Dithienophosphinine

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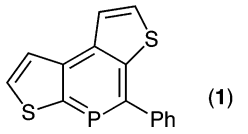
*Summary: Dithienophosphinine (**1**) was obtained in three steps starting with the ring expansion of dithienophosphole (**3**) by reaction with benzoyl chloride, triethylamine, and water. The three annellated rings of (**1**) are coplanar. Both the P═C(Ph) double bond (1.7281(17) Å) and the bridging C(Th)−C(Th) bond (1.426(2) Å) are indicative of electronic delocalization in the central ring. By comparison with parent phosphinine, (**1**) is less aromatic (NICS(1) −8.8 vs −10.8) and more easily reduced (at −1.94 V vs SCE in acetonitrile vs −2.27 V for the parent). Both the highest occupied molecular orbital and the lowest unoccupied molecular orbital are highly localized at the P═C(Ph) double bond and resemble the π and π* orbitals of a phosphaalkene.*

Introduction

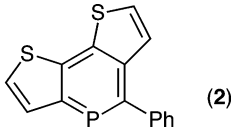
Molecules incorporating both thiophene and phosphinine rings are interesting on several counts. They can be seen as phosphorus-modified oligothiophenes. The work of Réau on thienyl-substituted phospholes[1] and Baumgartner on dithienophospholes[2] has convincingly shown the interest of these phosphorus-modified oligothiophenes as building blocks for optoelectronic materials.[3] From another standpoint, in these mixed thiophene-phosphinine molecules, the thiophene ring can be seen as a functionalizable carrier for the phosphinine ring. Neither electrophilic substitution nor metalation reactions are effective for the functionalization of phosphinines. The only two reasonably general functionlization methods reported to date are based on the palladium-catalyzed cross-coupling[4] and the zirconocene insertion[5] reactions of 2-halophosphinines. Several thienyl-substituted phosphinines have been reported in the literature, either made by ring expansion of phospholes,[6] cross-coupling reactions of 2-bromophosphinines,[4] or O to P exchange in pyrylium salts.[7] But, as far as we know, thieno-annellated phosphinines remain unknown today despite their obvious interest both from physicochemical and synthetic standpoints. In this report, we wish to describe our work on the synthesis and characterization of the first dithienophosphinine.

Results and Discussion

To get a more precise idea of the electronic properties of such dithienophosphinines, we first decided to perform a density functional theory (DFT) study of two representative species **1** and **2** at the B3LYP/6-311+G(d,p) level.[8] The lowest occupied molecular orbitals (LUMOs) of **1** and **2** appear at −2.04 and −1.85 eV, respectively, whereas the highest occupied molecular orbitals (HOMOs) are at −5.88 and −6.04 eV. The most significant result is that the HOMO−LUMO gap is smaller in **1** than in **2** by 0.35 eV. We thus focused our synthetic effort on the preparation of **1**.



(**1**)



(**2**)

Some time ago, we devised a three-step synthesis of phosphinines starting by the ring expansion of phospholes upon reaction with carboxylic acid chlorides.[9] This scheme was applied to dibenzophospholes to prepare phosphaphenanthrenes.[10] As expected, it proved possible to transpose this approach with dithienophosphole **3** to get dithienophosphinine **1** (eq 1).

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(1) Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812. Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau, R. *Org. Lett.* **2003**, *5*, 3467. Fave, C.; Cho, T. Y.; Hissler, M.; Chen, C. W.; Luh, T. Y.; Wu, C. C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254. Su, H. C.; Fadhel, O.; Yang, C. J.; Cho, T. Y.; Fave, C.; Hissler, M.; Wu, C. C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 983. Sebastian, M.; Hissler, M.; Fave, C.; Rault-Berthelot, J.; Odin, C.; Réau, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6152.

(2) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197. Baumgartner, T.; Bergmans, W.; Kárpáti, T.; Neumann, T.; Nieger, M.; Nyulászi, M. *Chem. Eur. J.* **2005**, *11*, 4687. Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495. Baumgartner, T.; Wilk, W. *Org. Lett.* **2006**, *8*, 503. Dienes, Y.; Durben, S.; Kárpáti, T.; Neumann, T.; Englert, U.; Nyulászi, L.; Baumgartner, T. *Chem. Eur. J.* **2007**, *13*, 7483−7500.

