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Structures of Dibenzocycloheptenylidene- and Fluorenylidene-(2,4,6-tri-*t*-butylphenyl)phosphines and Their Reactions with Sulfur

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ABSTRACT

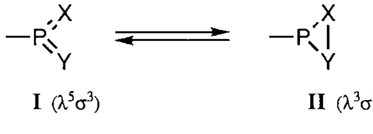
Dibenzocycloheptenylidene(2,4,6-tri-t-butylphenyl)-phosphine and fluorenylidene(2,4,6-tri-t-butylphenyl)-phosphine were prepared by the reactions of lithium silylphosphide with benzosuberenone and fluorenone, respectively. The reactions of the phosphines with sulfur were carried out to compare the results with those of the corresponding diphenyl derivative, and the new findings are discussed in terms of steric hindrance based on the results of the X-ray crystallographic analyses for dibenzocycloheptenylidenephosphine and its sulfide and the computational structure for the fluorenyl derivative. © 1997 John Wiley & Sons, Inc. Hereroatom Chem **8***: 375–382, 1997*

INTRODUCTION

Valence isomerization between low coordinated $\lambda^5\sigma^3$ phosphoranes (**I**) and $\lambda^3\sigma^3$ phosphiranes (**II**) have been of interest [1]. A sterically protected bis(2,4,6-tri-*t*-butylphenyl)diphosphene [2] was found to react with sulfur to give the corresponding diphosphene *P*-sulfide [3], which isomerized to the thiadiphosphirane by the action of heat or light [4] (Scheme 1).

Recently, we reported on the isomerization of a sterically protected (diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)phosphine *P*-sulfide (**2a**) to 3,3-diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane (**4a**) as shown in Scheme 2 [5]. We have also reported the X-ray structures of the two valence isomers, **2a** and **4a**, as well as the structure of the starting methylenephosphine **1a**, with discussion of the valence isomerism in terms of temperature dependence [5].

During this study, we noticed that the type of substituents on the thiaphosphirane *P*-sulfide **3a** might affect the course of the desulfurization reac-



SCHEME 1

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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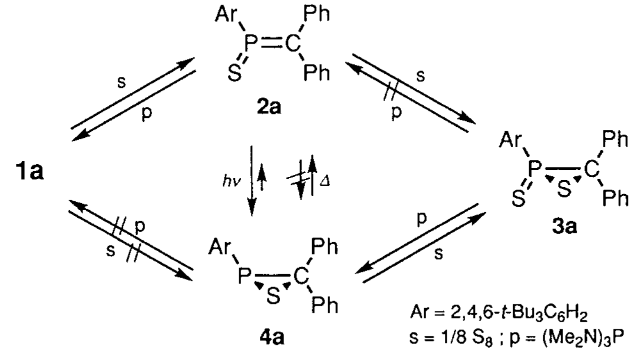


SCHEME 2

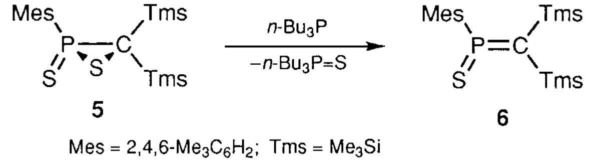
tion. Thus, 3,3-diphenyl-2-(2,4,6-tri-*t*-butylphenyl) derivative **3a** was desulfurized with tris(dimethylamino)phosphine (HMPT) to give thiaphosphirane **4a,** whereas Caira et al. reported that the desulfurization reaction of 2-mesityl-3,3-bis(trimethylsilyl)-1,2-thiaphosphirane (**5**) with tributylphosphine afforded the methylenephosphine *P*-sulfide **6** [6] (Scheme 3). These facts suggest that a restricted conformation about the diphenylmethylene moiety might affect the preference of formation of **2** or **4.**

We report here on the reaction of sulfur with conformationally restricted analogs of **1a**; viz., with the ethylene-bridged derivative, 5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene(2,4,6-tri-*t*-butylphenyl)phosphine (**1b**), and with the directly bound derivative, 9*H*-fluoren-9-ylidene(2,4,6-tri-*t*-butylphenyl)phosphine (**1c**) [7] (Formula 1).

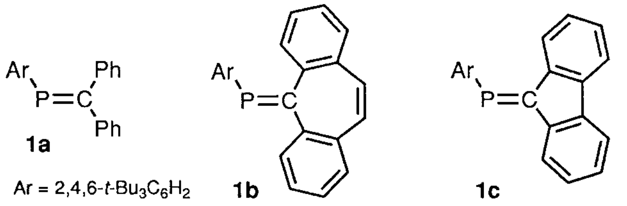
RESULTS AND DISCUSSION

5*H*-Dibenzo[*a,d*]cyclohepten-5-ylidene(2,4,6-tri-*t*-butylphenyl)phosphine (**1b**) was prepared by the phospha-Peterson reaction [8]. Thus, lithium (2,4,6-tri-*t*-butylphenyl(trimethylsilyl)phosphide (**7**) was allowed to react with 5*H*-dibenzo[*a,d*]cyclohepten-5-one (dibenzosuberenone) to give **1b** in 26% yield (Scheme 4).

