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Preparation of Some Multifunctionalized Methylenephosphines by Reactions of Chloro-[(2,4,6-tri-*t*-butylphenyl)phosphinidene]methyllithiums with Carbonyl Compounds

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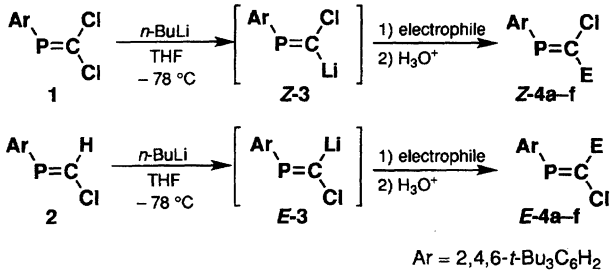
Either a (*Z*)- or (*E*)-chloro(phosphinidene)methyllithium reagent, prepared from dichloromethylene- or (*E*)-chloromethylene-phosphine with butyllithium, respectively, reacted with carbonyl compounds to give the corresponding functionalized methylenephosphines. Although the stereochemistry of the products was retained during the initial step of the reaction, in some cases *E*/*Z* isomerization reactions occurred to the resulting methylenephosphines. Imidazolidinediones bearing the P=C bond were obtained for the first time by a reaction of the *E*-lithium reagent with phenyl isocyanate; the structure of the *Z*-isomer was determined by X-ray analysis.

Kinetic stabilization of unstable chemical species with bulky substituents are of current interest. Utilizing the 2,4,6-tri-*t*-butylphenyl (abbreviated to Ar) group as a sterically protecting group, we have prepared various kinds of low-coordinated phosphorus compounds, such as diphosphenes,[1] as stable chemical species. During the course of our studies on phosphorus compounds in low-coordination states,[2] we have reported on the synthetic application of lithium trialkylsilyl(2,4,6-tri-*t*-butylphenyl)phosphide[3] and [(2,4,6-tri-*t*-butylphenyl)phosphinidene](trimethylsilyl)methyllithium[4] to the preparation of methylenephosphines via Peterson-type reactions. Chloro(phosphinidene)methyllithiums are also a promising reagent for introducing the P=C moiety. Thus, (dichloromethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (**1**)[5] and (*E*)-(chloromethylene)(2,4,6-tri-*t*-butylphenyl)phosphine (**2**)[6a,6b] were converted to (*Z*)-chloro[(2,4,6-tri-*t*-butylphenyl)phosphinidene]-methyllithium ***Z*-3**[5] and (*E*)-chloro[(2,4,6-tri-*t*-butylphenyl)phosphinidene]methyllithium ***E*-3**,[7] respectively, by reactions with butyllithium. Although the (phosphinidene)methyllithiums ***Z*-3** and ***E*-3** are expected to react with various electrophiles to yield substitution products, the reported reactions of **3** have been limited to those with iodomethane, chlorotrimethylsilane, chlorotrimethyltin, and methanol.[5,7] No reactions of **3** with carbonyl compounds have been reported so far. We now report on the reactions of ***E*-3** and ***Z*-3** with various carbonyl compounds, such as benzaldehyde, cyclohexanone, phenyl isocyanate, ethyl chloroformate, benzoyl chloride, and pivaloyl chloride, leading to multifunctionalized methylenephosphines **4**. Hereafter in this article, compounds bearing a P=C bond are trivially called phosphaethenes for **1**, **2**, and **4**, and 2-phosphaethenyllithium for **3**, instead of methylenephosphines and phosphinidenemethyllithium.

Results and Discussion

The starting phosphaethenes, 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**1**)[5b] and (*E*)-2-chloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**2**),[6a,6b] were prepared according to literature methods. (*Z*)-1-Chloro-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (***Z*-3**), prepared from **1**, was allowed to react with ca. 1.5 equiv of electrophiles to give the corresponding functionalized phosphaethenes ***Z*-4a—f** (Scheme 1). Similarly, (*E*)-1-chloro-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (***E*-3**), prepared from **2**, gave phosphaethenes ***E*-4a—f**. The results are summarized in Table 1.

In the ^{1}H NMR, NOE was observed between C*H*OH and one of the *o*-C(CH_3)$_3$'s for ***E*-4a**, whereas for ***Z*-4a**, a large coupling constant ($^3J_{PH}$) was observed (12.5 Hz)



Scheme 1.

Table 1. Reaction Products **4** from Reaction of **3** with Some Carbonyl Compounds

Entry	Reactant	Electrophile	ArP=C(E)Cl (**4**)			
				E	δ_P[a]	Yield/%[b]
1	***Z*-3**	PhCHO	***Z*-4a**	C(H)(OH)Ph	240.0	78
2	***Z*-3**	$(CH_2)_5CO$	***Z*-4b**	$C(OH)(CH_2)_5$	233.8	29
3	***Z*-3**	PhNCO	***Z*-4c**	C(O)NHPh	304.7	81
4	***Z*-3**	$ClCO_2Et$	***Z*-4d**	CO_2Et	316.0	86
5	***Z*-3**	PhCOCl	***Z*-4e**	C(O)Ph	334.4	91
6	***Z*-3**	*t*-BuCOCl	***Z*-4f**	C(O)*t*-Bu	304.1	74
7	***E*-3**	PhCHO	***E*-4a**	C(H)(OH)Ph	233.7	65
8	***E*-3**	$(CH_2)_5CO$	***E*-4b**	$C(OH)(CH_2)_5$	220.0	24[c]
9	***E*-3**	PhNCO	***E*-4c**	C(O)NHPh	257.4	16[d]
10	***E*-3**	$ClCO_2Et$	***E*-4d**	CO_2Et	282.7	78[c]
11	***E*-3**	PhCOCl	***E*-4e**	C(O)Ph	263.7	>50[e]
12	***E*-3**	*t*-BuCOCl	***E*-4f**	C(O)*t*-Bu	258.7	70

a) $^{31}P\{^1H\}$ NMR: 81 MHz, in $CDCl_3$. b) Isolated yield based on the starting **1** or **2**. c) Very slow isomerization from ***E*-4** to ***Z*-4** was observed. d) Compound ***E*-5** was obtained as a main product in 57% yield based on **2**. e) Intermediary formation of ***E*-4e** was observed according to the ^{31}P NMR spectroscopy, but the final product was ***Z*-4e** in 50% yield.