(3) Reviews: Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681. Hobbs, M. G.; Baumgartner, T. *Eur. J. Inorg. Chem.* **2007**, 3611.

(4) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1993**, *115*, 10665. Trauner, H.; Le Floch, P.; Lefour, J. M.; Ricard, L.; Mathey, F. *Synthesis* **1995**, 717.

(5) Le Floch, P.; Kolb, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2065. Rosa, P.; Le Floch, P.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1997**, *119*, 9417.

(6) Alcaraz, J. M.; Deschamps, E.; Mathey, F. *Phosphorus Sulfur* **1984**, *19*, 45.

(7) Müller, C.; Wasserberg, D.; Weemers, J. J. M.; Pidko, E. A.; Hoffmann, S.; Lutz, M.; Spek, A. L.; Meskers, S. C. J.; Janssen, R. A. J.; van Santen, R. A.; Vogt, D. *Chem. Eur. J.* **2007**, *13*, 4548.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(9) Mathey, F. *Tetrahedron Lett.* **1979**, 1753. Alcaraz, J.-M.; Brèque, A.; Mathey, F. *Tetrahedron Lett.* **1982**, *23*, 1565.

(10) Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *Tetrahedron Lett.* **1980**, *21*, 1441.

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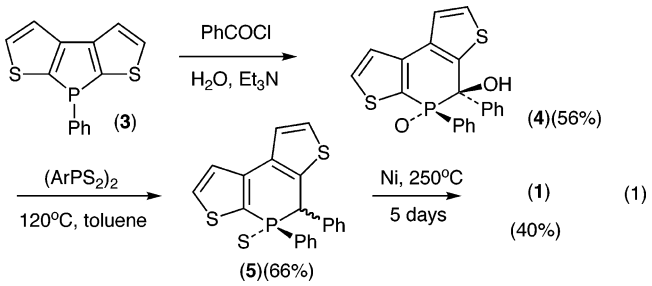
Publication on Web 10/25/2007



The starting dithienophosphole **3** was prepared by reaction of phenyldichlorophosphine with 2,2′-dilithio-3,3′-dithienyl.[11] The ring expansion gives **4** as a single diastereomer whose structure was established by X-ray crystal structure analysis (Figure 1). The P−C(OH) bond appears to be long and weak at 1.8751(8) Å. The P═O and C−OH bonds are on the opposite sides of the ring. This result gives some clue concerning the proposed mechanism of this ring expansion. In the proposed TBP intermediate, the phosphole ring occupies an apical-equatorial position due to its internal angle close to 90°. The acyl group in the equatorial plane tends to rotate so that the two negatively charged oxygen atoms stay as far as possible to reduce the electronic repulsion. This explains why only one diastereomer is formed when the phosphole apical P−C bond is cleaved (Scheme 1).

As previously observed in similar reactions, racemization occurs upon reductive sulfurization by the Lawesson reagent to give **5**. We have been able to crystallize out one of the two diastereomers. The X-ray crystal structure of this diastereomer **5a** is shown in Figure 2. In this isomer, the P−Ph occupies a pseudoaxial and the C−Ph a pseudo-equatorial position. The P−C(Ph) bond remains rather long at 1.8530(12) Å, although less than in **4**. To shed some light on this curious reaction, we decided to investigate it by DFT at the B3LYP/6-311+G(d,p) level on the non-annellated products. The conversion of carbinols into thiols by reaction with the Lawesson reagent is a well-known reaction.[12] Thus we admitted that the loss of sulfur takes place on thiols such as **6** (trans) or **7** (cis). Such a loss is unprecedented for ordinary thiols, so we looked for possible isomers of **6** and **7**. We detected two other genuine minima (no negative frequency) corresponding to the S−S derivative **8** and to the thiirane **9**. Their relative energies (ZPE included) are given in Scheme 2.

