

# Water-Soluble Phosphines. 17.<sup>1</sup> Novel Water-Soluble Secondary and Tertiary Phosphines with Disulfonated 1,1'-Biphenyl Backbones and Dibenzophosphole Moieties<sup>§</sup>

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Reaction of 2,2'-difluoro-1,1'-biphenyl with chlorosulfonic acid and subsequent hydrolysis followed by neutralization with potassium or sodium hydroxide affords disodium or dipotassium 5,5'-disulfonato-2,2'-difluoro-1,1'-biphenyl (**1a**, **1b**). On treatment of **1b** with diphenyl- or phenylphosphine in the superbasic medium DMSO/KOH, phosphine ligand **2** or **3** with a disulfonated 1,1'-biphenyl backbone or a dibenzophosphole moiety is formed. The structure of the oxide of 5-phenyldibenzophosphole **3**, which crystallizes as **4**·2.5H<sub>2</sub>O in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n* with *a* = 13.799(3) Å, *b* = 19.246(4) Å, *c* = 17.764(4) Å, β = 105.63(3)°, and *Z* = 4, has been determined by X-ray analysis. Nucleophilic phosphination of **1a** with NaPH<sub>2</sub> in liquid ammonia yields the sodium phosphide **5a** which on protonation gives the water-soluble 5*H*-dibenzophosphole **5**. Reaction of **1b** with PH<sub>3</sub> in the superbasic medium DMSO/KO*t*Bu affords **5b** in addition to the oxidation product **6a**. On oxidation of **5a** or **5b** with H<sub>2</sub>O<sub>2</sub>, the sodium or potassium salts of the sulfonated phosphinic acids **6a** or **6b**, respectively, are formed. Alkylation of the sodium dibenzophospholide **5a** with 2,2'-bis(chloromethyl)-1,1'-biphenyl or 1,4-di-*O*-*p*-toluenesulfonyl-2,3-*O*-isopropylidene-*D*-threitol yields the chiral water-soluble bidentate phosphine ligands **8** and **9**, respectively.

## Introduction

There is a sustained interest in biphasic catalysis using either water<sup>2</sup> or ionic liquids<sup>3</sup> as the polar phase. This is due to the application of organometallic complexes as catalysts in selective organic synthesis and the development of industrially important high performance catalysts. Aqueous biphasic catalysis has been preferred in the past decade for

economic reasons and because of its environmentally benign use of water as the solvent.<sup>4</sup> Because the catalyst can be immobilized in the aqueous phase without leaching into the organic phase, its separation from the product is typically achieved by phase separation. The water solubility of the organometallic catalyst is typically performed by incorporation of highly polar anionic or cationic groups such as SO<sub>3</sub><sup>-</sup> or [NH-C(NH<sub>2</sub>)(NMe<sub>2</sub>)]<sup>+</sup> into the peripheries of the phosphine ligands bound to the transition metal.<sup>4–6</sup> For the immobilization of the effective catalysts in aqueous biphasic media, sulfonic groups have been preferably employed for this purpose. Phosphines containing *meta*-sulfonated phenyl

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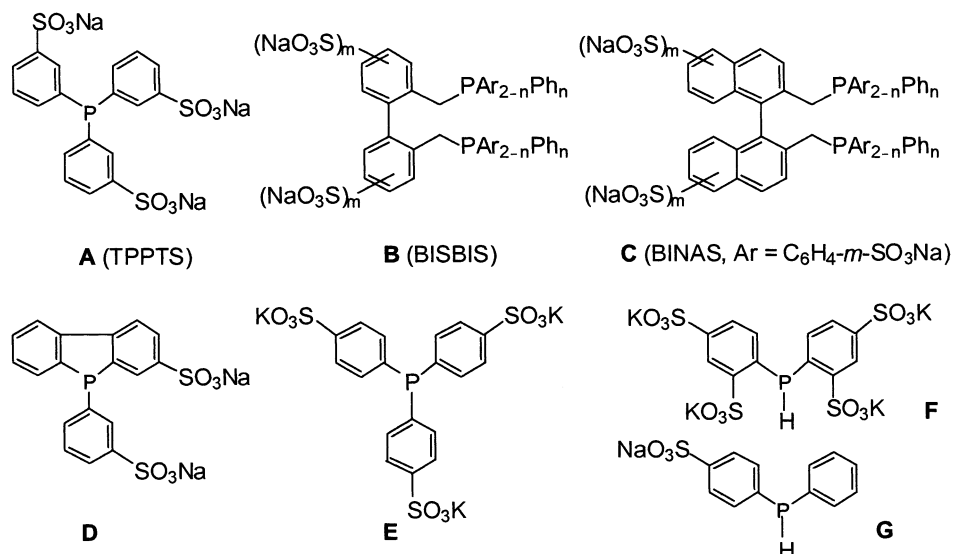
<sup>||</sup> Deceased.

<sup>§</sup> Dedicated to Prof. Dr. H. Bürger on occasion of his 65th birthday.

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Chart 1



groups and sulfonated backbones, for example, **A–D** in Chart 1,<sup>5,7–9</sup> have been obtained by direct sulfonation of the parent neutral phosphines with oleum.

The formation of derivatives of variable degrees of sulfonation and of phosphine oxides is, however, a serious drawback of this seemingly simple synthetic procedure. As shown by Herrmann et al.,<sup>9</sup> oxidation of the three-valent phosphorus can be suppressed in some cases by addition of boric acid. Nucleophilic aromatic phosphination of sulfonated fluorobenzene derivatives with PH<sub>3</sub> and primary and secondary phosphines (“indirect sulfonation”)<sup>10</sup> provides a more systematic approach to tertiary and secondary phosphines bearing aromatic substituents with sulfonic groups in 2- or 4-position or 2,4-disulfonated derivatives, for example, **E** or **F**, respectively.<sup>10,11</sup> Very recently, we have been able to show that sulfonated aromatic phosphines may also be obtained by Pd-catalyzed coupling reactions between sulfonated aryl iodides and primary or secondary phosphines.<sup>12</sup> Both methods provide an easy access to water-soluble phosphine ligands, for example, **G**, which cannot be obtained by the direct sulfonation method nor by its boric-acid variant.

Here, we report on the synthesis of water-soluble secondary and tertiary phosphines with a 1,1'-biphenyl backbone

and dibenzophosphole moieties by nucleophilic phosphination of sulfonated 2,2'-difluorobiphenyl with PH<sub>3</sub>, PhPH<sub>2</sub>, and Ph<sub>2</sub>PH in the superbasic medium<sup>13</sup> or in the presence of strong bases such as potassium *tert*-butoxide in aprotic dipolar solvents. For phosphination reactions with PH<sub>3</sub>, sodium phosphide (NaPH<sub>2</sub>) in liquid ammonia will alternatively be used as a reagent.