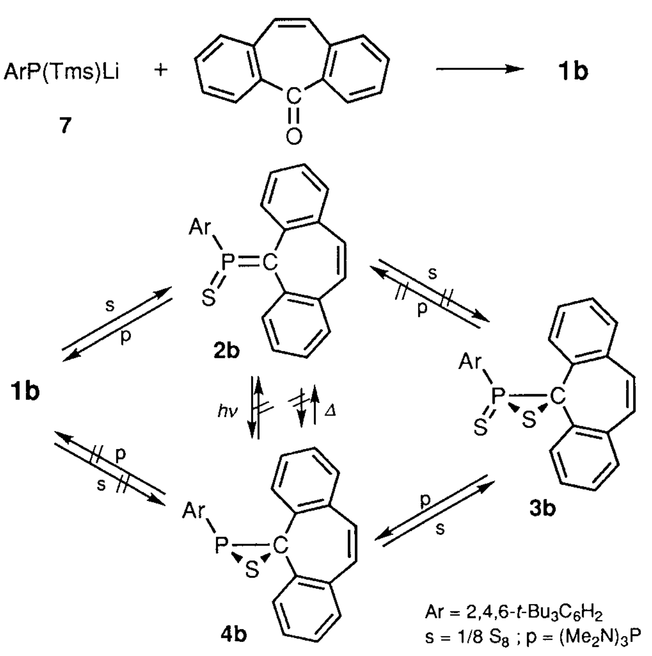
The compound **1b** thus obtained was then allowed to react with elemental sulfur (1 equiv.) in benzene at room temperature for 24 hours in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the corresponding methylenephosphine *P*-sulfide **2b** in 70% yield. The compound **2b** was obtained in better yields by reactions with excess of sulfur at room temperature (with 10 equiv. S, 91% yield) or at higher temperature (with 3 equiv. S, at 55°C, 96% yield). When **2b** was allowed to react with tris(dimethylamino)phosphine, the desulfurization reaction of **2b** occurred, and **1b** was obtained in 67% yield.



SCHEME 3



FORMULA 1



SCHEME 4

The structures of the methylenephosphine **1b** and its *P*-sulfide **2b** were confirmed by X-ray crystallography. Figure 1 shows an ORTEP [9] drawing of **1b.** The atoms P1, C1, C2, C15, and C16 of **1b** are almost planar within 0.05 Å, and the mean plane of the bulky Ar group forms an angle of 102.5° with this plane. The four atoms [C2, C7, C10, and C15] of the seven-membered ring are coplanar within 0.005 Å. The dihedral angle between the planes [C1, C2, and C15] and [C2, C7, C10, and C15] is 130.8° (α) and that of the planes [C7, C8, C9, and C10] and [C2, C7,

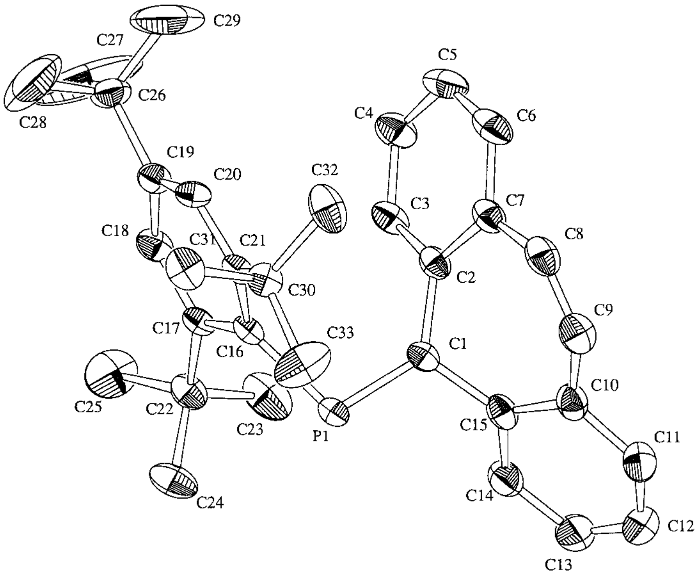


FIGURE 1 Molecular structure for **1b** with atom labeling scheme.

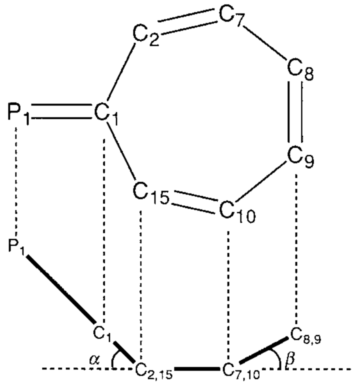


FIGURE 2 Side profile of the structures of **1b** and **2b** and definition of the angles *α* and *β*, indicating a boat-like cycloheptatriene framework.

C10, and C15] is 23.8° (*β*), indicating that the seven-membered ring is not planar but boat-shaped, as shown in Figure 2. The two phenyl rings attached to the seven-membered ring make a dihedral angle of 134.6°.

As for **2b,** the molecular structure is very similar to that of **1b,** as shown in Figure 3. The atoms P1, C1, C2, C15, C16, and S1 are almost planar within 0.04 Å, and the mean plane of the bulky Ar group forms an angle of 100.3° with this plane. The four atoms [C2, C7, C10, and C15] of the seven-membered ring are coplanar within 0.009 Å. The dihedral angles are 129.6° and 25.1° for *α* and *β* as defined in Figure 2, indicating that the seven-membered ring takes a boat form. The two phenyl rings attached to the seven-membered ring are inclined toward each other with a dihedral angle of 48.8°, whereas those for dibenzosuberenone itself are reported to form an angle of 39° [10]. Some important bond lengths and bond angles for **1b** and **2b** are listed in Tables 1 and 2, respectively.

It should be noted that **1b** resisted further sulfurization to **3b** even in the presence of an excess amount of sulfur. In fact, the product **2b** did not react with sulfur (3.2 equiv.) in refluxing benzene for 24 hours in the presence of DBU (76% recovery of **2b**), while **1a** was readily sulfurized to the corresponding thiaphosphirane *P*-sulfide **3a** under milder conditions. Thus, **1a** reacted with sulfur (0.9 equiv.) at room temperature for 24 hours in the presence of DBU to give a mixture of **1a, 2a,** and **3a** (**1a**:**2a**:**3a** =

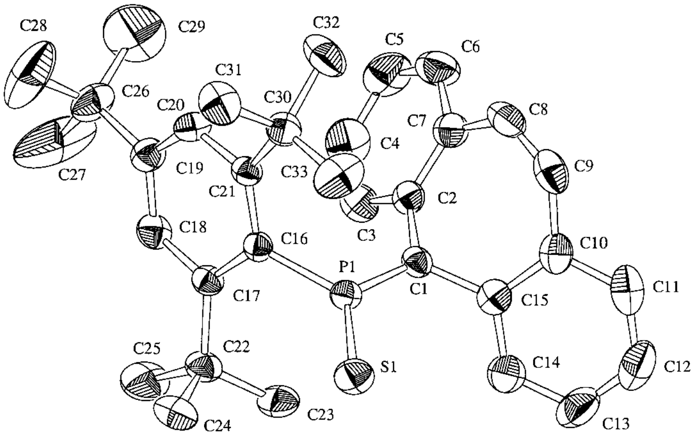


FIGURE 3 Molecular structure for **2b** with atom labeling scheme.