Since the reaction easily takes place in boiling toluene, only **8** is acceptable. Its computed structure is shown in Figure 3. It is stabilized by electronic delocalization as any λ^5-phosphinine.[13] The conversion of **7** into **8** via a concerted [1,3]-shift is possible but needs too much energy (barrier 42.2 Kcal mol^{-1}). Thus an ionization-recombination mechanism is probably involved. Indeed, the cation obtained by abstraction of SH^- from **6** or **7** shows a positive charge at sulfur of +0.33 (Mulliken). The loss of sulfur from organic S−S derivatives has been documented.[14] On this basis, we suggest that, in boiling toluene, an equilibrium exists between structures **6** and **7** on one side and structure **8** on the other side. The loss of sulfur displaces this equilibrium toward **10**. Our proposal is summarized in Scheme 3.

This mechanism nicely explains the racemization of the chiral center of **5** and the migration of the dienic system in the case of non-annellated dihydrophosphinines.[9]

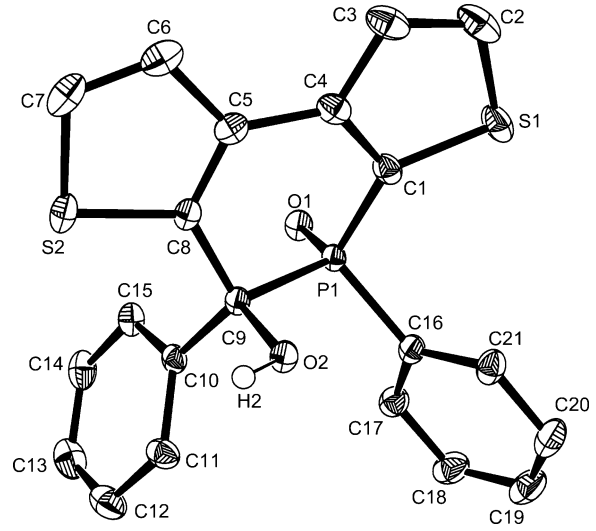


Figure 1. X-ray crystal structure of the ring-expanded product **4**. Main bond lengths (Å) and angles (deg.): P−C1, 1.7754(9); P−C9, 1.8751(8); P−C16, 1.7926(9); P−O1, 1.4952(6); C8−C9, 1.5146-(11); C9−O2, 1.4227(10); C5−C8, 1.3800(13); C4−C5, 1.4582-(13); C1−C4, 1.3871(13); C1−P−C9, 101.69(4).

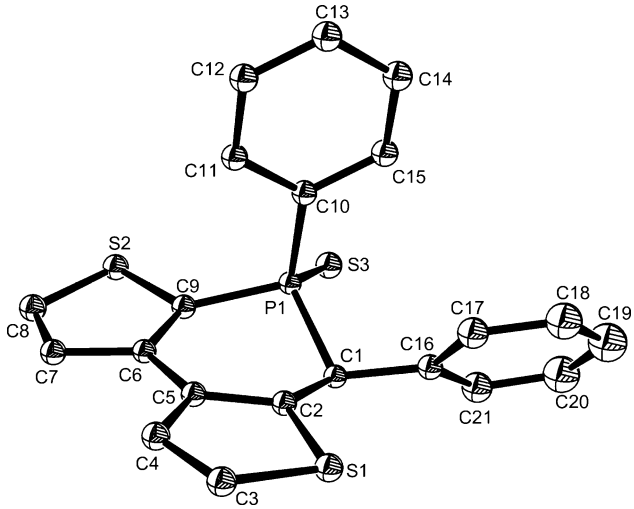


Figure 2. X-ray crystal structure of one of the two diastereomers of the dihydrophosphinine sulfide **5a**. Main bond lengths (Å) and angles (deg.): P−C1, 1.8530(12); P−C9, 1.7723(12); P−C10, 1.8138(12); P−S3, 1.9506(5); C1−C2, 1.5140(16); C2−C5, 1.3809-(16); C5−C6, 1.4627(16); C6−C9, 1.3823(17); C1−P−C9, 99.99-(6).

