Bidentate Phosphines of Heteroarenes: 4,6-Bis(diphenylphosphino)dibenzofuran and 4,6-Bis(diphenylphosphino)dibenzothiophene[1,2]

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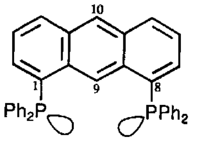
Twofold lithiation of dibenzofuran (**6**) and dibenzothiophene (**12**) with *n*-butyllithium/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) in *n*-hexane or *n*-pentane followed by the reaction with chlorodiphenylphosphine yielded the title compounds **4** and **5**, respectively. The monophosphines 4-(diphenylphosphino)dibenzofuran (**11**) and 4-(diphenylphosphino)dibenzothiophene (**15**) were obtained analogously via the monolithium compounds **9** and **14** of the heteroarenes. In the case of dibenzofuran (**6**), it was shown that mono- and dilithiation is controlled by temperature.

In a previous communication[3] we have reported on the synthesis of 1,8-bis(diphenylphosphino)anthracene (**1**) and preliminary studies of its behaviour as a ligand in metal complexation. By using the 1,8-disubstituted anthracene unit as a rigid carbon skeleton, it was intended that two phosphorus centres should be placed at a distance just too long to allow both to coordinate simultaneously to one metal nucleus. Alternatively, the formation of dimetallic complexes should bring two metal nuclei, each coordinated to one of the phosphorus centres, into close proximity, possibly introducing novel structural features and properties, especially with respect to catalytic processes. However, on reaction of **1** with nickel(II) chloride and bis(benzonitrile)palladium(II) chloride the concomitant cyclometallation of the carbon—hydrogen bond in position 9 of anthracene led to the formation of the extremely stable, square-planar monometallic chelat complexes **2** and **3**, respectively[3].



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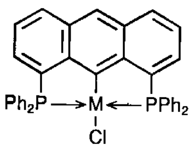
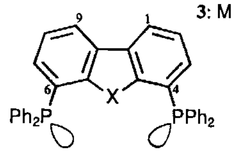


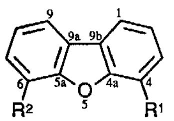
2: M = Ni
3: M = Pd



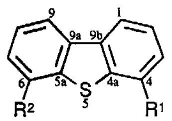
4: X = O
5: X = S

In pursuing our concept of rigid bidentate phosphine ligands for the formation of binuclear metal complexes we have been interested in 4,6-bis(diphenylphosphino)dibenzofuran (**4**) and 4,6-bis(diphenylphosphino)dibenzothiophene (**5**). The replacement of the 1,8-disubstituted anthracene skeleton of **1** by the 4,6-disubstituted heteroarenes dibenzofuran and dibenzothiophene in **4** and **5**, respectively, not only causes a small increase of the intramolecular distance between the phosphorus centres, but more importantly, it also alters the angle between the phosphorus lone pairs in such a way that a formation of monometallic chelate complexes should be rendered less favoured. Furthermore, the cyclometallation reaction, wich in the case of **1** leads to the formation of the very stable monometallic chelate complexes **2** and **3**, cannot occur in **4** and **5**, because the oxygen and sulphur heteroatoms are located in the position between the two phosphorus substituents.

On the other hand, the dibenzofuran oxygen and the dibenzothiophene sulphur atoms possess two lone pairs which might contribute additional weak coordinative bonds to metal atoms complexed by the phosphorus centres. Depending on the hybridization of the ring heteroatom, two idealized alternatives might be considered for this additionial coordination: With sp^2 hybridization one lone pair of the ring heteroatom is located in the p orbital perpendicular to the plane of the condensed ring system and contributes to the electron sextet of the five-membered heteroaromatic ring. Therefore, in this case only the other lone pair, located in the sp^2 orbital within the plane of the ring system and between the phosphorus centres, is expected to be available for an additional coordinative bond to a metal nucleus. If, on the other hand, sp^3 hybridization and hence tetrahedral geometry of the ring heteroatom is assumed, both lone pairs are located outside of the plane of the ring system and both might be capable of weak coordination to metal nuclei which in turn must also be located outside of the ring plane. A five-membered ring participating strongly in the aromaticity of the condensed ring system can be expected to require the sp^2 hybridization of the ring heteroatom, whereas sp^3 hybridization represents the case of a heteroatom-bridged biphenyl. The recently reported solid-state structure of a ruthenium(II) complex of 4-(diphenylphosphino)dibenzothiophene (**15**) shows the pyramidal geometry of the dibenzothiophenic sulphur atom, which, in addition to the phosphorus centre, is coordinated to the metal atom: The midpoint of the biphenyl linkage of the dibenzothiophene ligand, the sulphur, and the ruthenium atom define an angle of ca. 130°[4]. On this background the bidentate phosphine ligands **4** and **5** are



