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Iodine-Induced *E/Z* Isomerization of Sterically Protected 3,4-Diphosphinidenecyclobutenes and 1-Phosphaethenes

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ABSTRACT

Sterically protected (E,E)-3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)dialkylcyclobutenes were isomerized to the corresponding (E,Z) derivatives in the presence of catalytic amounts of iodine. Similar iodine-induced isomerizations were observed in the case of (E)- and (Z)-2-phenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaethenes.

INTRODUCTION

Low-coordinated phosphorus compounds having more than two phosphorus–carbon double bonds in their molecules are of interest because of their potential application as multidentate ligands. However, such phosphaethenes are generally unstable unless stabilized either kinetically by bulky substituents or thermodynamically by an electronic effect [1]. Utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) as a sterically protecting group [2,3], we successfully prepared 3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutenes **1** (via **3** and **4**) and their transition metal complexes **2aA–C** (Scheme 1). We were also successful in carrying out X-ray crystal structure analyses of both the ligand and the complex [4–6]. The compound **1** has a unique π system containing phosphorus–carbon $p\pi$–$p\pi$ double bonds and a rigid diphosphinidenecyclobutene skeleton. We have previously reported the *E/Z* isomerization of phosphaalkene **5** [7] and the diphosphinidenecyclobutenes **1a** and **1d** [4,8] by photoirradiation (Scheme 2). We now report here the iodine-induced *E/Z* isomerization of the diphosphinidenecyclobutenes.

RESULTS AND DISCUSSION

Sterically protected diphosphinidenecyclobutenes (*E,E*)-**1a** [4], (*E,E*)-**1c** [9], and (*E,E*)-**1d** [8] were prepared according to the methods in the literature. The 1,2-di-*t*-butyl-substituted derivative (*E,E*)-**1b** was similarly prepared from the corresponding ethynylphosphine **3b** in 23% overall yield. The diphosphinidenecyclobutenes thus obtained were then allowed to react with iodine (Scheme 3). Reaction of (*E,E*)-**1a** with ca. 1 mol equiv of iodine afforded the isomerization product, (*E,Z*)-**1a**, within 5 minutes in THF at room temperature (Table 1, entry 1). The isomerization also proceeded in the presence of a catalytic amount of iodine, although the conversion was relatively slow (entry 2). Either elongation of the reaction time or elevation of the reaction temperature led to a reduced yield of (*E,Z*)-**1a** because of partial decomposition (entries 3, 4).

Contrary to the case of the photo-isomerization, it seems likely that the iodine-induced isomerization of (*E,E*)-**1a** to (*E,Z*)-**1a** is irreversible or that the equilibrium balance is largely in favor of the (*E,Z*) form. Thus, attempted isomerization of

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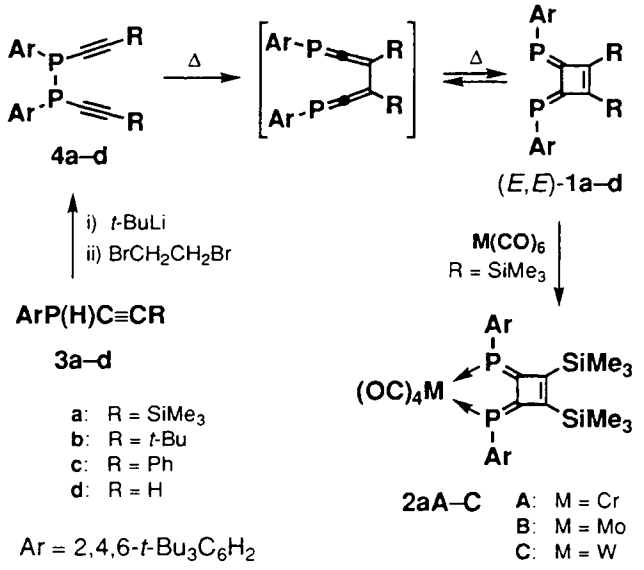
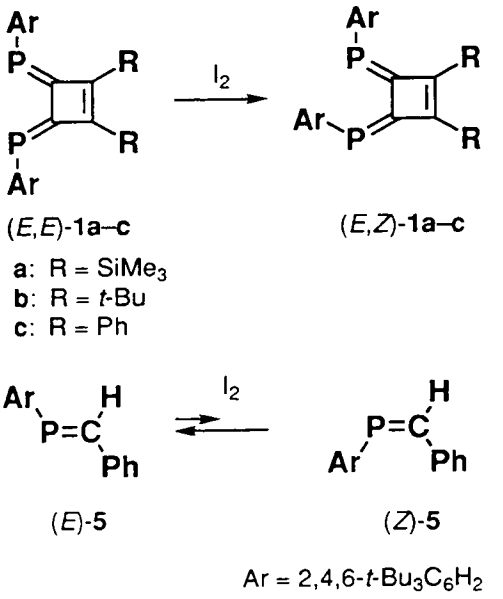