## Results and Discussion

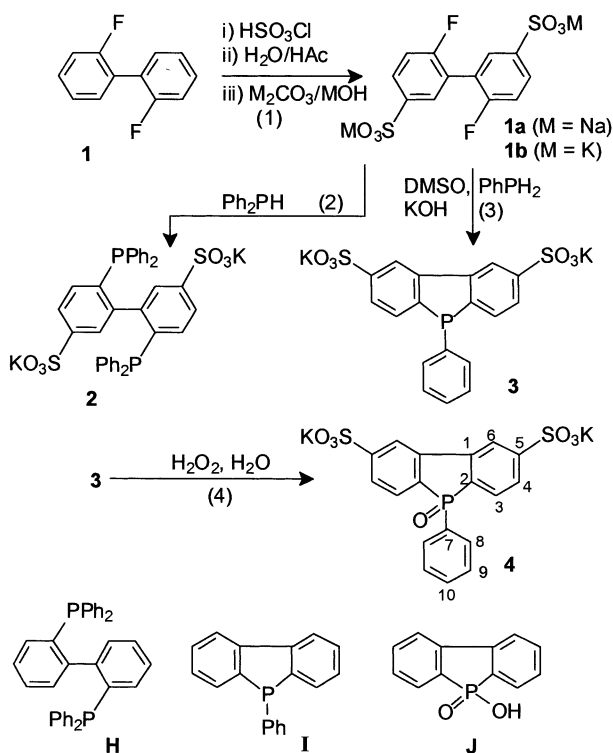
**Tertiary Water-Soluble Phospholes and Phosphines with a Biphenyl Backbone.** For the synthesis of the water-soluble sulfonated phosphines reported in this paper, disodium or dipotassium 2,2'-difluoro-1,1'-biphenyl-5,5'-disulfonate **1a** or **1b** was used as the starting material. These compounds were obtained by sulfonation of 2,2'-difluoro-1,1'-biphenyl with chlorosulfonic acid, hydrolysis of the intermediate sulfochloride, and subsequent neutralization of the sulfonic acid with sodium or potassium hydroxide or carbonate (eq 1, Scheme 1). Compounds **1a** and **1b** show a singlet at  $-111.4$  ppm in the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum. Five of the six resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum reveal higher order multiplet fine structure (X-parts of AB<sub>2</sub>X spin systems,<sup>14</sup> A = <sup>19</sup>F, X = <sup>13</sup>C); one resonance at  $\delta$ C = 141.3 ppm appears as a singlet and is assigned to carbon atom C5 bearing the sulfonic group. This assignment is supported by comparison with the pertinent <sup>13</sup>C{<sup>1</sup>H} NMR data of 2,2'-difluoro-1,1'-biphenyl and DEPT-<sup>13</sup>C{<sup>1</sup>H} NMR spectra. The attachment of the SO<sub>3</sub>M groups to C5 atoms is confirmed by the results of the X-ray structural analysis of the phosphole oxide **4** derived from **1a** (see later).

Nucleophilic phosphination of **1b** with diphenyl- or phenylphosphine in the superbasic medium DMSO/KOH affords the sulfonated phosphine **2** with a 1,1'-biphenyl backbone and the dibenzophosphole **3** in satisfying yields

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Scheme 1



(eqs 2 and 3 in Scheme 1). The neutral parent molecule **H**<sup>15</sup> of **2** has been obtained in a two-stage synthesis in ca. 50% yield using  $\text{Ph}_2\text{P}(\text{O})\text{-C}_6\text{H}_4\text{-2-I}$  as the starting material.<sup>15</sup> Attempts to synthesize **H** by treatment of 2,2'-dilithio-1,1'-biphenyl with  $\text{Ph}_2\text{PCl}$  resulted in the formation of 5-phenyldibenzophosphole (**I**).<sup>16a,b</sup> This ligand was obtained in a more simple way by ligand exchange at  $\text{Ph}_3\text{PO}$  with phenyllithium<sup>16c</sup> or by reaction of tetraphenylphosphonium bromide with lithium diethylamide.<sup>16d</sup>

In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, **2** and **3** show singlets at  $\delta\text{P} = -15.7$  ppm or  $-9.0$  ppm, respectively, the shift values of which may well be compared with those of **H** ( $\delta\text{P} = -14.1$  ppm)<sup>15</sup> or **I**<sup>16</sup> ( $\delta\text{P} = -12.7$  ppm). This is in line with our observations and those of others: introduction of a sulfonic group in *meta*- or *para*-position to phosphorus in the Ph substituents of aromatic phosphines causes no significant change in the  $\delta\text{P}$  values.<sup>17</sup> A surprisingly low field shift ( $\delta\text{P} = 17.42$  ppm)<sup>9</sup> was found for **D**, however.

Because of the axial chirality of **2**, the Ph groups of the  $\text{Ph}_2\text{P}$  substituents are inequivalent showing a doubling of the  $^{13}\text{C}\{^1\text{H}\}$  NMR resonances of the carbon atoms in *ipso*-

Table 1. Crystal Data of  $4 \cdot 2.5\text{H}_2\text{O}$ 

$\text{C}_{36}\text{H}_{32}\text{K}_4\text{O}_{19}\text{P}_2\text{S}_4$	fw: 1115.20
$a = 13.799(3)$ Å	space group: $P2_1/n$
$b = 19.246(4)$ Å	cryst syst: monoclinic
$c = 17.764(4)$ Å	$T = 293(2)$ K
$\beta = 105.63(3)^\circ$	$\lambda = 0.71073$ Å
$V = 4543(2)$ Å <sup>3</sup>	$\rho_{\text{calcd}} = 1.630$ g/cm <sup>3</sup>
$Z = 4$	$\mu = 0.722$ mm <sup>-1</sup>
$2\theta$ range: 4.24–54.38°	$F(000) = 2280$
reflins collected: 8273	cryst size: 0.75 × 0.38 × 0.30 mm
independent reflins: 7919	index ranges: $0 \leq h \leq 16$ ,
$[R(\text{int}) = 0.0509]$	$0 \leq k \leq 22$ , $-22 \leq l \leq 20$
obsd reflins ( $I = 2\sigma(I)$ ): 5472	GOF on $F^2$ : 1.046
abs correction: empirical	final $R$ indices <sup>a</sup> [ $I > 2\sigma(I)$ ]:
	$R1 = 0.0705$ , $wR2 = 0.1756$
	$R$ indices (all data):
	$R1 = 0.1088$ , $wR2 = 0.2032$
	largest diff. peak and hole:
	1.544 and $-1.319$ e Å <sup>-3</sup>

$$^a R1 = \sum(|F_o| - |F_c|)/\sum|F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}.$$

*ortho*-, and *meta*-position (C7/C7', C8/C8', C9/C9'). As expected, 10 signals are observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** showing in part  $^{13}\text{C}$ – $^{31}\text{P}$  coupling fine structure (for the numbering of the carbon atoms, see Scheme 1). They were tentatively assigned by comparison with the corresponding  $^{13}\text{C}\{^1\text{H}\}$  NMR data of 5-phenyldibenzophosphole.<sup>16a,b</sup>

The sulfonated 2,2'-bis(diphenylphosphino)-1,1'-biphenyl (**2**) and the dibenzophosphole (**3**) show a moderate solubility in water (**2**, 125 g/L; **3**, 63 g/L water at 25 °C). Compound **3** is slowly oxidized by oxygen; the oxide **4** was obtained analytically pure by treating an aqueous solution of **3** with hydrogen peroxide (eq 4 in Scheme 1). In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, **4** appears as a singlet at  $\delta\text{P} = 39.9$  ppm while for the oxide of **I** a  $\delta\text{P}$  value of 32.2 ppm was observed.<sup>16b</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of C1, C3–C6, and C8–C10 in **4** are shifted to low field on oxidation, while the resonances of C2 and C7 appear at high field compared with those in **3**. For C2 and C7, large P–C coupling constants ( $^1J(\text{C}–\text{P}) = 107.8, 106.1$  Hz) are observed (for the numbering of the carbon atoms in **3** and **4**, see Scheme 1).

#### X-ray Structure of the Sulfonated Phosphole Oxide **4**.

To obtain detailed information about the structure of the phosphole ring system in **4** and to confirm the position of the sulfonate groups, a structure determination has been performed. Crystals of composition  $4 \cdot 2.5\text{H}_2\text{O}$  suitable for X-ray structural analysis were obtained on recrystallization of **4** from a water/ethanol mixture. Compound  $4 \cdot 2.5\text{H}_2\text{O}$  crystallizes in the space group  $P2_1/n$ . The asymmetric unit contains two crystallographically different molecules of **4**, the geometrical parameters of which differ slightly; therefore, the structure of molecule 1 will only be discussed. The results are collected in Tables 1 and 2 and Figure 1. As shown by analysis of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4**, the sulfonate groups are in *para*-position to the phosphorus atom. This therefore also applies for **2** and **3** which, like **4**, are derivatives of **1b**.

