

Improved Preparative Method for 1,2-Diaryl-3,4-diphosphinidenecyclobutenes and Its Application to the Studies of 1,2-Bis(arylthienyl)-3,4-diphosphinidenecyclobutenes

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Sterically protected 1,2-diaryl-3,4-diphosphinidenecyclobutenes were prepared from 3-aryl-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-3-(trimethylsiloxy)-1-phosphapropene using *t*-butyllithium and 1,2-dibromoethane, and the properties of the products, such as 1,2-di(2,2′-bithienyl-5-yl)-3,4-diphosphinidenecyclobutene, were studied. This method is an excellent method for preparing these compounds.

Conjugated oligomers of aromatic 5- or 6-membered ring components are of current interest.[1] However, conjugated oligoarenes that contain components with multiply bonded heavier main group elements, such as phosphorus and silicon, are rare, mainly due to high reactivity of their π-bonds.[1f,g] The multiple bonds of heavier main group elements can be stabilized by bulky substituent (steric protection),[2] and many compounds with exotic structures have been successfully isolated by utilizing of steric protection methodology. Recently, we have reported preparation and properties of a sterically protected 1,2-di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (**1T** or DPCBT; hereafter, diphosphinidenecyclobutene is abbreviated to DPCB), bearing thiophene rings at the 1,2-positions of the cyclobutene ring (Chart 1).[3] Compound **1T** has a unique structure, in which the DPCB π-system is inserted into an oligothiophene **2** structure. The structure of **1T** can be also regarded as a 1,4-diphospha-1,3-butadiene system, which is coupled with 1,2-di(2-thienyl)ethene (**3**) structure. It is of interest to extend the π-system of **1T** by utilizing thienylene or phenylene spacer. We report here studies of extension of π-system of **1T** as well as an improved preparative method for 1,2-diaryl-3,4-diphosphinidenecyclobutenes, which gives **1T** and related compounds in good yield.

Results and Discussion

Preparative Methods for DPCB Derivatives. For the synthesis of DPCB derivatives, various preparative methods have been reported to date. The methods can be classified into three categories, Methods 1–3 (Scheme 1).

Method 1, from Chloro(ethynyl)phosphines: Appel et al. have prepared (*E*,*E*)-1,2-diphenyl-DPCB (**1P**) starting from dichloro(ethynyl)phosphine $Cl_2PC{\equiv}CR$, via a reaction of chloro(ethynyl)phosphine **4** with ethynylphosphide **5**.[4a,b] Reductive coupling of **4** using zinc powder was later developed by us.[4c]

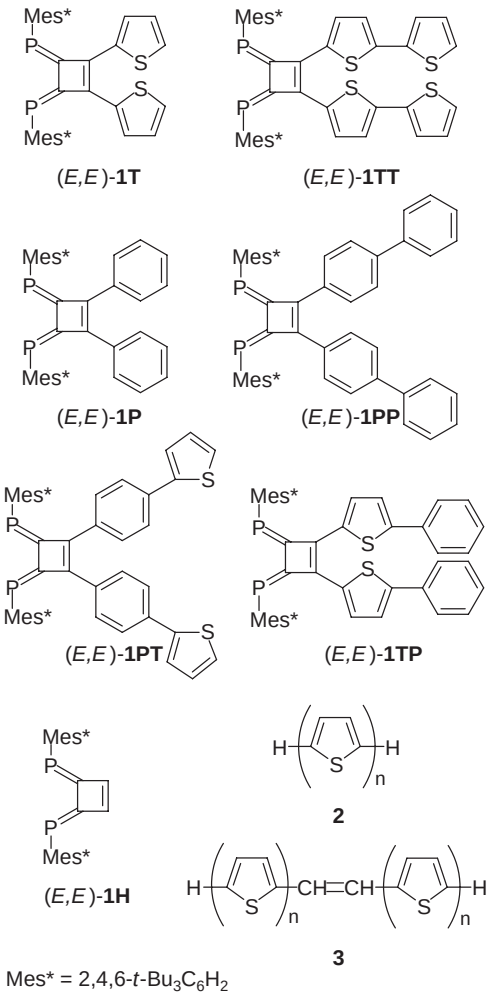

Chart 1.

Method 2, from Ethynylphosphines: Märkl and Hennig[5b] and we[5a] have prepared several DPCB derivatives from ethynylphosphine **7**, which is prepared starting from chloro-

