

Preparation, Methylation, and Coupling Reaction of 1,2-Dithienyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes

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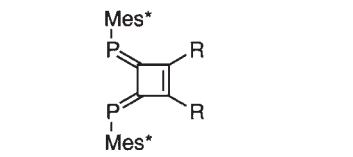
Sterically protected 1,2-di(2-thienyl)- and 1,2-di(3-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes were prepared and their properties were studied. When the dithienyldiphosphinidenecyclobutenes were allowed to react with butyllithium and then with iodomethane, the corresponding methylthienyl derivatives were obtained. The structure of (*E*,*E*)-1,2-bis(5-methyl-3-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene was analyzed by X-ray crystallography. Lithiation of the dithienyldiphosphinidenecyclobutenes, followed by treatment with $CuCl_2$, afforded the corresponding coupling products on the thiophene rings.

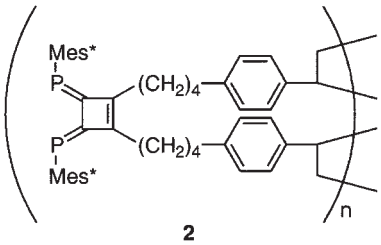
Sterically protected 3,4-diphosphinidenecyclobutenes (abbreviated as DPCB, **1** in Chart 1),[1] are unique ligands,[2] because of the relatively rigid framework that contains the phosphorus–carbon π-bonds.[3] Various transition metal complexes of DPCB have been prepared[2] and used as homogeneous catalysts;[4] however, there are only limited examples of compounds containing more than one DPCB unit in a molecule, although we previously reported the synthesis of a polymeric DPCB derivative **2**.[5] Although oligomeric DPCB derivatives have not been reported, they attract interest, from a viewpoint of modern transition metal complex chemistry, because they might form the 'metal assembled complexes' containing sp^2-hybridized phosphorus-bonded transition metals.

For the purpose of connecting the DPCB moieties, reactions under mild conditions are desirable, because the phosphorus–carbon π-bonds are essentially reactive and may decompose under severe reaction conditions. We report here preparations of 1,2-dithienyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes **1a** and **1b** as promising building blocks containing the DPCB skeleton.[6]

In a typical preparative method of 3,4-diphosphinidenecyclobutenes, alkynylphosphines were used as the starting material.[1] Thus, first we prepared (thienylethynyl)(2,4,6-tri-*t*-butylphenyl)phosphines (**3a**,**b**), which contain a bulky 2,4,6-tri-*t*-butylphenyl substituent (hereafter abbreviated to the Mes* group) as a sterically protecting auxiliary[7] (Scheme 1). Reaction of 2-ethynylthiophene[8] with ethylmagnesium bromide, followed by treatment with chloro(2,4,6-tri-*t*-butylphenyl)phosphine,[9] afforded **3a** in 44% yield. In some cases, phosphaallene **4a** was formed as a by-product, probably via base-induced allenic rearrangement of **3a**. Compound **3b** was also obtained by a similar method in 82% yield, starting from 3-ethynylthiophene[8b,10] and chloro(2,4,6-tri-*t*-butylphenyl)phosphine. In this case, only a trace amount of phosphaallene **4b** was formed.



1a: R = 2-thienyl, **1b**: R = 3-thienyl,
1c: R = Ph, **1d**: R = H



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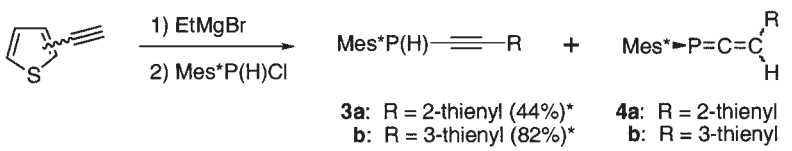
Mes* = 2,4,6-*t*-$Bu_3C_6H_2$

Chart 1.



3a: R = 2-thienyl (44%)* **4a**: R = 2-thienyl
b: R = 3-thienyl (82%)* **b**: R = 3-thienyl

* Isolated yield based on the starting Mes^*PH_2.

Scheme 1.

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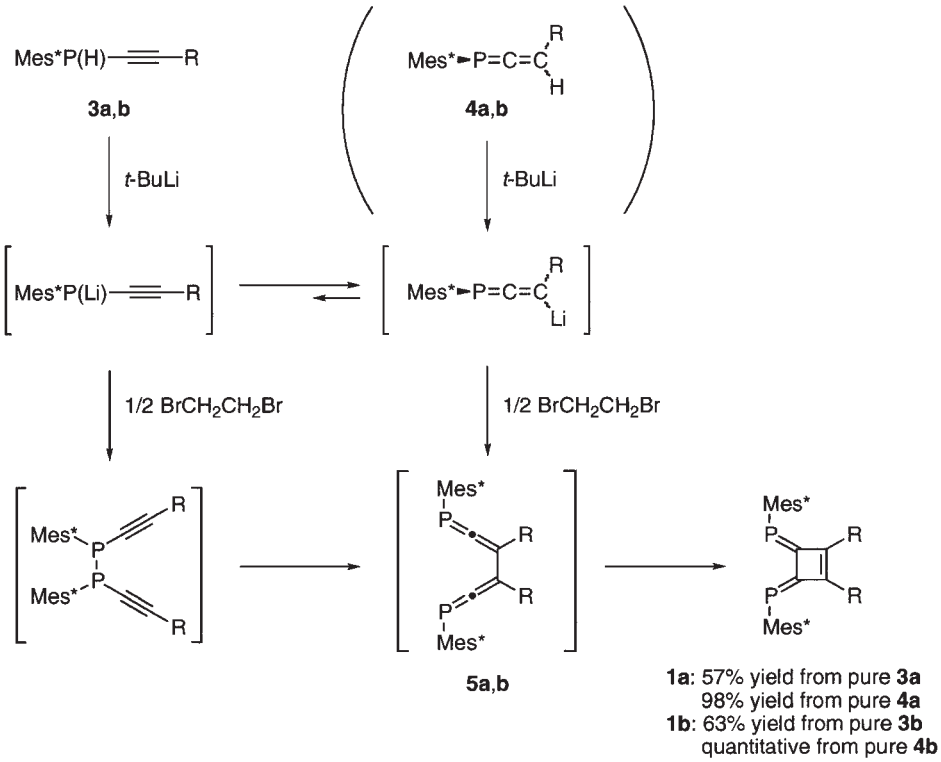


Scheme 2.