The carbon atoms of the dibenzophosphole ring system are almost coplanar; the dihedral angles between the best planes through the six-membered rings C1–C6 and C7–C12 and the planar central phosphole ring are  $3.25(52)^\circ$  or  $0.37(46)^\circ$ , respectively. A similar situation is observed in

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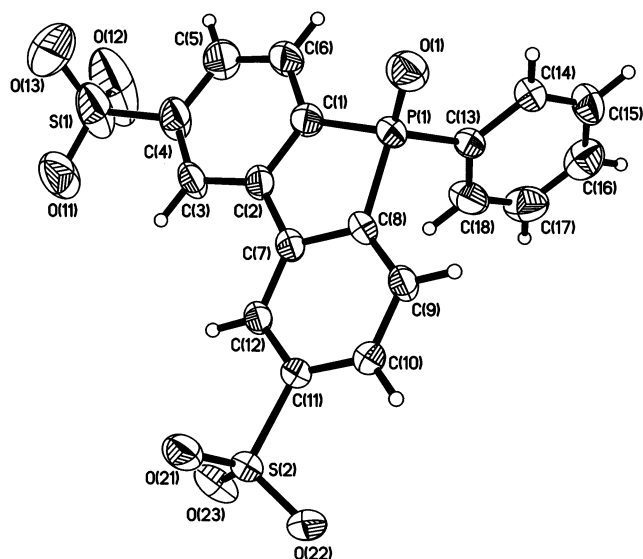


Figure 1.

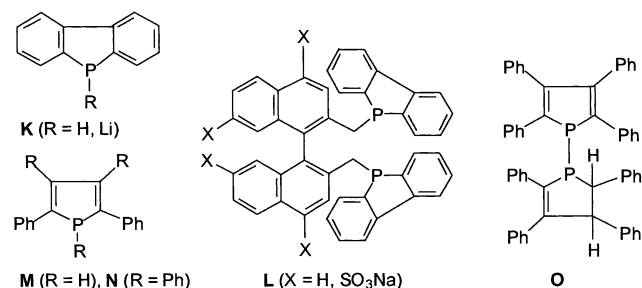
Table 2. Selected Interatomic Distances and Angles for 4·2.5H<sub>2</sub>O

Bond Lengths (Å)			
P(1)–C(1)	1.802(6)	C(7)–C(8)	1.414(7)
P(1)–C(8)	1.788(6)	S(2)–O(23)	1.441(4)
P(1)–C(13)	1.787(6)	S(2)–O(22)	1.444(4)
P(1)–O(1)	1.474(5)	S(2)–O(21)	1.448(4)
C(1)–C(2)	1.403(8)	S(2)–C(11)	1.779(5)
C(2)–C(7)	1.473(8)		
Bond Angles (deg)			
C(1)–P(1)–C(8)	92.1(3)	C(1)–C(2)–C(7)	113.2(5)
C(1)–P(1)–C(13)	109.8(3)	O(21)–S(2)–C(11)	104.3(3)
C(1)–P(1)–O(1)	116.3(3)	O(22)–S(2)–C(11)	107.0(2)
C(8)–P(1)–O(1)	118.5(3)	O(23)–S(2)–C(11)	106.2(3)
C(2)–C(1)–P(1)	110.8(4)	O(21)–S(2)–O(22)	113.0(3)
C(7)–C(8)–P(1)	110.7(5)	O(21)–S(2)–O(23)	113.1(3)
C(2)–C(7)–C(8)	113.3(5)	O(22)–S(2)–O(23)	112.5(3)

5-hydroxy-5*H*-dibenzophosphole-5 oxide (**J**).<sup>18</sup> In 5-phenyl-5*H*-dibenzophosphole (**I**),<sup>19</sup> the phosphole ring has a flat envelope conformation, with the P atom being 0.136(15) or 0.104(15) Å out of the relevant four-C-atom plane. The plane of the Ph group (C13–C18) is rotated by 82.3(2)° against the plane of the dibenzophosphole moiety. For the dibenzophosphole ring system in **4** and **J**, the P–C bond lengths are almost identical. A small intracyclic C–P–C bond angle (**4**, 92.1(3)°; **J**, 93.4(3)°) was found in both compounds. The phosphorus–oxygen distance P(1)–O(1) = 1.474(5) Å is in the range typical for tertiary phosphine oxides.<sup>20</sup>

**Synthesis of the Secondary Water-Soluble Phosphole 5 and Its Derivatives.** Alkali metal derivatives of dibenzophospholes **K**<sup>21,22</sup> (R = H, Li, Na) (see Chart 2) have been

Chart 2



employed for the synthesis of bidentate ligands with different backbones bearing terminal dibenzophosphole moieties, for example, **L**.<sup>22</sup> These ligands show a high conformational rigidity<sup>23</sup> and a pronounced P basicity<sup>24</sup> of the phosphole unit. They have been used as ligands in catalyst complexes for hydrocarboalkoxylation<sup>25a</sup> and hydroformylation.<sup>25b</sup> For the synthesis of water-soluble derivatives of these phosphine ligands, sulfonated dibenzophospholes of type **K** were of interest as building blocks. So far, there is only one report on water-soluble ligands of type **L** in the literature.<sup>22</sup>

If disodium 2,2'-difluoro-5,5'-disulfonato-1,1'-biphenyl (**1a**) is treated with NaPH<sub>2</sub> in liquid ammonia, the sodium salt **5a** of 5*H*-dibenzophosphole **5** is formed (eq 5 in Scheme 2). After removal of the solvent in vacuo, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the D<sub>2</sub>O solution of the reaction mixture shows a broad resonance at δP = 13.0 ppm which is not split into a doublet under proton coupling (<sup>31</sup>P NMR spectrum). An additional low intensity resonance is observed at δP = 33.0 ppm which corresponds to the phosphinate anion of **6b** (see later). The signal at δP = 13.0 ppm is assigned to the sodium phosphide **5a** which is in equilibrium with the phosphole **5**. The phosphole obviously shows a pronounced PH acidity due to the electron-withdrawing sulfonic groups in 5,5'-position stabilizing the anion of **5a** by delocalization of the negative charge on phosphorus (**5a'**). The assignment of the <sup>31</sup>P{<sup>1</sup>H} NMR resonance at δP = 13.0 ppm to **5a/5a'** is supported by comparison of its δP value with those of other phosphole anions,<sup>21a,c</sup> for instance, the nonsulfonated analogue of **5a** with its <sup>31</sup>P resonance at 14.3 ppm.<sup>26a</sup> As noted by Ricard, Quin, and Mathey,<sup>26a–c</sup> these phosphole anions show <sup>31</sup>P{<sup>1</sup>H} NMR resonances at much lower field compared with those of typical phosphide anions R<sub>2</sub>P<sup>–</sup>. The <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum of **5a/5a'** reveals six resonances at 134.9, 136.5, 120.2, 148.5 (*J* = 2.0 Hz), 121.4 (*J* = 11.2 Hz), and 129.8 ppm (*J* = 14.4 Hz) being split in part by <sup>31</sup>P–<sup>13</sup>C coupling.

