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Preparation and Properties of Some Stable Captodative Diphosphenes Carrying the *N*-(9-Fluorenyl)-*N*-mesitylamino Group as an Electron-Donating New Sterically Protecting Auxiliary

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ABSTRACT

The N-(9-fluorenyl)-N-mesitylamino group was utilized as an electron-donating new sterically protecting group and thus several captodative 1-amino-2-aryldiphosphenes were prepared. The push-pull substituent effect on the -P=P- bond was demonstrated by ^{31}P NMR, and the reactivities of the captodative diphosphenes were studied.

INTRODUCTION

Compounds with multiple bonds involving the heavier main-group elements, such as phosphorus [1], have attracted considerable attention because of their unusual physicochemical properties. Utilizing the extremely bulky 2,4,6-tri-*t*-butylphenyl group as a sterically protecting group, we have successfully prepared the diphosphene **1** as a stable compound [2]. We have recently reported the preparations and properties of some push-pull diphosphenes, such as 1-amino-2-aryldiphosphenes **2**, carrying either the 2,4,6-tris(trifluoromethyl)phenyl or the 2,6-bis(trifluoromethyl)phenyl group as an electron withdrawing substituent and a dialkylamino group as an electron donating substituent [3]. Such captodative diphosphenes are interesting, because each phosphorus atom is supposed to have an opposite electronic character. However, studies on the properties of these diphosphenes have been limited because of their instability. The instability of **2** may be partly due to the polarized -P=P- bond and partly to insufficient steric protection. Thus, it is of interest to introduce a bulky amino group as a protecting partner to stabilize such captodative diphosphenes. We report here the utilization of *N*-(9-fluorenyl)-*N*-mesitylamino group as a new sterically protecting group for low-coordinated organophosphorus compounds.

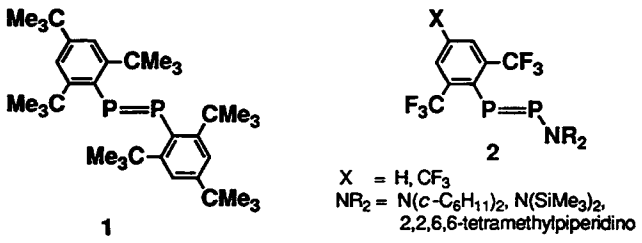

FIGURE 1

RESULTS AND DISCUSSION

The sterically hindered amino group was prepared as follows: mesidine (mesitylenamine) was allowed to react with fluorenone in the presence of boron trifluoride etherate [4] at 150°C under fusion

This article is dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

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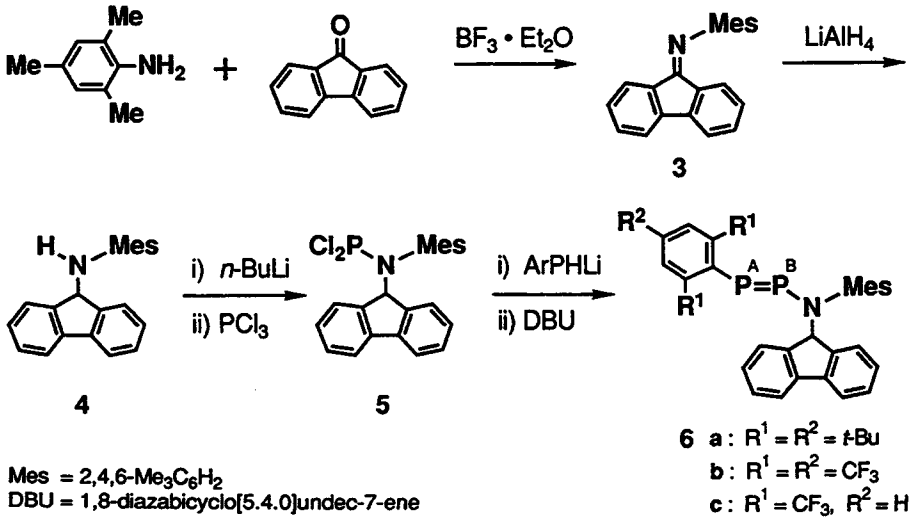
conditions to give *N*-9-fluorenylidenemesitylenamine **3** in 84% yield. The compound **3** thus obtained was reduced to the corresponding amine **4** by $LiAlH_4$ (87% yield). Then the diphosphenes bearing the (9-fluorenyl)mesitylamino group were prepared as follows. The amine **4** was lithiated with butyllithium, and the resulting lithium amide was allowed to react with phosphorus trichloride to give the phosphoramidous dichloride **5**. Because of its instability, the dichloride **5** was used for further reactions without isolation. Treatment of **5** with lithium 2,4,6-tri-*t*-butylphenylphosphide, followed by base-induced dehydrochlorination, afforded the diphosphene **6a**. Similarly, the diphosphenes **6b** and **6c** were prepared by the reaction of **5** with lithium 2,4,6-tris(trifluoromethyl)phenylphosphide or lithium 2,6-bis(trifluoromethyl)phenylphosphide, respectively, followed by dehydrochlorination [5].