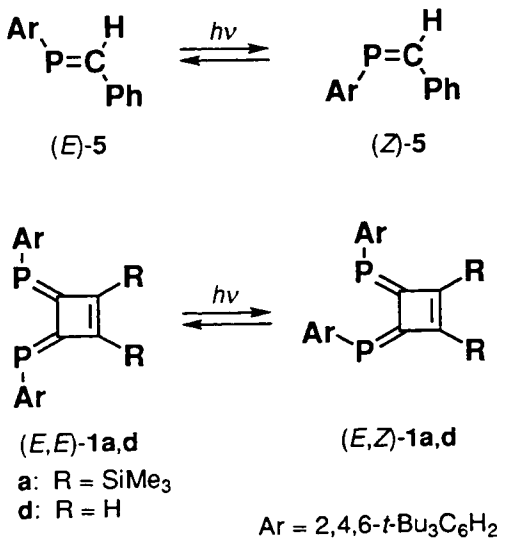
SCHEME 1



SCHEME 3

(*E*,*Z*)-**1a** under similar conditions resulted in the quantitative recovery of (*E*,*Z*)-**1a** (entry 5).

Similar results were obtained in the case of (*E*,*E*)-**1b**, **c**, although the reaction was slower than that of (*E*,*E*)-**1a** (entries 6–9). It should be noted that, in the photo-isomerization reaction of (*E*,*E*)-**1a** and **1b**, a slight amount of unidentified by-product was formed (δ_p = 165.5 and 152.3, respectively). However, no such by-products were formed in the case of iodine-induced isomerization. Reaction of iodine with the 1,2-nonsubstituted derivative (*E*,*Z*)-**1d** resulted in the decomposition of the diphosphinidenecyclobutene, suggesting that the steric bulk at the 1,2 positions of the cyclobutene ring is essential to prevent decomposition.



SCHEME 2

A probable mechanism of the isomerization is as follows (Scheme 4). Initially, a phosphonium iodide such as **6** or its valence isomer is formed, where the bond order of the –P=C< bond is lowered, making the rotation around the phosphorus–carbon bond easier. The predominant formation of the (*E*,*Z*) derivatives is ascribable to less steric repulsion between the 'Ar' group and the substituent at the cyclobutene-ring carbon that occurs in the (*E*,*Z*) derivatives more than that in the (*E*,*E*) derivatives.

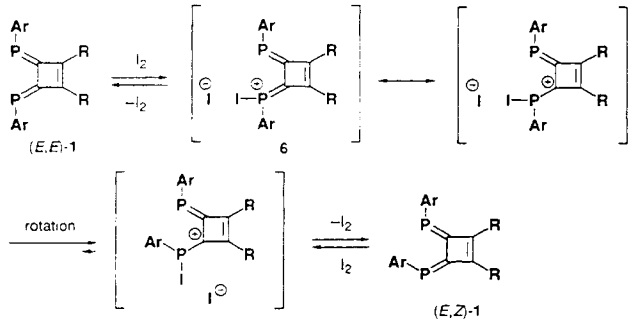
Iodine-induced *E*/*Z* isomerization of the phosphorus–carbon double bond was also demonstrated in the case of simple phosphaalkenes, (*E*)- and (*Z*)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethenes (**5**) (Scheme 3). Thus, (*Z*)-**5** isomerized to the *E* form within 12 minutes in THF in the presence of iodine (Table 1, entry 10). In this case, the isomerization was reversible, and (*Z*)-**5** was formed from (*E*)-**5** in the presence of iodine (entry 11). The *E*/*Z* ratio in the equilibrium state was found to be ca. 95 (*E*):5 (*Z*), while the photo-equilibrium ratio was 3 (*E*):7 (*Z*) [7]. Thus, the iodine-induced *E*/*Z* isomerization seems to be a general property of phosphaalkenes, affording the thermodynamically more stable isomer as a major product.