4: $R^1 = R^2 = PPh_2$
6: $R^1 = R^2 = H$
7: $R^1 = R^2 = Li$
8: $R^1 = R^2 = D$
9: $R^1 = Li$, $R^2 = H$
10: $R^1 = D$, $R^2 = H$
11: $R^1 = PPh_2$, $R^2 = H$



5: $R^1 = R^2 = PPh_2$
12: $R^1 = R^2 = H$
13: $R^1 = R^2 = Li$
14: $R^1 = Li$, $R^2 = H$
15: $R^1 = PPh_2$, $R^2 = H$

expected to bear interesting features with respect to metal complexation. Here we report on their syntheses and spectroscopic characterization.

Syntheses

A straightforward synthesis of **4** and **5** is conceivable by reaction of 4,6-dimetallated derivatives of dibenzofuran (**6**) or dibenzothiophene (**12**), respectively, with chlorodiphenylphosphine (Ph_2PCl). Gilman and co-workers, pioneering in the direct metallation reaction of **6** and **12** with organoalkali-metal reagents, have shown that the heteroatom facilitates the metallation especially in its neighbouring positions 4 and 6[5-11]. The conversion of dibenzofuran (**6**) into its 4,6-dimetallated product has been effected by organosodium reagents[5,9,12] while organolithium reagents have led only to the monometallated derivative[7]. In the case of the metallation of dibenzothiophene (**12**), the literature is contradictionary[9]. Gilman and Eidt have stated that the reaction of **12** with 2.2 equivalents of *n*-butyllithium in diethyl ether and subsequent termination with carbon dioxide yield exclusively 4-dibenzothiophenecarboxylic acid, the product of monometallation[7]. On the other hand, the reaction of **12** with a fourfold excess of *n*-butyllithium in di-*n*-butyl ether and termination with dimethyl sulphate yield 15% of 4,6-dimethyldibenzothiophene along with a material assumed to be 4-methyldibenzothiophene[13]. The product obtained from the reaction of **12** with a fourfold excess of *n*-butyllithium in diethyl ether and subsequent termination with deuterium oxide has been shown by mass spectrometry to contain 68% of [D_1]- and 22% of [D_2]dibenzothiophene; the latter compound has been presumed to be 4,6-disubstituted[14].

This previous work described in the literature prompted us to attempt the syntheses of **4** and **5** by twofold lithiation of the heteroarenes **6** and **12** and subsequent reaction of the dilithium compounds **7** and **13** with Ph_2PCl. However, by choosing the complex composed of equimolar quantities of *n*-butyllithium and TMEDA as the metallating reagent, it was thought to improve the lithiation step since metallation reactions of this complex are rapid even in unpolar aliphatic solvents like *n*-pentane or *n*-hexane[15-21]. Hence, it is possible to avoid using ether solvents which are sensitive towards organoalkali-metal reagents and thus might cause complications especially for multiple metallation reactions.

When two equivalents of *n*-butyllithium in *n*-hexane were added at room temperature to a solution of one equivalent of dibenzofuran (**6**) and two equivalents of TMEDA in *n*-hexane and the mixture was subsequently heated to reflux, a yellowish-beige suspension in a dark-brown solution was formed. The suspension consisted mainly of 4,6-dilithiodibenzofuran (**7**), so that **4** (50%, m.p. 212–216°C) could be prepared by reaction of **7** with Ph_2PCl. However, on adding one equivalent of **6**, dissolved in *n*-hexane, to a solution of two equivalents each of *n*-butyllithium and TMEDA in *n*-hexane at 0°C and keeping the mixture at this temperature, a brown solution was formed. Even though a twofold amount of the lithiation reagent had been applied, the brown solution apparently contained mainly the 4-lithiodibenzofuran (**9**) from which 4-(diphenylphosphino)dibenzofuran (**11**, 63%, m.p. 194–196°C) was obtained by the reaction with Ph_2PCl.