Finally, **5** was converted into the desired dithienophosphinine **1** by desulfurization and loss of benzene on nickel at 250 °C. The ^{31}P resonance of **1** appears at notably higher field than the resonance of the corresponding phosphaphenanthrene:[10] 149 vs 186 ppm. The X-ray crystal structure of **1** is shown in Figure 4. That the thiophene rings interact strongly with the central phosphinine nucleus is quite obvious from the significant inequivalencies of the two C−S and C═C bonds within each ring. This dissymmetry is well reproduced by the theoretical calculations. It is also interesting to point out that the C_4-C_5 bridge between the two thiophene rings is shorter than in a dithienophosphole[2] (1.426(2) vs 1.4397(19) Å), and also substantially shorter than in **4** (1.4582(13) Å) and **5a** (1.4627-(16) Å), thus highlighting the aromatization of the phosphinine ring. That the thiophene annulation reduces slightly the aromaticity of the P-ring is nevertheless quite obvious from the NICS-(1) value at −8.8 vs −10.8 for the parent phosphinine.[12] The

(11) Kellogg, R. M.; Schaap, A. P.; Wynberg, H. *J. Org. Chem.* **1969**, *34*, 343.
(12) Nishio, T. *J. Chem. Soc., Chem. Commun.* **1989**, 205.
(13) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229. Nyulászi, L.; Veszprémi, T. *J. Phys. Chem.* **1996**, *100*, 6456.
(14) Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1979**, *44*, 4135.

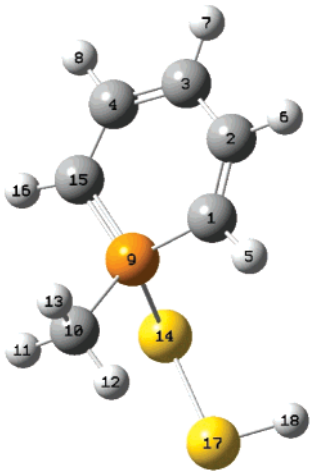


Figure 3. Computed structure of **8** at the B3LYP/6-311+G(d,p) level. Main bond lengths (Å) and angles (deg.): P−S14, 2.268; P−C1, 1.732; P−C15, 1.731; S14−S17, 2.118; C1−C2, 1.389; C2−C3, 1.399; C3−C4, 1.397; C4−C15, 1.391; C1−P−C15, 105.57; C1−P−S14, 115.76; P−S14−S17, 106.67.

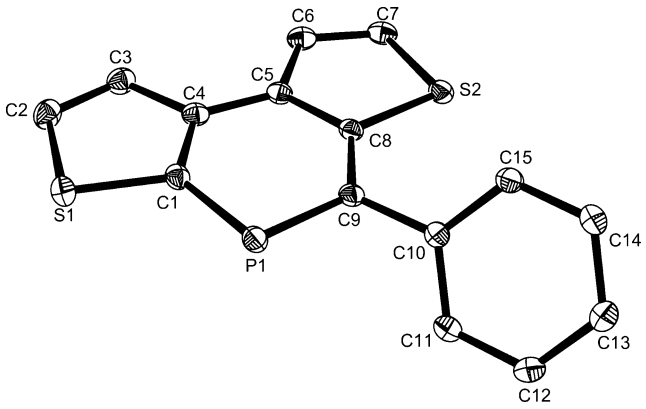


Figure 4. X-ray crystal structure of dithienophosphinine **1**. Main bond lengths (Å) and angles (deg.): P1−C1, 1.7513(17); P1−C9, 1.7281(17); C1−C4, 1.407(2); C4−C5, 1.426(2); C5−C8, 1.407-(2); C8−C9, 1.417(2); C1−S1, 1.7420(17); C2−S1, 1.7219(19); C2−C3, 1.358(3); C3−C4, 1.431(2); C8−S2, 1.7513(17); C7−S2, 1.7239(18); C6−C7, 1.356(2); C5−C6, 1.433(2); C1−P1−C9, 100.58(8); C1−S1−C2, 92.10(8); C7−S2−C8, 91.56(8); P1−C1−C4, 127.64(13); P1−C9−C8, 123.45(13); P1−C1−S1, 122.27(10).

