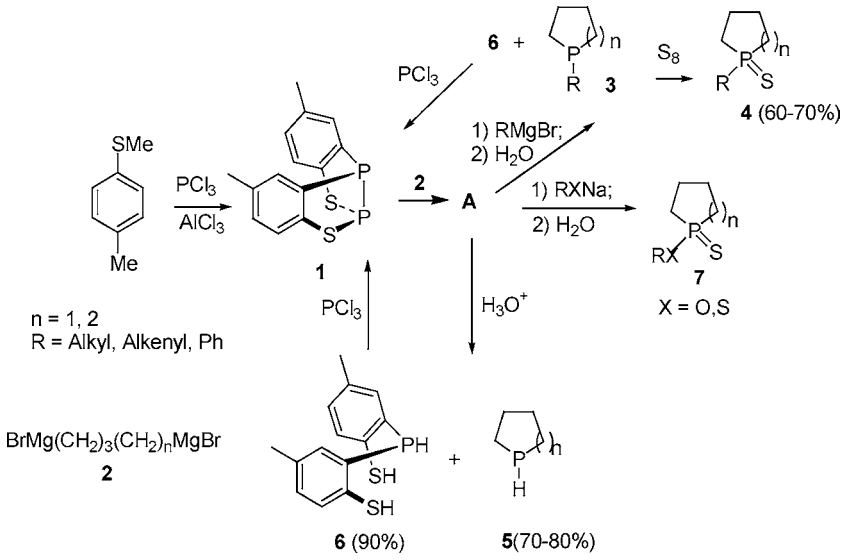
RESULTS AND DISCUSSION

In the past years, we reported [4] that benzothiadiphosphole **1** is easily obtained by an unexpected domino reaction treating p—methylthioanisole with PCl_3 and $AlCl_3$. Compound **1** was separated by simple crystallization from the reaction mixture [4b, 6b]. It is an air-stable solid which can be stored for several years without particular precaution and thus it is easy to handle. Subsequently, we found [5a] that compound **1** can be used as a phosphorus-donating reagent for obtaining diazaphosphole [5b] derivatives by the reaction of **1** with azalkenes.

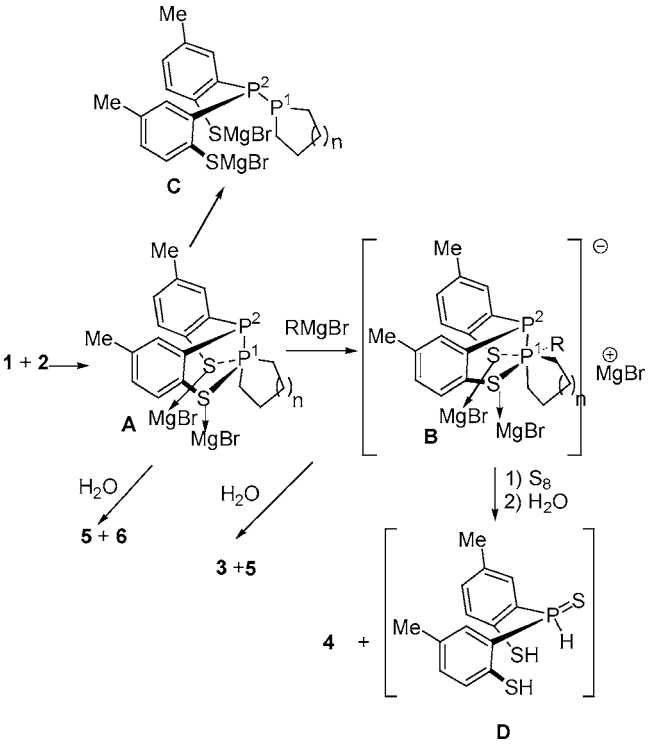
Recently, we reported [6] that the simultaneous or the sequential addition of equimolar amounts of a bis-Grignard **2** (n = 1, 2) and a mono-Grignard RMgBr (R = alkyl, phenyl, alkenyl) to one equivalent of **1** give phosphanes **3** or, after addition of elemental sulfur, their sulfides **4** in good yields at room temperature (Scheme 1). More recently [7], we have reported a very efficient and economic new method for the one-pot preparation of secondary cyclic phosphanes **5** (n = 1, 2) in 70–80% yields. This method consists in the treatment at room temperature of reagent **1** with one equivalent of bis-Grignard **2**. Treatment of the reaction mixture with acidic water gave secondary cyclic phosphanes **5** (70–80% yields) and the end product **6** (90% yields) which is the residue of reagent **1**. The separation of **5** from **6** can be performed by simple acid/base extraction or by distillation. Simple treatment of **6** with PCl_3 regenerates quantitatively and immediately the starting reagent **1**, which can be reused without further purification. The same end product **6** can be recovered also from the final reaction mixture obtained when we prepare phosphanes **3**.