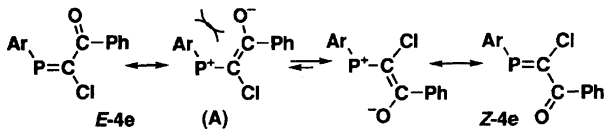
between C*H*OH and the phosphorus atom in contrast to a small $^3J_{PH}$ (1.6 Hz) for ***E*-4a**. These ^1H NMR results clearly confirm the *E*- and *Z*-configuration of **4**. The coupling constant ($^3J_{PH}$) is dependent on the configuration in the phosphaethene systems,[3c,6c] i.e., a proton which is closer to the lone pair of the phosphorus atom has a larger coupling constant, ($^3J_{PH}$).

^{31}P NMR data show that the *Z*-isomers resonate at a lower field than the *E*-isomers. This tendency is probably due to a steric effect of the substituents and an interaction of the phosphorus atom and lone-pair electrons of the chlorine atom. In the *E*-isomers ***E*-4**, the chlorine atom becomes closer to the phosphorus atom due to a buttressing effect because of the repulsion between a bulky substituent and the Ar group, causing the electron density on the phosphorus atom to be higher than that for the *Z*-isomers ***Z*-4**.

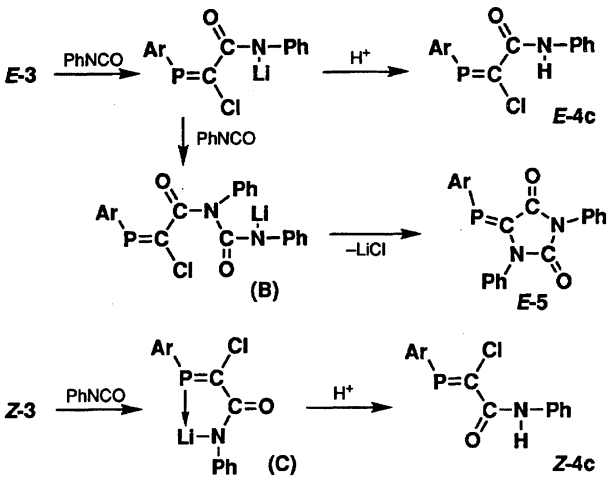
The reactions generally seem to proceed stereoselectively, at least during the initial step (see Scheme 1). The stereochemistry is completely retained if starting from ***Z*-3** (Table 1, Entries 1—6), and in some cases the same is true if starting from ***E*-3** (Entries 7—9). Some comments are as follows concerning the reaction of **3**. The yields were good except for in reactions with cyclohexanone (Entries 2 and 8). The reason for this seems to be due to competitive α-proton abstraction of cyclohexanone with ***Z*-3** or ***E*-3**.

In the reaction of ***E*-3** with benzoyl chloride (Entry 11), ^{31}P NMR spectroscopy indicated the initial formation of ***E*-4e** [δ_P (THF-d_8)=263.7]. However, this peak disappeared and a peak due to ***Z*-4e** [δ_P (THF-d_8)=323.7] appeared in about 0.5 h. The isomer ***Z*-4e** was isolated in 50% yield after column chromatography. This facile *E*/*Z* isomerization may be ascribed to the contribution of the zwitter ionic structure (**A** in Scheme 2) and the repulsion between the bulky Ar group and the acyl moiety. Similar isomerization was found in the case of ester ***E*-4d** (Entry 10), but very slowly, which is also explicable by this mechanism. Furthermore, ***E*-4b** (Entry 8) changed to a 1:1 mixture of ***E*-4b** and ***Z*-4b** at room temperature within a month, though the mechanism for this slow isomerization remains unclear.

The reaction of ***E*-3** with phenyl isocyanate led to



Scheme 2.



Scheme 3.

the formation of imidazolidine derivative ***E*-5** (Entry 9, see footnote d) in 57% yield based on the starting phosphaethene **2**. In this reaction, a small amount of ***E*-4c** was obtained (16% yield). Scheme 3 shows a plausible reaction mechanism for the formation of ***E*-5**. The reaction of ***E*-3** with the second isocyanate to form an intermediate **B** seems to proceed smoothly, since the reaction of ***E*-3** with a smaller amount of phenyl isocyanate (0.8 equiv) also gave ***E*-5** as a major product (39% yield based on the starting **2**). A similar hydantoin formation is known for sodium phenylacetylide.[8a] In contrast to ***E*-3**, the isomer ***Z*-3** did not afford the hydantoin derivative **5**, probably because a plausible reaction intermediate **C** is stabilized by coordination with the phosphorus atom to reduce the nucleophilicity, resulting in the exclusive formation of ***Z*-4c** upon hydrolysis. The formation of the hydantoin derivatives is of interest since there have been known several phenytoin-like anticonvulsant drugs, such as **6** (Chart 1).[8b,8c]

Furthermore, compound ***E*-5** was isomerized to ***Z*-5** either by light or by heat (Scheme 4). Irradiation of a benzene solution of ***E*-5** with a medium-pressure mercury lamp at 10 °C for 2 h gave a 2:3 mixture of ***E*-5** and ***Z*-5**. Heating of ***E*-5** in C_6D_6 in a sealed tube at 90 °C for 26 h in the dark gave a 1:1 mixture of ***E*-5** and ***Z*-5**. Pure ***Z*-5** was obtained by recrystallization from hexane. Moreover, the pure ***Z*-5** was isomerized to a 1:1 mixture of ***E*-5** and ***Z*-5** upon heating (90 °C for 26 h). A similar *E*/*Z* isomerization reaction of 5-benzylidenehydantoins, such as **7**,[9] is already known.