Finally, we studied the effect of iodine on the transition metal complex **2** (Scheme 5). Tetracarbonylmolybdenum complex **2aB** was prepared either by the previously reported reaction of (*E*,*E*)-**1a** with [bicyclo[2.2.1]hepta-2,5-diene]molybdenum(0) tetracarbonyl (**7**) [5] or by the reaction of (*E*,*Z*)-**1a** with **7** under photo-irradiation conditions. The molybdenum complex **2aB** thus obtained was allowed to react with iodine in THF at 50°C, and the reaction was followed by ^{31}P NMR

TABLE 1 Reactions of **1a–c**, **2aB**, and **5** with Iodine

Entry	*Reactant*	R^1	R^2	I_2 *(Mol Equiv)*	*Temperature (°C)*	*Time (hours)*	*Product*	*Yield (%)*
1	(*E,E*)-**1a**	TMS	TMS	1.3	RT	0.05	(*E,Z*)-**1a**	89
2	(*E,E*)-**1a**	TMS	TMS	0.2	RT	1	(*E,Z*)-**1a**	91
3	(*E,E*)-**1a**	TMS	TMS	1.2	RT	1	(*E,Z*)-**1a**	68
4	(*E,E*)-**1a**	TMS	TMS	1.2	50	1	(*E,Z*)-**1a**	11
5	(*E,Z*)-**1a**	TMS	TMS	1.2	RT	1	(*E,Z*)-**1a**	100[a]
6	(*E,E*)-**1b**	*t*-Bu	*t*-Bu	1.2	RT	5	(*E,Z*)-**1b**	88[b]
7	(*E,E*)-**1b**	*t*-Bu	*t*-Bu	0.3	RT	24	(*E,Z*)-**1b**	86
8	(*E,E*)-**1c**	Ph	Ph	1.2	RT	0.75	(*E,Z*)-**1c**	86[c]
9	(*E,E*)-**1c**	Ph	Ph	0.1	RT	9	(*E,Z*)-**1c**	46[d]
10	(*Z*)-**5**	Ph	H	0.1	RT	0.2	(*E*)-**5**	89[e]
11	(*E*)-**5**	H	Ph	0.1	RT	0.2	(*Z*)-**5**	7[f]
12	**2aB**	TMS	TMS	1.0[g]	50	63	(*E,Z*)-**1a**	59

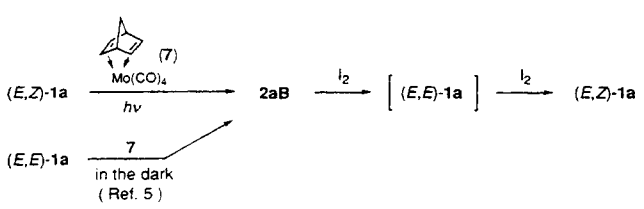
[a]Recovery.
[b]Recovery of (*E,E*)-**1b**: 3%.
[c]Recovery of (*E,E*)-**1c**: 2%.
[d]Recovery of (*E,E*)-**1c**: 49%.
[e]Determined by ^{1}H NMR, recovery of (*Z*)-**5**: 5%.
[f]Determined by ^{1}H NMR, recovery of (*E*)-**5**: 83%.
[g]Mol equiv based on the ligand diphosphinidenecyclobutene.