The lithium compounds **7** and **9** were characterized further by their reaction with ethan[D]ol. The suspension of **7** in *n*-hexane, which was obtained by performing the lithiation reaction at room temperature followed by heating at reflux, yielded 94% of dibenzofuran which by mass, ^1H-NMR, and ^{13}C-NMR spectra was shown to consist of about 88% of [4,6-D_2]dibenzofuran (**8**) [experiment a)]. On the other hand, the solution of **9**, which in the presence of a second equivalent of the lithiation reagent was obtained at 0°C, was on reaction with ethan[D]ol converted into 83% of dibenzofuran consisting to about 84% of [4-D_1]dibenzofuran (**10**) [experiment b)]. In experiment c) the solution of **9**, prepared at 0°C in the same manner as previously, was heated to reflux before ethan[D]ol was added. While the temperature was raised, **9** was metallated once more to give **7** which precipitated from the solution; accordingly, the dibenzofuran isolated in 97% yield from the reaction with ethan[D]ol was shown to consist again to about 90% of the dideuterated **8**. These experiments clearly demonstrate that in the metallation reaction of dibenzofuran (**6**) with the *n*-butyllithium/TMEDA complex in *n*-hexane the selective formation of the mono- and dilithium compound **9** and **7** is controlled by the temperature.

For the synthesis of 4,6-(diphenylphosphino)dibenzothiophene (**5**) two equivalents of *n*-butyllithium in *n*-hexane were added at room temperature to a suspension of one equivalent of dibenzothiophene (**12**) in *n*-pentane containing two eqivalents of TMEDA. A yellow-orange solution of 4,6-dilithio- and 4-lithiodibenzothiophene (**13** and **14**) was formed which was subsequently treated with Ph_2PCl to give a 1:2 mixture of **5** and 4-(diphenylphosphino)dibenzothiophene (**15**) as it was deduced from the ^{31}P-NMR spectrum. However, the separation of **5** and **15** on a preparative scale turned out to be difficult since both compounds behaved similarly in chromatography. So far only small yields of the pure compounds could be obtained by repeated crystallizations of fractions which before had been enriched in **5** and **15**, respectively, by chromatography on alumina with cyclohexane/toluene mixtures: **5** (2%), yellow crystals with m.p. 228–231°C and **15** (2%), colourless crystals with m.p. 215–218°C. The latter compound had been prepared already previously from the monolithium compound **14**[4,22].

Spectroscopic Characterization

The structures of **4** and **5** can be easily deduced from the ^1H-NMR spectra (CD_2Cl_2, 200 MHz) which show ABCX or ABCXX′ spin systems ($X = X' = {}^{31}P$), respectively, for the protons 1-, 9-H, 3-,.7-H and 2-, 8-H of the heteroarene. In the case of **4**, however, the B part for 3-, 7-H is obscured by the multiplet of the phenyl protons (for data see Experimental). It was not possible to assign completely the ^1H-NMR spectra of the monophosphines **11** and **15** measured at 200 MHz since these are complicated by the superposition of ABCX ($X = {}^{31}P$) and ABCD spin systems for the phosphorus-substituted and the unsubstituted six-membered ring of the heteroarenes, respectively. The assignments given in the Experimental are those of 400-MHz ^{1}H-NMR spectra (CD_2Cl_2) which were analyzed by H,H-correlated spectroscopy (COSY) and, in the case of **15**, additionally by simulation and iteration. The structure of **15** had been established previously by X-ray analyses of the free phosphine ligand[22] and two metal complexes[4,22].

The mass spectra (EI, 70 eV) of **4**, **11**, **15**, and of similar phosphines like **1** show the molecular ion peaks as the base peaks. In the mass spectrum of **5**, however, the very low intensity (1.5%) of the molecular ion peak $m/z = 552$ is striking. Instead, the fragment ion peak $m/z = 475$ is observed as the base peak which has to be attributed to an unusually strong fragmentation $[M^+ - 77]$ by the loss of a phenyl group from the molecular ion. In order to dispel last doubts about the structure, the ^{13}C-NMR spectrum of **5** ($CDCl_3$, 100 MHz) was also measured and found to be in full agreement with the structure **5** (see Experimental).

The diphosphine **5** is yellow in contrast to the colourless monophosphine **15** and the unsubstituted dibenzothiophene (**12**). Thus, the UV/Vis spectra (in cyclohexane, Figure 1) of the three compounds have been compared. Compound **12** exhibits three cleary separated absorption bands (β, p, and α band) in the wavelength ranges $\lambda = 220-265$, $275-290$, and $300-330$ nm, respectively. In the spectra of **15** and **5** the separations between the β and p bands have disappeared, and the p and α bands have been shifted increasingly to longer wavelengths. In comparison to **12**, the shifts of the p and the α bands of **15** are 5 and 9 nm, respectively, and in the case of **5** ca. 21 and 31 nm, respectively. The yellow colour of **5** is caused by the α band tailing to wavelengths of $\lambda > 400$ nm.