The structure of ***Z*-5** was confirmed by an X-ray analysis. Figure 1 depicts the molecular structure for ***Z*-5**. Some important bond lengths and angles are listed in Table 2. The imidazolidine ring is planar, which is common among the typical hydantoin derivatives.[10] The P(1)–C(1) bond length (1.693(7) Å) is normal for the P=C bond,[2] indicating that the conjugation of π-electrons of the P=C and the hydantoin system is not important. The bond lengths of C(1)–C(2) (1.498(9) Å) and N(2)–C(1) (1.398(8) Å) and bond angle of N(2)–C(1)–C(2) (105.8(6)°) are very similar to those for the benzylidene analog **8** (C(1)–C(2), 1.472(3) Å; N(1)–C(1), 1.404(3) Å; N(1)–C(1)–C(2), 105.5(2)°).[11] Additionally, the imidazolidine ring and the P=C plane is coplanar, which is also similar to **8**. The bulky Ar group of ***Z*-5** is almost perpendicular to the imidazolidine ring to avoid steric bulk. In fact, in the ^{1}H NMR, the aromatic protons of the 1-Ph group of ***Z*-5** (δ=6.8—7.0) show higher shifts than those of the 3-Ph group (δ=7.3—7.6), probably indicating the shielding effect of a ring current caused by the Ar group. On the other hand, the protons of the two phenyl groups of ***E*-5** appear in the ordinary region, δ=7.2—7.7.

In summary, several kinds of multifunctionalized phosphaethenes were obtained by the reactions of ***Z***-

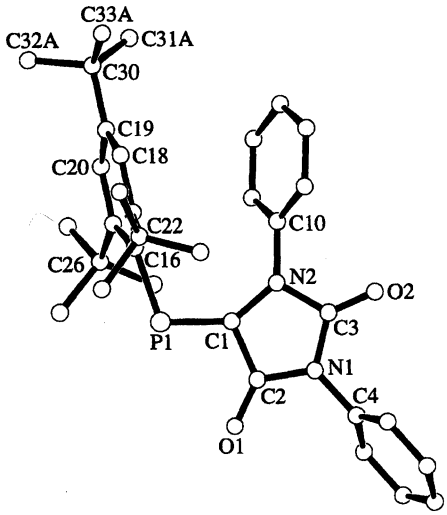


Fig. 1. Molecular structure of ***Z*-5** with atom labeling scheme. The *p*-*t*-butyl group (C31–C33) is disordered and the atoms with a predominant occupancy factor (0.67) are shown for clarity.

Table 2. Some Important Bond Lengths and Angles of ***Z*-5**[a]

Bond length/Å		Bond angle/°	
P(1)–C(1)	1.693(7)	C(1)–P(1)–C(16)	109.1(3)
O(1)–C(2)	1.204(8)	C(2)–N(1)–C(4)	124.2(6)
N(1)–C(2)	1.391(8)	C(1)–N(2)–C(3)	110.5(6)
N(1)–C(4)	1.441(8)	C(3)–N(2)–C(10)	119.8(6)
N(2)–C(3)	1.418(9)	P(1)–C(1)–C(2)	113.7(5)
C(1)–C(2)	1.498(9)	O(1)–C(2)–N(1)	125.1(7)
P(1)–C(16)	1.838(7)	N(1)–C(2)–C(1)	105.3(6)
O(2)–C(3)	1.193(8)	O(2)–C(3)–N(2)	126.5(8)
N(1)–C(3)	1.390(9)	P(1)–C(16)–C(17)	122.5(6)
N(2)–C(1)	1.398(8)	C(2)–N(1)–C(3)	112.1(6)
N(2)–C(10)	1.433(8)	C(3)–N(1)–C(4)	123.6(6)
		C(1)–N(2)–C(10)	129.0(6)
		P(1)–C(1)–N(2)	140.2(6)
		N(2)–C(1)–C(2)	105.8(6)
		O(1)–C(2)–C(1)	129.6(7)
		O(2)–C(3)–N(1)	127.3(7)
		N(1)–C(3)–N(2)	106.3(7)
		P(1)–C(16)–C(21)	119.0(5)

a) Numbers in parentheses are estimated standard deviations.

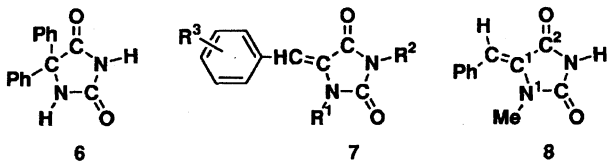
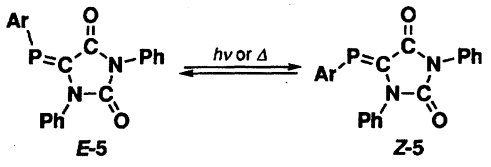


Chart 1.



Scheme 4.

3 and ***E*-3** with electrophiles, starting from **1** and **2**, respectively. In this method, since the starting materials already have the P=C moiety, this reaction enables us to prepare the corresponding multifunctionalized phosphaethenes. The products obtained in this research seem to attract further interest from the view points of synthetic application and structural chemistry since they have a low-coordinated P=C bond, halogen, and other reactive functional groups within their molecules, leading to subsequently interesting derivatives.

Experimental

The melting points were determined with a Yanagimoto micro melting-point apparatus MP-J3 and are not corrected. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200P or a Bruker AM600 spectrometer. ^{31}P NMR spectra were obtained with a Bruker AC200P spectrometer. Mass spectra were recorded on a JEOL HX-110, DX-303, AX-500, or a Hitachi M-2500S spectrometer. FT-IR and UV-vis spectra were taken on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively. X-Ray diffraction data were collected on a Rigaku AFC-7S four-circle diffractometer. All reactions were carried out under an argon atmosphere if necessary. Phosphaethenes **1**[5b] and **2**[6a] were prepared according to literature methods.