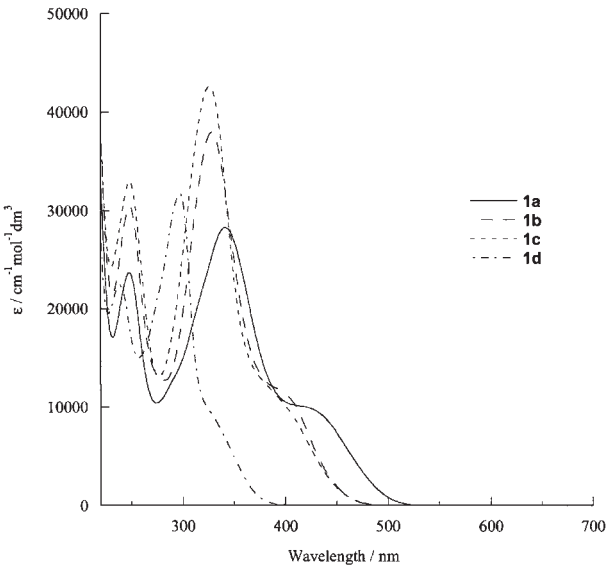


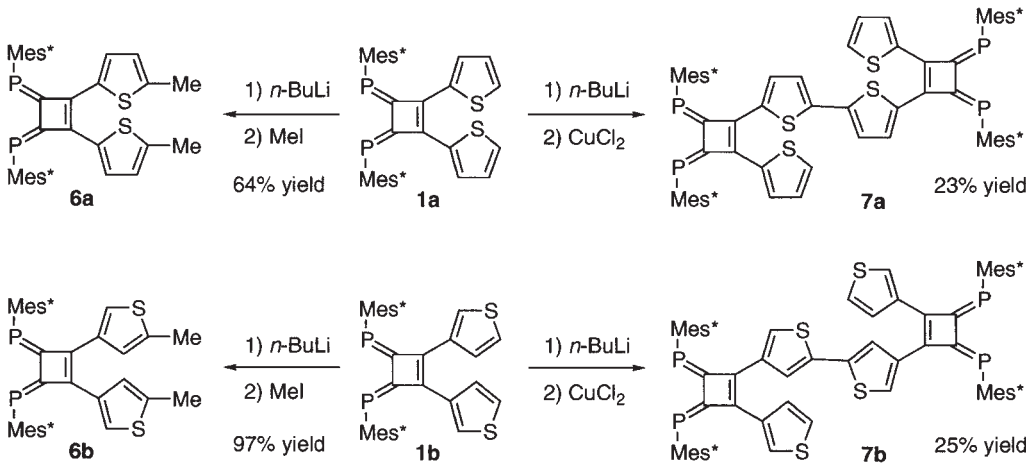
Fig. 1. UV–vis spectra of **1a**–**d** in hexane.

The ethynylphosphines **3a** and **3b** thus obtained were converted to the corresponding diphosphinidenecyclobutene **1a** and **1b** by the ordinary method[1b] using *t*-butyllithium (1 molar ratio) and 1,2-dibromoethane (0.5 molar ratio) [Scheme 2, **1a**: 57% yield, **1b**: 63% yield]. In the reaction of **3a**, formation of an intermediate **5a** was observed by ^{31}P NMR spectroscopic monitoring [**5a**: $\delta_P = 80.5$]. It should be noted that reactions of **4a** and **4b** with *t*-butyllithium (1 molar ratio) followed by addition of 1,2-dibromoethane (0.5 molar ratio) also gave **1a** and **1b**, respectively, in nearly quantitative yields.

Figure 1 shows the UV–vis spectra of **1a** and **1b** along with those of the 1,2-diphenyl derivative (**1c**)[1a] and 1,2-non-substituted DPCB (**1d**).[1c] The bathochromic effect was observed in the absorption of the aromatic ring-substituted DPCB (**1a**–**c**), compared with that of **1d**. Although the spectrum of **1b** was very similar to that of **1c**, the longest absorption band of **1a** showed an apparent red shift (ca. 30 nm), compared to the corresponding absorption bands of **1b** and **1c**. The red shift in 2,2′-bithienyl, compared with either 2,3′- or 3,3′-bithienyl, is well documented; this shift also appears in oligothiophenes of higher molecular weights.[11]

Lithiation of **1a** with butyllithium (2 molar ratio), followed by treatment with an excess amount of iodomethane, afforded the corresponding bis(5-methyl-2-thienyl) derivative **6a** in 64% isolated yield (Scheme 3). It should be mentioned that **6a** (*E*,*E*-form) isomerized relatively easily to the (*E*,*Z*)-form during the isolation process. This isomerization lowered the isolated yield of **6a**. In the case of methylation reaction of **1b**, bis(5-methyl-3-thienyl) derivative **6b** was obtained regioselectively in 97% yield. Introduction of a substituent at the position α to the bulky cyclobutene group seems to be retarded due to steric repulsion. The regioselective introduction of substituents in **1b** is promising in the viewpoint of the utilization of (3-thienyl)DPCB system as a building block for construction of more extended π systems.