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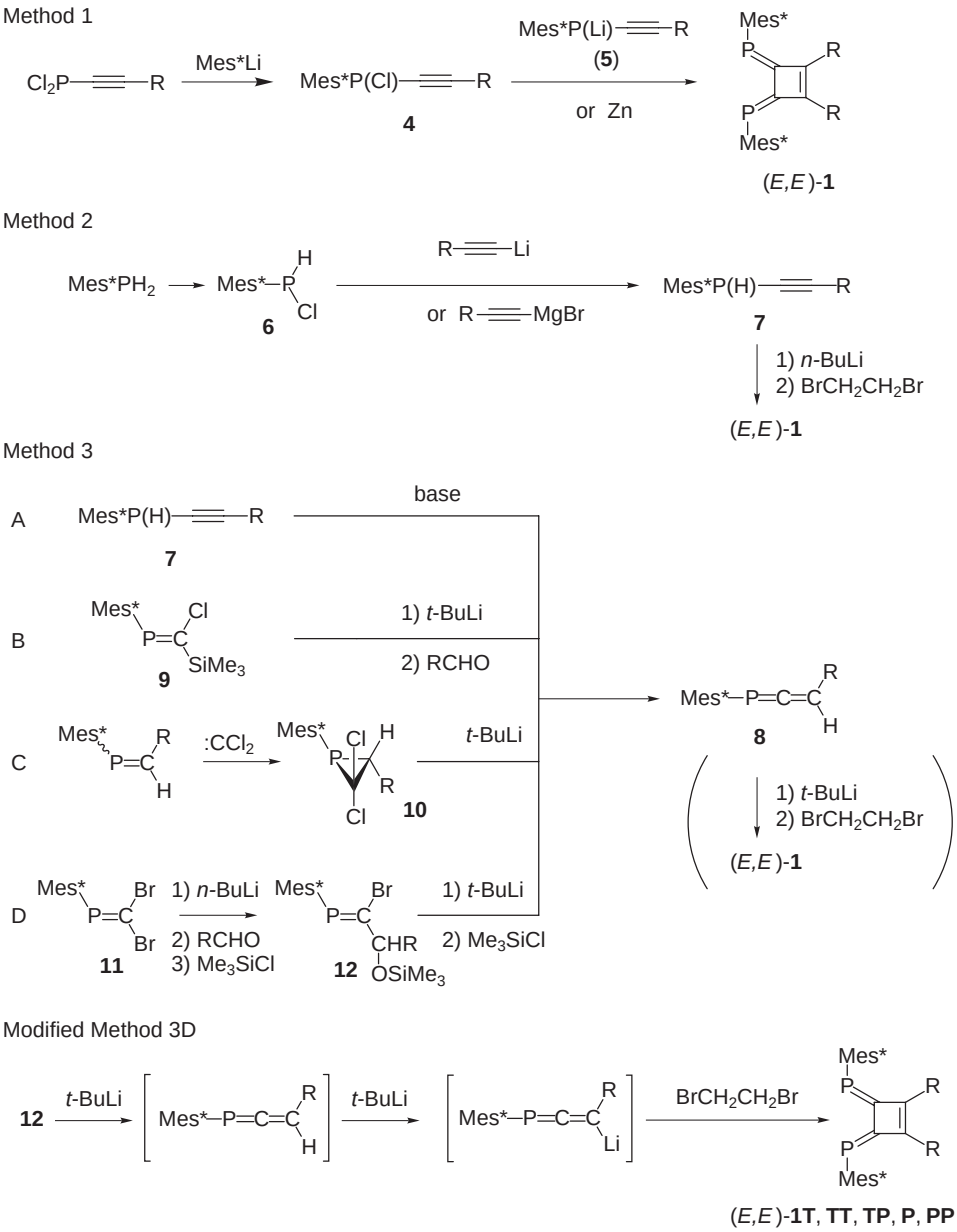

R = 2-thienyl (**T**), 2,2'-bithienyl-5-yl (**TT**), 5-phenyl-2-thienyl (**TP**), phenyl (**P**), biphenyl-4-yl (**PP**)

Scheme 1.

phosphine **6** and acetylide. In our preparation protocol for DPCB derivatives, lithiation with butyllithium (1 molar amount) followed by treatment with 1,2-dibromoethane (0.5 molar amount) is used.[5a] Corey–Fuchs alkyne synthesis[6] is also applicable to the preparation of ethynylphosphines **7**.[7,8]

Method 3, from 1-Phosphaallenes: As an alternative method, we have reported a preparation of **1T** via a direct lithiation of 3-mono-substituted-1-phosphaallenes **8** with *t*-butyllithium.[3] It should be noted here that the 1-phosphaallenes are obtainable through several methods:[9] base-induced isomerization of ethynylphosphines (Method 3A),[9c] Peterson-type reaction of **9** with aldehydes (Method 3B),[9d] and lithiation of 2,2-dichloro-1-phosphiranes **10**[9e] (Method 3C). Furthermore, a novel preparative method of 1-phosphaallene, starting from **11** via **12**, has recently reported by our laboratory (Method 3D).[10]

Thus, for the preparation of DPCB derivatives bearing a bulky aryl substituent Ar*, we can use one of the methods mentioned above; however, each method has merits and demerits. Methods 2 and 3A using ethynylphosphine intermediates are established and effective methods when the primary and secondary phosphines are stable enough to handle. If either primary phosphine Ar^*PH_2 or ethynylphosphine $Ar^*P(H)C{\equiv}CR$ is unstable and $Ar^*P{=}CBr_2$ or $Ar^*P{=}CCl_2$ is easy to handle, Methods 3B–3D are effective methods, because the phosphaallenes are prepared without using Ar^*PH_2 or $Ar^*P(H)C{\equiv}CR$. It should be noted that alkynes $RC{\equiv}CH$ as starting materials are used for introduction of the substituent R into the 1,2-positions of the DPCB in Methods 1, 2, and 3A, while aldehydes RCHO are used in Methods 3B and 3D

without conversion to alkynes. Thus, if alkynes are unstable in the reaction conditions or preparation of the alkyne is elaborate, Methods 3B and 3D without intermediary formation of alkynes are the methods of choice.