(*Z*)-2-Chloro-1-phenyl-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-ol (*Z*-4a): To a solution of the 2,2-dichlorophosphaethene **1** (126.0 mg, 0.351 mmol) in THF (12 mL) at −78 °C was added butyllithium (0.358 mmol; 1.63 M solution in hexane, 1 M=1 mol dm^{-3}), when the resulting solution turned light blue. Benzaldehyde (50 μL, 0.508 mmol) was added to the solution. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The solvent was evaporated in vacuo and the residue was extracted with ether (20 mL). The extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Silica-gel column chromatographic separation (hexane/ether, 2:1) of the residue gave ***Z*-4a** (119.0 mg, 78% yield based on **1**).

***Z*-4a:** Colorless needles, mp 129.0—129.5 °C (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ=1.31 (9H, s, *p*-*t*-Bu), 1.38 (9H, s, *o*-*t*-Bu), 1.49 (9H, s, *o*′-*t*-Bu), 2.50 (1H, brs, OH), 5.74 (1H, d, $^3J_{PH}$=12.5 Hz, C<u>H</u>OH), 7.29 (1H, t, $^3J_{HH}$=7.6 Hz, *p*-Ph), 7.35 (2H, dd, $^3J_{HH}$=7.6 and 7.2 Hz, *m*-Ph), 7.37 (1H, brs, *m*-Ar), 7.41 (1H, brs, *m*′-Ar), and 7.47 (2H, d, $^3J_{HH}$=7.2 Hz, *o*-Ph); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=31.3 (s, *p*-C(<u>C</u>H$_3$)$_3$), 32.5 (d, $^4J_{PC}$=6.7 Hz, *o*-C(<u>C</u>H$_3$)$_3$), 32.6 (d, $^4J_{PC}$=7.0 Hz, *o*′-C(<u>C</u>H$_3$)$_3$), 35.0 (s, *p*-<u>C</u>(CH$_3$)$_3$), 37.8 (s, *o*-<u>C</u>(CH$_3$)$_3$), 37.9 (s, *o*′-<u>C</u>(CH$_3$)$_3$), 79.1 (d, $^2J_{PC}$=38.0 Hz, <u>C</u>HOH), 122.0 (s, *m*-Ar), 122.1 (s, *m*′-Ar), 126.5 (s, *o*-Ph), 128.0 (s, *p*-Ph), 128.1 (s, *m*-Ph), 133.1 (d, $^1J_{PC}$=52.9 Hz, *ipso*-Ar), 140.0 (d, $^3J_{PC}$=10.2 Hz, *ipso*-Ph), 150.8 (s, *p*-Ar), 153.5 (d, $^2J_{PC}$=2.3 Hz, *o*-Ar), 153.8 (d, $^2J_{PC}$=2.3 Hz, *o*′-Ar), and 171.4 (d, $^1J_{PC}$=64.2 Hz, P=C); ^{31}P NMR (81 MHz, $CDCl_3$) δ=240.0 (d, $^3J_{PH}$=12.5 Hz); IR (KBr) 3536 cm^{-1}; UV (MeCN) 243 (log ε 4.30), 261 (4.21), 266 (4.21), and 308 nm (sh, 3.20); MS *m*/*z* (rel intensity) 432 (M^++2; 4), 430 (M^+; 12), 415 (M^+−OH+2; 5), 414 (M^+−OH+1; 4), 413 (M^+−OH; 10), 395 (M^+−Cl; 18), 377 (M^+−Cl−OH−1; 100), 275 (ArP$^+$−1; 65), and 57 (*t*-Bu$^+$; 71). Found: *m*/*z* 430.2188. Calcd for $C_{26}H_{36}{}^{35}ClOP$: M, 430.2192.

(*E*)-2-Chloro-1-phenyl-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-ol (*E*-4a): To a solution of the chlorophosphaethene **2** (149.0 mg, 0.459 mmol) in THF (12 mL) was added butyllithium (0.473 mmol) at −78 °C. After the solution turned pale yellow, 50 μL (0.508 mmol) of benzaldehyde was added. After being stirred for 1 h, the reaction mixture was warmed to room temperature. The solvent was evaporated in vacuo and the residue was extracted with ether (20 mL) and washed with water (10 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue underwent a silica-gel column chromatography (hexane/ether, 2:1) to give ***E*-4a** (128.6 mg, 65% based on **2**), along with the starting **2** (26.0 mg, 17% recovery).

***E*-4a:** Colorless crystals, mp 88—91 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ=1.14 (9H, s, *o*-*t*-Bu), 1.41 (9H, s, *p*-*t*-Bu), 1.57 (9H, s, *o*′-*t*-Bu), 2.09 (1H, brs, OH), 4.58 (1H, d, $^3J_{PH}$=1.6 Hz, C<u>H</u>OH), 6.83 (2H, d, $^3J_{HH}$=7.2 Hz, *o*-Ph), 7.16 (2H, dd, $^3J_{HH}$=7.5 and 7.2 Hz, *m*-Ph), 7.21 (1H, t, $^3J_{HH}$=7.5 Hz, *p*-Ph), 7.35 (1H, d, $^4J_{PH}$=1.6 Hz, *m*-Ar), and 7.53 (1H, d, $^4J_{PH}$=1.6 Hz, *m*′-Ar); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=31.4 (s, *p*-C(<u>C</u>H$_3$)$_3$), 32.9 (d, $^4J_{PC}$=8.0 Hz, *o*-C(<u>C</u>H$_3$)$_3$), 33.5 (d, $^4J_{PC}$=6.3 Hz, *o*′-C(<u>C</u>H$_3$)$_3$), 35.1 (s, *p*-<u>C</u>(CH$_3$)$_3$), 37.7 (s, *o*-<u>C</u>(CH$_3$)$_3$), 38.4 (s, *o*′-<u>C</u>(CH$_3$)$_3$), 74.0 (d, $^2J_{PC}$=15.6 Hz, <u>C</u>HOH), 122.2 (s, *m*-Ar), 122.6 (s, *m*′-Ar), 127.6 (s, *o*-Ph), 128.0 (s, *m*-Ph), 128.4 (s, *p*-Ph), 131.8 (d, $^1J_{PC}$=57.0 Hz, *ipso*-Ar), 139.2 (d, $^3J_{PC}$=8.0 Hz, *ipso*-Ph), 151.1 (s, *p*-Ar), 154.2 (s, *o*′-Ar), 154.9 (d, $^2J_{PC}$=3.3 Hz, *o*-Ar), and 174.5 (d, $^1J_{PC}$=50.7 Hz, P=C); ^{31}P NMR (81 MHz, $CDCl_3$) δ=233.7 (s); IR (KBr) 3361 cm^{-1}; UV (MeCN) 250 (log ε 4.10), 276 (4.10), and 320 nm (sh, 3.10); MS *m*/*z* (rel intensity) 430 (M^+; 5), 413 (6), 395 (45), 377 (25), 375 (24), 275 (72), and 57 (100). Found: *m*/*z* 430.2198. Calcd for $C_{26}H_{36}{}^{35}ClOP$: M, 430.2192.