The general synthesis of cyclic tertiary and secondary phosphanes reported in Scheme **1** is an atom-economic [8] and environmentally friendly methodology because the by-product **6** is easily transformed into the starting reagent **1**.

These results were tentatively explained by the intervention of hypervalent phosphorus intermediates [9] such as **A** and **B** (Scheme 2) in which the "dibenzo-butterfly" moiety of reagent **1**, as depicted in Scheme 1, might favor their formation. In intermediate **A**, the coordination of the Mg atom to sulfur would activate the P^1 atom to undergo the final nucleophilic attack giving a very unstable intermediate **B** (or its isomeric forms) that immediately collapses to the final phosphanic product. It should be noted that only in the second step we can use a nucleophilic reagent such as a sodium alcoholate or thiolate giving the corresponding cyclic phosphane derivatives **7** (see Scheme 1). But sodium alcoholate or thiolate



SCHEME 1



SCHEME 2

cannot be used in the first step of this reaction. In fact, we have found that reaction of several alcoholates as RONa with **1** does not give in appreciable amount the corresponding phosphite $(RO)_3P$.

This observation may be in agreement with our hypothesis that in the first step, the reaction of a bis-Grignard reagent with **1** may not be a conventional [10] double S_N2 substitution, which would give the expected form **C**, but might prefer to give the intermediate **A** with a hypervalent phosphorus atom as shown in Scheme 2. In the intermediate **A**, the formation of another additional ring around the P^1 atom, obtained by attack of the bis-Grignard, is a factor of further stability. In fact, when the reaction is carried out with simultaneous addition of a bis-Grignard reagent and mono-Grignard (RMgX) in equimolar amount, we have the almost exclusive formation of cyclic phosphanes **3** without acyclic PR_3 which, for three simple S_N2 reactions, would be favored. This observed favored cyclization might be in accord with a hypervalent intermediate in which the formation of a cyclic form is favored by a large factor (10^5–10^8) with respect to an acyclic form [11]. When we use only mono-Grignard reagents we have different results. In fact, the use of mono-Grignards also in the first step does not form a ring around the phosphorus and, consequently, causes instability of the intermediate **A** which might be transformed into the form **C** giving a very complex mixture of alkylphosphanes; this work is still in progress.

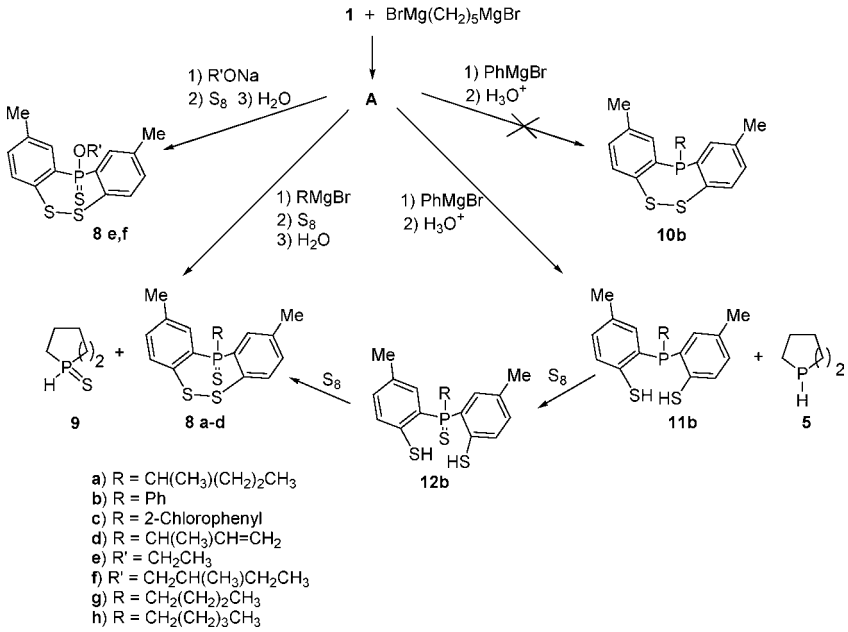
It should be noted that the end product, phosphane sulfide **D**, was supposed [2] and never isolated but the subsequent isolation of phosphane **6** also confirms **D**.