The structure of **6b** was unambiguously determined by X-ray crystallography. Figure 2 depicts a molecular structure of **6b** in the crystal.[12] In order to release the steric repulsion between the methyl group and the Mes* group, both of the methyl substituents of the thiophene rings locate apart from the sterically protecting groups. Atoms P(1), P(2), and C(1)–C(4) lie on almost the same plane, within ±0.03 Å. The interplanar angle between



Scheme 3.

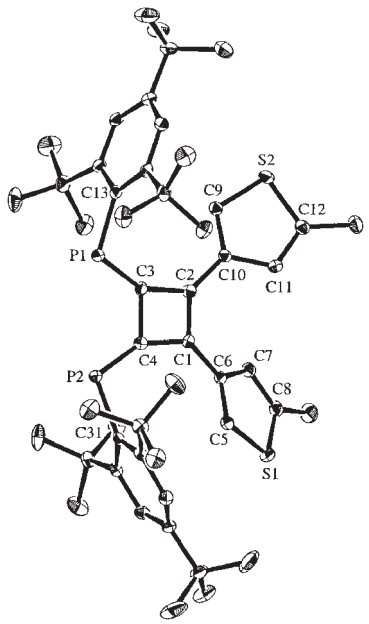


Fig. 2. Molecular structure of **6b**, showing the atomic labeling scheme with thermal ellipsoids (30% probability). Hydrogen atoms are omitted for clarity. Some selected bond lengths (Å) and angles (°): P(1)–C(3), 1.675(3); P(1)–C(13), 1.851(3); P(2)–C(4), 1.674(3); P(2)–C(31), 1.851(3); C(1)–C(2), 1.393(4); C(2)–C(3), 1.494(4); C(3)–C(4), 1.521(4); C(1)–C(4), 1.484(4); C(1)–C(6), 1.451(4); C(2)–C(10), 1.452(4); P(1)–C(3)–C(2), 148.8(2); P(1)–C(3)–C(4), 123.4(2); P(2)–C(4)–C(1), 149.5(5); P(2)–C(4)–C(3), 124.1(2); C(3)–P(1)–C(13), 106.8(1); C(4)–P(2)–C(31), 105.5(1); C(1)–C(2)–C(3), 92.1(2); C(1)–C(4)–C(3), 87.6(2); C(2)–C(1)–C(4), 92.8(2); C(2)–C(3)–C(4), 87.4(2).

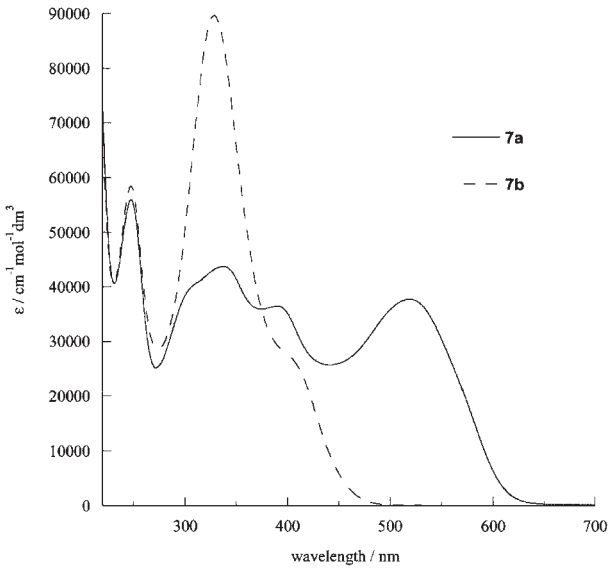


Fig. 3. UV–vis spectra of **7a**,**b** in hexane.

the DPCB plane [P(1), P(2), C(1)–C(4)] and one of the thiophene rings [S(1), C(5)–C(8)] is 34.2(1)°, while the angle between the DPCB plane and the other thiophene ring [S(2), C(9)–C(12)] is 21.5(1)°. The two aromatic rings of the Mes* group, [C(13)–C(18)] and [C(31)–C(36)], are almost perpendicular to the DPCB plane, whereas the interplanar angles between the aromatic planes and the DPCB plane are 84.5(1)° and 93.2(1)°, respectively.

Then we tried to combine the two 1,2-dithienyl-3,4-diphosphinidenecyclobutenes together. Compounds **1a** and **1b** were lithiated with butyllithium and the resulting thienyllithiums were treated with $CuCl_2$[13] to give compounds **7a** and **7b** in 23% and 25% yields, respectively. The ^{31}P NMR spectra of **7a** and **7b** showed an AB pattern (**7a**: $\delta_P = 170.9$ and 173.1, $^3J_{PP} = 102.3$ Hz; **7b**: $\delta_P = 167.3$ and 169.6, $^3J_{PP} = 96.1$ Hz). The large spin–spin coupling constants ($^3J_{PP}$) observed for **7a** and **7b** indicated all (*E*)-geometries around the Mes*P=C< moieties.[1b,d,f]

Figure 3 shows the UV–vis spectra of **7a** and **7b**. The spectrum of **7a** showed a red shift of π–π^* transition, compared with those of the isomer **7b** and the monomeric **1a** (Fig. 1), although the λ_{max} values of **7b** were very similar to those of the monomeric **1b**. This may be attributed to the efficient electron delocalization through the conjugation systems of the α-linked bithienyl moiety.[14] The delocalization through the bithienyl part appears to be more effective in **7a** (due to linear conjuga-

tion) than in **7b** (due to cross conjugation). Semi-empirical calculations (MOPAC, AM1) of **7a** showed the p orbitals of the α-carbons (carbon atoms bound to the other thiophene ring) are incorporated into both HOMO and LUMO of **7a**, while little contribution of the corresponding p orbitals at the α-carbons is indicated in the case of **7b**.

