

Preparation and photoisomerization of 2-phosphaethenylbenzenes having more than one phosphorus–carbon double bond

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Received 19 June 1996; revised 20 November 1996

Abstract

Phosphaethenes having more than one phosphorus–carbon double bond on a benzene ring were prepared. The *E/Z* photoisomerization reactions of these phosphaethenes were studied using ^{31}P NMR spectroscopy. The structure of 1,2-bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene was determined by X-ray crystallographic analysis. © 1997 Elsevier Science S.A.

Keywords: Phosphorus; Phosphaethene; 2,4,6-Tri-*t*-butylphenyl; Steric protection; X-ray crystallographic analysis

1. Introduction

Organophosphorus compounds in low coordination states are of current interest because they are highly reactive and unstable unless protected by bulky substituents such as the 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar). By using this protecting group, several unusual compounds have been prepared and characterized so far, including organophosphorus compounds such as diphosphenes [1], phosphaethenes [2], phosphaallenes [3], diphosphaallenes [4,5], and so on.

Since Bickelhaupt and coworkers reported the first phosphaethene stabilized with the mesityl group [6], many phosphaethenes carrying the P=C bond have been synthesized and their chemical properties have been studied [7]. Among the various reactivities of the phosphaethenes, one of the most fundamental reactions might be *E/Z* isomerization. We report here the synthesis and structure of phosphaethenes carrying more than one P=C double bond within a molecule, as well as their *E/Z* photoisomerization around each P=C bond [8],¹ while Geoffroy has recently reported on 1,3-bis(phosphaethenyl)benzene [9] as well as the 1,2-derivative [10].

2. Results and discussion

2.1. Preparation and spectral study of phosphaethenes carrying more than one P=C bond

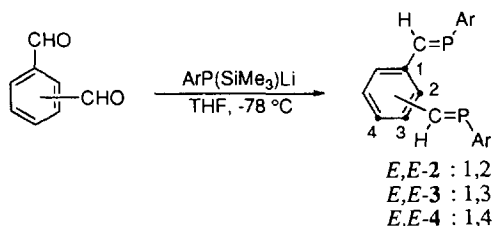
1,2-Bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (**2**) [8,10],¹ 1,3-bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (**3**) [8,9],¹ and 1,4-bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (**4**) were prepared, as shown in Scheme 1, according to the method employed for (*E*)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (*E*-**1**) in the dark [2]. Similarly, 1,3,5-tris[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (**5**) and 1,2,4,5-tetrakis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (**6**) were prepared from silylphosphide, $\text{ArP}(\text{SiMe}_3)\text{Li}$, and the corresponding aldehydes.

The configurations of **2–6** were all *E,E*-, *E,E,E*-, or *E,E,E,E*-isomers around the P=C bond respectively according to the NMR study, and no *Z*-isomers were detected in the reaction mixtures. ^{31}P NMR data of **2–6** are shown in Table 1, together with the corresponding *Z*-isomers obtained from the photoisomerization reactions. The assignments of configuration were done taking peak intensities as well as chemical shifts and coupling constants into account. For the *E,E*-isomers of **2–4**, they showed a downfield shift in the order **4**, **3**, **2**.

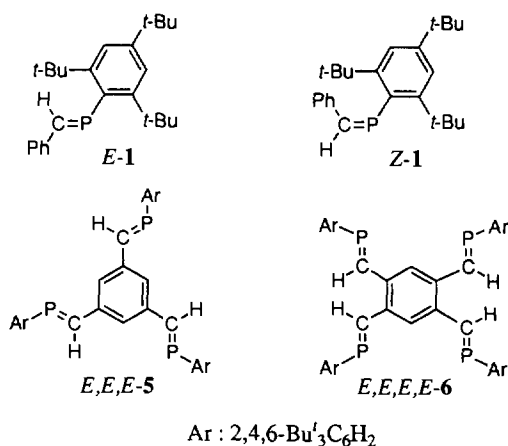
Fig. 1 shows UV–vis spectra of phosphaethenes **2–6** of all *E*-configurations together with *E*-**1** ($\lambda_{\text{max}} = 315 \text{ nm}$) as a reference compound, indicating that all the

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¹ A part of this work, including the X-ray analysis of *E,E*-**2**, was presented at the 69th Annual Meeting of the Chemical Society of Japan, March 1995, Kyoto, Abstr. 3H-706.



compounds carrying more than one P=C bond were red-shifted compared to *E*-1, and it is worthwhile noting that λ_{\max} of *E*-2, assignable to π - π^* absorption, was red-shifted by 350 nm from that of *E*-1. It might indicate that the P=C bonds have weak interaction with each other, delocalizing through the central benzene ring to some extent.