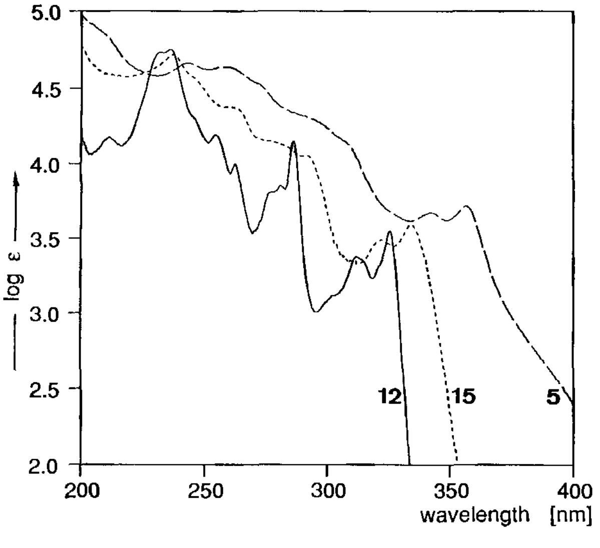


Figure 1. UV/Vis spectra (in cyclohexane) of dibenzothiophene (**12**), 4-(diphenylphosphino)dibenzothiophene (**15**), and 4,6-bis(diphenylphosphino)dibenzothiophene (**5**)

The structures of [4,6-D_2]dibenzofuran (**8**) and [4-D_1]-dibenzofuran (**10**), which had been prepared for the characterization of the di- and monolithium compounds **7** and **9** in the experiments a)−c) discussed above, were assigned by both their ^{1}H- and ^{13}C-NMR spectra (for data see Experimental). In the ^{13}C{^{1}H}-NMR spectra ($CDCl_3$, 50 MHz) the signals of the dibenzofuran carbon atoms C-4, -6[23] illustrate their degree of deuteration. In Figure 2a the strong signal of deuterium-substituted C-4, -6 at $\delta = 111.3$ (three lines 1:1:1 through deuterium coupling with $^1J_{CD} = 25.1$ Hz) and the very weak singlet of hydrogen-substituted C-4, -6 at $\delta = 111.6$ (marked by *) indicate that the product obtained from experiment a) was mainly the dideuterium compound **8**. For the product of experiment b), in which the lithiation and the subsequent reaction with ethan[D]ol was performed at 0°C, the approximately equal intensity of the signals for the deuterium-substituted C-4 and the hydrogen-substituted C-6 shows that the major product was [4-D_1]dibenzofuran (**10**, Figure 2b). In experiment c), which differed from b) only in that the temperature was raised before the addition of ethan[D]ol, **8** was again the major product. The deuterium isotope effect on ^{13}C-nuclear shielding[24] results in a shift of ca. 0.3 ppm for the deuterium-substituted aromatic carbon atom and ca. 0.1 ppm for its neighbouring carbon atoms. According to the latter effect, a splitting of the signals of C-3, -7 and C-4a, -5a is observed in the ^{13}C-NMR spectrum of **10** (for data see Experimental).

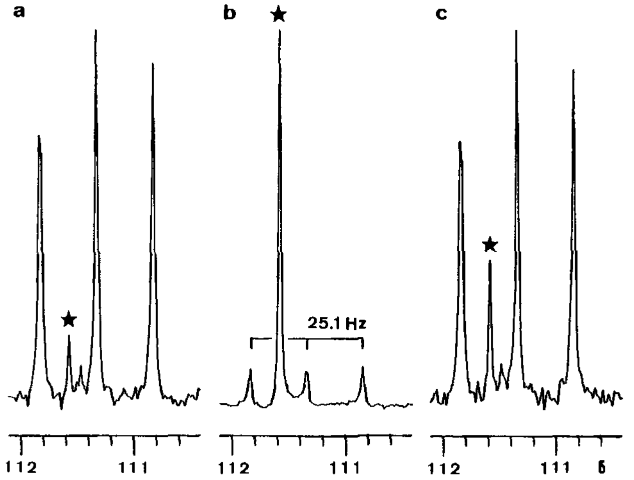


Figure 2. ^{13}C{^{1}H}-NMR spectra ($CDCl_3$, 50 MHz): Signal of the carbon atoms C-4, -6 for [4,6-D_2]dibenzofuran (**8**) obtained in experiments a), c) and for [4-D_1]dibenzofuran (**10**) obtained in experiment b); $\delta = 111.3$ (3 lines 1:1:1 with $^1J_{CD} = 25.1$ Hz for C−D), $\delta = 111.6$ (singlet for C−H, marked by *)[23]; for details see text to experiments a)−c)

