Notes

The Phosphaalkene-like Reactivity of Dithienophosphinines

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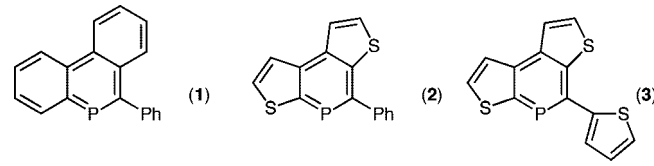
Received April 10, 2008

*Summary: 2-Thienyldithienophosphinine (**3**) has been prepared in three steps starting by the ring expansion of dithienophosphole (**4**) upon reaction with 2-thiophenecarboxylic acid chloride, triethylamine, and water. DFT calculations indicate that the replacement of the phenyl in 2-phenyldithienophosphinine (**2**) by the 2-thienyl substituent in **3** significantly reduces the HOMO−LUMO gap. Accordingly, **3** reacts cleanly and quantitatively with 2,3-dimethylbutadiene to give the [2+4] cycloadduct **11**, whose structure has been confirmed by X-ray crystal structure analysis, whereas **2** reacts slowly and gives the adduct in only 52% yield, and the analogous 2-phenylphosphaphenanthrene (**1**) gives only an untractable mixture.*

Introduction

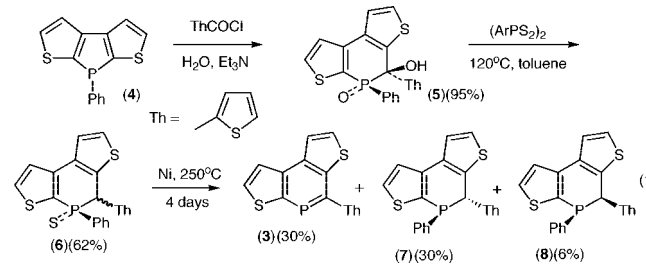
The work of Réau on thienyl-substituted phospholes[1] and Baumgartner on dithienophospholes[2] has convincingly shown the value of phosphorus-modified oligothiophenes as building blocks for optoelectronic materials.[3] On this basis, we have started an investigation of the synthesis and chemistry of the previously unknown dithienophosphinines.[4] During our preliminary investigation, we have noticed two clues that suggest that the thieno annellation sharply modifies the properties of dithienophosphinines by comparison with their benzo analogues, i.e., the phosphaphenanthrenes.[5] Whereas the final aromatization step leading to **1** takes place at 275 °C from the P-benzyl 1,2-dihydro derivative, the significantly easier aromatization leading to **2** takes place at 250 °C from the P-phenyl 1,2-dihydro derivative. In addition, the ^{31}P resonance of **2** (δ ^{31}P 149 ppm) is strongly shifted to higher fields when compared to the resonance of **1** (δ ^{31}P 186 ppm), which lies in the normal zone for phosphinines.



These observations led us to prepare 2-thienyldithienophosphinine (**3**) and to compare the chemistry of **1**, **2**, and **3**. This comparison demonstrates that the thiophene unit, both as substituent and annellating ring, significantly modifies the chemistry of phosphinines.

Results and Discussion

2-Thienyldithienophosphinine (**3**) was prepared as shown in eq 1. The phosphinine was isolated as yellow crystals (both **1** and **2** are colorless). The ^{31}P chemical shift of **3** (δ ^{31}P 150.6 ppm in $CDCl_3$) is very close to that of **2**. During the final aromatization step, notable quantities of the *trans* diastereomer of the 1,2-dhydrophosphinine **7** were recovered together with small quantities of the *cis* isomer **8**. The α-proton is coupled to ^{31}P in **8** (δ5.10, $^2J_{HP}$ = 9.4 Hz) and noncoupled in **7** (δ 4.83 $^2J_{HP}$ = 0 Hz). These results are in line with the known dependency of the $^2J_{HP}$ coupling constants on the H−C−P−lone pair dihedral angle in cyclic phosphines.[6] Their stereochemistry was definitively established by X-ray crystal structure analysis.



The structure of **8** is shown as an example (Figure 1). The H−C−P−Ph dihedral angle is 174.55°, and the Th−C−P−Ph angle is 72.43°. When **7** was heated at 250 °C over nickel powder, it was slowly transformed into phosphinine **3**. On this

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(1) (a) Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812. (b) Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau, R. *Org. Lett.* **2003**, *5*, 3467. (c) 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. (d) 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. (e) Sebastian, M.; Hissler, M.; Fave, C.; Rault-Berthelot, J.; Odin, C.; Réau, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6152.