2.2. *E*/*Z* photoisomerization of phosphathenes carrying more than one P=C bond

We have reported on the *E*/*Z* isomerization of **1** upon photoirradiation [2], suggesting that **2–6** are expected to be interesting compounds because of possessing two, three, and four P=C bonds. Chloroform-*d*₁ solutions of **2–6** of all *E*-configurations were irradiated using an Xe lamp at room temperature and were analyzed by means of ³¹P NMR. Fig. 2(a) and (b) show changes in peak intensities of ³¹P NMR during the irradiation of *E,E*-2 and *E,E,E*-5 (50 mg) respectively, taking unity as the starting intensity of *E*-configuration and employing 85% H₃PO₄ as a chemical shift standard as well as intensity standard. Fig. 2(a) shows intensity changes for *E,E*-2 upon irradiation. The *E,E*-2 appears to isomerized to the *E,Z*-isomer, eventually coming to an equilibrium mixture of *E,E*- and *E,Z*-isomers. Although the material balance was not complete and thus *E,E*-2 seemed to decompose slowly, the ratio of *E,E*-2

Table 1
³¹P and ¹H NMR data of some phosphathenes

Compound	δ_p (ppm)	² <i>J</i> _{PH} (Hz)
<i>E</i> -1	259.3	26.9
<i>Z</i> -1	241.6	39.1
<i>E,E</i> -2	264.2	22.1
<i>E,Z</i> -2	266.9 ^{a,b}	24.6
	247.6 ^{a,c}	36.1
<i>E,E</i> -3	262.1	25.4
<i>Z,Z</i> -3	242.2	38.0
<i>E,E</i> -4	259.5	25.1
<i>Z,Z</i> -4	239.6	38.0
<i>E,E,E</i> -5	263.7	22.7
<i>E,E,Z</i> -5	262.0 ^b	24.5
	243.9 ^c	40.2
<i>E,Z,Z</i> -5	259.7 ^b	25.3
	242.4 ^c	37.6
<i>Z,Z,Z</i> -5	240.8	37.8
<i>E,E,E,E</i> -6	267.1	17.6

^a ⁵*J*_{PP} = 9 Hz; ^b *E*-configuration; ^c *Z*-configuration.

to *E,Z*-2 was estimated to be 7:8, and even after 5 h irradiation the peak intensities did not change. Furthermore, no signals due to the *Z,Z*-isomer were observed during the photolysis. On the other hand, *E,E*-3 and *E,E*-4 appeared to be directly isomerized to the *Z,Z*-isomers, since no signals corresponding to either *E,Z*-isomers of **3** or **4** were observed during the photolysis. The ratios of *E,E*-isomer to *Z,Z*-isomer were 1:2, for both compounds after 10 h. *E,E,E*-5 showed complicated decay curves (Fig. 2(b)), indicating that photolysis of *E,E,E*-5 gave an equilibrium mixture of all the isomers of *E,E,E*-, *E,E,Z*-, *E,Z,Z*- and *Z,Z,Z*-configurations within 2 h, where the ratio was 1:8:14:13. At the early stage of photolysis, the *E,E,Z*-isomer seems to be a major product, while both the *E,E,Z*- and *E,Z,Z*-isomers become majors in a photoequilibrium state. *E,E,E,E*-6 appeared to decompose slowly but linearly