In summary, we have prepared 1,2-dithienyl- and 1,2-bis(methylthienyl)-3,4-diphosphinidenecyclobutenes, as well as compound **7** containing two DPCB moieties within a molecule. The results described here show that the thienyldiphosphinidenecyclobutenes are promising building blocks for the DPCB-based oligomers or polymers. Further studies on preparation and properties of DPCB oligomers are now in progress.

Experimental

Melting points were measured on a Yanagimoto MP-J3 micro melting point apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance-400 or a Bruker AM-600 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer. Gel permeation liquid chromatography (GPC, Japan Analytical Industry, JAIGEL H1+H2 column) was also used for the molecular weight determination using a polystyrene standard. X-ray diffraction data were collected on a Rigaku R-AXIS IV diffractometer. Reactions were performed under an argon atmosphere, unless otherwise specified.

(2-Thienylethynyl)(2,4,6-tri-*t*-butylphenyl)phosphine (3a). A mixture of (2,4,6-tri-*t*-butylphenyl)phosphine[15] (2.5 g, 9.0 mmol) and 2,2′-azobisisobutyronitrile (AIBN) (42 mg, 0.45 mmol) in carbon tetrachloride (31 mL) was refluxed for 4 h. The resulting mixture was concentrated in vacuo and 30 mL of tetrahydrofuran (THF) was added to the residual chloro(2,4,6-tri-*t*-butylphenyl)-phosphine. On the other hand, to a solution of 2-ethynylthiophene (11 mmol) in THF (10 mL) was added 12 mmol of ethylmagnesium bromide (0.89 M solution in hexane; 1 M = 1 mol dm^{-3}) at 0 °C. The resulting solution was stirred for 10 min, warmed to room temperature, and stirred for 20 min. Then the solution was added to the above THF solution of the chlorophosphine at 0 °C. The mixture was stirred at 0 °C for 10 min, warmed to room temperature, and stirred for 2 h. Then the solvent was removed under reduced pressure and the residue was submitted to a silica-gel column chromatographic treatment to give 1.53 g of **3a** (44% yield based on the starting Mes*PH$_2$). In some cases, (2-thienylethenylidene)(2,4,6-tri-*t*-butylphenyl)phosphine (**4a**) was obtained as a by-product.

3a: Pale yellow micro needles, mp 109–113 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (9H, s, *p*-*t*-Bu), 1.77 (18H, s, *o*-*t*-Bu), 6.06 (1H, d, $^1J_{PH}$ = 249.0 Hz, PH), 6.96–7.27 (3H, m, thiophene), and 7.62 (2H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 31.7 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.1 (d, $^4J_{PC}$ = 6.9 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 35.6 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.0 (s, *o*-$\underline{\mathrm{C}}Me_3$), 93.0 (d, $^1J_{PC}$ = 23.6 Hz, P$\underline{\mathrm{C}}\equiv$C), 95.9 (s, PC$\equiv\underline{\mathrm{C}}$), 123.3 (s, arom.), 124.1 (s, arom.), 125.7 (d, $^1J_{PC}$ = 25.6 Hz, *ipso*-Mes*), 127.3 (s, arom.), 127.7 (s, arom.), 132.6 (d, J_{PC} = 1.6 Hz, arom.), 151.2 (s, *p*-Mes*), and 156.1 (d, $^2J_{PC}$ = 10.8 Hz, *o*-Mes*); ^{31}P NMR (162 MHz, $CDCl_3$) δ −100.1 (d, $^1J_{PH}$ = 249.0 Hz); UV (hexane) 261 (log ε 4.13) and 282 nm (4.20); IR (KBr) 2974, 2403, 2156, 1595, 1537, 1464, 926, and 704 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 384 (M$^+$; 48) and 57 (*t*-Bu$^+$; 100). Found: *m*/*z* 384.2042. Calcd for $C_{24}H_{33}PS$: M, 384.2041.

4a: Pale yellow crystals, mp 133–136 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (9H, s, *p*-*t*-Bu), 1.74 (18H, s, *o*-*t*-Bu), 6.96 (1H, d, $^3J_{PH}$ = 26.4 Hz, P=C=CH), 6.98 (2H, m, thiophene), 7.26 (1H, t, $^3J_{HH}$ = 3.3 Hz, thiophene), and 7.49 (2H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 31.9 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.1 (d, $^4J_{PC}$ = 6.9 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 35.5 (s, *p*-$\underline{\mathrm{C}}Me_3$), 38.6 (s, *o*-$\underline{\mathrm{C}}Me_3$), 107.1 (d, $^2J_{PC}$ = 9.3 Hz, P=C=$\underline{\mathrm{C}}$), 122.7 (s, arom.), 126.9 (s, arom.), 127.0 (s, arom.), 127.7 (s, arom.), 131.1 (d, $^1J_{PC}$ = 66.3 Hz, *ipso*-Mes*), 138.3 (d, J_{PC} = 13.5 Hz, arom.), 150.4 (s, *p*-Mes*), 154.4 (d, $^2J_{PC}$ = 3.3 Hz, *o*-Mes*), and 239.6 (d, $^1J_{PC}$ = 23.7 Hz, P=$\underline{\mathrm{C}}$=C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 80.7 (d, $^3J_{PH}$ = 26.4 Hz); UV (hexane) 296 (log ε 4.31) and 310 nm (sh, 4.17); IR (KBr) 1591, 1473, 1400, 1363, 1240, 1205, 1130, 1041, 879, 835, 750, and 704 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 384 (M$^+$; 23), 328 (M$^+$ − *t*-Bu + 1; 100), and 313 (M$^+$ − *t*-Bu − Me; 50). Found: *m*/*z* 384.2040. Calcd for $C_{24}H_{33}PS$: M, 384.2041.