SCHEME 4

spectroscopy. After having been heated for 63 hours with iodine, **2aB** was oxidized to liberate the ligand, and the free ligand was isomerized by iodine to give (*E,Z*)-**1a** in 59% yield (Table 1, entry 12). It should be noted that heating of **2aB** in THF at 50°C for 67 hours in the absence of iodine resulted in the quantitative recovery of **2aB**. Thus, we have completed the metallation-demetallation cycle (*E,Z*)-**1a** → [(*E,E*)-**1a**] → **2aB** → (*E,Z*)-**1a** promoted with iodine.

In summary, we have described iodine-induced *E/Z* isomerization of phosphorus–carbon double bonds as well as a photo-induced metallation of diphosphinidenecyclobutene and an iodine-induced demetallation of the complex. The iodine-induced isomerization described above is the better method for preparation of (*E,Z*)-diphosphinidenecyclobutenes, because photoisomerization usually results in a mixture of (*E,E*) and (*E,Z*) derivatives.



SCHEME 5

EXPERIMENTAL

Instruments

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer and/or an AM-600 spectrometer. ^{31}P NMR spectra were measured on a Bruker AC-200P spectrometer. UV-Vis spectra were obtained on a Hitachi U-3210 spectrometer. IR spectra were recorded on a Horiba FT-300 spectrometer. MS were taken on either a JEOL HX-110 spectrometer or a Hitachi M-2500S spectrometer.

1,2-Bis(3,3-dimethyl-1-butynyl)-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphane (**4b**)

To a solution of (3,3-dimethyl-1-butynyl)(2,4,6-tri-*t*-butylphenyl)phosphine **3b** [10] (1.10 g, 3.08 mmol) in THF (27 mL) was added 3.08 mmol of *t*-butyllithium (1.57 M solution in pentane) at −78°C, and the resulting mixture was stirred for 5 minutes at this temperature. The solution was warmed to room temperature and stirred for 25 minutes. Then, the

solution was cooled to −78°C and 1.54 mmol of 1,2-dibromoethane was added. After being stirred at −78°C for 5 minutes, the mixture was warmed to room temperature and stirred for 20 minutes. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/pentane) afforded **4b** (864.9 mg, 79% yield).

4b: Pale yellow prisms, mp 121.5–124.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.14 (18H, br s, *o*-*t*-Bu), 1.26 (18H, s, *p*-*t*-Bu), 1.31 (18H, s, *t*-BuC≡C), 1.61 (18H, br s, *o'*-*t*-Bu), 7.14 (2H, br s, *m*-Ar), and 7.39 (2H, br s, *m'*-Ar); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ = 29.2 (s, C≡C$\underline{C}$Me$_3$), 31.0 (s, C≡CC$\underline{Me}_3$), 31.2 (s, *p*-C$\underline{Me}_3$), 33.9 (br s, *o*-C$\underline{Me}_3$), 34.6 (br s, *o'*-C$\underline{Me}_3$), 34.8 (s, *p*-$\underline{C}$Me$_3$), 38.7 (br s, *o*-$\underline{C}$Me$_3$), 39.7 (br s, *o'*-$\underline{C}$Me$_3$), 76.6 (pseudo t, J_{PC} = 20.8 Hz, P$\underline{C}$≡C), 121.2 (s, *m*-Ar), 121.3 (s, PC≡$\underline{C}$), 123.4 (s, *m'*-Ar), 131.2 (pseudo t, J_{PC} = 7.6 Hz, ipso-Ar), 150.1 (s, *p*-Ar), 156.9 (br s, *o*-Ar), and 159.1 (pseudo t, J_{PC} = 21.1 Hz, *o'*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = −38.9; UV (hexane) 249 (log ϵ 4.33), 257 (sh, 4.32), and 365 nm (3.56); IR (KBr) 2141 (C≡C), 1589, 1362, and 1252 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 714 (M^+, 0.5), 657 (M^+ − *t*-Bu, 0.4), 469 (M^+ − Ar, 0.9), and 357 (1/2 M^+, 100). Found: *m/z* 357.2712. Calcd for $C_{24}H_{38}P$: 1/2M, 357.2711.