Contrary to **2**, the diphosphenes **6b** and **6c**, as well as **6a**, are stable in the air and they can be stored without decomposition at ambient temperature. Moreover, both thermal and photochemical stabilities of the diphosphene **6b** were demonstrated as follows. An attempted thermal cleavage reaction of **6b** in C_6D_6 in a sealed tube at 80°C for 2 hours did not proceed. Irradiation of **6b** in C_6D_6 with a mercury lamp for 6 hours also resulted in the recovery of **6b**.

The ^{31}P NMR data of the diphosphenes **6a–c** are listed in Table 1. The spectra of the fluorine-containing diphosphenes **6b** and **6c** showed ABX_6 patterns, while the spectrum of **6a** showed an AB pattern. The peaks of **6a–c** were assigned from the empirical rule that the peak due to the phosphorus atom β to the nitrogen atom (P^A) appears at a higher field than the peak due to the nitrogen-substituted phosphorus atom (P^B) [3,6]. The values of the spin-spin couplings ($^4J_{PF}$ and $^5J_{PF}$) in **6b** and **6c** also support this assignment [3,7,8]. Similarly to the case of the previously reported captodative diphosphenes [3], the P^A atoms of **6b** and **6c** exhibit the shifts to higher field ($|\Delta\delta_P(A)|$ = 50–57 ppm) compared with P^A atom of **6a**, while the P^B atoms of **6b** and **6c** exhibit the shifts to lower field ($|\Delta\delta_P(B)|$ = 26–27 ppm). This indicates that the phosphorus-phosphorus double bonds of **6b** and **6c** are more polarized than that of **6a**. Thus, in the resonance structures of the PPN π-system, the contribution of the zwitterionic form (II) seems to be larger in **6b** and **6c** than that in **6a**, due to the polarization caused by push-pull substitution on the phosphorus-phosphorus double bond [3].

The captodative substitution effect was also demonstrated in the reaction of **6b** with nucleophiles, such as butyllithium. Thus, **6b** reacted with butyllithium to give the diphosphane **7**. In this reaction, the nucleophile attacks the relatively positive phosphorus atom, *i.e.*, the nitrogen-substituted phosphorus atom. The MS spectrum of **7** showed the base peak at m/z 386, which was assigned to $[BuP\text{-}N(Flu)Mes]^+$, where Flu is fluorenyl.