(3-Thienylethynyl)(2,4,6-tri-*t*-butylphenyl)phosphine (3b). A mixture of (2,4,6-tri-*t*-butylphenyl)phosphine (3.2 g, 11.6 mmol) and AIBN (65 mg, 0.58 mmol) in carbon tetrachloride (41 mL) was refluxed for 4 h. The resulting mixture was concentrated in vacuo and 40 mL of THF was added to the residual chloro(2,4,6-tri-*t*-butylphenyl)phosphine. On the other hand, to a solution of 3-ethynylthiophene (11 mmol) in THF (20 mL) was added 11 mmol of ethylmagnesium bromide (0.89 M solution in hexane) at 0 °C. The resulting solution was stirred for 10 min, warmed to room temperature, and stirred for 20 min. Then the solution was added to the above THF solution of the chlorophosphine at 0 °C. The mixture was stirred at 0 °C for 10 min, warmed to room temperature, and stirred for 2 h. Then the solvent was removed under reduced pressure and the residue was submitted to a silica-gel column chromatographic treatment to give 3.64 g (82% yield based on the starting Mes*PH$_2$) of the phosphine **3b**.

3b: Pale yellow crystals, mp 113–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (9H, s, *p*-*t*-Bu), 1.86 (18H, s, *o*-*t*-Bu), 6.22 (1H, d, $^1J_{PH}$ = 247.2 Hz, PH), 6.60 (1H, m, thiophene), 6.85 (1H, m, thiophene), 6.97 (1H, m, thiophene), and 7.27 (2H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 31.7 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.1 (d, $^4J_{PC}$ = 6.9 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 35.6 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.0 (s, *o*-$\underline{\mathrm{C}}Me_3$), 87.9 (d, $^1J_{PC}$ = 21.8 Hz, P$\underline{\mathrm{C}}\equiv$C), 98.0 (s, PC$\equiv\underline{\mathrm{C}}$), 123.3 (s, arom.), 125.6 (s, arom.), 126.1 (d, $^1J_{PC}$ = 25.7 Hz, *ipso*-Mes*), 129.4 (s, arom.), 130.3 (s, arom.), 130.5 (s, arom.), 151.1 (s, *p*-Mes*), and 156.0 (d, $^2J_{PC}$ = 10.4 Hz, *o*-Mes*); ^{31}P NMR (162 MHz, $CDCl_3$) δ −100.4 (d, $^1J_{PH}$ = 247.2 Hz); UV (hexane) 254 (log ε 4.16) and 268 nm (sh, 4.14); IR (KBr) 3104, 2958, 2927, 2869, 2399, 2362, 2337, 2154, 1594, 1473, 1394, 1361, 1236, 1209, 1187, 1164, 1126, 1079, 1024, 941, 923, 873, 781, and 622 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 384 (M$^+$; 93), 369 (M$^+$ − Me; 24), 327 (M$^+$ − *t*-Bu; 28), 231 (Mes*$^+$ − Me + 1; 100), and 57 (*t*-Bu$^+$; 98). Found: *m*/*z* 384.2040. Calcd for $C_{24}H_{33}PS$: M, 384.2041.

(*E*,*E*)-1,2-Di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1a). To a solution of **3a** (980 mg, 2.6 mmol) in THF (40 mL) was added 2.6 mmol of *t*-butyllithium (1.60 M solution in pentane) at −78 °C. The resulting mixture was stirred for 10 min at this temperature. Then the mixture was treated with 1,2-dibromoethane (1.3 mmol) and the resulting solution was stirred for 10 min, warmed to room temperature, stirred for 2 h; finally, the solvent was removed in vacuo. Chromatographic treatment (SiO_2/hexane) of the residue afforded 560 mg (57%) of (*E*,*E*)-**1a**: Orange prisms, mp 214–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (18H, s, *p*-*t*-Bu), 1.62 (36H, s, *o*-*t*-Bu), 6.00 (2H, d, $^3J_{HH}$ = 3.7 Hz, 3-thiophene), 6.60 (2H, dd, $^3J_{HH}$ = 5.0 Hz

and $^3J_{HH}$ = 3.7 Hz, 4-thiophene), 7.10 (2H, d, $^3J_{HH}$ = 5.0 Hz, 5-thiophene), and 7.50 (4H, s, *m*-Mes*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 32.1 (s, *p*-C$\underline{Me}_3$), 33.6 (s, *o*-C$\underline{Me}_3$), 35.5 (s, *p*-$\underline{C}Me_3$), 38.8 (s, *o*-$\underline{C}Me_3$), 122.5 (s, arom.), 127.3 (s, arom.), 128.2 (s, arom.), 130.2 (s, arom.), 133.2 (s, arom.), 135.1 (pseudo t, $^1J_{PC}$ = 27.5 Hz, *ipso*-Mes*), 147.5 (d, $^2J_{PC}$ = 5.7 Hz, P=C–$\underline{C}$), 150.9 (s, *p*-Mes*), 155.7 (s, *o*-Mes*), and 175.5 (d, $^1J_{PC}$ = 17.5 Hz, P=$\underline{C}$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 170.5; UV (hexane) 216 (log ε 4.60), 248 (4.37), 341 (4.45), and 428 nm (sh, 3.99); IR (KBr) 1593, 1529, 1475, 1396, 1363, 1240, 1211, 1126, and 906 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 766 (M^+; 23), 709 (M^+ − *t*-Bu; 10), 491 (M^+ − Mes*P + 1; 23), and 275 (Mes*P^+ − 1; 100). Found: C, 73.26; H, 8.43; S, 8.44%. Calcd for $C_{48}H_{64}P_2S_2 \cdot H_2O$: C, 73.43; H, 8.47; S, 8.17%.