Recently, in order to find further information about this reaction, we have observed a new type of transformation which occurs when the intermediate **A** reacts with RMgBr with high steric hindrance of the R group (Scheme 3). In these cases (cases **a, c, d**), we have the prevalent formation [2] of the new heterocyclic compounds **8** (75–80%) with the concomitant formation of cyclic phosphane sulfides **9**. When RMgX is sterically less demanding (case **b**) and the intermediate **A** was allowed to stand for about 3 h at room temperature before the reaction with RMgBr, we have the formation of both **8** and **4** in a ratio depending on the reaction time of the first step of the reaction with the formation of intermediate **A**. In fact, when PhMgBr is immediately added to **A** we have only **4b** while when we added PhMgBr to **A** after about 3 h at ambient temperature we also found **8b** in 50% yield. This fact indicates that the pathway for formation of **8** is more complex than the one for explaining the formation of **4**.

Presumably the new intermediate might be the isomeric ionic form **A′** (Scheme 4) which might explain the inversion of reactivity of the two P atoms. In this manner, the nucleophilic attack of the second reagent can occur on the P^2 atom which is now a very reactive phosphenium ion [12]. After this attack and addition of S_8 and water, the P^1 phosphoranide [13], an unstable hypervalent species, collapses to form compounds **8** and **9**. The decomposition pathway is still unclear. A possibility is the formation of phosphanethiols such as **11** and **12** and their subsequent oxidation by S_8, as reported in Scheme 3 and explained below.

In a similar manner we obtained the 11-alkoxy derivatives **8e,f** using alcoholates as nucleophilic reagents.

Compounds **8** represent the first examples of derivatives with a new heterocyclic system, namely 11*H*-dibenzo[c,f][1,2,5] dithiaphosphepine 11-thione derivatives. The only related compound reported in the literature [14] is the 11-phenyl-11-oxo-derivative, obtained by a two-step procedure from lithium 2-lithiobenzenethiolate at −78°C with phenylphosphonic dichloride. Then the 2-mercaptophenyl phosphane oxide obtained is oxidized to the cyclic disulfide by DMSO at 90°C. It is clear that with this reported procedure it is necessary to use, for every cyclic disulfide, various $RPOCl_2$ reagents, which are very difficult to prepare when R

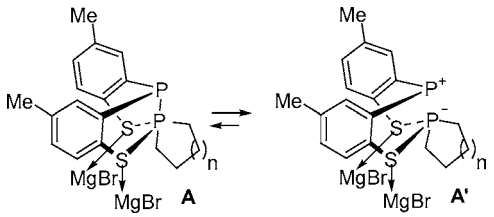


SCHEME 3

is a simple alkyl group. On the other hand, in our case, it is possible to obtain compounds **8** bearing several R or OR′ groups only using different mono-Grignard reagents or sodium alcoholates in a one-pot two-step procedure carried out at room temperature.

With the purpose to check whether our new method to obtain dibenzo[c,f][1,2,5]dithiaphosphepine 11-thione derivatives can be generalized, we carried out the reaction using mono-Grignard reagents RMgBr having not relevant steric hindrance, namely *n*-butyl- and *n*-pentyl-magnesium bromide (cases **g,h**). Also in these cases, we obtained the corresponding products **8g** and **8h**, thus confirming the possibility to prepare, through this new synthetic approach, a wide number of dithiaphosphepines.

In order to confirm unequivocally the structure of these new series of heterocyclic compounds by X-rays diffraction, we repeated the reaction to prepare compound **8b** and were able to obtain suitable crystals for a single crystal X-ray diffraction study.



SCHEME 4

Compound **8b** (Fig. 1) contains an unusual seven-membered heterocycle in which a phosphorus and two sulfur atoms forming an S—S bond are present. The molecule is asymmetric, and the central heterocycle is rather distorted, presumably in order to optimize the bonding interactions. The S—S distance [2.033(2) Å] is comparable to that found in S_8 [2.059 Å], and the P—S distance [1.936(2) Å] indicates double bond order. To the best of our knowledge, only one other compound showing a similar seven-membered ring has been reported in the literature: $[OPS_3]_2$, where $PS_3 = [P(C_6H_4\text{-}2\text{-}S)_3]$ [15] (see Fig. 2). In the latter case, the molecule is dimeric and the phosphorus atoms are oxidized.