(E,E)-1,2-Di-t-butyl-3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)cyclobutene [(*E,E*)-**1b**]

A solution of **4b** (735.9 mg, 1.03 mmol) in toluene (75 mL) was heated to reflux for 14 hours in the dark. The solvent was evaporated under reduced pressure, and the residue was separated by column chromatography to give 211.4 mg (29% yield) of (*E,E*)-**1b**. In this reaction, *trans*-3-*t*-butyl-4-(3,3-dimethyl-1-butynyl)-1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-diphosphet-3-ene (331.5 mg, 45% yield) was obtained along with (*E,E*)-**1b**.

(*E,E*)-**1b**: Yellow crystals, mp 203–204°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.67 (18H, s, 1,2-*t*-Bu), 1.30 (18H, s, *p*-*t*-Bu), 1.55 (36H, s, *o*-*t*-Bu), and 7.31 (4H, s, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 30.6 (s, 1,2-C$\underline{Me}_3$), 31.3 (s, *p*-C$\underline{Me}_3$), 33.1 (s, 1,2-$\underline{C}$Me$_3$), 33.3 (pseudo t, J_{PC} = 3.9 Hz, *o*-C$\underline{Me}_3$), 34.9 (s, *p*-$\underline{C}$Me$_3$), 38.3 (s, *o*-$\underline{C}$Me$_3$), 121.3 (s, *m*-Ar), 138.8 (pseudo t, J_{PC} = 29.0 Hz, ipso-Ar), 149.3 (s, *p*-Ar), 154.7 (s, *o*-Ar), 168.0 (br s, P=C–$\underline{C}$), and 179.3 (dd, $^1J_{PC}$ = 20.3 Hz and $^2J_{PC}$ = 16.9 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 142.6; UV (hexane) 259 (log ϵ 4.42), 288 (sh, 4.40), 308 (4.43), and 345 nm (sh, 3.95); IR (KBr) 1595, 1477, 1392, 1362, 1240, 1126, and 877 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 714 (M^+, 16), 657 (M^+ − *t*-Bu, 29), 469 (M^+ − Ar, 7), 439 (M^+ − ArP, 25), and 57 (*t*-Bu^+, 100). Found: *m/z* 714.5437. Calcd for $C_{48}H_{76}P_2$: M, 714.5422.

Iodine-Induced Isomerization of (E,E)-3,4-Bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutenes [(*E,E*)-**1**]

A solution of (*E,E*)-**1a** (83.8 mg, 0.112 mmol) in THF (12 mL) was added to 5.0 mg (0.0197 mmol) of iodine under argon in the dark. The resulting solution was stirred at room temperature for 1 hour and then poured into a 10% aqueous solution of $Na_2S_2O_3$ (50 mL). The solution was extracted with 50 mL of ether twice. The combined extract was washed with water (50 mL) and dried over $MgSO_4$. Removal of the solvent in vacuo afforded 76.5 mg (91% yield) of (*E,Z*)-**1a**. The diphosphinidenecyclobutenes (*E,Z*)-**1b,c** were also obtained from the corresponding (*E,E*) isomers by a similar method.