TABLE 1 Some Important Bond Lengths and Angles of **1b**

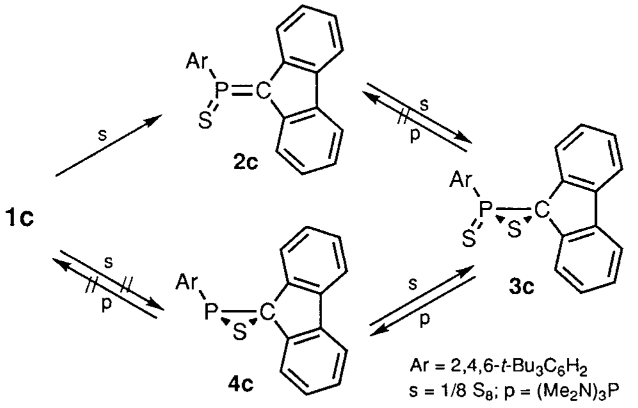
Bond Length (Å)		*Bond Angle (deg)*	
P(1)–C(1)	1.681(4)	C(1)–P(1)–C(16)	104.5(2)
P(1)–C(16)	1.850(5)	P(1)–C(1)–C(2)	128.9(3)
C(1)–C(2)	1.480(6)	P(1)–C(1)–C(15)	114.0(3)
C(1)–C(15)	1.497(6)	C(1)–C(2)–C(7)	121.1(4)
C(2)–C(7)	1.414(6)	C(1)–C(15)–C(10)	121.7(4)
C(7)–C(8)	1.471(7)	C(2)–C(7)–C(8)	123.5(5)
C(8)–C(9)	1.319(8)	C(7)–C(8)–C(9)	129.0(5)
C(9)–C(10)	1.451(7)	C(8)–C(9)–C(10)	129.5(6)
C(10)–C(15)	1.411(6)	C(9)–C(10)–C(15)	123.2(5)

Numbers in parentheses are estimated standard deviations.

TABLE 2 Some Important Bond Lengths and Angles of **2b**

Bond Length (Å)		*Bond Angle (deg)*	
P(1)–C(1)	1.663(3)	C(1)–P(1)–C(16)	111.4(1)
P(1)–C(16)	1.815(3)	P(1)–C(1)–C(2)	123.2(2)
P(1)–S(1)	1.921(1)	P(1)–C(1)–C(15)	118.4(2)
C(1)–C(2)	1.480(4)	C(1)–P(1)–S(1)	125.0(1)
C(1)–C(15)	1.493(4)	C(16)–P(1)–S(1)	123.5(1)
C(2)–C(7)	1.402(4)	C(1)–C(2)–C(7)	120.1(3)
C(7)–C(8)	1.459(5)	C(1)–C(15)–C(10)	120.6(3)
C(8)–C(9)	1.332(5)	C(2)–C(7)–C(8)	123.8(3)
C(9)–C(10)	1.456(5)	C(7)–C(8)–C(9)	128.6(4)
C(10)–C(15)	1.401(4)	C(8)–C(9)–C(10)	129.2(4)
		C(9)–C(10)–C(15)	123.1(3)

Numbers in parentheses are estimated standard deviations.



SCHEME 5

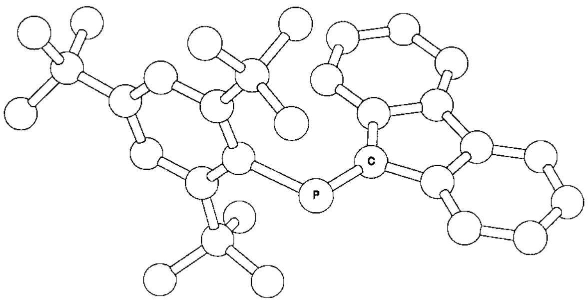


FIGURE 4 Energy-optimized structure calculated by PM3 SCF-MO method for **1c.**

4:2:1). Similarly, 9*H*-fluoren-9-ylidene(2,4,6-tri-*t*-butylphenyl)phosphine (**1c**) [7] reacted with sulfur (0.9 equiv.) to give a mixture of **1c, 2c,** and **3c** (**1c**:**2c**:**3c** = 5:4:2). When an excess amount of sulfur (ca. 10 equiv.) was used, **1a** and **1c** afforded **3a** and **3c** in good yields (96% and 95%, respectively) even at room temperature, making a sharp contrast to the case of **1b** (Scheme 5). The X-ray structural analyses of **2b** and **1b** indicate that the steric hindrance around the phosphorus atom in the **b** series is greater than that of the corresponding **2a** and **1a,** or **2c** and **1c,** probably due to the strongly restricted motion of the phenyl groups within the debenzocycloheptenyl group in the **b** series. However, the two phenyl groups in compounds in the **a** series can rotate freely. Although attempted X-ray analysis of **1c** was not successful, an energy-optimized structure, calculated by CAChe-MOPAC [11] using the PM3 SCF-MO method [12] for **1c,** indicated that both the $-P=C<$ and the fluorenyl groups are planar, respectively, forming a dihedral angle of 179.9° between the two planes, and that the Ar ring is perpendicular to those planes (89.7°), forming the C–P–C angle of 109.0° and with the $P=C$ bond length being 1.621 Å. Figure 4 suggests that there is much room around the phosphorus atom in **1c.** Thus the difference of the steric congestion might cause the difference in the reactivity toward sulfur.