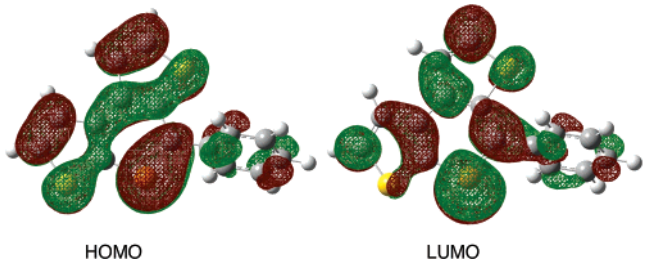


Figure 5. HOMO and LUMO of **1** as computed at the B3LYP/6-311+G(d,p) level.

shapes of the HOMO and LUMO are shown in Figure 5. They show a substantial localization at the P═C(Ph) bond and resemble the π and π^* orbitals of a phosphaalkene. This suggests that the chemistry of this species will, at least partly, resemble that of a stabilized P═C double bond. CV data in acetonitrile show one reversible reduction wave at −1.94 V vs SCE. The corresponding reduction wave for parent phosphinine occurs at −2.27 V.[15] The UV−vis spectrum of **1** shows four bands at 236.1, 268.1, 286.0, and 347.9 nm in dichloromethane. Upon excitation at 348 nm, a blue emission is observed at 426 nm. But the intensity of this emission is weak as already observed for thienyl-substituted phosphinines.[7] We are presently investigating the chemistry of this interesting new class of compounds.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Bruker Avance 300 and Varian Inova spectrometer operating at 300.13 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained on VG 7070 and Hewlett−Packard 5989A GC/Ms spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, Az.

Dithienophosphole (3). *n*-BuLi (25 mL, 40 mmol) was added dropwise to a solution of 2,2′-dibromo-3,3′-dithienyl[11] (6.2 g, 19 mmol) in Et_2O (150 mL) at −78 °C. The solution was stirred at −78 °C for 1 h before the temperature was raised to −30 °C. Subsequently, $PhPCl_2$ (2.7 mL, 20 mmol) dissolved in Et_2O (20 mL) was added slowly to the reaction mixture which was allowed to warm quickly to room temperature. The solvent was then removed under vacuum, and the residue was chromatographed on silica gel, with hexane/CH_2Cl_2 4:1 as the eluent. Compound **3** was obtained as white crystals (4 g, 75% yield). ^{31}P NMR ($CDCl_3$): δ −14.5. ^{13}C NMR ($CDCl_3$): δ 120.47 (s, = CH Th), 129.00 (d, $^3J_{C-P}$ = 7.6 Hz , *m* CH Ph), 129.85 (s, *p* CH Ph), 132.37 (d, $^2J_{C-P}$ = 21.0 Hz, *o* CH Ph), 133.60 (s, =CH Th), 134.98 (d, $^1J_{C-P}$ = 16.9 Hz, ipso C Ph), 142.66 (d, $^1J_{C-P}$ = 19.4 Hz, =CαTh), 147.26 (s, =Cβ Th) Anal. Calcd for $C_{14}H_9PS_2$: C, 61.75; H, 3.33. Found: C, 61.88; H, 3.05.

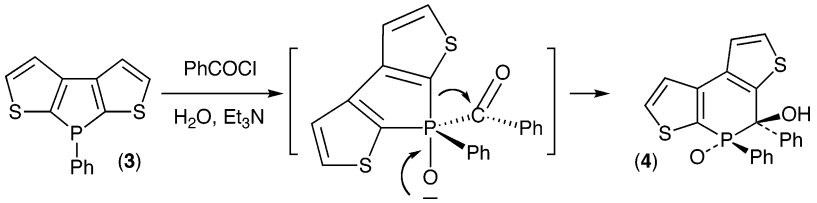
Ring-Expanded Product (4). To a solution of **3** (1.1 g, 4 mmol) in Et_2O (20 mL), was added subsequently 2 mL of NEt_3, then dropwise 2.5 mL of PhCOCl in Et_2O (5 mL). The mixture was stirred for 1 h at room temperature and cooled at 0 °C, and 15 mL of degassed, distilled H_2O was added. After stirring 1 h at room temp, the white precipitate was washed with H_2O (3 × 10 mL) and Et_2O (3 × 10 mL) and dried under vacuum (0.85 g, 56% yield). ^{31}P NMR ($CDCl_3$): δ 26.6. Mass: *m*/*z* 395 (MH+). Exact mass calcd for $C_{21}H_{16}O_2PS_2$, 395.0329; found, 395.0327. Because of its poor solubility, the product was recrystallized in CH_2Cl_2/toluene and mainly characterized by X-ray crystal structure analysis.