Improved Preparation of DPCB Derivatives. Taking the above-mentioned factors into account, preparation of **1T** by using a modified version of Method 3D was first investigated. Successive reaction of (dibromomethylene)phosphine **11**[11] with butyllithium, 2-thiophenecarbaldehyde, and chlorotrimethylsilane gave phosphaethene **12T** in 88% yield. Reaction of phosphaethene **12T** with 2 molar amounts of *t*-butyllithium followed by treatment with 1,2-dibromoethane gave (*E*,*E*)-**1T** nearly quantitatively.

The modified Method 3D for preparation of **1T** has an advantage, as mentioned above, over Method 2:[3] handling of volatile 2-ethynylthiophene is avoided. Furthermore, isolation of intermediate phosphaallene is not necessary in modified method 3D, making the experimental procedure simple and easy.

Similarly, (*E*,*E*)-**1TT** was prepared by using improved Method 3D in 96% yield, based on the corresponding phosphaalkenes **12TT**. (*E*,*E*)-**1P** and (*E*,*E*)-**1PP** were also prepared by using improved Method 3D in 91% and quantitative yield, respectively, based on the corresponding phosphaalkenes **12P** and **12PP**; however, 3 molar amounts of *t*-butyllithium were necessary in these cases.

In these reactions, phosphaallenes and phosphaallenyllithiums seem to be generated in situ. In the case of the reactions of **12P** and **12PP**, 2 molar amounts of *t*-BuLi probably participate in the halogen–metal exchange process to form phosphaallene, 2-methylpropene, and 2-methylpropane; the phosphaallenyl proton is then abstracted by another *t*-BuLi (1 molar amount). On the other hand, in the case of the reactions of **12T** and **12TT**, reaction of **12** with *t*-BuLi (1 molar amount), formation of phosphaallene, and abstraction of the phosphaallenyl proton by another *t*-BuLi (1 molar amount) seems to proceed rapidly enough to form phosphaallenyllithium.

It should be mentioned that a one-pot reaction of improved Method 3D also afforded DPCB, but in lower yield. Successive treatment of **11** with butyllithium, 2-thiophenecarbaldehyde, chlorotrimethylsilane, *t*-butyllithium, and 1,2-dibromoethane gave **1T** in 50% yield.

Furthermore, preparations of **1TP** and **1PT** were examined as follows. 5-Phenylthiophene-2-carbaldehyde[12] was subjected to the successive reaction according to the modified Method 3D to give **12TP**, which was then converted (3 molar amounts of *t*-butyllithium was used) to (*E*,*E*)-**1TP** in 58% yield. As for compound **1PT**, however, an attempted reaction of 4-(2-thienyl)benzaldehyde,[13] which was prepared from *o*-iodoxybenzoic acid (IBX) oxidation of 4-(2-thienyl)phenylmethanol,[14] with Mes*P=C(Br)Li followed by treatment with chlorotrimethylsilane did not give **12PT**. This might be explained taking into account the fact that the acidity of the proton (α to the sulfur atom) in 4-(2-thienyl)benzaldehyde is increased due to the formyl group. Nucleophilic attack at the carbonyl group does not seem to be efficient, resulting in the predominance of proton abstraction. It should be noted that conversion of 4-(2-thienyl)benzaldehyde to 2-[4-(2,2-dibromovinyl)phenyl]thiophene followed by reactions of Method 2 (using Corey–Fuchs method) was not satisfactory and **12PT** was not obtained, probably due to predominance of proton abstraction.

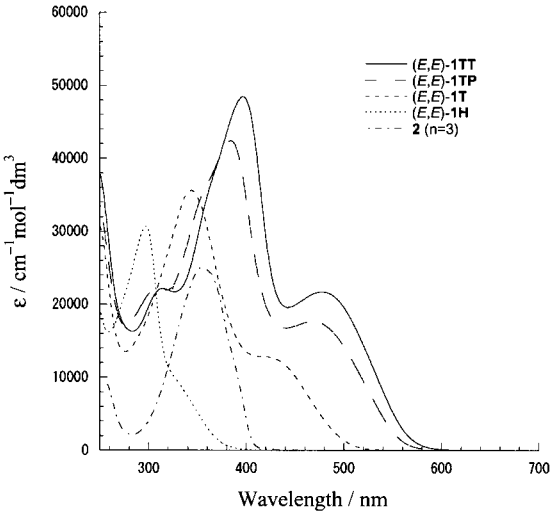

Fig. 1. UV–vis spectra for DPCB derivatives (*E*,*E*)-**1H**, -**T**, -**TP**, and -**TT** and 2,2′:5′,2″-terthiophene in CH_2Cl_2.

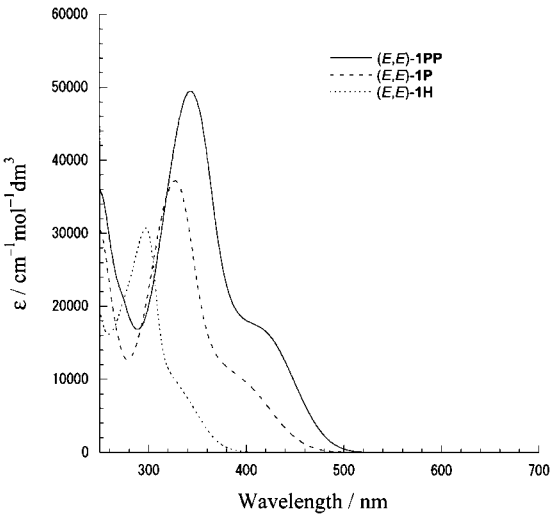

Fig. 2. UV–vis spectra for DPCB derivatives (*E*,*E*)-**1H**, -**P**, and -**PP** in CH_2Cl_2.