Although the attempted preparation of **3b** by a direct sulfurization reaction of **1b** failed, as described above, we could prepare **3b** by utilizing a valence isomerization reaction of **2b** to the corresponding thiaphosphirane **4b.** Thus, the compound **2b** in benzene solution was irradiated by use of a 300-W Xe lamp with a UV-37 filter, at room temperature for 10 hours, to give **4b** in 74% yield. It should be noted that the attempted thermal isomerization reaction (in *m*-xylene, at 130°C, 24 hours) of **2b** to **4b** resulted in the recovery (93%) of **2b.** On the other hand, **4b** decomposed by application of heat or photoirradiation. Although formation of **2b** was observed in the ^{31}P NMR spectrum during the thermal decomposition reaction of **4b,** it remained unclear whether **2b** was formed by a direct isomerization reaction of **4b** or by a multistep process, such as desulfurization–resulfurization.

The thiaphosphirane **4b** was allowed to react with elemental sulfur in the presence of DBU to give **3b,** which could not be obtained by the direct sulfurization reaction of **1b** as described earlier. The compound **3b** was desulfurized to **4b** by the action of tris(dimethylamino)phosphine, in a similar manner to the cases of **3a** and **3c.**

EXPERIMENTAL

Instruments

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer and/or a Bruker AM-600 spectrometer [13]. ^{31}P NMR spectra were measured on a Bruker AC-200P spectrometer. UV-Vis spectra were obtained on a Hitachi U-

3210 spectrometer. IR spectra were recorded on a Horiba FT-300 spectrometer. MS were taken on either a JEOL HX-110 spectrometer or a Hitachi M-2500S spectrometer.

5H-Dibenzo[a,d]cyclohepten-5-ylidene(2,4,6-tri-t-butylphenyl)phosphine (**1b**)

Lithium (2,4,6-tri-*t*-butylphenyl)(trimethylsilyl)-phosphide (**7**) was prepared from 2,4,6-tri-*t*-butylphenylphosphine (500.3 mg, 1.80 mmol) in THF (30 mL) according to the method reported previously [7]. To this solution of **7** was added a THF (15 mL) solution of dibenzosuberenone (420.5 mg, 1.98 mmol) at −78°C. The reaction mixture was warmed to room temperature and stirred overnight. Hexane (ca. 100 mL) was added to the solution, and the mixture was stirred for a few minutes. Then the solution was allowed to pass through a short silica-gel column, and the solvent was removed under reduced pressure. The residue was separated by silica-gel column chromatography (eluted with hexane) to give 218.8 mg (26% yield) of **1b.** Pale yellow prisms, mp 193.0–195.0°C (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.17 (9H, s, *o-t*-Bu), 1.28 (9H, s, *p-t*-Bu), 1.82 (9H, s, *o′-t*-Bu), 6.26 (1H, d, $^3J_{HH}$ = 7.6 Hz, H_d), 6.62 (1H, ddd, $^3J_{HH}$ = 7.6 Hz and $^5J_{PH}$ = 1.1 Hz, H_c), 6.70 (1H, d, $^3J_{HH}$ = 11.8 Hz, $H_{1''}$), 6.81 (1H, d, $^3J_{HH}$ = 11.8 Hz, H_1), 6.91 (1H, dd, $^3J_{HH}$ = 7.6 Hz, H_b), 6.95 (1H, d, $^4J_{PH}$ = 1.8 Hz, *m*-Ar), 7.08 (1H, d, $^3J_{HH}$ = 7.6 Hz, H_a), 7.25 (1H, d, $^3J_{HH}$ = 7.5 Hz, H_k), 7.31 (1H, dd, $^3J_{HH}$ = 7.4 Hz, H_j), 7.35 (1H, s, *m′*-Ar), 7.38 (1H, ddd, $^3J_{HH}$ = 7.5 Hz and $^5J_{PH}$ = 1.2 Hz, H_i), and 7.57 (1H, d, $^3J_{HH}$ = 7.5 Hz, H_h); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 31.4 (s, *p*-$C\underline{Me}_3$), 33.8 (d, $^4J_{PC}$ = 8.8 Hz, *o*-$C\underline{Me}_3$), 34.0 (d, $^4J_{PC}$ = 5.7 Hz, *o′*-$C\underline{Me}_3$), 34.7 (s, *p*-$\underline{C}Me_3$), 38.3 (s, *o*-$\underline{C}Me_3$), 38.3 (s, *o′*-$\underline{C}Me_3$), 120.3 (s, *m′*-Ar), 122.8 (s, *m*-Ar), 125.6 (s, C_b), 127.2 (s, C_c), 127.4 (d, $^3J_{PC}$ = 6.2 Hz, C_d), 127.6 (s, C_j), 128.3 (s, C_a), 128.3 (s, C_i), 128.4 (s, C_k), 128.8 (d, $^3J_{PC}$ = 20.2 Hz, C_h), 131.1 (s, $C_{l'}$), 132.4 (d, $^3J_{PC}$ = 7.7 Hz, C_m), 132.5 (s, $C_{l''}$), 134.2 (d, $^1J_{PC}$ = 63.4 Hz, *ipso*-Ar), 134.7 (d, $^2J_{PC}$ = 11.5 Hz, C_e), 140.8 (d, $^3J_{PC}$ = 14.5 Hz, C_l), 143.5 (d, $^2J_{PC}$ = 31.4 Hz, C_g), 150.0 (s, *p*-Ar), 154.9 (s, *o*-Ar), 155.2 (d, $^2J_{PC}$ = 3.2 Hz, *o′*-Ar), and 179.8 (d, $^1J_{PC}$ = 45.9 Hz, $P{=}C_f$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 261.4; UV (hexane) 246 (log ε 4.2), 294 (3.8), and 334 nm (3.5); IR (KBr) 2360, 1589, 1473, 1394, and 1361 cm^{-1}; MS (70 eV) *m/z* (rel. intensity) 466 (M^+; 7), 275 ($ArP^+{-}1$; 8), 191 ($C_{15}H_{11}^+$; 100), and 57 (*t*-Bu^+; 8). Found: *m/z* 466.2805. Calcd for $C_{33}H_{39}P$: M, 466.2789.