Dihydrophosphinine Sulfide (5a,b). The solution of **4** (0.6 g, 1.5 mmol) with the Lawesson reagent (0.4 g, 1 mmol) in toluene (25 mL) was heated under reflux overnight at 120 °C. The cooled solution was hydrolyzed with a saturated solution of Na_2CO_3 (10 mL), and the toluene phase was washed with H_2O (3 × 10 mL), dried on Na_2SO_4, and evaporated under vacuum. The residue was then chromatographed on silica gel with hexane/CH_2Cl_2 2:3 as the eluent. Compound **5** was isolated as a mixture of isomers, as yellow crystals (0.4 g, 66% yield). ^{31}P NMR (CH_2Cl_2): δ 31.3 (**a**) and 33.0 (**b**) (50:50). Pure monocrystals of **5a** were obtained by slow recrystallization in CH_2Cl_2/toluene. ^{1}H NMR ($CDCl_3$): δ 5.03 (d, $^2J_{HP}$ = 23.4 Hz, C*H*Ph). ^{13}C NMR ($CDCl_3$): δ 55.29 (d, $^1J_{CP}$ = 48.3 Hz, *C*HPh). Mass: *m*/*z* 395 (MH^+). Exact mass calcd for $C_{21}H_{16}PS_3$, 395.0151; found, 395.0154. The structure was confirmed by X-ray analysis.

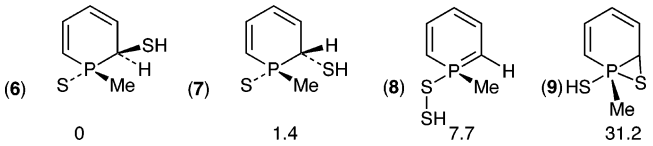
Dithienophosphinine (1). The solution of **5a**,**b** (0.4 g, 1 mmol) and Ni (0.5 g) in toluene (3 mL) was heated in a pressure tube at 250 °C for 5 days. The solution was diluted with CH_2Cl_2, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/CH_2Cl_2 9:1 as the eluent. Phosphinine (**1**) was isolated

(15) Elschenbroich, C.; Nowotny, M.; Metz, B.; Massa, W.; Graulich, J.; Biehler, K.; Sauer, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 547.

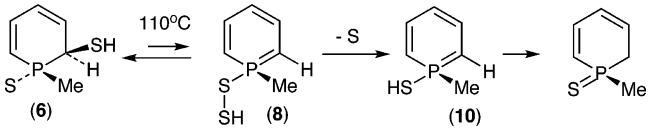
Scheme 1: Formation of 4



Scheme 2: Relative Energies in Kcal mol^{-1} (ZPE Included)



Scheme 3: Proposed Mechanism for the Loss of Sulfur



as white crystals (0.07 g, 40% yield). ^{31}P NMR (CD_2Cl_2): δ 149.0. ^{13}C NMR (CD_2Cl_2): δ 124.26 (s, CH β Th), 125.08 (d, $^3J_{CP} = 6.1$ Hz, *C*H β Th), 128.87 − 131.89 (CH), 137.60 (d, $J_{CP} = 10$ Hz, C), 139.20 (d, $J_{CP} = 10$ Hz, C), 142.78 (d, $J_{CP} = 26.4$ Hz, C ipso?), 155.50 (d, $^1J_{CP} = 59$ Hz, Cα), 165.90 (d, $^1J_{CP} = 48.3$ Hz, Cα). Exact mass calcd for $C_{15}H_{10}PS_2$, 284.9961; found, 284.9964. Anal. Calcd for $C_{15}H_9PS_2$: C, 63.36; H, 3.19. Found: C, 63.21; H, 2.86.

X-ray Structure Data. Measurements were carried out using a low-temperature device at $T = 100(2)$ K, on a BRUKER X8 APEX[16] KAPPA-CCD X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å). An automated strategy determination program COSMO[17] was used to define diffraction experiments on the basis of φ and ω scans. Frames were integrated using the Bruker SAINT version 7.06A software[18] and using a narrow-frame integration algorithm. The integrated frames yielded for the compounds the following:

1: A total of 9725 reflections collected at a maximum 2θ angle of 57.68° (2961 independent reflections, $R_{int} = 0.0259$, $R_{sig} = 0.0294$, completeness = 92.4%) and 2490 (84.09%) reflections were found greater than $2\sigma(I)$. Compound crystallizes in monoclinic cell, space group $P2(1)/n$, $a = 3.9855(6)$ Å, $b = 24.100(3)$ Å, $c = 12.6805(17)$ Å, $\alpha = 90.0°$, $\beta = 92.369(2)°$, $\gamma = 90.0°$, $V = 1216.9(3)$ Å^3, $Z = 4$, calculated density $D_c = 1.552$ Mg/m^3.