Concluding Remarks

The bidentate phosphines **4** and **5** could be synthesized by twofold lithiation of the heteroarenes dibenzofuran (**6**) and dibenzothiophene (**12**) with *n*-butyllithium/TMEDA in aliphatic solvents and subsequent reactions of the heteroaromatic dilithium compounds **7** and **13**, respectively, with Ph_2PCl. As it has been shown by deuterium labeling experiments, 4,6-dilithiodibenzofuran (**7**) can be generated effectively and in relatively high purity, so that **4** becomes accessible without major difficulties. In the case of dibenzothiophene (**12**), however, the reaction sequence has only led to 1:2 mixtures of the diphosphine **5** and the monophosphine **15** from which pure **5** could be isolated so far in only poor yield. The accessibility of **5** might be improved by raising the efficiency in the twofold metallation reaction of dibenzothiophene (**12**) by which in turn the amount of **5** in the final product mixture would increase. Since the temperature has been shown to influence strongly the lithiation reaction of dibenzofuran (**6**), an improvement might be achieved solely by replacing the solvent *n*-pentane by the higher boiling *n*-hexane or *n*-heptane. A more efficient separation technique of the diphosphine **5** and the monophosphine **15** is the other possible objective for further improvement. Ligand-exchange chromatography[25,26] and the formation of metal complexes offer the advantage to utilize the property of the compounds as ligands for separation. Work is in progress to improve the accessibility of **5** and to study the behaviour of **4** and **5** as ligands in metal complexes[27].

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Experimental

All operations were carried out under dry argon. Solvents were dried, distilled and stored under argon. *n*-Butyllithium in *n*-hexane (1.6 M) was purchased from Metallgesellschaft, Frankfurt/Main. TMEDA was distilled from calcium hydride under argon. Ph_2PCl (Fluka) was distilled in vacuo, dibenzofuran (**6**) and dibenzothiophene (**12**) were purchased from Merck-Schuchardt, dried in high vacuo for 24 h, and stored under argon. Elemental analyses were carried out by the microanalytical laboratory Dornis & Kolbe, W-4330 Mülheim/Ruhr. – ^{1}H NMR: Bruker WP 80, AM 200, and AMX 400; tetramethylsilane as internal standard. – ^{13}C NMR: Bruker AM 200 (50 MHz) and AMX 400 (100 MHz); tetramethylsilane as internal standard. – ^{31}P NMR: Bruker AM 200 (81 MHz); phosphoric acid as external standard. – IR: Nicolet 7199 FT spectrometer; pressed KBr discs. – UV/Vis: Varian 2300 spectrometer. – MS: Finnigan MAT 311 A; EI at 70 eV. – GC/MS: Hewlett-Packard HP 5890 A with HP 5970 MSD. – GC: Hewlett-Packard HP 5890 A, Packard 427, Siemens Sichromat; capillary columns coated with OV-1, PS-240, PS-428, SE-54, or CW-20.

4,6-Bis(diphenylphosphino)dibenzofuran (**4**): At room temp. 40.5 ml of *n*-butyllithium in *n*-hexane (1.6 M, 64.8 mmol) was added within 40 min to a solution of 3.36 g (20.0 mmol) of dibenzofuran (**6**) and 7.53 g (9.78 ml, 64.8 mmol) of TMEDA in 80 ml of *n*-hexane. With the addition of *n*-butyllithium the solution immediately became red. The colour then changed slowly to very dark brown, and towards the end of the addition a yellowish-beige solid started to precipitate from the dark solution. The mixture was heated at reflux for 1 h. To the yellowish-beige suspension, cooled to 0°C, a solution of 8.78 g (7.20 ml, 40.0 mmol) of Ph_2PCl in 50 ml of *n*-hexane was added within 1 h. After stirring the mixture at room temp. for 12 h, 100 ml of air-free 2 N aqueous hydrochloric acid was added, and the *n*-hexane/water mixture was concentrated in vacuo. The residue was extracted exhaustively with dichloromethane. After the combined organic extracts had been washed with aqueous sodium chloride solution and dried with sodium sulphate, the solvent was removed in vacuo. According to the ^{31}P-NMR spectrum the solid residue (9.38 g) contained **4** and 4-(diphenylphosphino)dibenzofuran (**11**) in a ratio of ca. 2:1. Fractional crystallization from dichloromethane yielded 5.37 g (50%) of **4** as a colourless crystal powder with m.p. 212–216°C. – ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 7.94, 7.00 (A and C part of ABCX with X = ^{31}P, J_{AB} = 1.2, J_{AC} = 7.5, J_{BC} = 5.9, J_{CX} = 1.3 Hz; each 2H for 1-, 9-H and 2-, 8-H); 7.29–7.20 (m, 22H, B part of ABCX for 3-, 7-H and phenyl H). – ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = –17.2 (s); ($CDCl_3$): δ = –16.6 (s). – MS (70 eV): *m/z* (%) = 537 (34), 536 (100) [M$^+$], 535 (36), 457 (4), 428 (5), 379 (6), 352 (9), 351 (10) [M$^+$ – PPh_2], 350 (5), 349 (12), 320 (8), 274 (6), 273 (14), 268 (14), 267 (10), 257 (6), 244 (12), 229 (4), 183 (30), 168 (4), 152 (5), 108 (13), 78 (15), 77 (7), 51 (7).