The reaction of **6a** with elemental sulfur in toluene gave a stable thiadiphosphirane **8a**. The diphosphene **6b** did not react with elemental sulfur under similar conditions. However, addition of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) activated the sulfurization reaction to give the thiadiphosphirane **6b**. Since formation of the intermediary diphosphene sulfide [9] has not been observed during the sulfurization reaction, monitored by ^{31}P NMR spectroscopy, the isomerization of the diphosphene sulfide seems to be rapid in this captodative diphosphene system. The fact that the diphosphenes **6** and the thiadiphosphiranes **8** are stable indicates that the *N*-(9-fluorenyl)-



SCHEME 1

TABLE 1 $^{31}P\{^1H\}$ NMR Data of the Diphosphenes **1** (in C_6D_6) and **6** (in $CDCl_3$)

Compounds	$\delta_P(A)$	$(^4J_{PF}/Hz)$	$\delta_P(B)$	$(^5J_{PF}/Hz)$	$^1J_{PP}/Hz$
1[a]	492.4	—	—	—	—
6a	310.3	—	452.1	—	544.1
6b	254.0	(25.8)	478.4	(18.7)	531.7
6c	259.6	(25.7)	478.8	(18.7)	534.6

[a]Taken from Ref. [2].

N-mesitylamino group is an efficient protecting auxiliary which also acts as an electron-donating group. Further application of this group to the preparation of low-coordinated phosphorus compounds is now in progress.

EXPERIMENTAL

Melting points were taken on a Yanagimoto MP-J3 micro melting-point apparatus and were uncorrected. ^1H (200 MHz), ^{13}C (50 MHz), and ^{31}P (81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer. Ultraviolet spectra were measured on a Hitachi U-3210 spectrometer. Infrared spectra were obtained on a Horiba FT-300 spectrometer. The MS (70 eV) spectra were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. 2,4,6-Tri-*t*-butylphenylphosphine [10], 2,4,6-tris(trifluoromethyl)phenylphosphine [7], and 2,6-bis(trifluoromethyl)phenylphosphine [8] were prepared according to literature methods. Reactions were performed under argon with anhydrous solvents unless otherwise noted. Column chromatographic separations were carried out using compressed air over silica gel (Fuji-Davison BW-300).

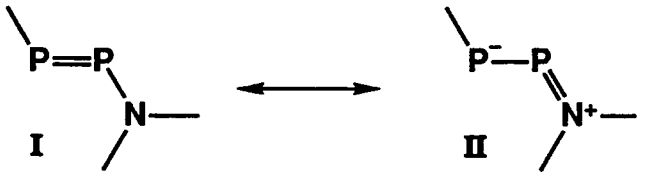


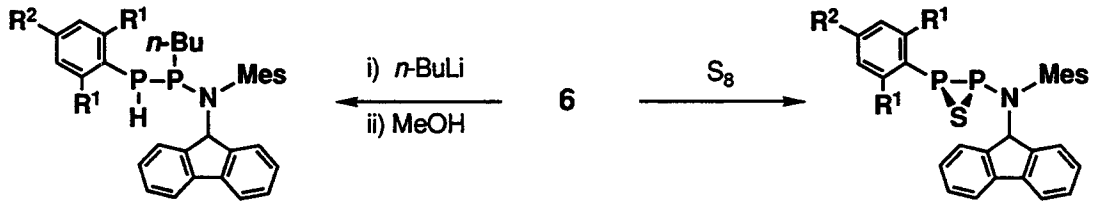
FIGURE 2

N-(9-Fluorenylidene)mesitylenamine (**3**)

A mixture of 9-fluorenone (9.05 g, 50.2 mmol), mesidine (13.5 g, 100.0 mmol), and boron trifluoride etherate (2.5 mL, 20.4 mmol) was fused in the air at 150°C and was kept at that temperature for 1.5 hours using a moisture trap to collect water as it formed during the reaction. The product was dissolved in benzene, and the resulting insoluble material was removed by filtration. The filtrate was dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation. Recrystallization of the residue from EtOH-$CHCl_3$ (3:1) afforded 12.6 g (84%) of **3**: Orange prisms; mp 196–197°C; ^1H NMR ($CDCl_3$) δ = 2.01 (6H, s, *o*-Me), 2.36 (3H, s, *p*-Me), 6.55 (1H, d, J = 7.7 Hz), 6.93 (2H, s, Mes), 6.97 (1H, t, J = 7.7 Hz), 7.30–7.53 (3H, m), 7.59–7.64 (2H, m), and 8.03 (1H, d, J = 7.7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 17.9 (*o*-Me), 20.9 (*p*-Me), 119.6, 120.0, 123.1, 124.8, 125.6, 128.4, 128.8, 131.6, 131.8, 132.0, 132.7, 137.3, 141.9, 143.0, 146.4, and 163.2; UV (CH_2Cl_2) 288 (log ϵ 3.9), 298 (3.9), and 411 nm (2.9); IR (KBr) 1653 cm^{-1} (C=N); MS *m/z* (*rel* intensity) 297 (M^+; 100) and 281 (M^+–Me–1; 17); found: *m/z* 297.1516. Calcd for $C_{22}H_{19}N$: M, 297.1518; found: C, 88.69; H, 6.57; N, 4.71%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%.