4: A total of 30098 reflections collected at a maximum 2θ angle of 80.52° (11308 independent reflections, $R_{int} = 0.0277$, $R_{sig} = 0.0343$, completeness = 99.7%) and 8606 (76.10%) reflections were found greater than $2\sigma(I)$. Compound crystallizes in monoclinic cell, space group $P2(1)/c$, $a = 13.2079(8)$, $b = 10.9300(6)$ Å, $c = 12.5030(7)$, $\alpha = 90.0°$, $\beta = 94.503(3)°$, $\gamma = 90.0°$, $V = 1799.39(18)$ Å,^{3} $Z = 4$, calculated density $D_c = 1.456$ Mg/m^3.

5a: A total of 13909 reflections collected at a maximum 2θ angle of 37.60° (4361 independent reflections, $R_{int} = 0.0121$, $R_{sig} = 0.0114$, completeness = 93.0%) and 4190 (96.07%) reflections were found greater than $2\sigma(I)$. Compound crystallizes in monoclinic cell, space group $P2(1)/n$, $a = 11.5695(18)$ Å, $b = 9.8629(15)$ Å, $c = 15.957(3)$ Å, $\alpha = 90.0°$, $\beta = 99.685(2)°$, $\gamma = 90.0°$, $V = 1794.9(5)$ Å,^{3} $Z = 4$, calculated density $D_c = 1.456$ Mg/m^3.

Absorption corrections were applied for all data using the SADABS program included in SAINTPLUS software package.[18] Direct methods using the Sir92 program[19] were used for resolution. Direct methods of phase determination followed by some subsequent difference Fourier map led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit. With subsequent isotropic refinement and some Fourier differences synthesis, all non-hydrogen atoms were identified; atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full-matrix least-squares procedure on F^2 using SHELXTL software.[20] Hydrogen atoms were included in the refinement in calculated positions with isotropic thermal parameters fixed at 20% and 50% higher than C_{sp^2} and C_{sp^3} atoms, respectively, to which they were connected, torsion angles were refined for methyl groups. The refinement converged at R1 = 0.0344, wR2 = 0.0860, with intensity $I > 2\sigma(I)$, largest peak/hole in the final difference map found to 0.756 and −0.281 e.Å^{-3} for **1**; R1 = 0.0404, wR2 = 0.1062, with intensity $I > 2\sigma(I)$, largest peak/hole in the final difference map found to 0.661 and −0.272 e.Å^{-3} for **4**; and R1 = 0.0275, wR2 = 0.0736, with intensity $I > 2\sigma(I)$, largest peak/hole in the final difference map found to 0.473 and −0.286 e.Å^{-3} for **5a**. Drawings of molecules were achieved using ORTEP32.[21]

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Note Added after ASAP Publication. In the version of this paper published on the Web on October 25, 2007, the crystal data for compound **3** were given in the Experimental Section instead of the crystal data for compound **1**. In addition, the CIF file deposited as Supporting Information also contained the data for compound **3** instead of compound **1**. The version of the paper that now appears correctly gives all data for compound **1**.

Supporting Information Available: X-ray crystal structure analyses of compounds **1**, **4**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) *APEX 2*, version 2.0−2; Bruker AXS Inc.: Madison, WI, 2004.
(17) *COSMO NT*, version 1.40; Bruker AXS Inc.: Madison, WI.
(18) *SAINTPLUS Software Reference Manual*, version 6.02A; Bruker AXS Inc.: Madison, WI, 1997−1998.
(19) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. SIR92−A program for crystal structure solution. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(20) *SHELXTL Software Reference Manual*, version 6.10; Bruker AXS Inc.: Madison, WI, Dec. 5, 2000.
(21) Farrugia, L. J. ORTEP3 for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.