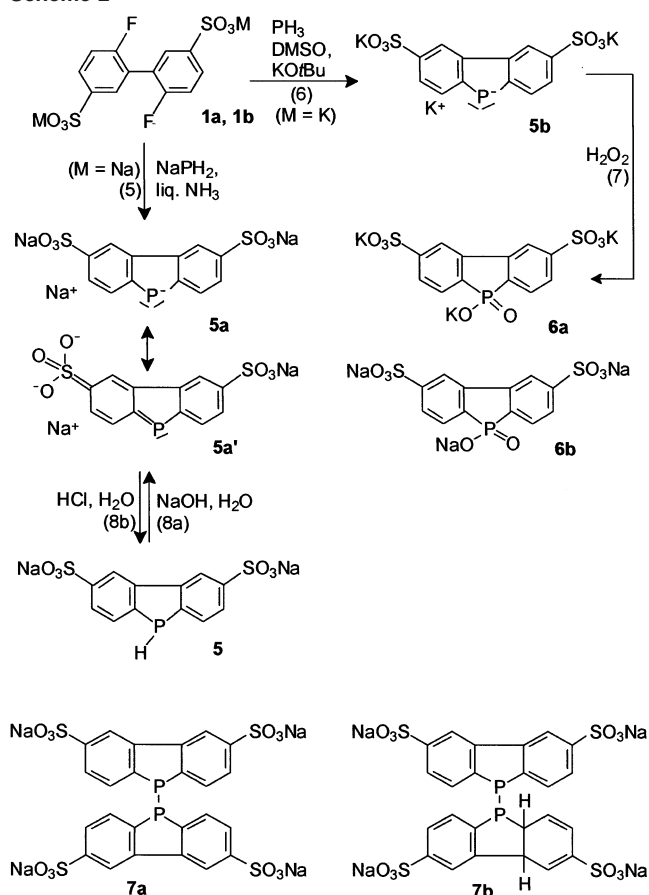
On protonation of the D<sub>2</sub>O solution of **5a/5a'** with aqueous HCl, the <sup>31</sup>P NMR spectrum shows a doublet and a 1:1:1 triplet which may be assigned to the phosphole **5** (δP = –65.7 ppm, <sup>1</sup>J(P–H) = 213.6 Hz) and its deuterium

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Scheme 2



isotopomer ( $\delta\text{P} = -66.8$  ppm,  $^1J(\text{P}-\text{D}) = 32.7$  Hz). The  $^{31}\text{P}$  NMR data of **5** may well be compared with those of 2,5-diphenylphosphole **M** ( $\delta\text{P} = -54.2$  ppm,  $^1J(\text{P}-\text{H}) = 232$  Hz)<sup>26</sup> and 2,3,4,5-tetraphenylphosphole **N** ( $\delta\text{P} = -40.9$  ppm,  $^1J(\text{P}-\text{H}) = 218$  Hz).<sup>26</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances of the anions derived from **M** or **N** appear at  $\delta\text{P} = 78.7$  or 97.0 ppm, respectively. Protonation of **5a/5a'** in aqueous solution is accompanied by formation of a side product showing a singlet  $\delta\text{P} = -21.7$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.

We tentatively assign this signal to the diphosphole **7a** possibly formed by oxidation of either the anion of **5a/5a'** or the phosphole **5**.<sup>27a</sup> A  $\delta\text{P}$  value of  $-21.5$  ppm has previously been reported for the nonsulfonated analogue of **7a**.<sup>26a</sup> The formation of the dimer **7b** of the phosphole **5a** (formed by addition of the PH bond of **5a** to its 2-isomer) is unlikely because it would require disruption of the delocalization within one of the benzene rings and can be excluded as it should give an AB-type  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The latter reaction pattern has been reported for 2,3,4,5-tetraphenylphosphole, the dimer with structure **O** being formed.<sup>27b</sup>

Reaction of **1b** with  $\text{PH}_3$  in the superbasic medium  $\text{DMSO}/\text{KO}t\text{Bu}$  (eq 6 in Scheme 2) affords considerable amounts of the oxidation product **6a** in addition to the potassium salt **5b** of the phosphole. Compounds **5b** and **6a** are assigned to the resonances at  $\delta\text{P} = 13.3$  or 32.8 ppm, respectively, in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture. Formation of **6a**, which precipitated from the reaction mixture, may be due to oxidation of **5b** by the solvent DMSO or by water

present in solution (the  $\text{KO}t\text{Bu}$  used contained 5% water). The oxidation of water-soluble phosphines and secondary phosphine oxides by aqueous alkali to the corresponding phosphine oxides or phosphinic acids with evolution of hydrogen has been reported by Lambert et al.<sup>28a</sup> and Stevens et al.<sup>28b</sup> Compound **6a** was obtained in a pure state by oxidation of the product precipitated from the reaction mixture with excess hydrogen peroxide. Because of  $^{31}\text{P}-^1\text{H}$  coupling ( $^nJ(\text{PH})$ ,  $n = 3, 4$ ), the  $^{31}\text{P}$  NMR signal of **6a** shows a fine structure which in a first-order approximation may be interpreted as an overlapping triplet of triplets of triplets. Six resonances are observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum each of which show doublet fine structure as a result of  $^{31}\text{P}-^{13}\text{C}$  coupling. Their assignment was achieved by running the  $^{13}\text{C}\{^1\text{H}\}$  NMR and  $^{13}\text{C}$ -DEPT NMR spectra at 100.6 and 62.9 MHz. Further support of the assignment comes from the comparison with the pertinent NMR data of **4**. As expected,<sup>29a</sup> a large coupling constant is obtained for the *ipso*-carbon atom ( $^1J(\text{P}-\text{C}) = 132.2$  Hz) which may be compared to the corresponding value in **4** ( $^1J(\text{P}-\text{C}) = 107.8$  Hz).

When  $\text{DMSO}/\text{KOH}$  (85%) was used instead of  $\text{DMSO}/\text{KO}t\text{Bu}$  as the base in the phosphination reaction of **1b** because of the higher concentration of water in the system, no formation of the phosphole system (**5b**) was observed. The  $^{31}\text{P}$  NMR spectrum of the reaction mixture shows an intense signal at  $\delta\text{P} = 32.3$  ppm and two very weak resonances at  $\delta\text{P} = 28.6$  and 42.7 ppm. While the signal at  $\delta\text{P} = 32.3$  ppm corresponds to the phosphinate anion of **6a**, the two weak resonances could not be assigned so far.

**Chiral Water-Soluble Phosphine Ligands with Sulfonated Dibenzophosphole Moieties.** Coupling of the sodium salt **5a** with 2,2'-bis(chloromethyl)-1,1'-biphenyl<sup>30a</sup> in DMF affords the bidentate ligand **8** containing sulfonated dibenzophosphole moieties (eq 9 in Scheme 3). The  $\delta\text{P}$  value ( $-12.4$  ppm) of **8** is comparable to that of **3** ( $-12.7$  ppm) and **L** ( $\text{X} = \text{H}$ ,  $\delta\text{P} = -9.16$  ppm;  $\text{X} = \text{SO}_3\text{Na}$ ,  $\delta\text{P} = -15.0$  ppm).<sup>22</sup> In the  $^{31}\text{P}$  NMR spectrum, only a broad singlet at  $\delta\text{P} = -12.4$  ppm is observed; no  $^{31}\text{P}-^1\text{H}$  coupling fine structure ( $^nJ(\text{P}-\text{H})$ ,  $n = 2, 3$ ) could be resolved. This is in line with the appearance of the  $^1\text{H}$  NMR spectrum of the  $\text{CH}_2$  groups as an AB quartet. The hydrogen atoms of the  $\text{CH}_2$  groups are diastereotopic because of the axial chirality of the biphenyl backbone, and therefore, they represent the AB part of an ABX spin system ( $\text{A}, \text{B} = ^1\text{H}$ ;  $\text{X} = ^{31}\text{P}$ ). Because  $^2J(\text{P}-\text{H}(\text{A}))$  and  $^2J(\text{P}-\text{H}(\text{B}))$  are small compared with the line width, only a somewhat broadened AB pattern is observed, however. The small values of  $^2J(\text{P}-\text{H}(\text{A}))$  and  $^2J(\text{P}-\text{H}(\text{B}))$  indicate that in the energetically favorable