$C_{36}H_{26}OP_2$ (536.55)			
Calcd.	C 80.59	H 4.88	P 11.55
Found	C 80.39	H 4.91	P 12.05

4-(Diphenylphosphino)dibenzofuran (**11**): 15.6 ml of *n*-butyllithium in *n*-hexane (1.6 M, 25.0 mmol) was added to a solution of 3.49 g (4.53 ml, 30.0 mmol) of TMEDA in 20 ml of *n*-hexane. To this mixture, cooled to 0°C, a solution of 1.82 g (10.8 mmol) of dibenzofuran (**6**) in 80 ml of *n*-hexane was added under stirring within 30 min. During the addition of **6** at 0°C the solution became slowly yellow-red, and later the colour changed to brown. After stirring the brown solution at 0°C for 1.5 h, a solution of 5.52 g (4.49 ml, 25.0 mmol) of Ph_2PCl in 25 ml of *n*-hexane was added at 0°C within 1 h. After stirring the mixture at room temp. for 10 h, 100 ml of a saturated aqueous ammonium chloride solution was added, and the mixture was extracted with dichloromethane. The organic solution was washed with aqueous sodium chloride solution and dried with sodium sulphate. The residue obtained by evaporating the solvent was recrystallized from dichloromethane/2-propanol to yield 2.40 g (63%) of **11** as a colourless crystal powder with m.p. 194–196°C. – ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 8.00, 7.29, 6.96 (ABCX with X = ^{31}P, J_{AB} = 7.7, J_{AC} = 1.3, J_{BC} = 7.5, J_{AX} = 0, J_{BX} = 0.3, J_{CX} = 5.3 Hz; each 1H for 1-H, 2-H, 3-H); 7.99, 7.51, 7.44, 7.35 (ABCD with J_{AB} = 0.7, J_{AC} = 1.4, J_{AD} = 7.7, J_{BC} = 8.2, J_{BD} = 1.2, J_{CD} = 7.2 Hz; each 1H for 9-H, 6-H, 7-H, 8-H); 7.35 (m, 10H, phenyl H); analyzed by H,H-correlated spectroscopy (COSY). – ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = –18.6 (s). – MS (70 eV): *m/z* (%) = 353 (22), 352 (100) [M$^+$], 351 (14), 274 (17), 273 (34), 244 (22), 215 (6), 198 (9), 197 (6), 183 (14), 170 (5), 152 (4), 139 (8), 108 (14), 78 (6), 77 (8), 51 (15).

$C_{24}H_{17}OP$ (352.37)			
Calcd.	C 81.81	H 4.86	P 8.79
Found	C 81.46	H 4.85	P 8.80

[4,6-D$_2$]Dibenzofuran (**8**) *and [4-D$_1$]dibenzofuran* (**10**): a) As described in the preparation of **4**, 40.5 ml of *n*-butyllithium in *n*-hexane (1.6 M, 64.8 mmol) was added within 40 min to a solution of 3.36 g (20.0 mmol) of dibenzofuran (**6**) and 7.53 g (9.78 ml, 64.8 mmol) of TMEDA in 80 ml of *n*-hexane at room temp., and the mixture was heated at reflux for 1 h. After the suspension of the yellowish-beige solid in the dark brown solution had been cooled to 0°C, 10 ml of ethan[D]ol was added. The mixture, which had turned to colourless again, was stirred at 0°C for 2 h and hydrolysed by adding 100 ml of a saturated aqueous solution of ammonium chloride. The organic layer was separated, the aqueous phase extracted with ether, and the combined organic solutions were washed several times with 5% aqueous hydrochloric acid and water. The solvent was evaporated and the residue dried in high vacuo to yield 3.16 g (94%) of **8**, m.p. 82–83°C [dibenzofuran (**6**): m.p. 86–87°C]. – MS: 0.4% D_0, 3% D_1, 88% D_2, 6% D_3, 3% D_4. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.94, 7.44, 7.32 [ABCX with X = D, J_{AB} = 1.6, J_{AC} = 8.0, J_{BC} = 7.1, J_{BX} ($^{3}J_{HD}$) ≈ 1.2 Hz; each 2H for 1-, 9-H, 3-, 7-H, 2-, 8-H]. – ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 156.06 (C-4a, -5a), 126.89 (C-