(*E,Z*)-**1b**: Pale yellow needles, mp 227–228°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.63 (9H, s, 1-*t*-Bu), 1.26 (9H, s, *p*-*t*-Bu), 1.29 (9H, s, *p'*-*t*-Bu), 1.38 (18H, s, *o*-*t*-Bu), 1.51 (9H, s, 2-*t*-Bu), 1.62 (18H, s, *o'*-*t*-Bu), 7.20 (2H, s, *m*-Ar), and 7.34 (2H, s, *m*-Ar'); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 30.7 (d, $^4J_{PC}$ = 3.3 Hz, 1-C$\underline{Me}_3$), 31.1 (dd, $^4J_{PC}$ = 9.8 Hz and $^5J_{PC}$ = 3.3 Hz, 2-C$\underline{Me}_3$), 31.2 (s, *p*-C$\underline{Me}_3$), 31.6 (s, *p'*-C$\underline{Me}_3$), 32.4 (d, $^3J_{PC}$ = 1.0 Hz, 1-$\underline{C}$Me$_3$), 32.9 (d, $^4J_{PC}$ = 8.1 Hz, *o*-C$\underline{Me}_3$), 33.2 (d, $^4J_{PC}$ = 7.3 Hz, *o'*-C$\underline{Me}_3$), 34.8 (s, *p*-$\underline{C}$Me$_3$), 34.9 (s, *p'*-$\underline{C}$Me$_3$), 35.2 (d, $^3J_{PC}$ = 3.4 Hz, 2-$\underline{C}$Me$_3$), 38.0 (s, *o*-$\underline{C}$Me$_3$), 38.2 (d, $^3J_{PC}$ = 1.3 Hz, *o'*-$\underline{C}$Me$_3$), 121.2 (s, *m*-Ar), 121.3 (s, *m*-Ar'), 135.3 (dd, $^1J_{PC}$ = 54.9 Hz and $^4J_{PC}$ = 2.3 Hz, ipso-Ar'), 139.9 (d, $^1J_{PC}$ = 70.4 Hz, ipso-Ar), 149.0 (s, *p*-Ar'), 149.5 (d, $^4J_{PC}$ = 0.6 Hz, *p*-Ar), 153.8 (d, $^2J_{PC}$ = 2.8 Hz, *o*-Ar'), 154.3 (dd, $^2J_{PC}$ = 4.6 Hz and $^5J_{PC}$ = 1.9 Hz, *o*-Ar), 166.2 (dd, $^2J_{PC}$ = 36.9 Hz and $^3J_{PC}$ = 28.5 Hz, P=C–C), 168.9 (dd, $^2J_{PC}$ = 36.5 Hz and $^3J_{PC}$ = 11.9 Hz, P=C–C), 178.1 (dd, $^1J_{PC}$ = 77.3 Hz and $^2J_{PC}$ = 18.9 Hz, P=C), and 182.0 (dd, $^1J_{PC}$ = 60.0 Hz and $^2J_{PC}$ = 31.7 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 158.8 and 176.6 (AB, $^3J_{PP}$ = 14.1 Hz); UV (hexane) 260 (sh, log ϵ 4.27), 291 (4.46), 298 (sh, 4.45), and 345 nm (sh, 3.82); IR (KBr) 1593, 1479, 1392, 1362, 1238, 1128, 876, 752, and 660 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 714 (M^+, 18), 657 (M^+ − *t*-Bu, 34), 469 (M^+ − Ar, 11), 439 (M^+ − ArP, 39), 275 (ArP^+ − 1, 78), and 57 (*t*-Bu^+, 100). Found: *m/z* 714.5406. Calcd for $C_{48}H_{76}P_2$: M, 714.5422.

(*E,Z*)-**1c**: Yellow prisms, mp 287.5–288.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.28 (18H, s, *o*-*t*-Bu), 1.33 (18H, s, *p*-*t*-Bu), 1.66 (18H, s, *o'*-*t*-Bu), 6.56 (2H, d, $^3J_{HH}$ = 7.4 Hz, *o*-Ph), 6.79 (2H, dd, $^3J_{HH}$ = 7.5 Hz, *m*-Ph), 6.95 (1H, t, $^3J_{HH}$ = 7.3 Hz, *p*-Ph), 7.12 (2H, d, $^4J_{PH}$ = 1.2 Hz, *m*-Ar), 7.28–7.32 (3H, m, *m*- and *p*-Ph'), 7.39 (2H, d, $^4J_{PH}$ = 1.4 Hz, *m*-Ar'), and 7.74 (2H, br d, $^3J_{HH}$ = 6.3 Hz, *o*-Ph'); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 31.56 (s, *p*-C$\underline{Me}_3$), 31.58 (s, *p'*-C$\underline{Me}_3$), 32.6 (d, $^4J_{PC}$ = 7.5 Hz, *o*-C$\underline{Me}_3$), 33.8 (d, $^4J_{PC}$ = 6.7 Hz, *o'*-C$\underline{Me}_3$), 34.87 (s, *p*-$\underline{C}$Me$_3$), 34.88 (s, *p'*-$\underline{C}$Me$_3$), 38.1 (s, *o*-$\underline{C}$Me$_3$), 38.3 (s, *o'*-$\underline{C}$Me$_3$), 121.3 (s, *m*-Ar), 121.5 (s, *m*-Ar'), 127.2 (s, *p*-Ph), 127.4 (s, *m*-Ph), 127.8 (d, $^4J_{PC}$ = 2.6 Hz, *o*-Ph), 128.2 (s, *m*-Ph'), 128.6 (br d,