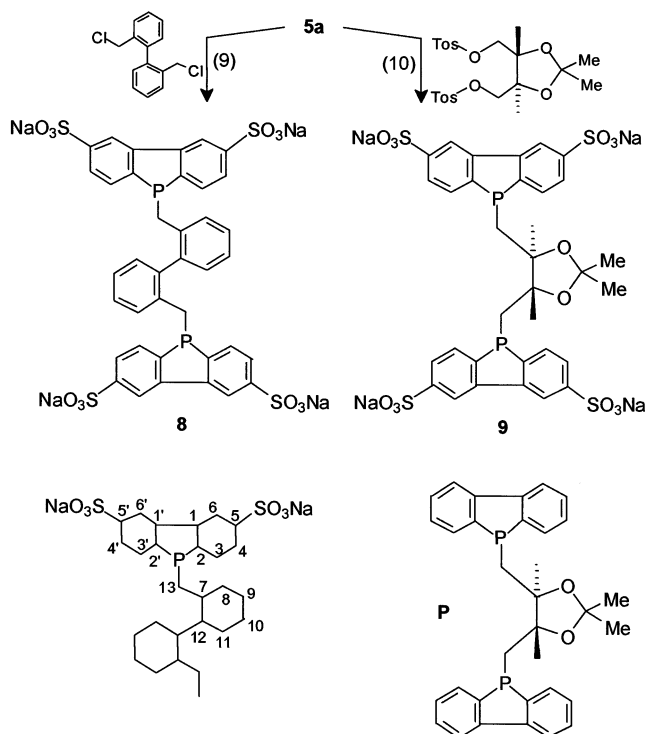
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Scheme 3



conformers of **8** with respect to the P–CH<sub>2</sub> axis the two hydrogen atoms are approximately in *anti*-position to the phosphorus lone pairs. In tertiary phosphines RR'<sub>2</sub>P–CH<sub>2</sub>–X, geminal phosphorus–proton coupling constants are small for protons in *anti*-positions to the phosphorus lone pair while they are large for protons in *syn*-position.<sup>31</sup>

As a result of the axial chirality of **8**, the two benzo groups of both dibenzophosphole substituents are inequivalent. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum therefore shows, instead of the expected 12 signals, 18 resonances in the shift range typical for aromatic carbon atoms. They were tentatively assigned by means of <sup>13</sup>C-DEPT NMR spectra as well as by comparison with the pertinent data of BISBI,<sup>32a</sup> **9** and **3** (see previous discussion; for the numbering of the carbon atoms in **8** and **9**, see Scheme 3).

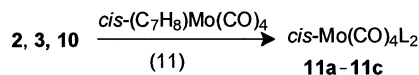
The DIOP-type<sup>32b</sup> water-soluble bidentate ligand **9** has been obtained by reaction of the sodium salt **5a** with 1,4-di-*O-p*-toluenesulfonyl-2,3-*O*-isopropylidene-*D*-threitol in dioxane or THF (eq 10 in Scheme 3). The vicinity of the chiral dioxolane bridging unit renders the carbon atoms C2, C3, and C4 of the dibenzophosphole substituent inequivalent, nine <sup>13</sup>C{<sup>1</sup>H} NMR signals being observed instead of the expected six resonances for the aromatic carbon atoms.

Water solubility has been attained for DIOP-type ligands by introducing *para*-trimethylammoniumphenyl groups instead of the unsubstituted phenyl groups.<sup>33a</sup> Neutral dibenzophospholyl derivatives, for example, **P**,<sup>33b</sup> of DIOP have

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Scheme 4



**a** (L = **2**), **b** (L = **3**), **c** (L = **10**)

PhP(C<sub>6</sub>H<sub>4</sub>-4-SO<sub>3</sub>K)<sub>2</sub> (**10**)

been employed in Rh-catalyzed hydroformylation of styrene. Replacement of the diphenylphosphino group by the dibenzophospholyl moiety increased the enantioselectivities and b/n-ratio in hydroformylation of styrene using a Pt/SnCl<sub>2</sub> catalyst.<sup>34</sup>

**Ligand Properties of the Sulfonated Phosphines 2, 3, and 10.** To obtain information on the influence of the sulfonic groups, different bridging units, and aromatic skeletons on the ligand properties, a comparative study of tetracarbonyl molybdenum(0) complexes of **2** and **3** was undertaken. For sake of comparison, Ph<sub>3</sub>P<sup>35a</sup> and the structurally related ligands (TPPTS,<sup>35b</sup> PhP(C<sub>6</sub>H<sub>4</sub>-4-SO<sub>3</sub>K)<sub>2</sub> (**10**)) have been included in these studies.

Reaction of the ligands **2**, **3**, and **10** with (bicyclo[2.2.1]-heptadiene)tetracarbonyl molybdenum(0) in a 1:10 2-propanol/water solution yields the molybdenum complexes **11a–11c** almost quantitatively as pale yellow air-stable solids (eq 11 in Scheme 4). The ν(CO)A<sub>1</sub>(1) stretching frequencies of the complexes cis-(CO)<sub>4</sub>Mo(PR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)<sub>2</sub> may be taken as a measure for the electronic donor–acceptor properties of the phosphorus ligands PR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>. The definition of the electronic parameters χ<sub>i</sub><sup>Mo</sup> of the individual substituents R<sup>i</sup> is given in eq 12, the strongly basic *t*Bu<sub>3</sub>P being used as the standard.<sup>36</sup> Because molybdenum carbonyl complexes cis-(CO)<sub>4</sub>Mo(PR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>)<sub>2</sub> are much more accessible than the corresponding nickel carbonyl complexes, it is more convenient to use the electronic parameters χ<sub>i</sub><sup>Mo</sup> as derived by us instead of the corresponding values χ<sub>i</sub><sup>Ni</sup> derived by Tolman<sup>37</sup> from (CO)<sub>3</sub>Ni(PR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>) complexes. Both sets of χ<sub>i</sub> values correlate very well, the correlation coefficient *R* being 0.9943.<sup>38</sup>

$$\nu(\text{CO})A_1(1) = 2005 + \sum_{i=1}^3 \chi_i^{\text{Mo}} \quad (12)$$

The electronic parameters Σχ<sub>i</sub><sup>Mo</sup> obtained for **11a–11c** are collected in Table 3, including the data for the corresponding complexes of Ph<sub>3</sub>P and TPPTS. Obviously, the Σχ<sub>i</sub><sup>Mo</sup> values do not differ significantly. This is also true for the coordination chemical shifts of the <sup>31</sup>P resonances and the coupling

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**Table 3.**  $\nu(\text{CO})$  Carbonyl Stretching Frequencies ( $\text{cm}^{-1}$ ),  $\Sigma\chi_i^{\text{Mo}}$  Parameters, and Coordination Chemical Shift Values  $\Delta\delta\text{P}^d$  for the Complexes *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> **11a–11c** for L = **2**, **3**, **10**, Ph<sub>3</sub>P, TPPTS

L	A <sub>1</sub> (2)	A <sub>1</sub> (1)	B <sub>1</sub>	B <sub>2</sub>	$\Sigma\chi_i^{\text{Mo}}$	$\Delta\delta\text{P}^d$	${}^2J(\text{PP})^e$
<b>2</b>	2021 <sup>a</sup>	1928	1907	1907	16	47.8 <sup>f</sup>	18
<b>3</b>	2016 <sup>a</sup>	1918	1901	1886	13	47.2 <sup>g</sup>	19
<b>10</b>	2021 <sup>a</sup>	1921	1908	1887	16	45.4 <sup>g</sup>	
Ph <sub>3</sub> P	2023 <sup>b</sup>	1929	1911	1899 <sup>35a</sup>	18		
TPPTS	2025 <sup>a</sup>	1931	1914	1898 <sup>35b</sup>	20		
	2023 <sup>c</sup>	1911	1909	1859 <sup>35b</sup>	18		

<sup>a</sup> 2-Methoxyethanol. <sup>b</sup> *n*-Hexane. <sup>c</sup> CH<sub>3</sub>CN, [Na-kryptofix-221]<sub>6</sub>[*cis*-(CO)<sub>2</sub>Mo{P(C<sub>6</sub>H<sub>4</sub>-*m*-SO<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]. <sup>d</sup>  $\Delta\delta\text{P} = \delta\text{P}_{\text{complex}} - \delta\text{P}_{\text{ligand}}$ . <sup>e</sup> In hertz, determined from the CO-<sup>13</sup>C{<sup>1</sup>H} NMR spectra (X parts of ABX spectra). <sup>f</sup> H<sub>2</sub>O/*d*<sub>6</sub>-acetone. <sup>g</sup> D<sub>2</sub>O/2-propanol.