N-(9-Fluorenyl)mesitylenamine (**4**)

To a stirred solution of lithium aluminum hydride (2.17 g, 57.2 mmol) in ether (50 mL) was added the solid fluorenylidenemesitylenamine **3** (8.35 g, 28.1 mmol) at 0°C. The solution was warmed to room temperature and refluxed for 48 hours. Water (20 mL) was carefully added to the reaction mixture at 0°C under argon, and the solution was diluted with ether (150 mL). To this mixture were added 20% aqueous sodium potassium tartrate (240 mL) and 10% aqueous sodium hydroxide (80 mL). The organic layer was separated, washed with brine,



7: $R^1 = R^2 = CF_3$

8 **a**: $R^1 = R^2 = t$-Bu
b: $R^1 = R^2 = CF_3$

SCHEME 2

and then dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, and recrystallization of the residue from EtOH afforded 7.30 g (87%) of **4**: Colorless needles; mp 94–95°C; ^{1}H NMR ($CDCl_3$) δ = 2.25 (6H, s, *o*-Me), 2.34 (3H, s, *p*-Me), 3.24 (1H, brs, NH), 5.34 (1H, s, Flu-H9), 6.92 (2H, s, Mes), 7.24–7.49 (6H, m, Flu), and 7.73 (2H, d, J = 7.5 Hz, Flu); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 18.9 (*o*-Me), 20.8 (*p*-Me), 61.8 (Flu-C9), 119.9, 125.2, 127.4, 128.3, 129.6, 129.7, 131.5, 140.1, 142.0, and 146.1; UV (hexane) 230 (log ϵ 4.3), 261 (4.3), 270 (4.3), and 306 nm (3.6); IR (KBr) 3334 cm^{-1} (NH); MS m/z (*rel* intensity) 299 (M^+; 27), 165 (Flu^+; 100), and 134 ($MesNH^+$; 30); found: m/z 299.1687. Calcd for $C_{22}H_{21}N$: M, 299.1674.

N-(9-Fluorenyl)-N-mesitylphosphoramidous Dichloride (**5**)

To a stirred solution of the mesidine **4** (559.5 g, 1.87 mmol) in ether (6 mL) was added 1.99 mmol of butyllithium (1.59 M in hexane) at 0°C, and then the resulting solution was warmed to room temperature and stirred for 30 minutes. This solution was added to a solution of phosphorus trichloride (2.06 mmol) in ether (4 mL) at −78°C, and then the mixture was warmed up to room temperature and stirred for 4 hours. The solvent was removed in vacuo, and 9 mL of toluene was added to the residue. Filtration of insoluble material followed by evaporation of the solvent gave 684.6 mg (92%) of **5**: Yellow prisms; mp 110–112°C (toluene); ^{1}H NMR (C_6D_6) δ = 1.73 (3H, s, *p*-Me), 2.00 (6H, s, *o*-Me), 6.01 (1H, s, Flu-H9), 6.33 (2H, s, Mes), 6.90–7.06 (4H, m, Flu-H2,H3,H6,H7), 7.17 (2H, d, J = 7.0 Hz, Flu-H1,H8), and 7.76 (2H, d, J = 7.2 Hz, Flu-H4,H5); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 158.3; MS m/z (*rel* intensity) 399 (M^+; 7), 297 (M^+–PCl_2–1; 81), and 165 (Flu^+; 100); found: m/z 399.0706. Calcd for $C_{22}H_{20}Cl_2NP$: M, 399.0710.