Properties of the DPCB Derivatives. Properties of oligothiophenes have been well investigated, however, π-conjugated oligomers reported in this paper contain a cisoid spacer with a 4-membered ring structure.[15] Thus, the effect of the 4-membered ring spacer on the oligothiophenes (and the related oligomers) is of interest. Figure 1 shows UV–vis spectra of (*E*,*E*)-**1H**, (*E*,*E*)-**1T**, (*E*,*E*)-**1TP**, and (*E*,*E*)-**1TT**, along with that of 2,2′:5′,2″-terthiophene (**2**, $n = 3$), while Figure 2 exhibits UV–vis spectra of (*E*,*E*)-**1H**, (*E*,*E*)-**1P**, and (*E*,*E*)-**1PP**. In the spectrum for the phenylene-linked DPCB (*E*,*E*)-**1PP**, there was a slight bathochromic shift compared to that of (*E*,*E*)-**1P**. It is likely that the co-planarity of the phenyl rings in these compounds is not good, making the π-conjugation less effective. In contrast, in the spectra for the thienylene-linked DPCB derivatives (*E*,*E*)-**1TP** and (*E*,*E*)-**1TT** there was a large bathochromic shifts compared to (*E*,*E*)-**1T**, suggesting good conjugation in the thienylene-linked system.[1b]

Theoretical calculations [Gaussian 03, DFT(B3LYP)][16] of

(*E*,*E*)-**1P** showed that the HOMO and LUMO of (*E*,*E*)-**1P** consisted of the π system of the diphosphinidenecyclobutene moiety and the 1,2-phenyl substituents. TD calculation[16] indicated that the longest absorption band mainly corresponded to the HOMO $\rightarrow$ LUMO transition. The situations seem to be general for other DPCBs reported in this paper, containing aromatic rings at the 1,2-positions. For example, MOPAC AM1 calculation showed that the frontier orbital of (*E*,*E*)-**1T** consisted of a π system of the diphosphinidenecyclobutene moiety and the thiophene moiety; the situation is similar to that of (*E*,*E*)-**1P**.

As for unsubstituted oligomeric 2,5-thienylenes **2**, those smaller than octamer are known.[1c,17] Compared to **2** ($n = 3$) with absorption at λ_{max} 354 nm, compound (*E*,*E*)-**1T** absorbed at a much longer wavelength (Fig. 1). Compound (*E*,*E*)-**1T** showed large bathochromic shift compared to 1,2-di(2-thienyl)ethenes (*E*)-**3** ($n = 1$, λ_{max} 338 nm ($\log \varepsilon$ 4.45) in cyclohexane)[18] or (*Z*)-**3** ($n = 1$, λ_{max} 322 nm ($\log \varepsilon$ 3.90) in acetonitrile),[19] and a slight bathochromic shift, compared to 1,2-di(bithienyl)ethene (*E*)-**3** ($n = 2$, λ_{max} 423 nm ($\log \varepsilon$ 4.65) in $CHCl_3$).[20] Similarly, (*E*,*E*)-**1TT** absorbed in a longer wavelength region, compared to **2** ($n = 5$; λ_{max} 416 nm ($\log \varepsilon$ 4.74) in $CHCl_3$)[21] or (*E*)-**3** ($n = 3$, λ_{max} 324 ($\log \varepsilon$ 4.13) and 460 nm (4.84) in $CHCl_3$).[20] Thus, compounds (*E*,*E*)-**1T** and (*E*,*E*)-**1TT** as well as other DPCB derivatives reported here seem to have well-conjugated π-systems, containing both the P=C bond and thiophenes. The thienylene linked system shows, as expected, better conjugation than the phenylene-linked system.

In conclusion, we prepared various DPCB derivatives, bearing thienylene or phenylene linkers at the 1,2-positions. The DPCB derivatives containing terminal thiophene rings are promising building blocks for more extended π-systems. Moreover, a convenient and efficient protocol for the synthesis of DPCB derivatives was developed (improved Method 3D). Although it has some limitation, this method is operationally simple and is considerably less labor intensive than the earlier methods.

Experimental

Apparatus. Melting points were measured on a Yanagimoto MP-J3 micro melting points apparatus and were not corrected. NMR spectra were recorded on a Bruker Avance-400 or a Bruker AM-600 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on a Hitachi M-2500S spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer. Elemental analyses were performed at Analytical Research Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials. 2-Thiophenecarbaldehyde (Tokyo Chemical Industry, Co., Ltd.), 2,2′:5′,2″-terthiophene-5-carbaldehyde (Tokyo Chemical Industry, Co., Ltd.), 2,2′-bithiophene-5-carbaldehyde (Aldrich Chemical Company), and 4-biphenylcarbaldehyde (Wako Pure Chemical Industries, Ltd.) were purchased and used as obtained. (Dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine was prepared according to the literature.[11c] Silica gel 60 (70–230 mesh, Merck, Ltd.) or alumina (Sumitomo Chemical, Co., Ltd, KCG-30) was used for column chromatography, and silica gel 60 F_{254} on aluminium sheet (Merck, Ltd.) was used for TLC.