5H-Dibenzo[a,d]cyclohepten-5-ylidene(2,4,6-tri-t-butylphenyl)phosphine P-Sulfide (**2b**)

To a solution of **1b** (59.5 mg, 0.13 mmol) and sulfur (4.2 mg, 0.13 mg-atom) in benzene (2 mL) was added DBU (ca. 0.08 mmol). The resulting solution was stirred for 24 hours at room temperature, and the solvent was removed in vacuo. Chromatographic separation (SiO_2/ pentane - Et_2O = 50:1) of the residue afforded 44.6 mg (70% yield) of **2b.** Pale yellow crystals, mp 167.0–167.5°C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.27 (9H, s, *p-t*-Bu), 1.38 (9H, s, *o′-t*-Bu), 2.02 (9H, s, *o-t*-Bu), 6.40 (1H, d, $^3J_{HH}$ = 7.7 Hz, H_h), 6.66 (1H, dd, $^3J_{HH}$ = 7.4 Hz, H_i), 6.74 (1H, d, $^3J_{HH}$ = 11.8 Hz, $H_{1'}$), 6.79 (1H, d, $^3J_{HH}$ = 11.8 Hz, $H_{1''}$), 6.93 (1H, dd, $^3J_{HH}$ = 7.6 Hz, H_j), 7.05 (1H, d, $^4J_{PH}$ = 3.6 Hz, *m′*-Ar), 7.10 (1H, d, $^3J_{HH}$ = 8.0 Hz, H_k), 7.30 (1H, dd, $^3J_{HH}$ = 7.4 Hz, H_b), 7.35 (1H, d, $^3J_{HH}$ = 8.2 Hz, H_a), 7.40 (1H, dd, $^3J_{HH}$ = 7.4 Hz, H_c), 7.51 (1H, d, $^4J_{PH}$ = 3.3 Hz, *m*-Ar), and 7.58 (1H, d, $^3J_{HH}$ = 7.4 Hz, H_d); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 31.1 (s, *p*-$C\underline{Me}_3$), 33.8 (s, *o*-$C\underline{Me}_3$), 34.0 (s, *o′*-$C\underline{Me}_3$), 35.0 (s, *p*-$\underline{C}Me_3$), 39.7 (d, $^3J_{PC}$ = 2.7 Hz, *o′*-$\underline{C}Me_3$), 39.7 (d, $^3J_{PC}$ = 2.7 Hz, *o′*-$\underline{C}Me_3$), 120.0 (d, $^1J_{PC}$ = 75.7 Hz, *ipso*-Ar), 121.9 (d, $^3J_{PC}$ = 12.5 Hz, *m*-Ar), 124.2 (d, $^3J_{PC}$ = 14.3 Hz, *m′*-Ar), 126.1 (d, $^5J_{PC}$ = 2.5 Hz, C_j), 127.2 (s, C_i), 127.5 (d, $^5J_{PC}$ = 2.7 Hz, C_b), 127.9 (d, $^3J_{PC}$ = 11.2 Hz, C_h), 128.3 (d, $^4J_{PC}$ = 1.2 Hz, C_c), 128.6 (s, C_k), 129.3 (s, C_a), 130.3 (d, $^3J_{PC}$ = 14.4 Hz, C_d), 131.6 (s, $C_{l'}$), 131.8 (s, $C_{l''}$), 134.5 (d, $^3J_{PC}$ = 16.9 Hz, C_l), 135.3 (d, $^3J_{PC}$ = 16.5 Hz, C_m), 137.4 (d, $^2J_{PC}$ = 49.1 Hz, C_g), 137.4 (d, $^2J_{PC}$ = 49.8 Hz, C_e), 142.2 (d, $^1J_{PC}$ = 134.0 Hz, $P{=}C_f$), 154.0 (d, $^4J_{PC}$ = 3.4 Hz, *p*-Ar), 155.4 (d, $^2J_{PC}$ = 6.9 Hz, *o*-Ar), and 156.5 (d, $^2J_{PC}$ = 3.1 Hz, *o′*-Ar); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 159.3; UV (hexane) 240 (log ε 4.5) and 359 nm (4.1); IR (KBr) 1477, 760, and 710 cm^{-1}; MS (70 eV) *m/z* (rel. intensity) 498 (M^+; 42), 223 ($C_{15}H_{10}P^+$ + 2; 100), 191 ($C_{15}H_{10}^+$ + 1; 96), and 57 (*t*-Bu^+; 50). Found: *m/z* 498.2509. Calcd for $C_{33}H_{39}PS$: M, 498.2510.