(*E*,*E*)-1,2-Di(3-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1b). To a solution of **3b** (1.13 g, 2.9 mmol) in THF (40 mL) was added 2.8 mmol of *t*-butyllithium (1.60 M solution in pentane) at −78 °C. The resulting mixture was stirred for 10 min at this temperature. Then the mixture was treated with 1,2-dibromoethane (1.4 mmol) and the resulting solution was stirred for 10 min, warmed to room temperature, stirred for 2 h; finally, the solvent was removed under reduced pressure. Chromatographic treatment (SiO_2/hexane) of the residue gave 710 mg (63% yield based on **3b**) of (*E*,*E*)-**1b**. (3-Thienylethenylidene)(2,4,6-tri-*t*-butylphenyl)phosphine (**4b**) was formed as a by-product.

(*E*,*E*)-**1b**: Red crystals, mp 249–252 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (18H, s, *p*-*t*-Bu), 1.56 (36H, s, *o*-*t*-Bu), 5.63 (2H, d, $^4J_{HH}$ = 2.8 Hz, 2-thiophene), 6.59 (2H, dd, $^3J_{HH}$ = 5.0 Hz and $^5J_{PH}$ = 1.1 Hz, 4-thiophene), 6.91 (2H, dd, $^4J_{HH}$ = 2.8 Hz and $^3J_{HH}$ = 5.0 Hz, 5-thiophene), and 7.47 (4H, s, *m*-Mes*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 32.0 (s, *p*-C$\underline{Me}_3$), 33.5 (s, *o*-C$\underline{Me}_3$), 35.6 (s, *p*-$\underline{C}Me_3$), 38.8 (s, *o*-$\underline{C}Me_3$), 122.6 (s, arom.), 124.3 (s, arom.), 127.2 (s, arom.), 127.9 (s, arom.), 129.9 (d, $^1J_{PC}$ = 26.3 Hz, *ipso*-Mes*), 132.8 (s, arom.), 149.4 (d, $^2J_{PC}$ = 5.6 Hz, P=C–$\underline{C}$), 150.9 (s, *p*-Mes*), 155.7 (s, *o*-Mes*), and 176.2 (d, $^1J_{PC}$ = 17.5 Hz, P=$\underline{C}$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 166.6; UV (hexane) 216 (sh, log ε 4.66), 248 (4.48), 328 (4.58), and 396 nm (sh, 4.07); IR (KBr) 1576, 1460, 1401, 1359, 1212, 873, and 784 cm^{-1}. Found: C, 75.35; H, 8.63; S, 8.62%. Calcd for $C_{48}H_{64}P_2S_2$: C, 75.16; H, 8.41; S, 8.36%.

4b: Colorless crystals, mp 134–135 °C (decomp); ^1H NMR (600 MHz, $CDCl_3$) δ 1.30 (9H, s, *p*-*t*-Bu), 1.64 (18H, s, *o*-*t*-Bu), 6.72 (1H, d, $^3J_{PH}$ = 27.0 Hz, P=C=CH), 7.09 (1H, dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.9 Hz, 4-thiophene), 7.11 (1H, d, $^4J_{HH}$ = 2.7 Hz, 2-thiophene), 7.23 (1H, dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{PH}$ = 2.7 Hz, 5-thiophene), and 7.39 (2H, d, $^4J_{PH}$ = 1.2 Hz, *m*-Mes*); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 31.3 (s, *p*-C$\underline{Me}_3$), 33.4 (d, $^4J_{PC}$ = 6.0 Hz, *o*-C$\underline{Me}_3$), 34.9 (s, *p*-$\underline{C}Me_3$), 38.1 (s, *o*-$\underline{C}Me_3$), 106.9 (d, $^2J_{PC}$ = 10.5 Hz, P=C=$\underline{C}$), 122.1 (s, arom.), 122.8 (d, J_{PC} = 1.5 Hz, arom.), 125.8 (s, arom.), 127.4 (s, arom.), 130.8 (d, $^1J_{PC}$ = 64.8 Hz, *ipso*-Mes*), 134.9 (d, J_{PC} = 12.0 Hz, arom.), 149.7 (s, *p*-Mes*), 153.7 (d, $^2J_{PC}$ = 4.5 Hz, *o*-Mes*), and 240.1 (d, $^1J_{PC}$ = 24.1 Hz, P=$\underline{C}$=C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 75.6 (d, $^3J_{PH}$ = 27.0 Hz); UV (hexane) 203 (log ε 4.69), 236 (4.43), 258 (4.46), and 266 nm (sh, 4.41); IR (KBr) 1589, 1469, 1394, 1361, 1240, 877, 827, 771, 617, and 487 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 385 (M^+ + 1; 6), 327 (M^+ − *t*-Bu; 100), 313 (M^+ − *t*-Bu − Me + 1; 55), 271 (M^+ − 2*t*-Bu + 1; 58), 257 (Mes*PCCH$^+$ − 3Me + 1; 52), 216 (M^+ − 3*t*-Bu; 42), and 173 (Mes*PC^+ − 2*t*-Bu − 1; 21). Found: *m*/*z* 384.2036. Calcd for $C_{24}H_{33}PS$: M, 384.2041.

Preparation of 1a,b from 4a,b. To a solution of **4a** (100 mg, 0.260 mmol) in THF (4 mL) was added 0.260 mmol of *t*-butyllithium (1.45 M solution in pentane) at −78 °C. The reaction mixture was stirred at −78 °C for 5 min and 0.130 mmol of 1,2-dibromoethane was added. The resulting mixture was stirred at this temperature for 10 min then warmed to room temperature and stirred for 1 h. Evaporation of the solvent under reduced pressure, followed by column chromatographic treatment, afforded 98.1 mg (98%) of **1a**. Compound **1b** was obtained from **4b**, by a similar procedure, in an almost quantitative yield.