3, -7), 124.14 (C-9a, -9b), 122.55 (C-2, -8), 120.52 (C-1, -9), 111.31 ($^1J_{CD}$ = 25.1 Hz, C-4, -6).

b) As described in the preparation of **11**, a solution of 1.82 g (10.8 mmol) of **6** in 80 ml of *n*-hexane was added within 30 min to a stirred solution of 15.6 ml of *n*-butyllithium in *n*-hexane (1.6 M, 25.0 mmol) and 3.49 g (4.53 ml, 30 mmol) of TMEDA in 20 ml of *n*-hexane at 0°C. After stirring the brown solution at 0°C for 1.5 h, 6.20 ml of ethan[D]ol was added. The mixture, which had turned to colourless again, was stirred at 0°C and hydrolyzed by adding 100 ml of a saturated aqueous solution of ammonium chloride. Workup as described under a) yielded 1.51 g (83%) of **10**, m.p. 84–85°C. – MS: 2% D_0, 84% D_1, 14% D_2, 0.4% D_3. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.93, 7.43, 7.31 [ABCX with X = D, J_{AB} = 1.5, J_{AC} = 7.6, J_{BC} = 7.0, J_{BX} ($^3J_{HD}$) ≈ 1.1 Hz; each 1H for 1-H, 3-H, 2-H]; 7.93, 7.55, 7.43, 7.31 (ABCD with J_{AB} ≈ 0.5, J_{AC} = 1.5, J_{AD} = 7.6, J_{BC} = 8.0, J_{BD} ≈ 1.5, J_{CD} = 7.0; each 1H for 9-H, 6-H, 7-H, 8-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ = 156.14, 156.08 (C-4a, -5a), 127.04, 126.93 (C-3, -7), 124.17 (C-9a, -9b), 122.59 (C-2, -8), 120.55 (C-1, -9), 111.58 (C-6), 111.34 ($^1J_{CD}$ = 25.1 Hz, C-4).

c) A solution of **6** in *n*-hexane was added within 30 min to a solution of *n*-butyllithium and TMEDA in *n*-hexane at 0°C by using the same quantities and procedure as described in b). In deviation from b), the brown solution obtained at 0°C was subsequently heated at reflux for 1 h. While the temperature was raised, a yellowish-beige solid started to precipitate from the solution. After cooling again to 0°C, 6.20 ml of ethan[D]ol was added. The workup as described above yielded 1.77 g (97%) of **8**, m.p. 82°C. – MS: 0.4% D_0, 4% D_1, 90% D_2, 5% D_3, 1% D_4. – ^1H- and ^{13}C-NMR spectra corresponded closely to those obtained for the product according to procedure a).

4-(Diphenylphosphino)dibenzothiophene (**15**) *and 4,6-bis(diphenylphosphino)dibenzothiophene* (**5**): 117 ml of *n*-butyllithium in *n*-hexane (1.6 M, 187 mmol) was added within 30 min at room temp. to a suspension of 17.7 g (93.3 mmol) of dibenzothiophene (**12**) in 21.7 g (28.2 ml, 187 mmol) of TMEDA in 400 ml of *n*-pentane. The originally colourless suspension changed to yellow and finally was dissolved to form a yellow-orange solution. The mixture was heated at reflux for 30 min and then cooled to 0°C. A solution of 41.2 g (33.5 ml, 187 mmol) of Ph_2PCl in 100 ml of *n*-pentane was added within 90 min, and the mixture was stirred at room temp. for 12 h. Hydrolysis with 100 ml of 2 N hydrochloric acid, extraction with dichloromethane, washing of the organic solution with aqueous sodium chloride solution, drying with sodium sulphate, and removal of the solvent yielded 33.0 g of crude material. According to the ^{31}P-NMR spectrum the product contained **15** and **5** in a ratio of ca. 2:1. Chromatography on alumina with cyclohexane/toluene mixtures gave only fractions which contained the two compounds in different ratios. Repeated crystallizations of fractions enriched in **15** and **5**, respectively, from dichloromethane/2-propanol led to small amounts of the pure compounds.