2-Bromo-3-(2-thienyl)-1-(2,4,6-tri-*t*-butylphenyl)-3-(trimethylsiloxy)-1-phosphapropene (12T). To a solution of (dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (2.00 g, 4.33 mmol) in THF (100 mL)[22] was added 4.33 mmol of butyllithium (1.59 M solution in hexane; 1 M = 1 mol dm^{-3}, 2.70 mL) at -98 °C. The resulting solution was stirred at -98 °C for 10 min, and then 4.33 mmol of 2-thiophenecarbaldehyde was added. The resulting mixture was then allowed to warm to room temperature and stirred for 30 min, and 4.33 mmol of chlorotrimethylsilane was added. After additional 30 min stirring, the solvent was removed in vacuo. Chromatographic treatment of the residue (SiO_2/hexane to hexane:EtOAc 50:1) afforded 2.12 g (88% yield) of **12T**: Colorless powder, mp 110–111 °C; R_f 0.45 (hexane:EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (9H, s, $SiMe_3$), 1.42 (9H, s, *p*-*t*-Bu), 1.54 (9H, s, *o*-*t*-Bu), 1.58 (9H, s, *o*′-*t*-Bu), 6.03 (1H, d, $^3J_{PH} = 12.5$ Hz, P=C–CH), 7.01 (1H, dd, $^3J_{HH} = 5.0$ Hz, $^3J_{HH} = 3.5$ Hz, 4-thienyl), 7.10 (1H, d, $^3J_{HH} = 3.5$ Hz, 3-thienyl), 7.28 (1H, d, $^3J_{HH} = 5.0$ Hz, 5-thienyl), 7.48 (1H, s, *m*-Mes*), and 7.50 (1H, s, *m*′-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.7 (s, $SiMe_3$), 31.9 (s, *p*-C*Me*$_3$), 33.2 (d, $^4J_{PC} = 5.2$ Hz, *o*-C*Me*$_3$), 33.3 (d, $^4J_{PC} = 6.6$ Hz, *o*′-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 38.5 (s, *o*′-*C*Me$_3$), 77.3 (d, $^2J_{PC} = 40.2$ Hz, COSi), 122.7 (s, *m*-Mes*), 124.8 (s, 4-thienyl), 125.0 (s, 3-thienyl), 126.7 (s, 5-thienyl), 137.2 (d, $^1J_{PC} = 54.1$ Hz, *ipso*-Mes*), 147.3 (d, $^3J_{PC} = 12.2$ Hz, 2-thienyl), 151.3 (s, *p*-arom.), 153.7 (s, *o*-arom.), 154.0 (s, *o*′-arom.), and 167.0 (d, $^1J_{PC} = 63.7$ Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 256.7; UV (hexane) 242 ($\log \varepsilon$ 4.29), 276 (4.06), and 309 nm (sh, 3.09); IR (KBr) 2958, 2902, 2868, 1593, 1473, 1398, 1363, 1252, 1099, 1065, 879, 847, 754, 704, 459, and 401 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 553 ($M^+ + 1$; 2), 551 ($M^+ - 1$; 2), 465 ($M^+ - OTms + 2$; 11), 463 ($M^+ - OTms$; 10), 327 (Mes*P=C–CHThienyl$^+$ − *t*-Bu; 19), 291 (Mes*PC$^+$ + 2; 32), 275 (Mes*P$^+$ − 1; 100), 219 (Mes*P$^+$ − *t*-Bu; 70), and 163 (Mes*P$^+$ − 2*t*-Bu + 1; 54). Found: *m*/*z* 551.1563. Calcd for $C_{27}H_{41}BrOPSSi$: M − H, 551.1568. Anal. Found: C, 58.58; H, 7.47; Br, 14.40; S, 6.03%. Calcd for $C_{27}H_{42}BrOPSSi$: C, 58.57; H, 7.65; Br, 14.43, S, 5.79%.

(*E*,*E*)-1,2-Di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1T). To a solution of **12T** (1.00 g, 1.81 mmol) in THF (42 mL) was added *t*-butyllithium (1.45 M solution in pentane, 3.63 mmol, 2.50 mL) at -78 °C. The resulting solution was stirred at -78 °C for 15 min, and 1,2-dibromoethane (0.078 mL, 0.91 mmol) was added. The reaction mixture was stirred for 10 min, allowed to warm to room temperature, and stirred for an additional 1 h. Removal of the solvent followed by column chromatography (Al_2O_3/hexane) afforded 0.688 g (99% yield) of (*E*,*E*)-**1T**.[3]

One-Pot Method for 1T. To a solution of (dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (200 mg, 0.433 mmol) in THF (10 mL) was added butyllithium in hexane (1.59 M, 0.27 mL, 0.43 mmol) at -98 °C. The resulting solution was stirred at -98 °C for 10 min, and 0.433 mmol of 2-thiophenecarbaldehyde was added. The resulting mixture was then allowed to warm to room temperature and stirred for 30 min, and chlorotrimethylsilane (0.055 mL, 0.43 mmol) was added. After stirring for an additional 30 min, the mixture was cooled to -78 °C, and *t*-butyllithium in pentane (1.58 M, 0.58 mL, 0.87 mmol) was added at -78 °C. The resulting solution was stirred at -78 °C for 15 min, and 1,2-dibromoethane (0.019 mL, 0.22 mmol) was added. The reaction mixture was stirred for 10 min, allowed to warm to room temperature, and stirred for an additional 1 h. Removal of the solvent followed by column chromatography (Al_2O_3/hexane to hexane–EtOAc 50:1) afforded 82.2 mg (50% yield) of (*E*,*E*)-**1T**.