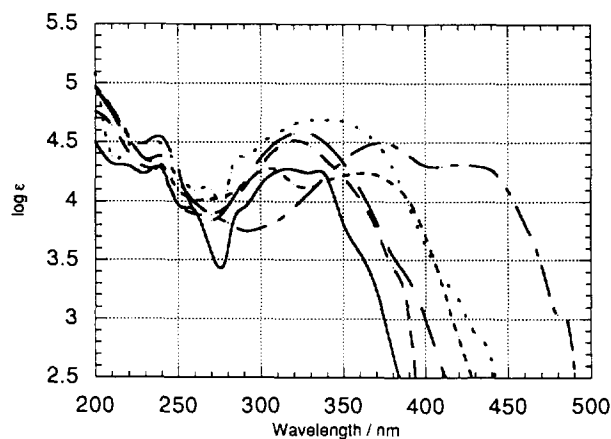


Fig. 1. UV-vis spectra of **1–6** of all *E*-configurations in hexane: — *E*-1; --- *E,E*-2; - · - · *E,E*-3; · · · *E,E*-4; · · · · *E,E,E*-5; - - - *E,E,E,E*-6.

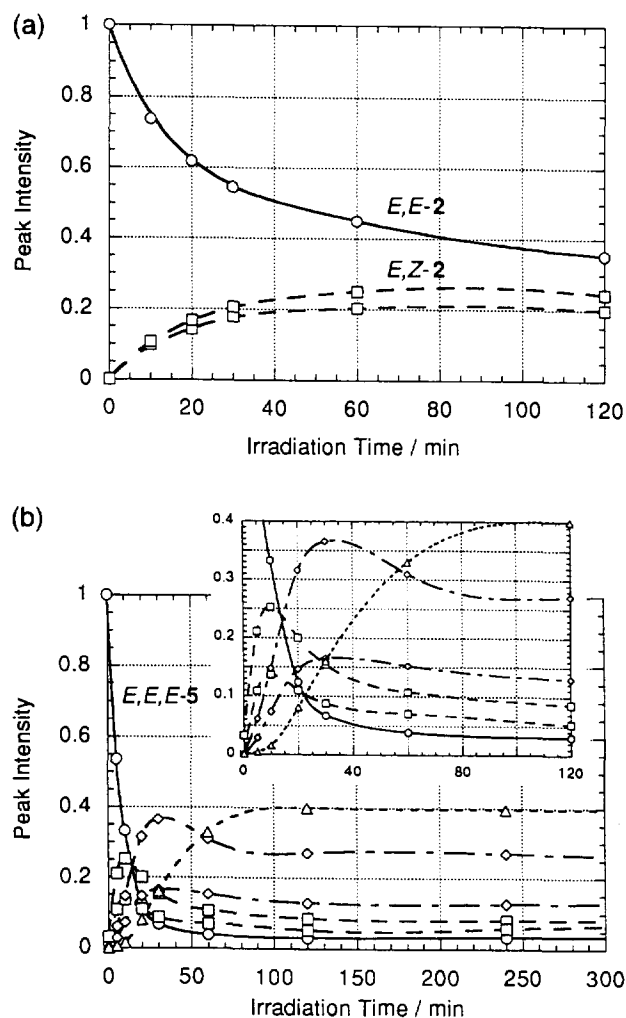


Fig. 2. ^{31}P NMR signal intensity changes upon irradiation of a chloroform solution of some phosphathenylbenzenes: (a) *E,E*-2 (○) where the legend □ is for *E,Z*-2; (b) *E,E,E*-5 (○) where the legends □ are for *E,E,Z*-5, ◇ for *E,Z,Z*-5, and △ for *Z,Z,Z*-5.

with irradiation time only to give intractable materials within 17 h. The difference of photoisomerization of the compounds **2** to **6** might be caused by interaction of each $\text{P}=\text{C}$ double bond and the bulky protective group.

2.3. X-ray structural analysis of *E,E*-2

The structure of *E,E*-2 was confirmed by X-ray crystallographic analysis.¹ Fig. 3 shows the molecular structure [11], where the $\text{P}=\text{C}$ bond length is 1.662(5) Å, which is almost the same value for *E*-1 (1.674(2) Å) [2] or *E,E*-3 (1.667 Å) [9]. The structure analysis for *E,E*-2 was independently carried out by Geoffroy and coworkers [10]. Some important bond lengths and angles and dihedral angles are listed in Table 2. Both the configurations were determined to be *E,E*. The benzene ring [C(3)–C(8)] is planar within 0.01 Å and the two adja-