15: 0.67 g (2%) of colourless crystals, m.p. 215–218°C (m.p. in ref.[4,22] not given). – ^1H NMR (CD_2Cl_2, 400 MHz): δ = 8.18, 7.43, 7.06 (ABCX with X = ^{31}P, J_{AB} = 7.9, J_{AC} = 1.1, J_{BC} = 7.3, J_{AX} ≈ 0.2, J_{BX} = 0.5, J_{CX} = 4.8 Hz; each 1H for 1-H, 2-H, 3-H); 8.18, 7.82, 7.47, 7.45 (ABCD with J_{AB} = −0.7, J_{AC} = 1.2, J_{AD} = 8.0, J_{BC} = 8.0, J_{BD} = 1.2, J_{CD} = 7.2 Hz; each 1H for 9-H, 6-H, 7-H, 8-H), 7.40–7.36 (m, 10H, phenyl H); analyzed by H,H-correlated spectroscopy (COSY), simulation, and iteration. – ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = −9.4 (s). – MS (70 eV): *m/z* (%) = 369 (31), 368 (100) [M^+], 367 (11), 291 (11) [M^+ – Ph], 290 (12), 289 (42), 260 (18), 259 (17), 258 (9), 214 (11), 213 (7), 183 (13), 152 (2), 139 (7), 108 (4), 107 (4), 78 (3), 77 (5), 51 (11). – UV/Vis (cyclohexane): λ_{max} (lg ε) = 238 nm (4.717), 260 (4.376), 276 (sh, 4.150), 292 (4.051), 323 (3.485), 335 (3.589).

$C_{24}H_{17}PS$ (368.44)
Calcd. C 78.24 H 4.65 P 8.41 S 8.70
Found C 78.07 H 4.49 P 8.26 S 8.76

5: 1.14 g (2%) of yellow crystals, m.p. 228–231°C. – ^1H NMR (CD_2Cl_2, 200 MHz): δ = 7.88, 7.57, 7.41 [ABCXX′ with X and X′ = ^{31}P, J_{AB} = 1.2, J_{AC} = 7.8, J_{BC} = 7.6, $\Sigma J_{BX(X')}$ = 3.2, J_{CX} = 0 Hz; each 2H for 1-, 9-H, 3-, 7-H, 2-, 8-H]; 7.25–7.20 (m, 20H, phenyl H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ [multiplicity with respect to $^1J_{CH}$, coupling to ^{31}P with apparent multiplicity ("m")[28]] = 140.5 [s, $J_{CP+CP'}$ = 31.3 Hz ("t"), C-4a, -5a (or C-4, -6)], 140.2 [s, $J_{CP+CP'}$ = 9.0 Hz ("t"), C-4, -6 (or C-4a, -5a)], 140.0 [s, $J_{CP+CP'}$ = 0.6 Hz ("d"), C-9a, -9b], 135.4 [s, $J_{CP+CP'}$ = 12.5 Hz ("t"), phenyl C_{ipso}], 135.0 [d, $^1J_{CH}$ = 163 Hz, $J_{CP+CP'}$ = 1.8 Hz ("t"), C-3, -7], 133.0 (d, $^1J_{CH}$ = 160 Hz, $J_{CP+CP'}$ = 21.0 Hz ("t"), phenyl C_{ortho}], 127.8 [d, $^1J_{CH}$ = 160 Hz, $J_{CP+CP'}$ = 6.7 Hz, phenyl C_{meta}], 127.6 [d, $^1J_{CH}$ = 160 Hz, phenyl C_{para}], 126.4 [d, $^1J_{CH}$ = 163 Hz, C-2, -8], 123.4 [d, $^1J_{CH}$ = 163 Hz, C-1, -9]. – ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = −10.0 (s). – MS (70 eV): *m/z* (%) = 553 (0.6), 552 (1.5) [M^+], 476 (33), 475 (100) [M^+ – Ph], 398 (3.5) [M^+ – 2 Ph], 367 (1.3) [M^+ – Ph_2P], 321 (18), 289 (9), 276 (8), 258 (5), 244 (4), 213 (3), 183 (12), 152 (1), 107 (1), 77 (2), 51 (2). – UV/Vis (cyclohexane): λ_{max} (lg ε) = 244 nm (4.663), 259 (4.637), 271 (sh, 4.538), 290 (sh, 4.319), 308 (sh, 4.141), 343 (3.668), 357 (3.717).

$C_{36}H_{26}P_2S$ (552.62)
Calcd. C 78.25 H 4.74 P 11.21 S 5.80
Found C 77.71 H 4.75 P 11.40 S 5.95

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[1] Dedicated to Professor *Heinz A. Staab* on the occasion of his 65th birthday.

[2] Phosphine ligands, 2; for part 1 see ref.[3]. The present work is part of the doctoral thesis of D. Jakubik, University of Düsseldorf, 1990.

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[28] The coupling with the two phosphorus atoms results in deceptively simple spectra, because $^6J_{PP}$ is large compared with J_{CP} and $J_{CP'}$.

[125/91]