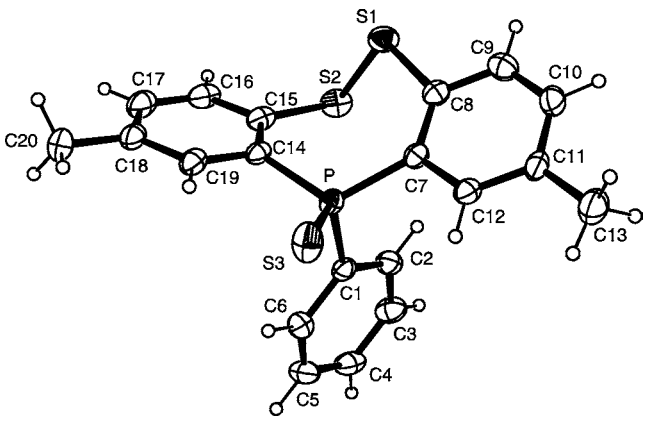


FIGURE 1 ORTEP drawing of **8b**

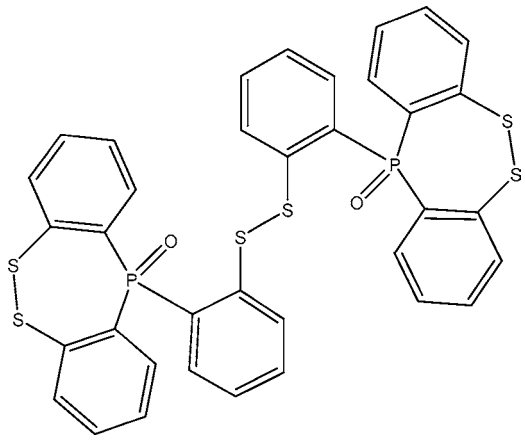


FIGURE 2 Representation of structure of compound reported in literature [15] as $[OPS_3]_2$.

With the aim to obtain compound **10b**, which is the phosphinic form of **8b**, we have carried out the reaction in a similar manner but without the final treatment with sulfur. The final reaction mixture was treated with aqueous acid to recover also the secondary cyclic phosphane **5** ($n = 2$), but surprisingly we obtained the phosphanethiol **11b** together with phosphane **5**, which can be completely purified by bulb-to-bulb distillation. Compound **11b** was separated from the residue by column chromatography and obtained in 50% yield. Compound **10b** was not obtained. Small amounts of **3** (R=Ph) and **6** were also observed.

When we treated compound **11b** with a stoichiometric amount of elemental sulfur, we obtained quantitatively the corresponding sulfide **12b** which was completely characterized. Further treatment of **12b** with sulfur gave the heterocyclic compound **8b**.

In addition, we found that compounds **11b** and **12b**, when analyzed by GC-MS, showed mainly the presence of compounds **10b** and **8b**, respectively, thus revealing a probable oxidation reaction from the thiolic to the disulfidic form in the mass injector. From this result, we hope to find other reaction conditions to obtain also **10b**.

The importance of this new simple route to phosphanylthiols suggests us to try to synthesize also alkyl derivatives, which probably are less stable than the phenyl ones: work is still in progress to this objective.

In conclusion, with these new transformations of compound **1**, it is possible to have a general method to produce the 1,2,5-dithiaphosphepinic system and to also obtain its precursor phosphanethiols **11b** and **12b**, which are known as pincer ligands. Recently, the chemistry of this kind of S—P—S pincer ligands has attracted increasing interest, augmented by the observation of unusual structures containing a "dibenzo-butterfly" moiety, very similar to our intermediate **A**, in the resulting transition metal complexes [3].