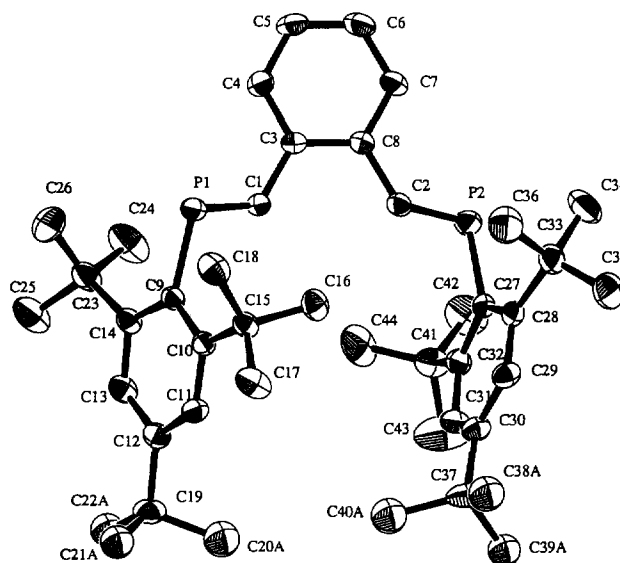


Fig. 3. Molecular structure of *E,E*-2 determined by X-ray analysis. The *p-t*-butyl groups are disordered and only positions with the predominant occupancy factors are displayed for clarity.

cent carbon atoms C(1) and C(2) are almost on the benzene plane within 0.008 and 0.04 Å respectively. Furthermore, the atoms [C(9), P(1), C(1), C(3)] and [C(27), P(2), C(2), C(8)] are almost coplanar within 0.005 and 0.002 Å respectively. The planes of the phosphathene system make dihedral angles of 37.9° and 31.8° with the benzene ring [C(3)–C(8)]. The two Ar groups are perpendicular to the plane [C(9), P(1), C(1), C(3)] (91.3°) or [C(27), P(2), C(2), C(8)] (84.1°) respectively, and the two Ar groups appear to be parallel with each other, making a dihedral angle of 22° and a distance between them of 6.49 Å.

Table 2

Some important bond lengths and bond and dihedral angles for *E,E*-2 (numbers in parentheses are estimated standard deviations)

Bond length (Å)		Bond angle or dihedral angle (°)	
P(1)–C(1)	1.662(5)	C(1)–P(1)–C(9)	101.9(2)
P(1)–C(9)	1.850(4)	C(2)–P(2)–C(27)	99.3(2)
P(2)–C(2)	1.661(5)	P(1)–C(1)–C(3)	124.2(3)
P(2)–C(27)	1.837(4)	P(2)–C(2)–C(8)	124.8(3)
C(1)–C(3)	1.478(6)	C(1)–C(3)–C(4)	120.6(4)
C(2)–C(8)	1.468(6)	C(1)–C(3)–C(8)	120.9(4)
C(3)–C(4)	1.399(6)	P(1)–C(9)–C(10)	120.3(3)
C(3)–C(8)	1.407(6)	P(1)–C(9)–C(14)	120.1(3)
C(4)–C(5)	1.372(6)	P(2)–C(27)–C(28)	120.4(4)
C(5)–C(6)	1.376(7)	P(2)–C(27)–C(32)	120.5(4)
C(6)–C(7)	1.370(7)	C(3)–C(1)–P(1)–C(9)	179.2(4)
C(7)–C(8)	1.388(6)	C(8)–C(2)–P(2)–C(27)	–179.7(4)
C(9)–C(10)	1.426(6)		
C(9)–C(14)	1.419(6)		
C(27)–C(28)	1.425(6)		
C(27)–C(32)	1.418(6)		

3. Experimental details

All experiments were carried out under argon atmosphere with dry solvents, unless otherwise specified. All melting points were determined with a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were measured by either a Bruker AC-200P or AM-600 spectrometer. ^{31}P NMR spectra were obtained with a Bruker AC-200P spectrometer using 85% H_3PO_4 as an external standard. IR spectra were recorded on a Horiba FT-300 spectrometer. The UV-vis spectra were obtained with a Hitachi U-3210 spectrometer. X-ray reflections were recorded on a Rigaku AFC-7S four-circle diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation.