(*Z*)-2-Chloro-2-(1-hydroxycyclohexyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (*Z*-4b): Similarly to the case of ***Z*-4a**, starting from **1** (97.0 mg, 0.270 mmol), butyllithium (0.293 mmol), and cyclohexanone (50 μL, 0.482 mmol), ***Z*-4b** (33.1 mg) was obtained in 29% yield.

***Z*-4b:** Colorless crystals, mp 104—106 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.33 (9H, s, *p*-*t*-Bu), 1.47 (18H, d, $^5J_{PH}$=0.6 Hz, *o*-*t*-Bu), 1.2—2.5 (10H, m, −(CH$_2$)$_5$−), 2.2 (1H, brs, OH), and 7.46 (2H, d, $^4J_{PH}$=1.6 Hz, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=21.8 (d, $^5J_{PC}$=2.9 Hz, CH$_2$), 25.4 (s, CH$_2$), 31.3 (s, *p*-C(<u>C</u>H$_3$)$_3$), 32.5 (d, $^4J_{PC}$=7.2 Hz, *o*-C(<u>C</u>H$_3$)$_3$), 35.0 (s, *p*-<u>C</u>(CH$_3$)$_3$), 36.4 (d, $^3J_{PC}$=12.4 Hz, CH$_2$), 37.9 (d, $^3J_{PC}$=0.7 Hz, *o*-<u>C</u>(CH$_3$)$_3$), 78.6 (d, $^2J_{PC}$=16.6 Hz, <u>C</u>(OH)), 122.0 (d, $^3J_{PC}$=1.3 Hz, *m*-Ar), 134.7 (d, $^1J_{PC}$=53.3 Hz, *ipso*-Ar), 150.4 (s, *p*-Ar), 153.4 (d, $^2J_{PC}$=3.0 Hz, *o*-Ar), and 180.8 (d, $^1J_{PC}$=68.6 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=233.8; IR (KBr) 3430 cm^{-1}; UV (MeCN) 211 (log ε 4.32), 243 (4.01), 263 (3.98), and 310 nm (2.93); MS *m*/*z* (rel intensity) 424 (M^++2; 3), 422 (M^+; 7), 404 (M^+−OH−1; 10), 387 (M^+−Cl; 45), 369 (M^+−Cl−OH−1; 17), 275 (ArP$^+$−1; 100), and 57 (*t*-Bu$^+$; 89). Found: *m*/*z* 422.2514. Calcd for $C_{25}H_{40}{}^{35}ClOP$: M, 422.2505.

(*E*)-2-Chloro-2-(1-hydroxycyclohexyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (*E*-4b): Similarly to the case of ***E*-4a**, starting from **2** (111.4 mg, 0.343 mmol), butyllithium (0.293 mmol), and cyclohexanone (55 μL, 0.515

mmol), ***E*-4b** (36.2 mg) was obtained in 24% yield. The alcohol ***E*-4b** changed to a 1:1 mixture of ***E*-4b** and ***Z*-4b** at room temperature in the dark after 1 month according to the ^{31}P NMR analysis.

***E*-4b:** Colorless crystals, mp 82—85 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.95 (1H, brs, OH), 1.33 (9H, s, *p*-*t*-Bu), 1.54 (18H, d, $^{5}J_{PH}$=0.8 Hz, *o*-*t*-Bu), 1.2—1.6 (10H, m, $-(CH_2)_5-$), and 7.34 (2H, d, $^{4}J_{PH}$=1.6 Hz, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=21.5 (s, CH_2), 25.1 (s, CH_2), 31.2 (s, *p*-C($\underline{C}H_3)_3$), 33.6 (d, $^{4}J_{PC}$=7.6 Hz, *o*-C($\underline{C}H_3)_3$), 33.9 (d, $^{3}J_{PC}$=4.6 Hz, CH_2), 35.0 (s, *p*-$\underline{C}(CH_3)_3$), 38.2 (d, $^{3}J_{PC}$=1.1 Hz, *o*-$\underline{C}(CH_3)_3$), 80.8 (d, $^{2}J_{PC}$=18.6 Hz, $-\underline{C}$(OH)–), 121.7 (d, $^{3}J_{PC}$=0.7 Hz, *m*-Ar), 132.3 (d, $^{1}J_{PC}$=64.4 Hz, *ipso*-Ar), 151.5 (s, *p*-Ar), 154.6 (d, $^{2}J_{PC}$=2.7 Hz, *o*-Ar), and 179.4 (d, $^{1}J_{PC}$=61.8 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=220.0; IR (KBr) 3562 and 3400 cm^{-1}; UV (MeCN) 220 (sh, log ε 4.20), 268 (4.00), and 320 nm (3.00); MS *m*/*z* (rel intensity) 423 (M^++1; 2), 422 (M^+; 3), 421 (M^+−1; 4), 405 (M^+−OH; 7), 387 (M^+−Cl; 100), 369 (21), 275 (94), and 57 (61). Found: *m*/*z* 422.2506. Calcd for $C_{25}H_{40}{}^{35}ClOP$: M, 422.2505.

(*Z*)-2-Chloro-1-anilino-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-one (*Z*-4c): Similarly to the case of ***Z*-4a**, starting from **1** (72.1 mg, 0.201 mmol), butyllithium (0.217 mmol), and phenyl isocyanate (20 μL, 0.217 mmol), ***Z*-4c** (69.0 mg) was obtained in 81% yield.