constants  ${}^2J(\text{PP})$ . These results suggest that the donor properties of the ligands are not greatly changed by introduction of the sulfonic groups into the skeletons. Compared with  $\nu(\text{CO})\text{A}_1(1)$  (2021  $\text{cm}^{-1}$ ) obtained for **11c** (ligand L = **10**), the complex of the dibenzophosphole **3** shows a significantly lower value (2016  $\text{cm}^{-1}$ ) indicating a greater  $\sigma$ -donor capability for this ligand. Complete characterization of chromium, molybdenum, and tungsten carbonyl complexes of phenyldibenzophosphole has been reported.<sup>39</sup>

## Experimental Section

**Physical Measurements and General Procedures.** <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F{<sup>1</sup>H} NMR spectra were recorded on a Bruker AC 250 and Bruker ARX 400 at 250.0, 62.9, and 100.6 MHz or 400.1, 100.6, 160.0, and 376.5 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported relative to tetramethylsilane; for <sup>31</sup>P{<sup>1</sup>H} NMR spectra, external phosphoric acid was used as the reference, while for <sup>19</sup>F{<sup>1</sup>H} NMR spectra CCl<sub>3</sub>F was employed as reference. Mass spectra were run on a Varian MAT 311 A. Air-sensitive materials were manipulated in an inert gas atmosphere using Schlenk techniques. Solvents were purified using standard methods.<sup>40</sup>

**Materials.** DMSO was purchased from Aldrich Chemicals, 2,2'-difluoro-1,1'-biphenyl, from Fluorochem. Ph<sub>3</sub> was donated by Messer Griesheim. Ph<sub>2</sub>PH, <sup>41a</sup> PhPH<sub>2</sub>, <sup>41b</sup> and C<sub>7</sub>H<sub>8</sub>Mo(CO)<sub>4</sub><sup>42</sup> were prepared according to literature methods. 2,2'-Bis(chloromethyl)-1,1'-biphenyl<sup>30a</sup> was obtained by Cl/Br exchange of 2,2'-bis-(bromomethyl)-1,1'-biphenyl<sup>30b</sup> using LiCl in DMF.

**Syntheses. 5,5'-Bis(sulfonato)-2,2-difluoro-1,1'-biphenyl Disodium Salt (1a) and Dipotassium Salt (1b).** A solution of 10.0 g (53.0 mmol) of 2,2-difluoro-1,1'-biphenyl in 60 mL of chloroform was added to 21 mL (320 mmol) of chlorosulfonic acid at 25 °C within 1 h. After the evolution of HCl ceased, the reaction mixture was stirred for 2 h at ambient temperature. Thereafter, the reaction mixture was poured onto 30 g of ice. The organic phase was separated, and the aqueous phase was extracted with three aliquots of 50 mL of chloroform. The combined organic phases were washed with 30 mL of a saturated NaHCO<sub>3</sub> solution. After removal of the solvent in vacuo, the remaining residue was recrystallized from ethyl acetate. Yield: 11.7 g (57%) 5,5'-bis(chlorosulfonyl)-2,2-difluoro-1,1'-biphenyl.

A 19.5 g (50.4 mmol) portion of 5,5'-bis(chlorosulfonyl)-2,2-difluoro-1,1'-biphenyl was dissolved in 50 mL of water, the solution was heated to reflux, and 80 mL of acetic acid was added at this temperature. After the reaction mixture was heated for 2 h, all volatiles were removed in vacuo. Yield: 17.5 g (99%) 2,2-difluoro-1,1'-biphenyl-5,5'-bis(sulfonic acid).

Neutralization of a solution of 5.6 g (16.0 mmol) or 17.5 g (50.0 mmol) of 2,2-difluoro-1,1'-biphenyl-5,5'-bis(sulfonic acid) in 7.0 or 50 mL of water with dilute NaOH solution or solid KOH (85%, 1.8 g, 32.0 mmol) gave, after evaporation of the solvent in vacuo, 5,5'-bis(sulfonato)-2,2-difluoro-1,1'-biphenyl disodium (**1a**) or 5,5'-bis(sulfonato)-2,2-difluoro-1,1'-biphenyl dipotassium (**1b**) as colorless crystalline powders. Yields: 6.58 g (98%) **1a**, 18.5 g (87%) **1b**. For a further purification, **1b** was recrystallized from a 1:2 water/ethanol mixture.

Anal. Calcd for C<sub>12</sub>H<sub>6</sub>F<sub>2</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O (*M*<sub>r</sub> = 412.3) (**1a**): C, 34.96; H, 1.96. Found: C, 34.86; H, 1.81. <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  7.30–8.00 (arom, 6 H). <sup>19</sup>F NMR (D<sub>2</sub>O):  $\delta$  -111.4 (m). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O):  $\delta$  (C1–C6) 124.8 ( ${}^2J(\text{CF}) = 10.2$ ,  ${}^3J(\text{CF}) = 6.1$  Hz), 163.2 ( ${}^1J(\text{CF}) = 253.3$ ,  ${}^4J(\text{CF}) = 2.0$  Hz), 131.5 (m, *N*(CF) = 5.3 Hz), 130.6 (m, *N*(CF) = 9.2 Hz), 141.3, 118.8 ( ${}^3J(\text{CF}) = 26.0$ ,  ${}^4J(\text{CF}) = 2.3$  Hz,  ${}^5J(\text{FF}) = 23.7$  Hz). Anal. Calcd for C<sub>12</sub>H<sub>6</sub>F<sub>2</sub>K<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (*M*<sub>r</sub> = 426.5) (**1b**): C, 33.79; H, 1.42. Found: C, 33.29; H, 2.01. <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  7.39–7.99 (arom, 6 H). <sup>19</sup>F NMR (D<sub>2</sub>O):  $\delta$  01.5 (m). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O):  $\delta$  (C1–C6) 125.0 ( ${}^2J(\text{CF}) = 10.2$ ,  ${}^3J(\text{CF}) = 6.1$  Hz), 163.7 ( ${}^1J(\text{CF}) = 253.6$ ,  ${}^4J(\text{CF}) = 1.8$  Hz), 132.0 (m, *N*(CF) = 5.4 Hz), 131.2 (m, *N*(CF) = 9.6 Hz), 141.9, 119.4 ( ${}^3J(\text{CF}) = 26.2$ ,  ${}^4J(\text{CF}) = 2.5$ ,  ${}^5J(\text{FF}) = 24.0$  Hz).

**5,5'-Bis(sulfonato)-2,2'-bis(diphenylphosphino)-1,1'-biphenyl Dipotassium Salt (2).** The solution of 7.90 g (42.2 mmol) of diphenylphosphine in 60 mL of DMSO was charged with 2.4 g (42.2 mmol) of KOH powder (85%). After the red solution was stirred for 1 h, 12.0 g (28.1 mmol) of finely powdered **1b** was added, and the reaction mixture was heated to 50–60 °C for 12 h. Thereafter, 100 mL of 2-propanol was added dropwise until **2** was precipitated completely from the reaction mixture. The precipitate was filtered off, washed with three aliquots of 50 mL of methanol, and dried in vacuo. For a further purification, **2** was recrystallized from a minimum of water. Yield: 9.7 g (43%). Anal. Calcd for C<sub>36</sub>H<sub>26</sub>K<sub>2</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>·2H<sub>2</sub>O (*M*<sub>r</sub> = 794.9): C, 54.40; H, 3.80. Found: C, 54.78; H, 3.85. <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>6</sub>-DMSO):  $\delta$  (C1–C10) 147.0 (t, *N* = 48.7 Hz), 137.4 (t, *N* = 13.2 Hz), 133.6, 127.6 (t, *N* = 9.2 Hz), 148.2, 125.2, 136.6 (t, *N* = 11.2 Hz), 136.4 (t, *N* = 10.2 Hz), 133.0 (t, *N* = 19.3 Hz), 132.9 (t, *N* = 20.3 Hz), 128.3, 128.2, 128.5. <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>6</sub>-DMSO):  $\delta$  -15.7.