$^4J_{PC}$ = 2.6 Hz, *o*-Ph'), 128.8 (br s, *p*-Ph'), 132.2 (s, ipso-Ph), 132.3 (s, ipso-Ph'), 134.2 (d, $^1J_{PC}$ = 53.1 Hz, ipso-Ar'), 134.2 (d, $^1J_{PC}$ = 64.5 Hz, ipso-Ar), 149.4 (s, *p*-Ar'), 150.4 (s, *p*-Ar), 153.8 (s, *o*-Ar'), 154.2 (dd, $^2J_{PC}$ = 39.7 Hz and $^3J_{PC}$ = 25.6 Hz, P=C–C), 154.6 (dd, $^2J_{PC}$=38.8 Hz and $^3J_{PC}$ = 13.2 Hz, P=C–C), 155.2 (d, $^2J_{PC}$ = 3.1 Hz, *o*-Ar), 175.0 (dd, $^1J_{PC}$ = 67.7 Hz and $^2J_{PC}$ = 18.3 Hz, P=C), and 180.8 (dd, $^1J_{PC}$ = 54.3 Hz and $^2J_{PC}$ = 26.5 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 176.5 and 195.2 (AB, $^3J_{PP}$ = 14.9 Hz); UV (hexane) 245 (log ϵ 4.32), 324 (4.53), and 377 nm (sh, 3.97); IR (KBr) 1593, 1475, 1394, 1362, 1240, 1211, 1128, and 694 cm^{-1}; FAB–MS *m/z* 755 (M^+), 622 (M^+ – *t*-Bu–Ph), and 480 (M^+ – ArP).

Iodine-Induced Isomerization of 2-Phenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaethene (**5**)

To a solution of (*Z*)-**5** (38.9 mg, 0.106 mmol) in THF (10 mL) was added 2.1 mg (0.0083 mmol) of iodine, and the resulting solution was stirred at room temperature for 12 minutes. The solution was poured into a 10% aqueous solution of $Na_2S_2O_3$ (50 mL) and extracted with hexane. The organic phase was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure to give 36.3 mg of a mixture of (*E*)- and (*Z*)-**5**. (*E*:*Z* = 95:5, determined by ^1H NMR spectroscopy). By a similar procedure, (*E*)-**5** (17.5 mg, 0.048 mmol) was allowed to react with iodine (0.0032 mmol) to give a mixture of (*E*)- and (*Z*)-**5** (15.7 mg, *E*:*Z* = 92:8, determined by ^1H NMR spectroscopy).

Preparation of [(E,E)-3,4-Bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene]tetracarbonylmolybdenum(0) (**2aB**)

A mixture of (*E,Z*)-**1b** (9.5 mg, 0.013 mmol) and [bicyclo[2.2.1]hepta-2,5-diene]molybdenum(0) tetracarbonyl (**7**) (4.3 mg, 0.014 mmol) in C_6D_6 (0.4 mL) was irradiated with a medium-pressure mercury lamp (100 W) at room temperature for 7.5 hours. After removal of the solvent in vacuo, the residue was chromatographed (SiO_2/hexane) to give 1.8 mg (15%) of **2aB**.

Attempted Thermal Reaction of **2aB**

A THF-d_8 (0.4 mL) solution of **2aB** (17.5 mg, 0.0183 mmol) was sealed in a Pyrex tube (5 mmϕ) under argon and heated at 50°C for 67 hours. No significant change was observed in ^1H and ^{31}P NMR spectra of the resulting solution, and 17.3 mg (99%) of **2aB** was recovered after short column chromatography (SiO_2/hexane).

Reaction of **2aB** *with Iodine*

To a THF (3 mL) solution of iodine (4.3 mg, 0.017 mmol) was added a THF (7 mL) solution of **2aB** (16.3 mg, 0.017 mmol), and the mixture was heated at 50°C for 63 hours. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/pentane) afforded 7.5 mg (59% yield) of (*E,Z*)-**1a**.

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