1-[N-(9-Fluorenyl)-N-mesitylamino]-2-(2,4,6-tri-t-butylphenyl)diphosphene (**6a**)

To a stirred solution of 2,4,6-tri-*t*-butylphenylphosphine (158.2 mg, 0.568 mmol) in THF (2.5 mL) was added 0.616 mmol of butyllithium (1.62 M in hexane) at 0°C, and the solution was stirred at this temperature for 10 minutes and then warmed to room temperature. The resulting solution was added to a stirred solution of **5** (325.4 mg, 0.816 mmol) in THF (2.5 mL) at 0°C, and the mixture was allowed to warm to room temperature. The resulting solution was treated with DBU (0.090 mL, 0.60 mmol) and stirred for 1.5 hours. Evaporation of the solvent, followed by chromatographic separation (SiO_2/pentane-Et_2O 150:1), afforded **6a** (139.3 mg, 41%) as pale yellow crystals: mp 73–76°C (pentane); ^{1}H NMR ($CDCl_3$) δ = 1.30 (9H, s, *p*-Bu^t), 1.46 (18H, s, *o*-Bu^t), 2.39 (3H, s, *p*-Me), 2.42 (6H, s, *o*-Me), 5.61 (1H, d, $^3J_{PH}$ = 5.9 Hz, Flu-H9), 7.11 (2H, s, Mes), 7.16–7.39 (4H, m, Flu-H2,H3,H6,H7), 7.34 (2H, s, Ar), 7.49 (2H, d, J = 7.5 Hz, Flu-H1,H8), and 7.65 (2H, d, J = 7.5 Hz, Flu-H4,H5); UV (CH_2Cl_2) 262 (log ϵ 4.1), 305 (3.5), 370 (3.4), and 391 nm (3.3); IR (KBr) 1475, 1450, 1055, 1022, and 739 cm^{-1}; MS m/z (*rel* intensity) 605 (M^+; 4), 297 ($Mes(Flu)N^+$ − 1; 100), 277 (ArP^+ + 1; 20), 164 (Flu^+ − 1; 72), and 57 (Bu^{t+}; 52); found: m/z 605.3350. Calcd for $C_{40}H_{49}NP_2$: M, 605.3340.

1-[N-(9-Fluorenyl)-N-mesitylamino]-2-[2,4,6-tris (trifluoromethyl)phenyl]diphosphene (**6b**)

To a stirred solution of 2,4,6-tris(trifluoromethyl)phenylphosphine (898.3 mg, 2.86 mmol) in THF (7 mL) was added 2.86 mmol of butyllithium (1.59 M in hexane) at −78°C, and the mixture was stirred at this temperature for 10 minutes. The resulting solution was added to a stirred solution of **5** (684.6 mg, 1.72 mmol) in THF (4 mL) at −78°C and then warmed to room temperature. The resulting solution was treated with DBU (0.25 mL, 1.7 mmol) and stirred for 2 hours. The solvent was removed in vacuo, and the residue was chromatographed (SiO_2/pentane-Et_2O 200:1) to give **6b** (567.2 mg, 52%): Pale yellow crystals; mp 167–169°C (hexane); ^{1}H NMR ($CDCl_3$) δ = 2.36 (6H, s, *o*-Me), 2.41 (3H, s, *p*-Me), 5.62 (1H, dd, $^3J_{PH}$ = 5.9 Hz, $^4J_{PH}$ = 2.9 Hz, Flu-H9), 7.16 (2H, s, Mes), 7.20–7.40 (4H, m, Flu-H2,H3,H6,H7), 7.42 (2H, d, J = 7.4 Hz, Flu-H1,H8), 7.69 (2H, d, J = 7.4 Hz, Flu-H4,H5), and 8.01 (2H, s, Ar); UV (CH_2Cl_2) 272 (log ϵ 4.4), 348 (3.9), and 379 nm (4.0); IR (KBr) 1274 and 741 cm^{-1}; MS m/z (*rel* intensity) 641 (M^+; 9) and 164 (Flu^+ − 1; 100); found: m/z 641.1110. Calcd for $C_{31}H_{22}F_9NP_2$: M, 641.1084.