**5-Phenyl-2,2'-bis(sulfonato)-5H-dibenzophosphole Dipotassium Salt (3).** This compound was obtained in an analogous way as **2** using 2.6 g (23.5 mmol) of phenylphosphine, 10.0 g (23.5 mmol) of **1b**, and 2.90 g (51.7 mmol) of KOH in 60 mL of DMSO. Yield: 7.1 g (60%), colorless solid. Anal. Calcd for C<sub>18</sub>H<sub>11</sub>K<sub>2</sub>O<sub>6</sub>PS<sub>2</sub> (*M*<sub>r</sub> = 496.6): C, 43.54; H, 2.23. Found: C, 43.48; H, 2.30. <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O):  $\delta$  (C1–C10) 142.8 (*J* = 4.1 Hz), 142.6 (*J* = 3.0 Hz), 130.4 (*J* = 22.4 Hz), 125.6 (*J* = 7.1 Hz), 148.5, 119.2, 135.2 (*J* = 19.3 Hz), 131.9 (*J* = 19.3 Hz), 129.1 (*J* = 8.1 Hz), 129.6.

**5-Phenyl-2,2'-bis(sulfonato)-5H-dibenzophosphole-5-oxide Dipotassium Salt (4).** To 0.35 g (0.70 mmol) of **3**, dissolved in 10 mL of water, was added 0.5 mL of a 3% solution of H<sub>2</sub>O<sub>2</sub> (1.10 mmol). After the mixture was stirred for 2 h, all volatiles were removed in vacuo. The remaining solid was dissolved in methanol and precipitated by addition of 2-propanol. The residue was filtered off and dried in vacuo. Yield: 0.35 g (92%). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>K<sub>2</sub>O<sub>7</sub>PS<sub>2</sub>·3H<sub>2</sub>O (*M*<sub>r</sub> = 566.6): C, 38.16; H, 3.02. Found:

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C, 38.21; H, 2.73.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  (C1–C10) 144.0 ( $J = 23.4$  Hz), 135.3 ( $J = 107.8$  Hz), 132.8 ( $J = 10.2$  Hz), 129.7 ( $J = 12.2$  Hz), 150.5 ( $J = 3.0$  Hz), 121.8 ( $J = 10.2$  Hz), 128.7 ( $J = 106.1$  Hz), 133.0 ( $J = 11.2$  Hz), 131.7 ( $J = 13.2$  Hz), 136.1 ( $J = 3.0$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  39.0.

The prismatic crystals used for the X-ray structural analysis were obtained by slow oxidation of an ethanol/water solution of **3** on contact with air.

**5-Phenyl-2,2'-bis(sulfonato)-5H-dibenzophosphole-5-oxide Tripotassium Salt (6a).** The solution of 2.2 g (19.6 mmol) of  $\text{KOtBu}$  in 50 mL of DMSO was saturated at 20 °C with  $\text{PH}_3$  under a pressure of 0.1 bar. To the yellow solution was added 4.0 g (9.4 mmol) of **1b**, dissolved in 20 mL of DMSO. The pressure in the reaction flask was kept constant by addition of further  $\text{PH}_3$ . The yellow-orange precipitate was collected on a glass fritted funnel under nitrogen, washed with 2-propanol, and dried in vacuo. Thereafter, it was dissolved in 50 mL of water, and hydrogen peroxide (30%) was added until the color of the solution disappeared. All volatiles were removed in vacuo (20–50 °C, 0.01 mbar). Yield: 1.9 g (41%), colorless powder. Anal. Calcd for  $\text{C}_{12}\text{H}_6\text{K}_3\text{O}_8\text{P}_2\text{S}_2\cdot 4\text{H}_2\text{O}$  ( $M_r = 562.6$ ): C, 25.62; H, 2.51; P, 5.51. Found: C, 25.04; H, 1.71; P, 4.90.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  (C1–C6) 141.0 ( $J = 26.5$  Hz), 139.7 ( $J = 132.2$  Hz), 129.7 ( $J = 9.2$  Hz), 128.9 ( $J = 12.2$  Hz), 148.4 ( $J = 2.0$  Hz), 120.7 ( $J = 11.2$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  33.1.

**Bis-[2,2'-bis(sulfonato)-5H-dibenzophospholyl)methyl]-1,1'-biphenyl Tetrasodium Salt (8).** A solution of 0.73 g (31.8 mmol) of sodium in 100 mL of liquid ammonia was saturated with  $\text{PH}_3$  under a pressure of 0.1 bar until the original blue color changed to yellow. To release the hydrogen formed, the system was depressurized from time to time. Thereafter, the ammonia was evaporated, and the remaining yellowish residue was dissolved in 25 mL of DMF. To this solution, 4.2 g (10.6 mmol) of **1a** dissolved in 25 mL of DMF was added. The suspension was stirred for 12 h and charged with a solution of 1.35 g (5.4 mmol) of 2,2'-bis(chloromethyl)-1,1'-biphenyl in 20 mL of DMF. After stirring for 12 h at ambient temperature, the reaction mixture was heated for 1 h at 80 °C. The solvent was distilled off in vacuo, and the remaining residue was dried at 100 °C in vacuo. Then, 50 mL of water was added, and the aqueous phase was extracted with 50 mL of dichloromethane. The aqueous phase was separated, concentrated in vacuo to 10 mL, and charged with 10 mL of ethanol. The precipitate formed was filtered off and dried in vacuo. Yield: 5.2 g (94%). Anal. Calcd for  $\text{C}_{38}\text{H}_{24}\text{Na}_4\text{O}_{12}\text{P}_2\text{S}_4\cdot 4\text{H}_2\text{O}$  ( $M_r = 1026.8$ ): C, 44.45; H, 3.14. Found: C, 44.15; H, 3.06.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  6.5–8.3, 2.47 ( $J(\text{HH}) = 12.6$  Hz,  $\text{CH}_2$ ), 2.83 ( $J(\text{HH}) = 12.6$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  (C1–C12) 144.8, 145.0, 148.2 ( $J = 10.2$  Hz), 147.9 ( $J = 10.2$  Hz), 132.7 ( $J = 7.9$  Hz), 132.5 ( $J = 7.1$  Hz), 126.9 ( $J = 7.9$  Hz), 126.8 ( $J = 7.4$  Hz), 145.84, 145.76, 121.01, 121.97, 136.6, 132.1 ( $J = 5.8$  Hz), 128.7, 129.9, 132.8, 142.0 ( $J = 2.8$  Hz), 36.1 ( $J = 22.6$  Hz,  $\text{CH}_2$ ).