3.1. Synthesis of bis(phosphaethenyl)benzenes (2–4)

Butyllithium in hexane solution (2.8 ml, 4.5 mmol) was added to 2,4,6-tri-*t*-butylphenylphosphine (1.1 g, 4.0 mmol) in THF (50 ml) solution under argon gas at -78°C in the dark and stirred. Chlorotrimethylsilane (0.6 ml, 4.7 mmol) was added dropwise and warmed up to room temperature. Butyllithium (2.8 ml, 4.5 mmol) was added again at 0°C into the solution and cooled down to -78°C . *o*-Phthalaldehyde (0.26 g, 1.9 mmol) in THF (10 ml) was added dropwise. After addition, the solution was warmed up to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography with hexane/ CHCl_3 and recrystallization from hexane to give 0.68 g (54%) of (*E,E*)-1,2-bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (*E,E*-2). *E,E*-2: ^1H NMR (600 MHz, CDCl_3) $\delta = 1.37$ (18H, s, *p*-¹Bu), 1.41 (36H, s, *o*-¹Bu), 7.27 (2H, m, 3,6-Ph), 7.37 (4H, s, *m*-Ar), 7.85 (2H, m, 4,5-Ph), and 8.14 (2H, d, $^2J_{\text{PH}} = 22.4$ Hz, P=CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) $\delta = 31.4$ (*p*-C(CH_3)₃), 33.8 (*o*-C(CH_3)₃), 34.9 (*p*-C(CH_3)₃), 38.1 (*o*-C(CH_3)₃), 121.5 (*m*-Ar), 126.1 (3,6-Ph), 128.2 (4,5-Ph), 136.7 (t, $^2J_{\text{PC}} = 13$ Hz, 1,2-Ph), 139.5 (d, $J_{\text{PC}} = 57$ Hz, *ipso*-Ar), 149.6 (*p*-Ar), 153.9 (*o*-Ar), and 173.7 (d, $J_{\text{PC}} = 35$ Hz, P=CH); ^{31}P NMR (81 MHz, CDCl_3) $\delta = 263.8$ (d, $^2J_{\text{PH}} = 22.8$ Hz); IR (KBr) 3099, 3070, 2906, 2865, 1592, 1471, 1361, and 877 cm^{-1} ; UV (hexane) 236 (log ϵ 4.34), 306 (4.27), and 356 nm (4.23). MS (70 eV) m/z (rel. int.) 654 (M^+ , 1.5), 597 (51), 541 (13), 471 (9.1), 409 (100), 275 (30), and 57 (88). Found: m/z 654.4489. $\text{C}_{44}\text{H}_{64}\text{P}_2$ Calc.: M, 654.4480. Anal. Found: C, 79.95; H, 9.84. $\text{C}_{44}\text{H}_{64}\text{P}_2$ Calc.: C, 80.69; H, 9.85%.

Very similarly using *m*-phthalaldehyde, (*E,E*)-1,3-bis[2-(2,4,6-tri-*t*-butylphenyl)phosphaethenyl]benzene (*E,E*-3) was obtained in 50% yield. *E,E*-3: Yellow prisms, m.p. 195–195.3 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) $\delta = 1.35$ (18H, s, *p*-¹Bu), 1.51 (36H, s, *o*-¹Bu), 7.44 (4H, s, *m*-Ar), 7.54 (m, 4H, Ph), and 8.10 (2H, d,

$^2J_{\text{PH}} = 26.0$ Hz, P=CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3) $\delta = 31.4$ (*p*-C(CH_3)₃), 33.8 (*o*-C(CH_3)₃), 34.9 (*p*-C(CH_3)₃), 38.3 (*o*-C(CH_3)₃), 121.8 (*m*-Ar), 123.6 (t, $J_{\text{PC}} = 21$ Hz, 1,3-Ph), 125.0 (m, 2-Ph), 129.0 (5-Ph), 138.9 (d, $J_{\text{PC}} = 54$ Hz, *ipso*-Ar), 140.5 (m, 4,6-Ph), 149.7 (*p*-Ar), 154.1 (*o*-Ar), and 175.4 (d, $J_{\text{PC}} = 34$ Hz, P=CH); ^{31}P NMR (81 MHz, CDCl_3) $\delta = 260.6$ (d, $^2J_{\text{PH}} = 25.4$ Hz); IR (KBr) 2690, 2952, 2864, 1587, 1362 and 877 cm^{-1} ; UV (hexane) 212 (log ϵ 4.63), 232 (4.29), and 320 nm (4.51). MS (70 eV) m/z (rel. int.) 654 (M^+ , 18), 598 (11), 541 (13), 380 (16), 275 (100), and 57 (35). Found: m/z 654.4448. $\text{C}_{44}\text{H}_{64}\text{P}_2$ Calc.: M, 654.4480. Anal. Found: C, 80.66; H, 9.61. $\text{C}_{44}\text{H}_{64}\text{P}_2$ Calc.: C, 80.69; H, 9.85%.