1-[2,6-Bis(trifluoromethyl)phenyl]-2-[N-(9-fluorenyl)-N-mesitylamino]diphosphene (**6c**)

To a stirred solution of 2,6-bis(trifluoromethyl)phenylphosphine (289.6 mg, 1.18 mmol) in THF (3 mL) was added 1.18 mmol of butyllithium (1.59 M in hexane) at −78°C, and the mixture was stirred at that temperature for 10 minutes. The resulting solution was added to a stirred solution of **5** (279.3 mg, 0.70 mmol) in THF (2.5 mL) at −78°C, and then the solution was warmed to room temperature. The resulting solution was treated with DBU (0.10 mL, 0.67 mmol) and stirred for 2 hours. The solvent was removed in vacuo, and the residue was chromatographed (SiO_2/pentane-Et_2O 200:1) to give **6c** (80.7 mg, 20%) as pale yellow crystals: mp 135–137°C (pentane); ^{1}H NMR ($CDCl_3$) δ = 2.38 (6H, s, *o*-Me), 2.40 (3H, s, *p*-Me), 5.63 (1H, dd, $^3J_{PH}$ = 5.3 Hz and $^4J_{PH}$ = 2.5 Hz, Flu-H9), 7.15 (2H, s, Mes), 7.20–7.50 (5H, m, *p*-Ar and Flu-H2,H3,H6,H7), 7.46 (2H, d, J = 7.7 Hz, Flu-H1,H8), 7.68 (2H, d, J = 7.7 Hz, Flu-H4,H5), and 7.79 (2H, d, J = 8.0 Hz,

m-Ar); UV (CH_2Cl_2) 268 (log ϵ 4.4), 342 (3.7), and 376 nm (3.8); IR (KBr) 1288 and 739 cm^{-1}; MS *m/z* (*rel* intensity) 573 (M^+; 5) and 297 ($N(Flu)Mes^+ - 1$; 100); found: *m/z* 573.1232. Calcd for $C_{30}H_{23}F_6NP_2$: M, 573.1210.

1-Butyl-1-[N-(9-fluorenyl)-N-mesitylamino]-2-[2,4,6-tris(trifluoromethyl)phenyl]diphosphane (**7**)

To a stirred solution of the diphosphene **6b** (211.8 mg, 0.330 mmol) in THF (3 mL) was added 0.33 mmol of butyllithium (1.59 M in hexane) at −78°C, and the resulting violet solution was stirred at this temperature for 10 minutes. To this solution was added 13 μL (0.33 mmol) of absolute methanol at −78°C, and the solution was allowed to warm to room temperature and stirred for 2 hours. The solvent was removed in vacuo, and 7 mL of hexane was added to the residue. Insoluble material was removed by filtration, and the solvent was evaporated to give 216.5 mg (94%) of **7** (diastereomeric mixture, 6:1): Yellow viscous oil; ^{31}P NMR ($CDCl_3$) major: δ = −44.1 (d of sept, $^1J_{PH}$ = 220.0 Hz and $^4J_{PF}$ = 28.2 Hz, ArP) and 90.4 (sept, $^5J_{PF}$ = 21.0 Hz, MesNP), $^1J_{PP}$ = 330.8 Hz; minor: δ = −66.9 (d of sept, $^1J_{PH}$ = 223.4 Hz and $^4J_{PF}$ = 28.8 Hz, ArP) and 92.3 (sept, $^5J_{PF}$ = 24.9 Hz, MesNP), $^1J_{PP}$ = 223.6 Hz; MS *m/z* (*rel* intensity) 699 (M^+; 2), 386 ($P(Bu)N(Flu)Mes^+$; 100), and 298 ($N(Flu)Mes^+$; 61); found: *m/z* 699.1878. Calcd for $C_{35}H_{32}F_9NP_2$: M, 699.1866.