EXPERIMENTAL

General

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 300 (or Inova 400) spectrometer at 300 (or 400) MHz, 75.46 (or 100.56) MHz, and 121.47 (or 161.90) MHz, respectively, in $CDCl_3$. Chemical shifts are referenced to internal standard TMS (^1H NMR), to solvent (77.0 ppm for ^{13}C NMR), and to external standard 85% H_3PO_4 (^{31}P NMR). J values are given in Hz. Multiplicities were obtained from DEPT experiments (the symbols used are as follows: (+) for CH and CH_3, (−) for CH_2) I.R. spectra were recorded on a Perkin-Elmer spectrometer model 1600 FT-IR. MS spectra were recorded at an ionization voltage of 70 eV on a VG 7070 E spectrometer. GC-MS analyses were performed on a HP-5890 gas chromatograph equipped with a methyl silicone capillary column and an HP-5970 mass detector. Thin-layer chromatography was performed on Merck Kieselgel 60 F_{254}. Melting points were measured with a Büchi apparatus and are uncorrected. THF was distilled from sodium benzophenone ketyl. All Grignard reagents used, both commercially available and prepared from the corresponding alkyl halide and magnesium turnings, were titrated immediately prior to use by standard methods [16]. 2-Chlorophenylmagnesium iodide (for the synthesis of compound **8c**) was prepared by adding dropwise, at −30°C, an equimolar amount of *iso*-propylmagnesium chloride to a solution of 1-chloro-2-iodobenzene in anhydrous THF and keeping this solution at −30°C for 60 min. Air and moisture sensitive solutions and reagents were handled in a dried apparatus under an atmosphere of dry nitrogen.

Typical Procedure for the Synthesis of Compounds **8**

A solution of $BrMg(CH_2)_5MgBr$ (**2**, 1.0 mmol) in THF was added dropwise under dry nitrogen atmosphere to a solution of **1** (1.0 mmol) in THF (15–25 mL) at room temperature. The mixture was stirred for 30 min and allowed to stand for an additional 150 min, always at room temperature. A solution of mono-Grignard reagent (1.1 mmol) (or alcoholate, 2.0 mmol) was then added. The reaction mixture was allowed to stand for 25 h at room temperature then

treated with elemental sulfur (2.0 mmol) for 60 min, quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate and concentrated "in vacuo." Compounds **8** were isolated by FC on a silica gel column. According to spectral data their purity is higher than 98%. Characterization data for compounds **8a,c,d,e,f** were reported previously [2].

*2,9-Dimethyl-11-(butyl)-11H11λ⁵-dibenzo[c,f][1,2,5]dithiaphosphepine-11-thione (**8g**).* Greasy solid, 35% yield, $R_f = 0.44$ (petroleum light: dichloromethane 2:1); δ_H (300 MHz, $CDCl_3$): 8.74 (dd, 2H, $J_{P-H} = 17.0$ Hz, $J_{H-H} = 2.2$ Hz), 7.36 (dd, 2H, $J = 7.5$ Hz, $J = 4.4$ Hz), 7.26–7.16 (m, 2H), 2.85–2.70 (m, 2H), 2.45 (s, 6H, CH_3), 2.40–1.40 (m, 4H), 0.90–0.70 (m, 3H); δ_C (75.56 MHz, $CDCl_3$): 139.8 (d, $J = 12.2$ Hz, (+)), 139.3 (d, $J = 12.4$ Hz), 138.2 (d, $J = 5.8$ Hz), 133.7 (d, $J = 75.6$ Hz), 132.4 (d, $J = 2.4$ Hz, (+)), 131.3 (d, $J = 8.9$ Hz, (+)), 40.1 (d, $J = 56.0$ Hz, (−)), 24.2 (d, $J = 3.4$ Hz, (−)), 23.4 (d, $J = 18.1$ Hz, (−)), 21.3 (+), 13.6 (+); δ_P (121.47 MHz, $CDCl_3$): 53.7; MS (*m/z*, %): 364 (M^+, 25), 331 (25), 308 (30), 275 (100), 243 (50), 211 (18), 185 (21); IR, ν (cm^{-1}): 617, 728, 1111, 1450, 1583; HRMS calcd. For $C_{18}H_{21}PS_3$: 364.0543, found: 364.0541.