(2) (a) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197. (b) Baumgartner, T.; Bergmans, W.; Kárpáti, T.; Neumann, T.; Nieger, M.; Nyulászi, M. *Chem.−Eur. J.* **2005**, *11*, 4687. (c) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495. (d) Baumgartner, T.; Wilk, W. *Org. Lett.* **2006**, *8*, 503. (e) Dienes, Y.; Durben, S.; Kárpáti, T.; Neumann, T.; Englert, U.; Nyulászi, L.; Baumgartner, T. *Chem.−Eur. J.* **2007**, *13*, 7487.

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

(4) Tran Huy, N. H.; Donnadieu, B.; Mathey, F. *Organometallics* **2007**, *26*, 6497.

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

(6) Albrand, J. P.; Gagnaire, D.; Robert, J. B. *J. Chem. Soc., Chem. Commun.* **1968**, 1469.

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Publication on Web 06/26/2008

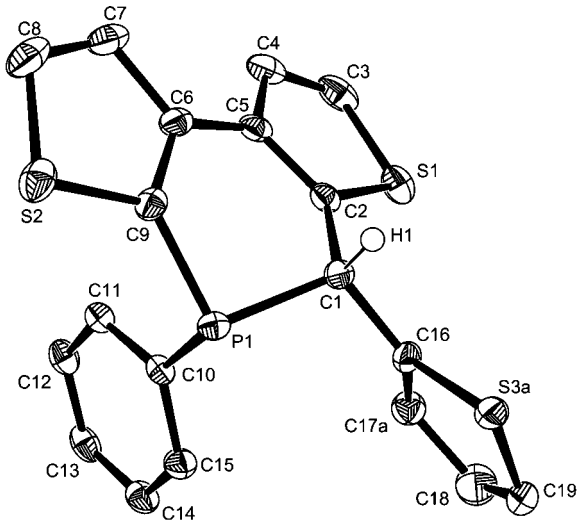
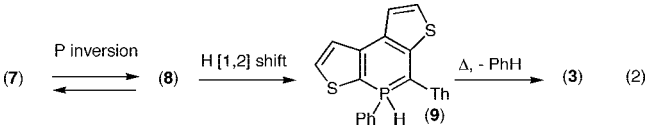


Figure 1. Stereochemistry of 1,2-dihydrodithiophosphinine (**8**) as determined by X-ray crystal structure analysis.

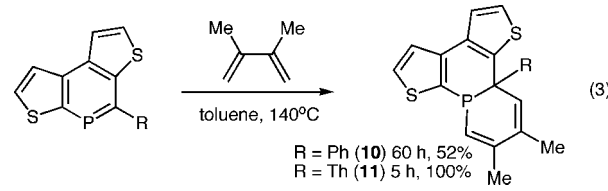
basis, we propose the intermediacy of the λ^5-phosphinine **9** in the aromatization reaction (eq 2).



The [1,2] suprafacial shift of the α-H from C to P can take place only in the *cis* isomer **8**, and **7** must first undergo a pyramidal inversion at P before being converted into the phosphinine **3**.

Since **3** is yellow whereas **1** and **2** are colorless, we recorded the UV−vis spectrum of **3**. The four bands of the spectrum of **2** at 236.1, 268.1, 286.0, and 347.9 nm are shifted in most cases toward longer wavelengths at 234.0, 271.0, 306.1, and 360.0 nm, confirming the significant influence of the substituent on the electronic structure of the phosphinine. In the same vein, DFT computations[7] at the B3LYP/6-311+G(d,p) level indicated that the HOMO−LUMO gap is reduced by 0.16 eV when replacing Ph in **2** by Th in **3**. This reduction mainly results from the lowering of the LUMO. A closer inspection of the computed structural data and Mulliken charges indicates that a significant charge transfer takes place from the thienyl substituent to the P=C double bond (Scheme 1).

In our previous paper, we noticed that the HOMO and LUMO of **2** are highly localized at the P=C double bond and are shaped like the π and π^* orbitals of a phosphaalkene. This observation suggested that **2** could react as a dienophile, contrary to nonannellated λ^3-phosphinines. Thus, we decided to study the reactivity of **1**−**3** toward 2,3-dimethylbutadiene. Phosphaphenanthrene **1** reacts to give a complex mixture of products including the expected cycloadduct in low yield. On the contrary, dithienophosphinine (**2**) reacts cleanly but slowly with the diene at 140 °C, and 2-thienyldithienophosphine (**3**) gives a fast and quantitative reaction under the same conditions (eq 3).



The structure of **11** is depicted in Figure 2. It shows some disorder due to the presence of two orientations of the 2-thienyl substituent. The two annellating thieno rings are almost coplanar (interplane angle ca. 16°). The phosphorus atom is highly pyramidal: ∑C−P−C angles = 295.7°.