Reaction of **1b** *with an Excess Amount of Elemental Sulfur*

Method a. To a solution of **1b** (55.9 mg, 0.12 mmol) and sulfur (39.9 mg, 1.24 mg-atom) in benzene (2 mL) was added DBU (ca. 0.08 mmol). The resulting solution was stirred at room temperature for 24 hours. Then the solution was allowed to pass through a short silica-gel column (eluent: CH_2Cl_2), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/ pentane-Et_2O = 50:1) of the reaction mixture afforded 54.7 mg (91% yield) of **2b.**

Method b. To a solution of **1b** (851.2 mg, 1.82 mmol) and sulfur (179.3 mg, 5.59 mg-atom) in benzene (50 mL) was added DBU (0.20 mmol). The resulting solution was stirred in the dark at 55°C for 21 hours. Then the solution was allowed to pass through a short silica-gel column (eluent: benzene), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/ hexane-Et_2O = 100:1) of the reaction mixture afforded 871.0 mg (96% yield) of **2b.**

Desulfurization Reaction of 2b

To a solution of **2b** (35.4 mg, 0.071 mmol) in benzene (15 mL) was added tris(dimethylamino)phosphine (0.35 mmol). The resulting solution was stirred in the dark at room temperature for 45 hours. Then the solution was allowed to pass through a short silica-gel column (eluent: benzene), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/hexane) of the reaction mixture gave 22.2 mg (67% yield) of **1b.**

Attempted Sulfurization Reaction of 2b

To a solution of **2b** (35.2 mg, 0.071 mmol) and sulfur (7.4 mg, 0.23 mg-atom) in benzene (2 mL) was added DBU (ca. 0.003 mmol). The resulting solution was refluxed in the dark for 24 hours. No significant change was observed in the ^{31}P NMR spectra of the solution. Removal of the solvent in vacuo followed by chromatographic separation (SiO_2/ hexane-benzene) of the residue afforded 26.9 mg (76% recovery) of **2b.**

2′-(2,4,6-Tri-t-butylphenyl)spiro[5H-dibenzo-[a,d]cycloheptene-5,3′-[1,2]thiaphosphirane] (4b)

A solution of **2b** (77.1 mg, 0.16 mmol) in benzene (1.5 mL) was irradiated by use of a 300 W Xe lamp with a UV-37 filter for 10 hours. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/hexane) of the residue afforded 56.9 mg (ca. 74% yield) of crude **4b.** Because of the partial decomposition in the solution, **4b** was not obtained in pure form. **4b:** ^{1}H NMR (600 MHz, C_6D_6) δ = 1.14 (9H, s, *p-t*-Bu), 1.53 (18H, s, *o-t*-Bu), 6.54 (1H, d, $^3J_{HH}$ = 11.4 Hz, $H_{1''}$), 6.64 (1H, dd, $^4J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 5.6 Hz, H_a), 6.78 (2H, dd, $^4J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 5.6 Hz, H_b and H_c), 6.80 (2H, s, *m*-Ar), 6.81 (1H, d, $^3J_{HH}$ = 11.4 Hz, $H_{1'}$), 6.95 (1H, pseudo t, $^3J_{HH}$ = 7.6 Hz, H_j), 7.01 (1H, d, $^3J_{HH}$ = 7.6 Hz, H_k), 7.07 (1H, pseudo t, $^3J_{HH}$ = 7.6 Hz, H_i), 7.46 (1H, dd, $^4J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 5.6 Hz, H_d), and 7.75 (1H, d, $^3J_{HH}$ = 7.6 Hz, H_h); ^{13}C{^{1}H} NMR (150 MHz, C_6D_6) δ = 31.5 (s, *p*-C$\underline{\mathrm{Me}}_3$), 33.8 (s, *o*-C$\underline{\mathrm{Me}}_3$), 34.1 (s, *p*-$\underline{\mathrm{C}}Me_3$), 35.8 (s, *o′*-C$\underline{\mathrm{Me}}_3$), 40.1 (s, *o*-$\underline{\mathrm{C}}Me_3$), 64.0 (d, $^1J_{PC}$ = 59.1 Hz, P=C_f), 126.6 (s, C_b and C_c), 126.8 (s, C_j), 127.8 (s, *m*-Ar), 128.1 (s, C_a), 128.4 (s, C_k), 128.8 (s, C_i), 130.4 (s, C_h), 132.9 (s, $C_{l''}$), 133.8 (d, $^1J_{PC}$ = 99.7 Hz, *ipso*-Ar), 134.1 (s, $C_{l'}$), 135.9 (s, C_m), 136.1 (s, C_l), 136.4 (s, C_e), 139.7 (d, $^2J_{PC}$ = 13.0 Hz, C_g), 149.2 (s, *p*-Ar), 159.1 (s, *o*-Ar), and 159.9 (s, *o′*-Ar); ^{31}P{^{1}H} NMR (81 MHz, C_6D_6), δ = −34.1 (accompanied by a signal at −42.2).

Attempted Thermal Reaction of 2b

A solution of **2b** (36.6 mg, 0.073 mmol) in *m*-xylene (5 mL) was heated at 130°C for 24 hours. No significant change was observed in the ^{31}P NMR spectra of the solution. Removal of the solvent in vacuo, followed by chromatographic separation (SiO_2/ hexane-benzene) of the residue, afforded 34.1 mg (93% recovery) of **2b.**

2′-(2,4,6-Tri-t-butylphenyl)spiro[5H-dibenzo-[a,d]cycloheptene-5,3′-[1,2]thiaphosphirane] 2′-Sulfide (3b)

To a solution of crude **4b** (58 mg, 0.11 mmol) and sulfur (35.6 mg, 1.11 mmol) in benzene (10 mL) was added DBU (0.17 mmol). The resulting solution was stirred for 46 hours at room temperature. Then the solution was allowed to pass through a short silica-gel column (eluent: benzene), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/hexane) of the residue afforded 20.8 mg (ca. 36% yield) of crude **3b.** Because of the instability of **3b** in the solution, it was not obtained in pure form: **3b:** ^{1}H NMR (200 MHz, C_6D_6) δ = 1.07 (9H, s, *p-t*-Bu), 1.44 (9H, s, *o-t*-Bu), 2.10 (9H, s, *o-t*--Bu), and 6.5–8.7 (12H, m, =CH); ^{31}P {^{1}H} NMR (81 MHz, $CDCl_3$) δ = 19.9.

Irradiation of 4b

A solution of **4b** (10 mg) in hexane (0.5 mL) was irradiated with a 100 W medium pressure mercury lamp for 2 hours. The reaction was monitored by ^{31}P NMR spectroscopy, which showed formation of **2b** along with many unidentified compounds. No evidence for the formation of **2b** was obtained.