***Z*-4c:** Yellow needles, mp 208.0—208.5 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.36 (9H, s, *p*-*t*-Bu), 1.48 (18H, s, *o*-*t*-Bu), 7.15 (1H, t, $^{3}J_{HH}$=7.4 Hz, *p*-Ph), 7.35 (2H, dd, $^{3}J_{HH}$=7.4 and 7.6 Hz, *m*-Ph), 7.46 (2H, d, $^{4}J_{PH}$=1.7 Hz, *m*-Ar), 7.65 (2H, d, $^{3}J_{HH}$=7.6 Hz, *o*-Ph), and 8.29 (1H, brs, NH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.2 (s, *p*-C($\underline{C}H_3)_3$), 32.8 (d, $^{4}J_{PC}$=7.1 Hz, *o*-C($\underline{C}H_3)_3$), 35.0 (s, *p*-$\underline{C}(CH_3)_3$), 37.8 (d, $^{3}J_{PC}$=0.7 Hz, *o*-$\underline{C}(CH_3)_3$), 119.9 (s, *m*-Ph), 122.4 (d, $^{3}J_{PC}$=0.9 Hz, *m*-Ar), 124.7 (s, *p*-Ph), 129.0 (s, *o*-Ph), 133.6 (d, $^{1}J_{PC}$=53.0 Hz, *ipso*-Ar), 137.3 (s, *ipso*-Ph), 151.4 (s, *p*-Ar), 153.4 (d, $^{2}J_{PC}$=2.7 Hz, *o*-Ar), 156.5 (d, $^{1}J_{PC}$=60.3 Hz, P=C), and 161.7 (d, $^{2}J_{PC}$=22.6 Hz, C=O); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=304.7; IR (KBr) 3379 and 1645 cm^{-1}; UV (THF) 236 (log ε 4.25), 308 (4.01), and 360 nm (sh, 3.50); MS *m*/*z* (rel intensity) 444 (M^++1; 1.3), 429 (M^+−Me+1; 2), 387 (M^+−*t*-Bu+1; 44), 303 ($ArPCC^+$+3; 16), 275 (ArP^+−1; 4), 173 ($ArPC^+$−2*t*-Bu−1; 100), and 57 (*t*-Bu^+; 10). Found: C, 70.01; H, 7.88; N, 3.15; Cl, 8.09%. Calcd for $C_{26}H_{35}ClNOP$: C, 70.34; H, 7.95; N, 3.15; Cl, 7.99%.

(*E*)-2-Chloro-1-anilino-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-one (*E*-4c) and (*E*)-1,3-Diphenyl-5-(2,4,6-tri-*t*-butylphenylphosphinidene)-imidazolidine-2,4-dione (*E*-5): To a solution of **2** (108.2 mg, 0.333 mmol) in THF (10 mL) at −78 °C were successively added butyllithium (0.343 mmol) and phenyl isocyanate (55 μL, 0.500 mmol). After being stirred for 30 min, the reaction mixture was warmed to room temperature and the solvent was evaporated in vacuo. ^{31}P NMR spectrum of the residue showed ***E*-4c** (δ_P=257.4) and ***E*-5** (δ_P=198.3) in a 1:2 ratio. Silica-gel column chromatographic treatment (hexane/ether, 6:1) gave ***E*-5** (100.2 mg, 57% based on **2**) and ***E*-4c** (29.9 mg, 16%). A similar reaction with 0.8 equiv of phenyl isocyanate gave ***E*-5** (39%) together with ***E*-4c** (7%) and a trace of **2**.

***E*-4c:** Yellow crystals, mp 135—137 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.30 (9H, s, *p*-*t*-Bu), 1.55 (18H, s, *o*-*t*-Bu), 6.6 (1H, brs, NH), 6.88 (2H, d, $^{3}J_{HH}$=7.3 Hz, *o*-Ph), 7.00 (1H, t, $^{3}J_{HH}$=7.3 Hz, *p*-Ph), 7.14 (2H, dd, $^{3}J_{HH}$=7.3 Hz, *m*-Ph), and 7.58 (2H, d, $^{4}J_{PH}$=1.6 Hz, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.0 (s, *p*-C($\underline{C}H_3)_3$), 33.1 (d, $^{4}J_{PC}$=7.2 Hz, *o*-C($\underline{C}H_3)_3$), 35.2 (s, *p*-$\underline{C}(CH_3)_3$), 38.4 (d, $^{3}J_{PC}$=0.7 Hz, *o*-$\underline{C}(CH_3)_3$), 119.5 (s, *m*-Ph), 123.8 (d, $^{3}J_{PC}$=0.7 Hz, *m*-Ar), 124.3 (s, *p*-Ph), 128.6 (s, *o*-Ph), 131.2 (d, $^{1}J_{PC}$=63.6 Hz, *ipso*-Ar), 137.1 (s, *ipso*-Ph), 153.2 (s, *p*-Ar), 155.0 (d, $^{2}J_{PC}$=2.7 Hz, *o*-Ar), 157.8 (d, $^{2}J_{PC}$=15.1 Hz, C=O), and 162.7 (d, $^{1}J_{PC}$=61.7 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=257.4; IR (KBr) 3356 and 1670 cm^{-1}; UV (THF) 234 (log ε 4.35), 295 (4.00), and 360 nm (sh, 3.60); MS *m*/*z* (rel intensity) 445 (M^++2; 1), 443 (M^+; 2), 430 (M^+−Me+2; 0.2), 428 (M^+−Me; 0.7), 408 (M^+−Cl; 3), 388 (M^+−*t*-Bu+2; 29); 386 (M^+−*t*-Bu; 84), 275 (ArP^+−1; 100), and 57 (48). Found: C, 69.96; H, 7.81; N, 3.33%. Calcd for $C_{26}H_{35}ClNOP$: C, 70.34; H, 7.95; N, 3.15%.