Apart from demonstrating the significant influence of thieno annellation and thienyl substitution on the chemistry of phosphinines, the synthesis of the highly annellated phosphines **10** and **11** could be of interest in homogeneous catalysis. Very bulky and highly annellated phosphines indeed seem to be very efficient as ligands in palladium-catalyzed reactions.[8]

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.

2-Hydroxy-1-phenyl-2-thienyl-1,2-dihydrodithienophosphinine Oxide (5). To a solution of dithienophosphole (**4**)[4] (2.3 g, 8.4 mmol) in Et_2O (50 mL) was added 4.5 mL of NEt_3, then dropwise 5 mL of ThCOCl in Et_2O (20 mL). The mixture was stirred for 1 h at room temperature and cooled at 0 °C, and 35 mL of degassed, distilled H_2O was added. After stirring for 3 h at RT, the white precipitate was washed with H_2O (3 × 30 mL) and Et_2O (3 × 30 mL) and dried under vacuum (3.2 g, 95% yield). ^{31}P NMR (THF): δ 20.6 ppm. MS: *m*/*z* 401 (MH^+, 100%). Anal. Calcd for $C_{19}H_{13}O_2PS_3$: C, 56.98; H, 3.27. Found: C, 57.06; H, 3.69.

1-Phenyl-2-thienyl-1,2-dihydrodithienophosphinine Sulfide (6). A solution of **5** (3.2 g, 8 mmol) with Lawesson reagent (3 g, 7.5 mmol) in toluene (150 mL) was heated under reflux overnight at 120 °C. The cooled solution was hydrolyzed with a saturated solution of Na_2CO_3 (75 mL), and the toluene phase was washed with H_2O (3 × 80 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 eluent. Compound **6** was isolated as a mixture of isomers, as light salmon crystals (2 g, 62% yield).

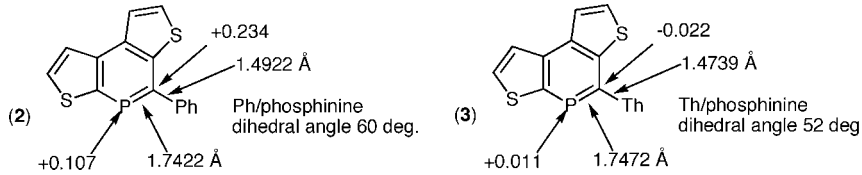
^{31}P NMR ($CDCl_3$): δ 32.2. ^{1}H NMR ($CDCl_3$): δ 5.06 (d, $^2J_{HP}$ = 14.1 Hz, C*H*Th). ^{13}C NMR ($CDCl_3$): δ 46.62 (d, $^1J_{CP}$ = 50.1 Hz, *C*HTh). MS: *m*/*z* 401 (MH^+, 100%). Anal. Calcd for $C_{19}H_{13}PS_4$: C, 56.97; H, 3.27. Found: C, 57.00; H, 3.27.

2-Thienyldithienophosphinine (3) and Dihydro Derivatives 7 and 8. A solution of **6** (1.2 g, 3 mmol) and Ni (1.5 g) in toluene (5 mL) was heated in a pressure tube at 250 °C for 4 days. The

(7) 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.; 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.: Pittsburgh, PA, 2003.

(8) See, for example:Iwasawa, T.; Komano, T.; Tajima, A.; Tokunaga, M.; Obora, Y.; Fujihara, T.; Tsuji, Y. *Organometallics* **2006**, *25*, 4665.

Scheme 1



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 eluent.

(a) Phosphinine **3** (first eluted product) was isolated as yellow crystals (0.26 g, 30% yield). ^{31}P NMR ($CDCl_3$): δ 150.6. ^{13}C NMR ($CDCl_3$): δ 137.53 (d, $^3J_{C-P}$ = 10.3 Hz, C_γ phosphinine), 138.87 (d, $^2J_{C-P}$ = 10.4 Hz, P−C=*C*), 141.35 (d, $^2J_{C-P}$ = 13.8 Hz, P=C-*C*S thieno), 144.06 (d, $^2J_{C-P}$ = 32.2 Hz, P=C-*C*S thienyl), 155.08 (d, $^1J_{C-P}$ = 59.9 Hz, P−C_α thienyl), 156.56 (d, $^1J_{C-P}$ = 48.3 Hz, P−C_α thieno). The assignments have been made on the basis of a simulation by DFT (B3LYP/6-311+G(d,p)). MS: *m*/*z* 291 (MH^+, 100%). Anal. Calcd for $C_{13}H_7PS_3$: C, 53.77; H, 2.43. Found: C, 53.52; H, 2.31.