(*E*,*E*)-1,2-Diphenyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1P). To a solution of **12P** (333 mg, 0.61 mmol)[10] in THF (10 mL) was added *t*-butyllithium in pentane (1.59 M, 1.2 mL, 1.9 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 10 min, and 1,2-dibromoethane (0.027 mL, 0.31 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. Removal of the solvent followed by column chromatography (SiO_2/hexane to hexane: EtOAc 50:1) afforded 210 mg (91%) of (*E*,*E*)-**1P**.[4]

3-(2,2′-Bithienyl-5-yl)-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-3-(trimethylsiloxy)-1-phosphapropene (12TT). To a solution of (dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (3.00 g, 6.49 mmol) in THF (100 mL) was added butyllithium in hexane (1.59 M, 4.10 mL, 6.49 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 10 min, and 2,2′-bithiophene-5-carbaldehyde (1.26 g, 6.49 mmol) was added. The resulting mixture was then allowed to warm to room temperature, stirred for 30 min, and chlorotrimethylsilane (0.82 mL, 6.49 mmol) was added. After stirring for an additional 30 min, the solvent was removed in vacuo. Chromatographic treatment of the residue (SiO_2/hexane to hexane:EtOAc 50:1) afforded 3.31 g (80% yield) of **12TT**: Pale yellow powder, mp 148–149 °C; R_f 0.40 (hexane:EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (9H, s, $SiMe_3$), 1.35 (9H, s, *p*-*t*-Bu), 1.49 (9H, s, *o*-*t*-Bu), 1.52 (9H, s, *o*′-*t*-Bu), 5.91 (1H, d, $^3J_{PH}$ = 12.2 Hz, P=C–CH), 6.93 (1H, m, thienyl), 7.00–7.10 (2H, m, thienyl), 7.16 (1H, m, thienyl), 7.20 (1H, m, thienyl), 7.42 (1H, s, *m*-Mes*), and 7.44 (1H, s, *m*′-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.6 (s, $SiMe_3$), 31.7 (s, *p*-C*Me*$_3$), 33.1 (d, $^4J_{PC}$ = 6.7 Hz, *o*-C*Me*$_3$), 33.2 (d, $^4J_{PC}$ = 7.0 Hz, *o*′-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 38.4 (s, *o*′-*C*Me$_3$), 77.1 (d, $^2J_{PC}$ = 40.9 Hz, COSi), 122.6 (s, *m*-Mes*), 123.4 (s, thienyl), 123.8 (s, thienyl), 124.5 (s, thienyl), 125.3 (s, thienyl), 128.1 (s, thienyl), 136.9 (d, $^1J_{PC}$ = 54.1 Hz, *ipso*-Mes*), 137.0 (thienyl), 138.2 (thienyl), 146.4 (d, $^3J_{PC}$ = 12.4 Hz, thienyl), 151.3 (s, *p*-arom.), 153.6 (d, $^2J_{PC}$ = 2.2 Hz, *o*-arom.), 153.9 (d, $^2J_{PC}$ = 2.1 Hz, *o*′-arom.), and 166.3 (d, $^1J_{PC}$ = 64.0 Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 257.7; UV–vis (CH_2Cl_2) 247 (log ε 4.31), 276 (4.05), 320 (4.27), and 383 nm (sh, 3.39); IR (KBr) 2962, 2871, 1593, 1473, 1398, 1363, 1252, 1070, 877, 843, 795, and 688 cm^{-1}. Found: *m*/*z* 657.1414. Calcd for $C_{31}H_{44}{}^{79}BrNaOPS_2Si$: M^+ + Na, 657.1416.

(*E*,*E*)-1,2-Di(2,2′-bithienyl-5-yl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1TT). To a solution of **12TT** (2.00 g, 3.15 mmol) in THF (73 mL) was added *t*-butyllithium in pentane (1.45 M, 4.30 mL, 6.29 mmol) at −78 °C. The resulting solution was stirred at −78 °C for 15 min, and 1,2-dibromoethane (0.14 mL, 1.6 mmol) was added. The reaction mixture was stirred for 10 min, allowed to warm to room temperature, and stirred for additional 1 h. Removal of the solvent followed by column chromatography (Al_2O_3/hexane) afforded 1.41 g (96% yield) of (*E*,*E*)-**1TT**: Red powder, mp 265–266 °C (decomp); R_f 0.14 (hexane: EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (18H, s, *p*-*t*-Bu), 1.59 (36H, s, *o*-*t*-Bu), 5.54 (2H, d, $^3J_{HH}$ = 3.9 Hz, 3-thienyl), 6.58 (2H, d, $^3J_{HH}$ = 3.9 Hz, 4-thienyl), 6.96 (2H, dd, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 3.7 Hz, 4′-thienyl), 7.03 (2H, m, 3′-thienyl), 7.19 (2H, dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.1 Hz, 5′-thienyl), and 7.44 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 32.0 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 122.5 (s, *m*-arom.), 124.3 (s, thienyl), 124.6 (s, thienyl), 125.3 (s, thienyl), 128.3 (s, thienyl), 131.6 (s, thienyl), 131.8 (s, thienyl), 137.2 (d, $^1J_{PC}$ = 26.4 Hz, *ipso*-Mes*), 146.2 (pseudo t, ($^2J_{PC}$ + $^3J_{PC}$)/2 = 5.5 Hz, P=C–*C*), 151.0 (s, *p*-Mes*), 155.7 (s, *o*-Mes*), and 175.3 (dd, $^1J_{PC}$ = 18.0 Hz, $^2J_{PC}$ = 9.2 Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 171.4; UV–vis (CH_2Cl_2) 248 (log ε 4.58), 315 (4.35), 359 (sh, 4.53), 397 (4.68), and 478 nm (4.34); IR (KBr) 2960, 2904, 2868, 1593, 1479, 1454, 1394, 1362, 1238, 1215, 879, 840, 802, and 696 cm^{-1}. Found: C, 72.16; H, 7.47; S, 13.80%. Calcd for $C_{56}H_{68}P_2S_4$: C, 72.22; H, 7.36; S, 13.77%.