2-[N-(9-Fluorenyl)-N-mesitylamino]-3-(2,4,6-tri-t-butylphenyl)-1,2,3-thiadiphosphirane (**8a**)

To a solution of elemental sulfur (9.0 mg, 0.28 mg-atom) in toluene (1 mL) was added a solution of the diphosphene **6a** (139.3 mg, 0.230 mmol) in toluene (2.5 mL), and the mixture was stirred at room temperature for 80 hours. The solvent was removed under reduced pressure, and the residue was chromatographed (SiO_2/pentane-Et_2O 100:1) to give 20.0 mg of **8a** (14%): Colorless crystals; mp 64–67°C (pentane); ^1H NMR ($CDCl_3$) δ = 1.21 (9H, s, *p*-Bu^t), 1.53 (18H, s, *o*-Bu^t), 2.24 (6H, s, *o*-Me), 2.32 (3H, s, *p*-Me), 5.33 (1H, s, Flu-H9), 6.91 (2H, s, Mes), 7.15–7.62 (6H, m, Flu-H1,H2,H3,H6,H7,H8), 7.35 (2H, s, Ar), and 7.73 (2H, d, J = 7.4 Hz, Flu-H4,H5); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −106.3 (ArP) and −8.4 (MesNP), ABq, $^1J_{PP}$ = 260.7 Hz; UV (CH_2Cl_2) 264 (log ϵ 4.5) and 307 (3.8); IR (KBr) 1477, 1450, 1261, 1099, 1030, 802, and 733 cm^{-1}; MS *m/z* (*rel* intensity) 637 (M^+; 1), 297 ($Mes(Flu)N^+ - 1$; 41), 276 (ArP^+; 22), 164 ($Flu^+ - 1$; 20), 119 (Mes^+; 5), and 57 (Bu^{t+}; 100); found: *m/z* 637.3047. Calcd for $C_{40}H_{49}NP_2S$: M, 637.3060.

2-[N-(9-Fluorenyl)-N-mesitylamino]-3-[2,4,6-tris(trifluoromethyl)phenyl]-1,2,3-thiadiphosphirane (**8b**)

To a solution of elemental sulfur (8.0 mg, 0.25 mg-atom) in toluene (2 mL) was added a solution of the diphosphene **6b** (150.0 mg, 0.234 mmol) in toluene (3 mL). A catalytic amount (ca. 9 mg, 0.06 mmol) of DBU was added to the solution, and the mixture was stirred at room temperature for 60 hours. The solvent was removed in vacuo and the residue was chromatographed (SiO_2/pentane-Et_2O 100:1) to give **8b** (37.9 mg, 24%): Colorless crystals; mp 50–53°C (pentane); ^1H NMR ($CDCl_3$) δ = 2.24 (6H, s, *o*-Me), 2.33 (3H, s, *p*-Me), 5.33 (1H, s, Flu-H9), 6.92 (2H, s, Mes), 7.19–7.46 (6H, m, Flu-H1,H2,H3,H6,H7,H8), 7.73 (2H, d, J = 7.6 Hz, Flu-H4,H5), and 7.82 (2H, s, Ar); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −124.8 (sept, $^4J_{PF}$ = 36.9 Hz, ArP) and −28.4 (sept, $^5J_{PF}$ = 21.0 Hz, MesNP), ABX_6, $^1J_{PP}$ = 258.0 Hz; UV (CH_2Cl_2) 263 (log ϵ 4.6) and 307 (4.0); IR (KBr) 1263, 1193, 1141, 1020, 802, and 739 cm^{-1}; MS *m/z* (*rel* intensity) 673 (M^+; 13), 297 ($(Mes(Flu)N^+ - 1$; 87), and 165 (Flu^+; 100); found *m/z* 673.0817. Calcd for $C_{31}H_{22}F_9NP_2S$: M, 673.0805.

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