(b) Phosphine **8** (second eluted product) was isolated as light yellow crystals (0.08 g, 6% yield). ^{31}P NMR ($CDCl_3$): δ −41.7. ^{1}H NMR ($CDCl_3$): δ5.10 (s, $^2J_{HP}$ = 9.4 Hz, *H cis* to lone pair, C*H*Th). ^{13}C NMR ($CDCl_3$): δ 39.80 (d, $^1J_{CP}$ = 18.4 Hz, C*H*Th). Anal. Calcd for $C_{19}H_{13}PS_3$: C, 61.93; H, 3.56. Found: C, 62.34; H, 3.89.

(c) Phosphine **7** (third eluted product) was isolated as light orange crystals (0.40 g, 30% yield). ^{31}P NMR ($CDCl_3$): δ −30.6. ^{1}H NMR ($CDCl_3$): δ 4.83 (s, $^2J_{HP}$ = 0 Hz, *H trans* to lone pair, C*H*Th). ^{13}C NMR ($CDCl_3$): δ 39.04 (d, $^1J_{CP}$ = 16.9 Hz, C*H*Th). MS: *m*/*z* 385 (MH^+ + O, oxidized species, 100%). Anal. Calcd for $C_{19}H_{13}PS_3$: C, 61.93; H, 3.56. Found: C, 62.03; H, 3.80. X-ray monocrystals were obtained from CH_2Cl_2/hexane.

[4+2] Cycloadducts 10 and 11. A solution of **2** (0.015 g, 0.05 mmol) and 2,3-dimethylbutadiene in excess (0.5 mL) in toluene (2 mL) was heated in a pressure tube at 140 °C and monitored by ^{31}P NMR; the cycloaddition was complete after 50 h heating at 140 °C. The solution was then evaporated and chromatographed on silica gel with hexane/CH_2Cl_2 (4:1) as eluent. The cycloadduct **10** was isolated as white crystals (10 mg, 52% yield).

^{31}P NMR ($CDCl_3$): δ −58.8. ^{13}C NMR ($CDCl_3$): δ 20.45 (s, Me), 22.10 (s, Me), 30.73 (d, $^2J_{CP}$ = 13.8 Hz, CH_2), 47.18 (d, $^1J_{CP}$ = 12.27 Hz, CH_2). MS: *m*/*z* 367 (MH^+, 100%), 383 (MH^+ + O, oxidized species, 90%).

A solution of **3** (0.03 g, 0.1 mmol) and 2,3-dimethylbutadiene in excess (1 mL) in toluene (3 mL) was heated in a pressure tube at 140 °C for 5 h, then evaporated and chromatographed on silica gel with hexane/CH_2Cl_2 (4:1) as eluent. The cycloadduct **11** was isolated as white crystals (40 mg, quantitative yield).

^{31}P NMR ($CDCl_3$): δ −55.5. ^{13}C NMR ($CDCl_3$): δ 20.47 (s, Me), 21.95 (d, $^3J_{CP}$ = 6.14 Hz, Me), 31.48 (d, $^2J_{CP}$ = 13.80 Hz, CH_2), 47.64 (d, $^1J_{CP}$ = 12.27 Hz, CH_2). MS: *m*/*z* 373 (MH^+, 100%); 389 (MH^+ + O, oxidized species, 35%). Anal. Calcd for $C_{19}H_{17}PS_3$: C, 61.26; H, 4.60. Found: C, 61.61; H, 4.99. X-ray monocrystals were obtained from CH_2Cl_2/Et_2O/hexane.

X-ray Structure Determination of 8 and 11. Measurements were carried out using a low-temperature device at T = 100(2) K, on a Bruker X8-APEX[9] KAPPA-CCD X-ray diffractometer system (Mo radiation, λ = 0.71073 Å). The automated strategy determination program COSMO[10] was used to define diffraction experiments on the basis of phi and omega scans. Frames were integrated using the Bruker SAINT version 7.06A software[11] and using a narrow-frame integration algorithm.

8: a total of 13 999 reflections collected at a maximum 2θ angle of 58.66° (4320 independent reflections, R_{int} = 0.0171, R_{sig} = 0.0182, completeness = 92.8%) and 3890 (90.05%) reflections were found greater than 2σ(*I*). Compound crystallized in the monoclinic cell, space group *P*2(1)/*n*, *a* = 8.5061(7) Å, *b* = 13.0337(11) Å, *c* = 15.2990(13) Å, α = 90.0°, β = 90.0370(10)°, γ = 90.0°, *V* = 1696.1(2) Å^3, *Z* = 4, calculated density D_c = 1.443 Mg/m^3.