(*E,E*)-1,4-Bis[2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyl]benzene (*E,E*-4) was obtained similarly using *p*-phthalaldehyde in 70% yield. *E,E*-4: Pale yellow needles, m.p. 144.5–145.5 $^\circ\text{C}$ (decomp.); ^1H NMR (600 MHz, CDCl_3) $\delta = 1.36$ (18H, s, *p*-¹Bu), 1.52 (36H, s, *o*-¹Bu), 7.45 (4H, s, *m*-Ar), 7.53 (4H, dd, $J = 8.3$ and 3.4 Hz, Ph), and 8.11 (2H, d, $^2J_{\text{PH}} = 25.8$ Hz, P=CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) $\delta = 31.3$ (*p*-C(CH_3)₃), 33.7 (*o*-C(CH_3)₃), 34.9 (*p*-C(CH_3)₃), 38.2 (*o*-C(CH_3)₃), 121.7 (*m*-Ar), 126.2 (1,4-Ph), 139.5 (*ipso*-Ar), 144.6 (2,3,5,6-Ph), 149.6 (*p*-Ar), 153.9 (*o*-Ar), and 173.7 (P=CH); ^{31}P NMR (81 MHz, CDCl_3) $\delta = 259.2$ (d, $^2J_{\text{PH}} = 25.1$ Hz); IR (KBr) 2962, 2906, 1593, 1363, and 848 cm^{-1} ; UV (hexane) 238 (log ϵ 4.49) and 326 nm (4.53). Anal. Found: C, 79.02; H, 9.60. $\text{C}_{44}\text{H}_{64}\text{P}_2$ Calc.: C, 80.69; H, 9.85%.

3.2. Synthesis of tris- and tetrakis(phosphaethenyl)benzenes (*E,E,E*-5 and *E,E,E,E*-6)

Using 1,3,5-benzene tricarboxaldehyde [12], (*E,E,E*)-1,3,5-tris[2-(2,4,6-tri-*t*-butylphenyl)phosphaethenyl]benzene (*E,E,E*-5) was similarly obtained in 18% yield. *E,E,E*-5: Yellow prisms, m.p. 208.5–208.7 $^\circ\text{C}$ (decomp.); ^1H NMR (600 MHz, CDCl_3) $\delta = 1.35$ (18H, s, *p*-¹Bu), 1.51 (36H, s, *o*-¹Bu), 7.43 (6H, s, *m*-Ar), 7.61 (3H, s, 2,4,6-Ph), and 8.10 (3H, d, $^2J_{\text{PH}} = 24.2$ Hz, P=CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) $\delta = 31.4$ (*p*-C(CH_3)₃), 33.9 (*o*-C(CH_3)₃), 35.0 (*p*-C(CH_3)₃), 38.3 (*o*-C(CH_3)₃), 121.7 (*m*-Ar), 122.5 (2,4,6-Ph), 138.9 (d, $J_{\text{PC}} = 55.4$ Hz, *ipso*-Ar), 140.8 (1,3,5-Ph), 149.5 (*p*-Ar), 154.1 (*o*-Ar), and 175.0 (d, $J_{\text{PC}} = 33.4$ Hz, P=CH); ^{31}P NMR (81 MHz, CDCl_3) $\delta = 263.7$ (d, $^2J_{\text{PH}} = 22.7$ Hz); IR (KBr) 3085, 2962, 2906, 2865, 1591, 1361, 1128, 877, and 754 cm^{-1} ; UV (hexane) 235 (log ϵ 4.50), and 333 nm (4.69). Anal. Found: C, 80.24; H, 10.34. $\text{C}_{63}\text{H}_{93}\text{P}_3$ Calc.: C, 80.21; H, 9.94%.