*2,9-Dimethyl-11-(pentyl)-11H-11λ⁵-dibenzo[c,f][1,2,5]dithiaphosphepine-11-thione (**8h**).* Greasy solid, 45% yield, $R_f = 0.44$ (petroleum light: dichloromethane 2:1); δ_H (300 MHz, $CDCl_3$): 8.74 (dd, 2H, $J_{P-H} = 16.3$ Hz, $J_{H-H} = 1.6$ Hz), 7.37 (dd, 2H, $J = 7.8$ Hz, $J = 4.7$ Hz), 7.25–7.16 (m, 2H), 2.80–2.62 (m, 2H), 2.45 (s, 6H, CH_3), 1.70–1.00 (m, 4H), 0.98–0.88 (m, 2H), 0.83–0.74 (m, 3H); δ_C (75.56 MHz, $CDCl_3$): 139.8 (d, $J = 12.2$ Hz, (+)), 139.3 (d, $J = 12.2$ Hz), 138.2 (d, $J = 5.4$ Hz), 133.8 (d, $J = 75.7$ Hz), 132.4 (d, $J = 3.2$ Hz, (+)), 131.4 (d, $J = 9.1$ Hz, (+)), 40.2 (d, $J = 55.6$ Hz, (−)), 32.4 (d, $J = 17.8$ Hz, (−)), 22.1 (−), 22.0 (d, $J = 3.6$ Hz, (−)), 21.4 (+), 13.9 (+); δ_P (121.47 MHz, $CDCl_3$): 53.6; MS (*m/z*, %): 378 (M^+, 24), 345 (30), 308 (32), 275 (100), 243 (31), 211 (16), 185 (25); IR, ν (cm^{-1}): 613, 717, 1117, 1456, 1583; HRMS calcd. For $C_{19}H_{23}PS_3$: 378.0700, found: 378.0698.

*Physical and Crystallographic Data of 11-(Phenyl)-2,9-dimethyl-11H-11λ⁵-dibenzo[c,f][1,2,5]dithiaphosphepine-11-thione(**8b**).* The reaction was carried out following the typical procedure described above. Compound **8b** was obtained in 50% yield, mp: 162–164°C (from dichloromethane) $R_f = 0.45$ (petroleum light: dichloromethane 2:1); δ_H (300 MHz, $CDCl_3$): 8.58 (dm, 2H, $^3J_{P-H} = 16.6$ Hz), 7.42–7.20 (m, 9H), 2.43 (s, 6H, CH_3); δ_C (75.56 MHz, $CDCl_3$): 139.8 (d, $J = 70.1$ Hz), 139.5 (d, $J = 12.8$ Hz, (+)), 139.1 (d, $J = 13.1$ Hz), 139.0 (d, $J = 7.4$ Hz), 133.7 (d, $J = 83.0$ Hz), 132.8 (d, $J = 2.9$ Hz, (+)), 131.3 (d, $J = 8.9$ Hz, (+)), 130.7 (d, $J = 3.3$ Hz, (+)), 130.3 (d, $J = 11.3$ Hz, (+)), 128.3 (d, $J = 13.3$ Hz, (+)), 21.3 (+); δ_P (121.47 MHz, $CDCl_3$): 49.0; MS (*m/z*, %): 384 (M^+, 59), 352 (14), 320 (74), 275 (70), 243 (100), 211 (51), 185 (62); IR, ν (cm^{-1}): 488 (S—S), 690 and 745 (P═S), 1100 (PC), 1583; HRMS calcd. for $C_{20}H_{17}PS_3$: 384.0230, found: 384.0221.

Crystal structure of **8b**: $C_{20}H_{17}PS_3$, $F_w = 384.49$, monoclinic, space group Cc, $a = 9.351(2)$, $b = 16.050(3)$, $c = 12.474(3)$ Å, $\beta = 102.93(3)°$, $V = 1824.5(6)$ Å^3, $Z = 4$, $D = 1.400$ mg/m^3, μ(Mo K_α) = 0.493 mm^{-1}, $R_1 = 0.0348$, $[I > 2\sigma(I)]$, absolute structure parameter = 0.05(11), $R_w = 0.0911$ (all data), GOF = 1.002.

CCDC 254796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Synthesis of Compounds **11b** *and* **12b**

A solution of $BrMg(CH_2)_5MgBr$ (**2**, 1.0 mmol) in THF was added dropwise under a dry nitrogen atmosphere to a solution of **1** (1.0 mmol) in THF (15–25 mL) at room temperature. The mixture was stirred for 30 min and allowed to stand for an additional 150 min at room temperature. A solution of phenylmagnesium bromide (1.1 mmol) was then added. The reaction mixture was allowed to stand for 25 h at room temperature then treated with aqueous acid and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate and concentrated "in vacuo." Compound **11b** was isolated by FC on a silica gel column (eluent: petroleum light: dichloromethane 2:1). It contains small amounts (about 3%) of its oxide **13b**, probably formed during the work-up and/or the chromatographic purification process. The oxide **13b** was characterized only by ^{1}H, ^{31}P NMR, and MS spectroscopy as reported below.