***E*-5:** Yellow crystals, mp 215—220 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.38 (9H, s, *p*-*t*-Bu), 1.58 (18H, s, *o*-*t*-Bu), 7.37 (2H, d, $^{4}J_{PH}$=1.3 Hz, *m*-Ar), and 7.2—7.7 (10H, m, Ph); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.3 (s, *p*-C($\underline{C}H_3)_3$), 33.0 (d, $^{4}J_{PC}$=6.5 Hz, *o*-C($\underline{C}H_3)_3$), 35.1 (s, *p*-$\underline{C}(CH_3)_3$), 38.1 (s, *o*-$\underline{C}(CH_3)_3$), 122.7 (d, $^{4}J_{PC}$=1.8 Hz, 1-*o*-Ph), 126.1 (s, *m*-Ar), 128.0 (s, 1-*p*-Ph), 128.0 (d, $^{1}J_{PC}$=48.8 Hz, *ipso*-Ar), 128.1 (s, 3-*p*-Ph), 128.9 (s, 3-*m*-Ph), 129.9 (s, 3-*o*-Ph), 131.5 (s, 3-*ipso*-Ph), 134.4 (d, $^{3}J_{PC}$=3.0 Hz, 1-*ipso*-Ph), 151.1 (s, *p*-Ar), 153.8 (d, $^{2}J_{PC}$=2.7 Hz, *o*-Ar), 155.9 (s, 2-C=O), 156.1 (s, 4-C=O), and 161.4 (d, $^{1}J_{PC}$=44.5 Hz, P=C); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=198.3; IR (KBr) 1763 and 1720 cm^{-1}; UV (MeCN) 235 (log ε 4.16), 359 (3.74), and 408 nm (sh, 3.20); MS *m*/*z* (rel intensity) 526 (M^+, 25), 469 (M^+−*t*-Bu; 100), 275 (ArP^+−1; 36), and 57 (*t*-Bu^+; 5). Found: *m*/*z* 526.2748. Calcd for $C_{33}H_{39}N_2O_2P$: M, 526.2749.

(*Z*)-1,3-Diphenyl-5-(2,4,6-tri-*t*-butylphenylphosphinidene)imidazolidine-2,4-dione (*Z*-5): Compound ***E*-5** (5.0 mg, 0.095 mmol) was dissolved in hexane (100 mL) and refluxed in the dark. After 24 h this solution changed to a 1:1 mixture of ***E*-5** and ***Z*-5**; this ratio remained unchanged after 26 h. This hexane solution was then cooled to room temperature and ***Z*-5** was crystallized and washed with hexane (15.2 mg, 30% yield from ***E*-5**). Similarly, a solution of ***E*-5** (5.0 mg, 9.5 μmol) in benzene-d_6 (1 mL) was sealed in an NMR sample tube under argon. The solution was heated at 90 °C and monitored by ^{31}P NMR spectroscopy. After 24 h ***E*-5** changed to a 1:1 mixture of ***E*-5** and ***Z*-5**; this ratio remained unchanged after 26 h. In addition, a solution of ***Z*-5** (5.0 mg, 9.5 μmol) in benzene (1 mL) was heated in a sealed sample tube under argon at 90 °C for 24 h to give a 1:1 mixture of ***E*-5** and ***Z*-5**.

***Z*-5:** Yellow prisms, mp 210—214 °C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.24 (9H, s, *p*-*t*-Bu), 1.50 (18H, s, *o*-*t*-Bu), 6.8—7.0 (5H, m, 1-Ph), 7.03 (2H, d, $^{4}J_{PH}$=1.9 Hz, *m*-Ar), and 7.3—7.6 (5H, m, 3-Ph); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.3 (s, *p*-C($\underline{C}H_3)_3$), 33.5 (d, $^{4}J_{PC}$=7.2 Hz, *o*-C($\underline{C}H_3)_3$), 34.8 (s, *p*-$\underline{C}(CH_3)_3$), 38.1 (d, $^{3}J_{PC}$=0.6 Hz, *o*-$\underline{C}(CH_3)_3$), 121.8 (d, $^{4}J_{PC}$=1.3 Hz, 1-*o*-Ph), 126.0 (s, *m*-Ar), 127.6 (s, 1-*p*-Ph), 127.6 (s, 3-*m*-Ph), 127.9 (s, 1-*m*-Ph), 128.1 (s, 3-*p*-Ph), 128.9 (s, 3-*o*-Ph), 129.4 (d, $^{1}J_{PC}$=54.5 Hz, *ipso*-Ar), 131.6 (d, $^{3}J_{PC}$=1.0 Hz, 1-*ipso*-

Ph), 132.8 (d, $^4J_{PC}$=0.5 Hz, 3-*ipso*-Ph), 151.2 (s, *p*-Ar), 151.4 (s, 2-C=O), 153.1 (s, 4-C=O), 154.4 (d, $^2J_{PC}$=3.0 Hz, *o*-Ar), and 164.0 (d, $^1J_{PC}$=34.9 Hz, P=C); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ=191.4; IR (KBr) 1765 and 1714 cm^{-1}; UV (MeCN) 244 (log ε 4.11), 285 (3.65), and 352 nm (4.13); MS *m/z* (rel intensity) 526 (M^+; 23), 469 (76), 275 (100), and 57 (69). Found: C, 75.02; H, 7.45; N; 5.32%. Calcd for $C_{33}H_{39}O_2N_2P$: C, 75.26; H, 7.46; N, 5.32%.

Photoisomerization of 5. A solution of ***E*-5** (5.0 mg, 9.5 μmol) in benzene (1 mL) was sealed in an NMR sample tube under argon. The solution was irradiated at 10 °C with a 100-W medium-pressure mercury lamp and was monitored by ^{31}P NMR spectroscopy. After 2 h this solution gave a 2:3 mixture of ***E*-5** and ***Z*-5** and this ratio remained unchanged after 13 h. Similarly, a solution (benzene, 1 mL) of ***Z*-5** (5.0 mg, 9.5 μmol) was irradiated at 10 °C with the mercury lamp for 2 h to give a 2:3 mixture of ***E*-5** and ***Z*-5**.