3-(Biphenyl-4-yl)-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-3-(trimethylsiloxy)-1-phosphapropene (12PP). To a solution of (dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (1.35 g, 3.02 mmol) in THF (30 mL) was added butyllithium in hexane (1.60 M, 2.06 mL, 3.30 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 10 min, and a solution of 4-biphenylcarbaldehyde (627 mg, 3.44 mmol) in THF (6 mL) was added. Then the resulting mixture was allowed to warm to room temperature, stirred for 30 min, and chlorotrimethylsilane (0.46 mL, 3.6 mmol) was added. After stirring for an additional 30 min, an appropriate amount of hexane was added, and the mixture was washed successively with water and brine and dried over $MgSO_4$. The solvent was removed in vacuo. Chromatographic treatment of the residue (SiO_2/hexane:EtOAc 100:1) afforded 1.55 g (82% yield) of **12PP**: Pale yellow powder, mp 139–141 °C; R_f 0.52 (hexane:EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (9H, s, $SiMe_3$), 1.33 (9H, s, *p*-*t*-Bu), 1.43 (9H, s, *o*-*t*-Bu), 1.51 (9H, s, *o*′-*t*-Bu), 5.76 (1H, d, $^3J_{PH}$ = 12.9 Hz, P=C–CH), and 7.33–7.66 (11H, m, arom.); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.79 (s, $SiMe_3$), 31.9 (s, *p*-C*Me*$_3$), 33.1 (d, $^4J_{PC}$ = 6.1 Hz, *o*-C*Me*$_3$), 33.3 (d, $^4J_{PC}$ = 7.4 Hz, *o*′-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 38.5 (s, *o*′-*C*Me$_3$), 80.4 (d, $^2J_{PC}$ = 36.9 Hz, COSi), 122.6 (s, arom.), 126.9 (s, arom.), 127.6 (s, arom.), 127.7 (s, arom.), 129.2 (s, arom.), 137.4 (d, $^1J_{PC}$ = 54.1 Hz, *ipso*-Mes*), 140.7 (s, arom.), 141.3 (s, arom.), 141.4 (s, arom.), 151.2 (s, *p*-Mes*), 153.7 (s, *o*-Mes*), 154.0 (s, *o*′-Mes*), and 168.2 (d, $^1J_{PC}$ = 65.3 Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 253.1; UV (CH_2Cl_2) 251 (log ε 4.44) and 274 nm (4.44); IR (KBr) 2958, 2904, 2868, 1703, 1595, 1479, 1398, 1362, 1252, 1209, 1076, 877, 843, 760, 737, and 696 cm^{-1}. Found: *m*/*z* 645.2288. Calcd for $C_{35}H_{48}{}^{79}BrNaOPSi$: M^+ + Na, 645.2288.

(*E*,*E*)-1,2-Di(biphenyl-4-yl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1PP). To a solution of **12PP** (500 mg, 0.80 mmol) in THF (3 mL) was added *t*-butyllithium in pentane (1.42 M, 1.70 mL, 2.41 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 30 min and 0.40 mmol of 1,2-dibromoethane was added. The reaction mixture was stirred for 1 h and refluxed for 1 h. Appropriate amount of hexane was added and the mixture was washed successively with water and brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatographic treatment of the residue (SiO_2/hexane) afforded (*E*,*E*)-**1PP** quantitatively: Orange powder, mp 234–236 °C; R_f 0.14 (hexane:EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (18H, s, *p*-*t*-Bu), 1.59 (36H, s, *o*-*t*-Bu), 6.64 (4H, d, $^3J_{PH}$ = 8.4 Hz, arom.), 7.10 (4H, d, $^3J_{HH}$ = 8.4 Hz, arom.), 7.32 (2H, t, $^3J_{HH}$ = 7.3 Hz, arom.), 7.38–7.43 (8H, m, arom.), and 7.50 (4H, d, $^3J_{HH}$ = 7.2 Hz, arom.); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 32.2 (s, *p*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 39.1 (s, *o*-*C*Me$_3$), 122.4 (s, arom.), 126.6 (s, arom.), 127.1 (s, arom.), 128.0 (s, arom.), 129.28 (s, arom.), 129.31 (s, arom.), 131.4 (s, arom.), 136.2 (d, $^1J_{PC}$ = 27.5 Hz, *ipso*-Mes*), 140.6 (s, arom.), 140.7 (s, arom.), 150.8 (s, *p*-Mes*), 155.3 (pseudo t, ($^2J_{PC}$ + $^3J_{PC}$)/2 = 4.9 Hz, P=C–*C*), 155.4 (s, *o*-Mes*), and 176.7 (dd, $^1J_{PC}$ = 17.2 Hz, $^2J_{PC}$ = 9.9 Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 170.3; UV–vis (CH_2Cl_2) 250 (log ε 4.55), 343 (4.69), and 420 nm (sh, 4.22); IR (KBr) 2960, 2362, 2337, 1479, 1396,