Thermal Reaction of 4b

A solution of **4b** (25.5 mg, 0.051 mmol) in toluene-d_8 (0.5 mL) was heated at 60°C for 217 hours. The formation of **2b** and **1b,** along with some unidentified products, was observed by ^{31}P NMR spectroscopic monitoring.

Desulfurization Reaction of 3b

To a solution of **3b** (48.3 mg, 0.091 mmol) in benzene (20 mL) was added tris(dimethylamino)phosphine (0.94 mmol). The resulting solution was stirred in the dark at room temperature for 12 hours. Then the solution was allowed to pass through a short silica-gel column (eluent: benzene), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/hexane) of the reaction mixture gave 25.9 mg (57% yield) of **4b.**

Reaction of 1a *with Elemental Sulfur*

To a solution of **1a** (61.1 mg, 0.14 mmol) and sulfur (3.8 mg, 0.12 mg-atom) in benzene (2 mL) was added DBU (ca. 0.08 mmol), and the mixture was stirred at room temperature for 24 hours. The ^{31}P NMR spectrum of the reaction mixture showed signals due to **1a, 2a,** and **3a** in a 4:2:1 ratio.

Reaction of 1c *with Elemental Sulfur*

To a solution of **1c** (29.2 mg, 0.066 mmol) and sulfur (2.0 mg, 0.06 mg-atom) in benzene (15 mL) was added DBU (ca. 0.003 mmol), and the mixture was stirred at room temperature for 24 hours. The ^{31}P NMR spectrum of the reaction mixture showed signals due to **1c, 2c,** and **3c** in a 5:4:2 ratio. **2c:** ^{31}P{^{1}H} NMR (81 MHz, C_6D_6) $\delta = 154.1$.

2′-(2,4,6-Tri-t-butylphenyl)spiro[9H-fluorene-9,3′- [1,2]thiaphosphirane] 2′-Sulfide (3c)

To a solution of **1c** (32.3 mg, 0.073 mmol) and sulfur (25.1 mg, 0.78 mg-atom) in benzene (12 mL) was added DBU (ca. 0.003 mmol). The resulting solution was stirred at room temperature for 24 hours. Then the solution was allowed to pass through a short silica-gel column (eluent: benzene), and the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/ hexane-Et_2O = 100:1) of the reaction mixture afforded 35.3 mg (95% yield) of **3c.** Pale yellow plates, mp 172.5–173.5°C (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.02$ (9H, s, *o*-*t*-Bu), 1.39 (9H, s, *p*-*t*-Bu), 1.85 (9H, s, *o′*-*t*-Bu), 5.02 (1H, d, $^3J_{HH} = 7.6$ Hz, H_d), 6.70 (1H, ddd, $^3J_{HH} = 7.6$ Hz and $^4J_{PH} = 1.0$ Hz, H_c), 7.06 (1H, dd, $^4J_{HH} = 1.9$ Hz and $^4J_{PH} = 7.2$ Hz, *m*-Ar), 7.22 (1H, dd, $^3J_{HH} = 7.6$ Hz, H_b), 7.40 (1H, ddd, $^3J_{HH} = 7.6$ Hz and $^4J_{PH} = 1.1$ Hz, H_i), 7.45 (1H, dd, $^3J_{HH} = 7.6$ Hz, H_j), 7.64 (1H, d, $^3J_{HH} = 7.6$ Hz, H_a), 7.64 (1H, dd, $^4J_{HH} = 1.9$ Hz and $^4J_{PH} = 7.6$ Hz, *m′*-Ar), 7.75 (1H, d, $^3J_{HH} = 7.6$ Hz, H_k), and 8.13 (1H, d, $^3J_{HH} = 7.6$ Hz, H_h); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.2$ (s, *p*-$\mathrm{C\underline{Me}_3}$), 32.1 (s, *o*-$\mathrm{C\underline{Me}_3}$), 34.3 (s, *o′*-$\mathrm{C\underline{Me}_3}$), 35.0 (s, *p*-$\mathrm{\underline{C}Me_3}$), 39.2 (d, $^3J_{PC} = 3.1$ Hz, *o*-$\mathrm{\underline{C}Me_3}$), 41.4 (d, $^3J_{PC} = 3.4$ Hz, *o′*-$\mathrm{\underline{C}Me_3}$), 52.2 (d, $^1J_{PC} = 24.8$ Hz, P = C_f), 119.4 (s, C_a), 119.9 (s, C_k), 122.7 (d, $^3J_{PC} = 16.7$ Hz, *m*-Ar), 124.5 (d, $^3J_{PC} = 1.1$ Hz, C_d), 126.0 (d, $^3J_{PC} = 14.8$ Hz, *m′*-Ar), 126.2 (d, $^3J_{PC} = 2.2$ Hz, C_h), 126.4 (d, $^4J_{PC} = 1.3$ Hz, C_c), 127.0 (d, $^4J_{PC} = 1.2$ Hz, C_i), 128.2 (s, C_b), 128.3 (d, $^1J_{PC} = 80.2$ Hz, *ipso*-Ar), 128.8 (s, C_j), 141.1 (d, $^3J_{PC} = 3.6$ Hz, C_m), 141.3 (d, $^3J_{PC} = 4.1$ Hz, C_l), 141.3 (d, $^2J_{PC} = 1.2$ Hz, C_g), 142.9 (d, $^2J_{PC} = 4.9$ Hz, C_e), 153.2 (d, $^4J_{PC} = 4.0$ Hz, *p*-Ar), 155.1 (d, $^2J_{PC} = 12.0$ Hz, *o*-Ar), and 157.8 (d, $^2J_{PC} = 7.4$ Hz, *o′*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) $\delta = -0.51$; UV (hexane) 251 (sh, log ε 4.4), 281 (sh, 4.0), 302 (sh, 3.8), and 421 nm (1.9); IR (KBr) 1477, 1442, 737, and 708 cm^{-1}; MS (70 eV) *m/z* (rel. intensity) 504 (M^+; 0.5), 472 (M^+ − S; 2), 196 (Flu-P + 1; 100), and 57 (*t*-Bu^+; 82). Found: *m/z* 504.2028. Calcd for $C_{31}H_{37}PS_2$: M, 504.2074.