(*E*,*E*)-1,2-Bis(5-methyl-2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (6a). To a solution of (*E*,*E*)-**1a** (80 mg, 0.10 mmol) in THF (5 mL) was added 0.20 mmol of butyllithium (1.56 M solution in hexane) at ambient temperature. The resulting mixture was stirred for 30 min at this temperature. Then the mixture was treated with an excess amount of iodomethane (2.0 mmol) and the resulting solution was stirred for 45 min. Removal of the solvent in vacuo, followed by chromatographic treatment (SiO_2/hexane–Et_2O) of the residue, afforded 53 mg (64%) of (*E*,*E*)-**6a**: Orange solid, mp 220–223 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (18H, s, *p*-*t*-Bu), 1.54 (36H, s, *o*-*t*-Bu), 2.28 (6H, s, Me), 5.51 (2H, d, $^3J_{HH}$ = 3.3 Hz, thiophene), 6.16 (2H, d, $^3J_{HH}$ = 3.3 Hz, thiophene), and 7.41 (4H, s, *m*-Mes*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.9 (thienyl-Me), 32.1 (s, *p*-C$\underline{Me}_3$), 33.6 (s, *o*-C$\underline{Me}_3$), 35.6 (s, *p*-$\underline{C}Me_3$), 38.8 (s, *o*-$\underline{C}Me_3$), 122.4 (s, arom.), 126.2 (s, arom.), 131.1 (s, arom.), 131.1 (s, arom.), 135.7 (pseudo t, J_{PC} = 29.0 Hz, *ipso*-Mes*), 142.8 (s, arom.), 147.1 (pseudo t, J_{PC} = 5.7 Hz, P=C–$\underline{C}$), 150.8 (s, *p*-Mes*), 155.7 (s, *o*-Mes*), and 175.9 (dd, $^1J_{PC}$ = 17.4 Hz and $^2J_{PC}$ = 8.8 Hz, P=$\underline{C}$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 165.3; UV (hexane) 348 (log ε 4.53) and 428 nm (4.10); IR (KBr) 1466, 1394, 1362, 1244, 1207, and 800 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 794 (M^+; 90), 737 (M^+ − *t*-Bu; 15), 519 (M^+ − Mes*P; 24), and 57 (*t*-Bu^+; 100).

(*E*,*E*)-1,2-Bis(5-methyl-3-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (6b). To a solution of (*E*,*E*)-**1b** (100 mg, 0.13 mmol) in THF (5 mL) was added 0.55 mmol of butyllithium (1.56 M solution in hexane) at ambient temperature. The resulting mixture was stirred for 30 min at this temperature. Then the mixture was treated with an excess amount of iodomethane (1.3 mmol) and the resulting solution was stirred for 45 min. Removal of the solvent in vacuo, followed by chromatographic treatment (SiO_2/hexane–Et_2O) of the residue, afforded 97 mg (97%) of (*E*,*E*)-**6b**: Yellow crystals, mp 216–223 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (18H, s, *p*-*t*-Bu), 1.56 (36H, s, *o*-*t*-Bu), 2.26 (6H, s, Me), 5.17 (2H, s, thiophene), 6.43 (2H, s, thiophene), and 7.47 (4H, s, *m*-Mes*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.5 (s, thienyl-Me), 32.1 (s, *p*-C$\underline{Me}_3$), 33.5 (s, *o*-C$\underline{Me}_3$), 35.6 (s, *p*-$\underline{C}Me_3$), 38.8 (s, *o*-$\underline{C}Me_3$), 122.6 (s, arom.), 125.9 (s, arom.), 126.1 (s, arom.), 132.6 (s, arom.), 136.0 (d, $^1J_{PC}$ = 28.0 Hz, *ipso*-Mes*), 138.2 (s, arom.), 150.9 (s, *p*-Mes*), 155.6 (m, P=C–$\underline{C}$), 155.7 (s, *o*-Mes*), and 176.7 (m, P=$\underline{C}$); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 164.0; UV (hexane) 216 (sh, log ε 4.61), 249 (4.43), 331 (4.52), and 406 nm (sh, 4.05); IR (KBr) 1593, 1533, 1473, 1394, 1363, 1242, 1207, 877, 833, and 760 cm^{-1}.

Compound 7a. To a solution of (*E*,*E*)-**1a** (200 mg, 0.261 mmol) in THF (1.2 mL) was added 0.521 mmol of butyllithium (1.58 M solution in hexane) at −78 °C. The resulting mixture was stirred for 30 min at −78 °C. Then the mixture was treated with an anisole (1.2 mL) solution of $CuCl_2$ (0.130 mmol) at −78 °C and the resulting solution was stirred for 1 h. The solution

was warmed to room temperature and ca. 0.5 mL of 3% hydrochloric acid was added. The resulting mixture was extracted with ether. The organic phase was washed with 15% aqueous ammonia and dried over $MgSO_4$. Removal of the solvent in vacuo, followed by gel permeation chromatographic treatment, afforded 22.7 mg (23%) of **7a**. **7a**: Dark red powder, mp 156–157 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (18H, s, *p*-*t*-Bu), 1.37 (18H, s, *p*-*t*-Bu), 1.54 (36H, s, *o*-*t*-Bu), 1.55 (36H, s, *o*-*t*-Bu), 5.30 (2H, d, $^3J_{HH} = 3.9$ Hz, thiophene), 6.06 (2H, d, $^3J_{HH} = 3.8$ Hz, thiophene), 6.33 (2H, d, $^3J_{HH} = 3.9$ Hz, thiophene), 6.58 (2H, dd, $^3J_{HH} = 5.0$ Hz and $^3J_{HH} = 3.8$ Hz, thiophene), 7.05 (2H, d, $^3J_{HH} = 5.0$ Hz, thiophene), 7.38 (4H, s, *m*-Mes*), and 7.39 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 31.6 (s, *p*-C<u>Me</u>$_3$), 33.1 (s, *o*-C<u>Me</u>$_3$), 35.1 (s, *p*-<u>C</u>Me$_3$), 38.3 (s, *o*-<u>C</u>Me$_3$), 122.0 (s, *m*-Mes*), 124.2 (s, thiophene), 126.8 (s, thiophene), 128.0 (s, thiophene), 129.6 (s, thiophene), 131.6 (s, thiophene), 132.0 (s, thiophene), 132.5 (s, thiophene), 134.4 (d, $^1J_{PC} = 57.4$ Hz, *ipso*-Mes*), 135.0 (d, $^1J_{PC} = 57.4$ Hz, *ipso*-Mes*), 138.3 (s, thiophene), 146.3 (m, P=C–<u>C</u>), 150.4 (s, *p*-Mes*), 150.6 (s, *p*-Mes*), 155.2 (s, *o*-Mes*), 155.3 (s, *o*-Mes*), 174.5 (dd, $^1J_{PC} = 50.6$ Hz and $^2J_{PC} = 20.4$ Hz, P=<u>C</u>), and 175.1 (dd, $^1J_{PC} = 49.1$ Hz and $^2J_{PC} = 21.9$ Hz, P=<u>C</u>); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 170.9 and 173.1 (AB, $^3J_{PP} = 102.3$ Hz); UV (hexane) 248 (log ε 4.75), 315 (sh, 4.62), 336 (4.64), 390 (4.56), and 518 nm (4.58); IR (KBr) 2962, 2904, 2868, 1591, 1531, 1475, 1435, 1394, 1362, 1240, 1209, 1126, 877, 798, 758, and 700 cm^{-1}; MW (GPC, vs the polystyrene standard) 1350. Found: C, 75.05; H, 8.30; S, 8.49%. Calcd for $C_{96}H_{126}P_4S_4$: C, 75.25; H, 8.29; S, 8.37%.