11: a total of 15 730 reflections collected at a maximum 2θ angle of 67.40° (6921 independent reflections, R_{int} = 0.0296, R_{sig} 0.0442, completeness = 99.0%) and 5345 (77.23%) reflections were found greater than 2σ(*I*). Compound crystallized in the monoclinic cell, space group *P*2(1)/*c*, *a* = 8.0053(3) Å, *b* = 8.6885(4) Å, *c* = 14.3922(9) Å, α = 103.068(4)°, β = 92.171(3)°, γ = 114.772(2)°, *V* =875.37(8) Å^3, *Z* = 4, calculated density D_c = 1.413 Mg/m^3.

Absorption corrections were applied for all data using the SADABS program included in the SAINTPLUS software package.[11] Direct methods using the Sir92 program[12] were used for resolution. Direct methods of phase determination followed by a 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 difference synthesis, all non-hydrogen atoms were identified, and 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

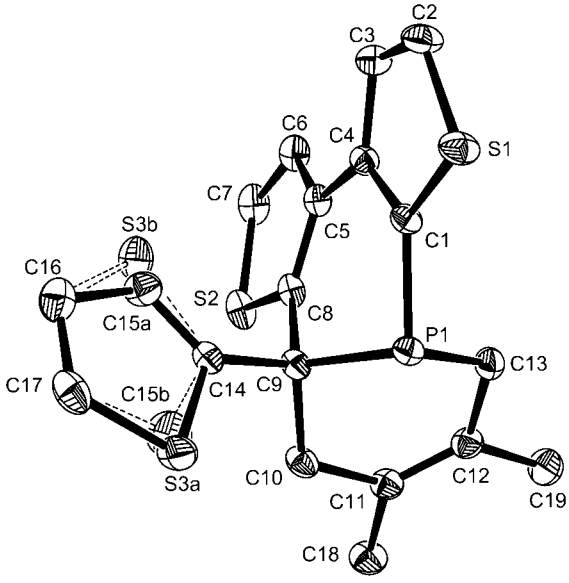


Figure 2. X-ray crystal structure of [4+2] cycloadduct **11**. Main bond lengths (Å) and angles (deg): P1−C1 1.8079(14), P1−C9 1.8790(14), P1−C13 1.8504(14), C1−C4 1.3833(18), C4−C5 1.4602(19), C5−C8 1.3816(19), C8−C9 1.5126(19), C9−C10 1.5405(19), C10−C11 1.5154(19), C11−C12 1.338(2), C12−C13 1.512(2); C1−P1−C9 98.06(6), C1−P1−C13 100.50(6), C9−P1−C13 97.13(6), C3−C4−C5−C6 15.99.

(9) Bruker. *APEX 2* version 2.0-2; Bruker AXS Inc.: Madison, WI, 2004.
(10) *COSMO NT* Version 1.40; Bruker AXS Inc.: Madison, WI, XXXX.
(11) *SAINTPLUS Software Reference Manual*, Version 6.02A; Bruker Analytical X-Ray System, Inc.: Madison, WI, 1997−1998.
(12) *SIR92*, A program for crystal structure solution: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

software.[13] Hydrogen atoms were included in the refinement in calculated positions with isotropic thermal parameters fixed at 20% and 50% higher than Csp^2 and Csp^3 atoms, respectively, to which they were connected. Torsion angles were refined for methyl groups. The H(1) atom was isotropically refined for compound **8**. For both compounds a statistical disorder generated by a free rotation was found for the thiophene ring. These were refined using restraints put on distances and bond angles in order to get a chemically correct model. The refinement converged at R1 = 0.0331, wR2 = 0.0829, with intensity $I > 2\sigma(I)$, largest peak/hole in the final difference map 0.666 and −0.548 e $Å^{-3}$ for **7** and R1 = 0.0427, wR2 = 0.1042, with intensity $I > 2\sigma(I)$, largest peak/hole in the final difference map 0.698 and −0.302 e.$Å^{-3}$ for **11**. Drawings of molecules were achieved using ORTEP32.[14] Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ UK, on quoting the full journal citation.

Acknowledgment. The authors thank the CNRS and the University of California Riverside for the financial support of this work. Thanks are also due to Dr. Dan Borchardt for the UV/vis spectra.

Supporting Information Available: X-ray crystal structure analyses of compounds **8** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8003256

(13) *SHELXTL Software Reference Manual*, Version 6.10; Bruker Analytical X-Ray System, Inc.: Madison, WI, 2000.

(14) *ORTEP3* for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.