2′-(2,4,6-Tri-t-butylphenyl)spiro[9H-fluorene-9,3′-[1,2]thiaphosphirane] (4c)

To a solution of **3c** (41.4 mg, 0.082 mmol) in benzene (2 mL) was added tris(dimethylamino)phosphine (2.2 mmol). The resulting solution was stirred at room temperature for 3 hours. Then the solvent was removed under reduced pressure. Chromatographic separation (SiO_2/hexane) of the reaction mixture gave 21.3 mg (55% yield) of **4c.** Pale yellow plates, mp 204.5–205.5°C (decomp., hexane); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 0.81$ (9H, s, *o*-*t*-Bu), 1.39 (9H, s, *p*-*t*-Bu), 1.73 (9H, s, *o′*-*t*-Bu), 5.04 (1H, d, $^3J_{HH} = 7.5$ Hz, H_d), 6.68 (1H, dd, $^3J_{HH} = 7.5$ Hz, H_c), 6.93 (1H, s, *m*-Ar), 7.17 (1H, dd, $^3J_{HH} = 7.5$ Hz, H_b), 7.30 (1H, d, $^3J_{HH} = 7.3$ Hz, H_i), 7.33 (1H, d, $^3J_{HH} = 7.3$ Hz, H_h), 7.37 (1H, dd, $^3J_{HH} = 7.3$ Hz, H_j), 7.44 (1H, d, $^4J_{PH} = 1.5$ Hz, *m′*-Ar), 7.65 (1H, d, $^3J_{HH} = 7.5$ Hz, H_a), and 7.74 (1H, d, $^3J_{HH} = 7.3$ Hz, H_k); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.3$ (s, *p*-$\mathrm{C\underline{Me}_3}$), 33.8 (d, $^4J_{PC} = 12.4$ Hz, *o*-$\mathrm{C\underline{Me}_3}$), 34.1 (d, $^4J_{PC} = 6.7$ Hz, *o′*-$\mathrm{C\underline{Me}_3}$), 34.6 (s, *p*-$\mathrm{\underline{C}Me_3}$), 38.9 (s, *o*-$\mathrm{\underline{C}Me_3}$), 39.8 (s, *o′*-$\mathrm{\underline{C}Me_3}$), 55.7 (d, $^1J_{PC} = 55.9$ Hz, P=C_f), 119.2 (s, C_a), 119.7 (s, C_k), 122.0 (d, $^3J_{PC} = 7.9$ Hz, C_h), 122.6 (s, *m*-Ar), 123.9 (s, *m′*-Ar), 124.6 (s, C_d), 126.2 (s, C_c), 127.1 (s, C_b), 127.2 (s, C_i), 127.4 (s, C_j), 133.9 (d, $^1J_{PC} = 93.0$ Hz, *ipso*-Ar), 139.9 (s, C_l), 140.7 (s, C_m), 144.0 (s, C_e), 146.9 (d, $^2J_{PC} = 10.6$ Hz, C_g), 150.0 (s, *p*-Ar), 157.1 (d, $^2J_{PC} = 6.6$ Hz, *o*-Ar), and 159.2 (d, $^2J_{PC} = 5.0$ Hz, *o′*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) $\delta = -43.2$; UV (hexane) 252 (log ε 4.5), 293 (4.7), and 420 nm (1.4); IR (KBr) 1473, 1442, and 737 cm^{-1}; MS (70 eV) *m/z* (rel. intensity) 472 (M^+; 33), 440 (M^+ − S; 10), 307 ($ArPS^+$ − 1; 16), 275 (ArP^+ − 1; 100), 220 (ArP^+ − *t*-Bu + 1; 48), and 57 (*t*-Bu^+; 54). Found: *m/z* 472.2367. Calcd for $C_{31}H_{37}PS$: M, 472.2354.

X-ray Crystal Structure Determination of 1b *and* 2b

1b: $C_{33}H_{39}P$, $M_r = 466.64$. Monoclinic, space group $P2_1/c$, $a = 20.081(4)$, $b = 9.027(5)$, $c = 16.813(4)$ Å;

$\beta = 113.02(2)°$; $V = 2804(1)$ Å^3, $Z = 4$, $\rho = 1.105$ g cm^{-3}, $\mu = 1.16$ cm^{-1}; 4904 unique reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (Mo Kα radiation, graphite monochrometer), Rigaku AFC5S. Of these, 3298 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86 [14]. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R = 0.069$, $R_w = 0.074$.

2b: $C_{33}H_{39}PS$, $M_r = 498.70$. Monoclinic, space group $P2_1/a$, $a = 16.246(4)$, $b = 9.349(4)$, $c = 20.642(3)$ Å; $\beta = 112.76(1)°$; $V = 2890(1)$ Å^3, $Z = 4$, $\rho = 1.146$ g cm^{-3}, $\mu = 1.86$ cm^{-1}; 5436 unique reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (Mo Kα radiation, graphite monochrometer), Rigaku AFC7S. Of these, 3483 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86 [14]. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but only some were refined. $R = 0.047$, $R_w = 0.033$.

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SUPPLEMENTARY MATERIAL AVAILABLE

Further details of the crystal structure investigation of **1b** and **2b** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, (UK), on quoting the full journal citation.

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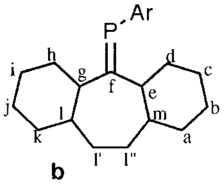
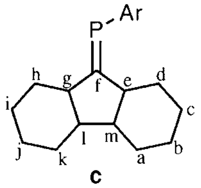


b



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