Treatment of a solution of **11b** in dichloromethane with an equimolar amount of elemental sulfur gave quantitatively the corresponding sulfide **12b**, which was isolated and fully characterized. Further addition of sulfur to this solution gave formation of compound **8b**. Also when the solution containing pure **11b** was treated with a large excess of elemental sulfur, the reaction, monitored by ^{1}H NMR

analysis, showed the presence of both **12b** and **8b**, with gradual decreasing of **12b** and the parallel increasing of **8b** until the presence of the latter alone.

*4-Methyl-2-[(5-methyl-2-sulfanylphenyl)(phenyl)-phosphino]benzenethiol(***11b***).* 50% yield, $R_f = 0.10$ (petroleum light: dichloromethane 1:2); δ_H (400 MHz, $CDCl_3$): 7.42–7.34 (m, 3H), 7.32–7.24 (m, 4H), 7.08–7.03 (m, 2H), 6.61–6.57 (m, 2H), 3.94 (d, 2H, $J = 1.3$ Hz, disappears after addition of D_2O), 2.17 (s, 6H); δ_C (100.56 MHz, $CDCl_3$) (selected data): 136.0, 134.7 (d, $J = 6.5$ Hz), 134.4 (+), 134.2 (d, $J = 20.2$ Hz, (+)), 130.9 (d, $J = 3.2$ Hz, (+)), 130.5 (+), 129.2 (+), 128.8 (d, $J = 7.3$ Hz, (+)), 21.1 (+); δ_P (161.90 MHz, $CDCl_3$): −18.3; MS (*m/z*, %): 353 (M^+ −1, 2), 352 (9), 320 (6), 243 (100), 211 (17); IR, ν (cm^{-1}): 696, 746, 807, 1038, 1111, 1263, 1434, 1453, 2487, 2547; HRMS calcd. for $C_{20}H_{19}PS_2$: 354.0666, found: 354.0662.

*4-Methyl-2-[(5-methyl-2-sulfanylphenyl)(phenyl)-phosphorothioyl]benzene Thiol (***12b***).* mp: 169–171°C (from dichloromethane), quantitative yield from **11b**, $R_f = 0.30$ (petroleum light: dichloromethane 1:2); δ_H (400 MHz, $CDCl_3$): 7.80 (dd, 2H, $J = 13.7$ Hz, $J = 7.1$ Hz), 7.64–7.44 (m, 3H), 7.38–7.28 (m, 2H), 7.22–7.14 (m, 2H), 6.95 (dd, 2H, $J = 15.2$ Hz, $J = 1.3$ Hz), 6.13 (s, 2H, disappears after addition of D_2O), 2.18 (s, 6H); δ_C (100.56 MHz, $CDCl_3$): 135.3 (d, $J = 7.3$ Hz), 135.0 (d, $J = 11.3$ Hz), 134.6 (d, $J = 11.3$ Hz, (+)), 133.2 (d, $J = 10.5$ Hz, (+)), 133.0 (d, $J = 9.7$ Hz, (+)), 132.8 (d, $J = 2.4$ Hz, (+)), 132.1 (d, $J = 3.2$ Hz, (+)), 129.4 (d, $J = 86.6$ Hz), 128.6 (d, $J = 13.0$ Hz, (+)), 127.4 (d, $J = 89.1$ Hz), 21.0 (+); δ_P (161.90 MHz, $CDCl_3$): 44.5; MS (*m/z*, %): 386 (M^+, 12), 385 (20), 384 (80), 352 (10), 320 (100), 275 (97), 243 (86), 185 (85); IR, ν (cm^{-1}): 692, 715, 730, 814, 905, 1118, 1267, 1380, 1434, 1464, 2373; HRMS calcd. for $C_{20}H_{19}PS_3$: 386.0387, found: 386.0384.

*4-Methyl-2-[(5-methyl-2-sulfanylphenyl)(phenyl)-phosphoryl]benzenethiol (***13b***).* δ_H (400 MHz, $CDCl_3$): 7.70–7.05 (m, 9H), 6.79 (d, 2H, $J = 14.3$ Hz), 5.95 (s, 2H, disappears after addition of D_2O), 2.19 (s, 6H); δ_P (161.90 MHz, $CDCl_3$): 39.0; MS (*m/z*, %): 370 (M^+, 11), 369 (25), 368 (100), 335 (13), 259 (63), 244 (18), 211 (22).

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