**Bis-[2,2'-bis(sulfonato)-5H-dibenzophospholyl]-2,3-O-isopropylidene-D-threitol Tetrasodium Salt (9).** A solution of 0.88 g (38.3 mmol) of sodium in 200 mL of liquid ammonia was saturated with  $\text{PH}_3$  under a pressure of 0.1 bar until the original blue color changed to yellow. To release the hydrogen formed, the system was depressurized from time to time. Thereafter, the ammonia was evaporated, and the remaining yellowish residue was dissolved in 25 mL of DMF. To this solution, 5.1 g (12.7 mmol) of **1a** dissolved in 20 mL of DMF was added. The suspension was stirred for 12 h and charged with 2.81 g (6.0 mmol) of 1,4-di-O-*p*-toluenesulfonyl-2,3-O-isopropylidene-D-threitol. After stirring for 3 days at ambient temperature, the solvent was distilled off, and the remaining residue

was suspended in 15 mL of water. Fractional precipitation with *i*-propanol leads to **9**. The precipitate formed was filtered off and dried in vacuo. Yield: 1.05 g (20%). Anal. Calcd for  $\text{C}_{31}\text{H}_{24}\text{Na}_4\text{O}_{14}\text{P}_2\text{S}_4\cdot \text{H}_2\text{O}$  ( $M_r = 920.7$ ): C, 40.44; H, 2.85. Found: C, 39.96; H, 2.74.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  8.42–8.36, 7.65–7.82, 3.78 (m, CH), 1.85 ( $J(\text{HH}) = 4.1$  Hz,  $\text{CH}_2$ ), 1.25 ( $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  (C1–C6) 145.0, 148.4 ( $J = 11.2$  Hz), 148.3 ( $J = 9.2$  Hz), 133.2 ( $J = 21.4$  Hz), 133.0 ( $J = 20.4$  Hz), 127.2 ( $J = 8.1$  Hz), 127.1 ( $J = 8.3$  Hz), 145.8, 121.2, 112.0 ( $\text{CMe}_2$ ), 80.8 ( $J = 7.6$  Hz, CH), 32.9 ( $J = 21.4$  Hz,  $\text{CH}_2$ ), 28.7 ( $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  –19.7.  $[\alpha]^{20}_{\text{D}} + 6.44$  ( $c$  0.45,  $\text{H}_2\text{O}$ ).

**cis-Tetracarbonyl(5,5'-bis(sulfonato)-2,2'-bis(diphenylphosphino)-1,1-biphenyl)molybdenum(0) Dipotassium Salt (11a).** A 250 mg (0.33 mmol) portion of **2** was added to a 20 mL aqueous suspension of 100 mg (0.33 mmol) of tetracarbonyl(bicyclo[2.2.1]-hepta-2,5-dien)molybdenum(0). The mixture was stirred for 24 h at room temperature, affording a viscous yellow solution, whose  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum still indicated the presence of free ligand. After addition of 2 mL of 2-propanol, 24 h of stirring led to completion of the reaction.

After the solids were centrifuged, the volatiles were removed in vacuo, and the resulting yellow product was washed with dichloromethane and diethyl ether. Yield: 274 mg (80%). Anal. Calcd for  $\text{C}_{40}\text{H}_{26}\text{K}_2\text{MoO}_{10}\text{P}_2\text{S}_2\cdot 4\text{H}_2\text{O}$  ( $M_r = 1038.93$ ): C, 46.24; H, 3.30. Found: C, 45.68; H, 3.85.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_6$ -acetone/ $\text{D}_2\text{O}$ ):  $\delta$  (C1–C10) 144.2 (q,  $N = 14.2$  Hz), 140.0 (q,  $N = 29.5$  Hz,  $^1J(\text{PC}) = 32$  Hz,  $^3J(\text{PC}) = -2$  Hz,  $^2J(\text{PP}) = 18$  Hz), 132.9, 131.7, 145.6, 125.1, 136.1/131.9 (q,  $N = 39.8$  Hz,  $^1J(\text{PC}) = 37$  Hz,  $^3J(\text{PC}) = 3$  Hz,  $^2J(\text{PP}) = 18$  Hz/ $N = 35$  Hz), 135.2/134.7 (q,  $N = 13.4$  Hz/q,  $N = 19.1$  Hz), 129.4/129.2 (t,  $N = 9.5$  Hz/t,  $N = 8.6$  Hz), 131.2;  $\delta(\text{CO})$  212.2 (t,  $^2J(\text{PC}) = 9.2$  Hz), 216.8 (q,  $N = 16.2$  Hz,  $^2J(\text{PC trans}) = 26$  Hz,  $^2J(\text{PC cis}) = -10$  Hz,  $^2J(\text{PP}) = 17$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_6$ -acetone/ $\text{D}_2\text{O}$ ):  $\delta$  36.9(s).

**cis-Tetracarbonyl-bis(5-phenyl-2,2'-bis(sulfonato)-5H-dibenzophosphole)molybdenum(0) Tetrapotassium Salt (11b).** Compound **11b** was prepared in an analogous manner to **11a** using 328 mg (0.66 mmol) of **3**. Yield of **11b**: 368 mg (85%) yellow solid. Anal. Calcd for  $\text{C}_{40}\text{H}_{22}\text{K}_4\text{MoO}_{16}\text{P}_2\text{S}_4\cdot 6\text{H}_2\text{O}$  ( $M_r = 1309.26$ ): C, 36.69; H, 2.61. Found: C, 36.41; H, 2.44.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}/2$ -propanol):  $\delta$  (C1–C10) 143.3 (t,  $N = 6.11$  Hz), 144.4 (q,  $N = 37.6$  Hz,  $^1J(\text{PC}) = 38$  Hz,  $^3J(\text{PC}) = 0$  Hz,  $^2J(\text{PP}) = 19$  Hz), 132.3 (t,  $N = 12.2$  Hz), 128.4 (t,  $N = 9.2$  Hz), 147.3, 121.7, 136.1 (q,  $N = 35.6$  Hz,  $^1J(\text{PC}) = 35$  Hz,  $^3J(\text{PC}) = 2$  Hz,  $^2J(\text{PP}) = 19$  Hz), 132.9 (q,  $N = 16.3$  Hz), 131.2 (t,  $N = 10.2$  Hz), 132.4;  $\delta(\text{CO})$  211.2 ( $^2J(\text{CP}) = 9.2$  Hz), 215.4 (q,  $N = 24.4$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}/2$ -propanol): 7.0–8.5(m).

**cis-Tetracarbonyl-bis(phenyl-bis(4,4'-sulfonatophenyl)phosphine)molybdenum(0) Tetrapotassium Salt (11c).** Compound **11c** was prepared in an analogous manner to **11a** using 309 mg (0.66 mmol) of  $\text{PhP}(\text{C}_6\text{H}_4\text{-4-SO}_3\text{K})_2$ , **10**. Yield of **11c**: 445 mg (82%) as a yellow solid. Anal. Calcd for  $\text{C}_{40}\text{H}_{26}\text{K}_4\text{MoO}_{16}\text{P}_2\text{S}_4\cdot 6\text{H}_2\text{O}$  ( $M_r = 1349.32$ ): C, 35.61; H, 3.13. Found: C, 34.65; H, 2.53.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}/2$ -propanol):  $\delta$  (C1–C8) 139.5 (q,  $N = 36.1$  Hz), 134.7 (t,  $N = 13.8$  Hz), 126.9 (t,  $N = 11.3$  Hz), 144.6, 135.3 (q,  $N = 35.8$  Hz), 135.0 (t,  $N = 11.7$  Hz), 131.5.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}/2$ -propanol): 7.3–7.8(m).

**X-ray Crystallography.** Diffraction data for  $\mathbf{4}\cdot 2.5\text{H}_2\text{O}$  were collected at 293 K on a Siemens P4 four-circle diffractometer in the  $\omega$  scan mode using graphite-monochromated  $\text{Mo K}\alpha$  radiation. The experimental data are collected in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$  using the SHELX-93 program.<sup>43</sup> H atoms of the aromatic rings are included in geometrically calculated positions (riding



model, C–H = 0.93 Å). One of the potassium cations [K(4)] is disordered with site occupation factors (sof's) of 0.75 and 0.25 for the two different sites. The water oxygen atom O(6) participates in this disorder and could only be located at the preferred site with an sof of 0.75. As a result of this static disorder and the torsional motion of the sulfonyl oxygens O(11)–O(13) about S(1)–C(4) in the first molecule of 4·2.5 H<sub>2</sub>O, the final *R* factors of, respectively, *R*1 = 0.109 and *wR*2 = 0.207 for all data are relatively high.

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**Supporting Information Available:** X-ray crystallographic file in CIF format for compound 4·2.5H<sub>2</sub>O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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