Using 1,2,4,5-benzene tetracarboxaldehyde [13], (*E,E,E,E*)-1,2,4,5-tetrakis[2-(2,4,6-tri-*t*-butylphenyl)phosphaethenyl]benzene (*E,E,E,E*-6) was obtained in 10% yield. *E,E,E,E*-6: Yellow prisms, m.p. 244–245 $^\circ\text{C}$

(decomp.); ^1H NMR (600 MHz, CDCl_3) δ = 1.35 (36H, s, *p*-^tBu), 1.42 (72H, s, *o*-^tBu), 7.38 (8H, s, *m*-Ar), 8.18 (4H, d, $^2J_{\text{PH}} = 17.5$ Hz, P=CH), and 8.23 (2H, s, 3,6-Ph); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ = 31.4 (*p*- $\text{C}(\text{CH}_3)_3$), 33.8 (*o*- $\text{C}(\text{CH}_3)_3$), 34.9 (*p*- $\text{C}(\text{CH}_3)_3$), 38.1 (*o*- $\text{C}(\text{CH}_3)_3$), 121.6 (*m*-Ar), 124.1 (3,6-Ph), 136.9 (1,2,5,6-Ph), 139.7 (d, $J_{\text{PC}} = 55.5$ Hz, *ipso*-Ar), 149.6 (*p*-Ar), 154.0 (*o*-Ar), and 172.9 (d, $J_{\text{PC}} = 34.1$ Hz, P=CH); ^{31}P NMR (81 MHz, CDCl_3) δ = 267.1 (d, $^2J_{\text{PH}} = 17.6$ Hz); IR (KBr) 3095, 2962, 2906, 2867, 1592, 1361, 1128, and 877 cm^{-1} ; UV (hexane) 236 (log ϵ 4.38), 374 (4.49), 420 (4.31), and 442 nm (4.42).

3.3. Photolysis of phosphathenes (2–6)

Chloroform-*d*₁ solutions (0.5 ml) of 2–6 (50 mg) of all *E*-configurations in an NMR sample tube were irradiated using a 500-W Xe lamp through a Toshiba filter (L-39S for 2 and 5, UV-35 for 3 and 4, and Y-48 for 6) at an ambient temperature (25 °C) and were analyzed at an appropriate time interval by means of ^{31}P NMR using 85% H_3PO_4 as a chemical shift standard as well as intensity standard. The irradiation was stopped when the NMR peak intensities became apparently constant. Photolysis of both 3 and 4 was performed by using a sample of 95% *E,E*-configuration and the photoequilibrium seemed to be reached in 10 h. Upon irradiation, 6 appeared to decompose linearly to intractable materials within 17 h. The results of the photolysis of 2 and 5 are shown in Fig. 2(a) and (b) respectively.

3.4. X-ray structure determination of *E,E*-2

The compound *E,E*-2 was recrystallized from chloroform. Crystal data for *E,E*-2: $\text{C}_{44}\text{H}_{64}\text{P}_2$, FW = 654.94, triclinic, $P\bar{1}$ (No. 2), $a = 11.951(2)$, $b = 18.037(3)$, $c = 10.177(1)$ Å, $\alpha = 103.32(1)^\circ$, $\beta = 90.78(1)^\circ$, $\gamma = 79.61(1)^\circ$, $V = 2098.9(5)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.036$ g cm⁻³, $R = 0.072$, $R_w = 0.095$; 4965 unique reflections with $I > 3\sigma(I)$. The structure was solved with SHELXS-86 [14]. The methyl carbon atoms of both *p*-*t*-butyl groups (C20–C22) and (C38–C40) are disordered. These disordered groups were resolved into two positions from the difference maps. The predominant occupancy factor for (C20A–C22A) was refined to be 0.559, while that for (C20B–C22B) was 0.441; the predomi-

nant occupancy factor for (C38A–C40A) was refined to be 0.604, while that for (C38B–C40B) was 0.396.

4. Supplementary material available

Tables of atomic coordinates, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, structure factors for *E,E*-2 are available on request from the authors.

Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 05236204, 06227209, and 06303002) from the Ministry of Education, Science, Sports and Culture, Japan.

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