Compound 7b. To a solution of (*E*,*E*)-**1b** (100 mg, 0.130 mmol) in THF (0.6 mL) was added 0.261 mmol of butyllithium (1.58 M solution in hexane) at −78 °C. The resulting mixture was stirred for 30 min at this temperature. Then the mixture was treated with an anisole (0.6 mL) solution of $CuCl_2$ (0.065 mmol) at −78 °C and the resulting solution was stirred for 1 h. The solution was warmed to room temperature and ca. 0.5 mL of 3% hydrochloric acid was added. The resulting mixture was extracted with ether. The organic phase was washed with 15% aqueous ammonia and dried over $MgSO_4$. Removal of the solvent in vacuo followed by gel permeation chromatographic treatment afforded 24.5 mg (25%) of **7b**. **7b**: Yellow powder, mp 168–169 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.34 (18H, s, *p*-*t*-Bu), 1.41 (18H, s, *p*-*t*-Bu), 1.51 (36H, s, *o*-*t*-Bu), 1.52 (36H, s, *o*-*t*-Bu), 5.11 (2H, s, thiophene), 5.65 (2H, d, $^4J_{HH} = 2.5$ Hz, thiophene), 6.50 (2H, dd, $^3J_{HH} = 5.1$ Hz and $^4J_{HH} = 1.2$ Hz, thiophene), 6.65 (2H, d, $^4J_{HH} = 1.2$ Hz, thiophene), 6.82 (2H, dd, $^3J_{HH} = 5.1$ Hz and $^4J_{HH} = 2.5$ Hz, thiophene), 7.39 (4H, s, *m*-Mes*), and 7.42 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 31.5 (s, *p*-C<u>Me</u>$_3$), 31.6 (s, *p*-C<u>Me</u>$_3$), 33.0 (s, *o*-C<u>Me</u>$_3$), 33.1 (s, *o*-C<u>Me</u>$_3$), 35.1 (s, *p*-<u>C</u>Me$_3$), 35.1 (s, *p*-<u>C</u>Me$_3$), 38.3 (s, *o*-<u>C</u>Me$_3$), 122.1 (s, *m*-Mes*), 123.5 (s, thiophene), 123.9 (s, thiophene), 126.2 (s, thiophene), 126.8 (s, thiophene), 127.4 (s, thiophene), 132.2 (s, thiophene), 132.8 (s, thiophene), 135.1 (d, $^1J_{PC} = 34.7$ Hz, *ipso*-Mes*), 135.4 (d, $^1J_{PC} = 36.2$ Hz, *ipso*-Mes*), 135.3 (s, thiophene), 148.1 (m, P=C–<u>C</u>), 149.9 (m, P=C–<u>C</u>), 150.5 (s, *p*-Mes*), 155.2 (s, *o*-Mes*), 155.3 (s, *o*-Mes*), and 175.8 (dd, $^1J_{PC} = 49.6$ Hz and $^2J_{PC} = 22.6$ Hz, P=<u>C</u>); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 167.3 and 169.6 (AB, $^3J_{PP} = 96.1$ Hz); UV (hexane) 258 (log ε 4.46), 328 (4.93), and 398 nm (sh, 4.44); IR (KBr) 3113, 2956, 2906, 2868, 1593, 1539, 1475, 1396, 1362, 1238, 1207, 1126, 876, 827, 793, 758, 696, and 625 cm^{-1}; MW (GPC, vs the polystyrene standard) 1430.

X-ray Crystallographic Analysis of 6b. $C_{50}H_{68}P_2S_2$, $M_r = 795.15$, monoclinic, space group $P2_1/n$ (#14), $a = 15.035(4)$, $b = 10.848(2)$, $c = 30.40(3)$ Å, $\beta = 102.181(5)°$, $V = 4847(4)$ Å^3, $Z = 4$, $\rho = 1.090$ g cm^{-3}, $\mu = 2.06$ cm^{-1}; $R1 = 0.062$, $R = 0.111$, $R_W = 0.144$; 5767 unique reflections with $2\theta \leq 50.0°$ were recorded on an imaging plate diffractometer (Mo Kα radiation, graphite monochrometer) at −120 °C. Of these, 5317 with $I > 2\sigma(I)$ were used for $R1$ calculation. The structure was solved by heavy-atom direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (no. CCDC 224042).

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