1361, 1240, 1209, 1012, 877, 842, 804, and 759 cm^{-1}. Found: m/z 929.5318. Calcd for $C_{64}H_{76}NaP_2$: $M^+ + Na$, 929.5314.

2-Bromo-3-(5-phenyl-2-thienyl)-1-(2,4,6-tri-*t*-butylphenyl)-3-(trimethylsiloxy)-1-phosphapropene (12TP). To a solution of (dibromomethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (225 mg, 0.502 mmol) in THF (5 mL) was added butyllithium in hexane (1.60 M, 0.35 mL, 0.56 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 10 min, and a solution of 5-phenylthiophene-2-carbaldehyde (103 mg, 0.547 mmol) in THF (2 mL) was added. Then, the resulting mixture was allowed to warm to room temperature, stirred for 30 min, and chlorotrimethylsilane (0.077 mL, 0.60 mmol) was added. After stirring for an additional 30 min, an appropriate amount of hexane was added, and the mixture was washed successively with water and brine, dried over $MgSO_4$. The solvent was removed in vacuo. Chromatographic treatment of the residue (SiO_2/hexane:EtOAc 100:1) afforded 151 mg (48% yield) of **12TP**: Pale yellow powder, mp 150–154 °C; R_f 0.40 (hexane:EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (9H, s, $SiMe_3$), 1.34 (9H, s, *p*-*t*-Bu), 1.48 (9H, s, *o*-*t*-Bu), 1.51 (9H, s, *o*′-*t*-Bu), 5.93 (1H, d, $^3J_{PH}$ = 12.4 Hz, P=C–CH), 6.98 (1H, d, $^3J_{HH}$ = 3.7 Hz, thienyl), 7.17 (1H, d, $^3J_{HH}$ = 3.7 Hz, thienyl), 7.35–7.43 (5H, m, arom.), 7.59 (2H, s, *m*-Mes*), and 7.61 (2H, s, *m*′-Mes*); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 257.1; UV (CH_2Cl_2) 237 (log ε 4.32), 285 (3.81), and 347 nm (4.50); IR (KBr) 2956, 1251, 873, 842, and 754 cm^{-1}. Found: m/z 651.1852. Calcd for $C_{33}H_{46}BrNaOPSSi$: $M^+ + Na$, 651.1852.

(*E*,*E*)-1,2-Bis(5-phenyl-2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (1TP). To a solution of **12TP** (144 mg, 0.229 mmol) in THF (1.5 mL) was added *t*-butyllithium in pentane (1.42 M, 0.50 mL, 0.71 mmol) at −98 °C. The resulting solution was stirred at −98 °C for 30 min, and 1,2-dibromoethane (0.011 mL, 0.13 mmol) was added. The reaction mixture was stirred for 1 h and then refluxed for 1 h. An appropriate amount of hexane was added, and the mixture was washed successively with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. Chromatographic treatment of the residue (SiO_2/hexane) followed by gel-permeation column chromatography (JAIGEL 1H+2H column) afforded 61 mg (58%) of (*E*,*E*)-**1TP**: Red powder, mp 228–230 °C; R_f 0.14 (hexane:EtOAc = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (18H, s, *p*-*t*-Bu), 1.62 (36H, s, *o*-*t*-Bu), 6.77 (2H, d, $^3J_{HH}$ = 3.9 Hz, thienyl), and 7.24–7.48 (16H, m, arom.); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 170.3; UV–vis (CH_2Cl_2) 308 (log ε 4.35), 342 (sh, 4.47), 384 (4.63), and 468 nm (4.25); IR (KBr) 2960, 2906, 2867, 1594, 1477, 1361, and 745 cm^{-1}. Found: m/z 918.4550. Calcd for $C_{60}H_{72}P_2S_2$: M^+, 918.4545. ^{13}C{^{1}H} NMR spectrum of **1TP** was unclear due to partial *E*/*Z*-isomerization during the measurement process.[23] (*E*,*Z*)-**1TP**: ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 178.6 (d, $^3J_{PP}$ = 17.4 Hz) and 196.7 (d, $^3J_{PP}$ = 17.4 Hz).

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23 This fact may indicate that steric hindrance between the Mes* groups and the substituents at the 1,2-positions (of the cyclobutene ring) is larger in (*E*,*E*)-**1TP** than in (*E*,*E*)-**1TT**, causing facile isomerization of (*E*,*E*)-**1TP**, in order to release the congestion. In the case of (*E*,*E*)-**1PP**, the UV–visible absorption spectrum was blue-shifted compared to those of (*E*,*E*)-**1TP** and (*E*,*E*)-**1TT**. Consequently, isomerization of (*E*,*E*)-**1PP** is not as easy as that of (*E*,*E*)-**1TP**.