Ethyl (*Z*)-2-Chloro-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propenoate (*Z*-4d): Similarly to the case of ***Z*-4a**, starting from **1** (84.3 mg, 0.235 mmol), butyllithium (0.245 mmol), and ethyl chloroformate (28 μL, 0.267 mmol), ***Z*-4d** (80.4 mg) was obtained in 86% yield.

***Z*-4d:** Yellow crystals, mp 97—100 °C; ^1H NMR (200 MHz, $CDCl_3$) δ=1.34 (9H, s, *p*-*t*-Bu), 1.39 (3H, t, $^3J_{HH}$=7.2 Hz, $CH_2C\underline{H}_3$), 1.46 (18H, d, $^5J_{PH}$=0.5 Hz, *o*-*t*-Bu), 4.34 (2H, q, $^3J_{HH}$=7.0 Hz, $C\underline{H}_2CH_3$), and 7.45 (2H, d, $^4J_{PH}$=1.7 Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=14.2 (s, $CH_2\underline{C}H_3$), 31.2 (s, *p*-C($\underline{C}H_3)_3$), 32.8 (d, $^4J_{PC}$=7.2 Hz, *o*-C($\underline{C}H_3)_3$), 35.0 (s, *p*-$\underline{C}(CH_3)_3$), 37.8 (d, $^3J_{PC}$=0.7 Hz, *o*-$\underline{C}(CH_3)_3$), 62.3 (d, $^4J_{PC}$=1.1 Hz, $\underline{C}H_2CH_3$), 122.4 (d, $^3J_{PC}$=1.1 Hz, *m*-Ar), 133.3 (d, $^1J_{PC}$=53.7 Hz, *ipso*-Ar), 151.4 (s, *p*-Ar), 153.1 (d, $^2J_{PC}$=2.8 Hz, *o*-Ar), 155.2 (d, $^1J_{PC}$=67.4 Hz, P=C), and 164.4 (d, $^2J_{PC}$=24.5 Hz, C=O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ=316.0; IR (KBr) 1714 and 1693 cm^{-1}; UV (hexane) 209 (log ε 4.16), 237 (3.66), 294 (3.63), and 360 nm (2.50); MS *m/z* (rel intensity) 398 (M^++2; 0.6), 275 (ArP^+−1; 100), and 57 (*t*-Bu^+; 35). Found: *m/z* 396.1985. Calcd for $C_{22}H_{34}{}^{35}ClO_2P$: M, 396.1985.

Ethyl (*E*)-2-Chloro-3-(2,4,6-tri-*t*-butylphenyl)-1-phospha-2-propenoate (*E*-4d): Similarly to the case of ***E*-4a**, starting from **2** (72.3 mg, 0.223 mmol), butyllithium (0.240 mmol), and ethyl chloroformate (30 μL, 0.286 mmol), ***E*-4d** (68.9 mg) was obtained in 78% yield. The compound ***E*-4d** changed to a 1:2 mixture of ***E*-4d** and ***Z*-4d** at room temperature in the dark after 2 months according to the ^{31}P NMR analysis.

***E*-4d:** Yellow crystals, mp 105—110 °C; ^1H NMR (200 MHz, $CDCl_3$) δ=0.76 (3H, t, $^3J_{HH}$=7.2 Hz, $CH_2C\underline{H}_3$), 1.33 (9H, s, *p*-*t*-Bu), 1.47 (18H, d, $^5J_{PH}$=0.6 Hz, *o*-*t*-Bu), 3.64 (2H, q, $^3J_{HH}$=7.2 Hz, $C\underline{H}_2CH_3$), and 7.40 (2H, d, $^4J_{PH}$=1.8 Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=13.6 (s, $CH_2\underline{C}H_3$), 31.2 (s, *p*-C($\underline{C}H_3)_3$), 33.4 (d, $^4J_{PC}$=7.2 Hz, *o*-C($\underline{C}H_3)_3$), 35.0 (s, *p*-$\underline{C}(CH_3)_3$), 38.1 (d, $^3J_{PC}$=0.9 Hz, *o*-$\underline{C}(CH_3)_3$), 61.6 (s, $\underline{C}H_2CH_3$), 122.1 (d, $^3J_{PC}$=1.4 Hz, *m*-Ar), 132.7 (d, $^1J_{PC}$=58.5 Hz, *ipso*-Ar), 151.1 (s, *p*-Ar), 153.7 (d, $^2J_{PC}$=3.1 Hz, *o*-Ar), 156.0 (d, $^1J_{PC}$=58.8 Hz, P=C), and 161.7 (d, $^2J_{PC}$=13.4 Hz, C=O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ=282.7; IR (KBr) 1704 cm^{-1}; UV (hexane) 210 (sh, log ε 4.4), 238 (4.01), 294 (3.92), and 360 nm (2.90); MS *m/z* (rel intensity) 396 (M^+; 5), 275 (ArP^+−1; 100), and 57 (*t*-Bu^+; 44). Found: *m/z* 396.1985. Calcd for $C_{22}H_{34}{}^{35}ClO_2P$: M, 396.1985.

(*Z*)-2-Chloro-1-phenyl-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-one (*Z*-4e): Similarly to the case of ***Z*-4a**, starting from **1** (171.0 mg, 0.475 mmol), butyllithium (0.505 mmol), and benzoyl chloride (50 μL, 0.508 mmol), ***Z*-4e** (185.0 mg) was obtained in 91% yield.

***Z*-4e:** Yellow crystals, mp 100—105 °C; ^1H NMR (200 MHz $CDCl_3$) δ=1.30 (9H, s, *p*-*t*-Bu), 1.48 (18H, s, *o*-*t*-Bu), 7.47 (2H, d, $^4J_{PH}$=1.6 Hz, *m*-Ar), and 7.4—7.8 (5H, m, Ph); $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δ=31.4 (s, *p*-C($\underline{C}H_3)_3$), 32.9 (d, $^4J_{PC}$=6.9 Hz, *o*-C($\underline{C}H_3)_3$), 35.3 (s, *p*-$\underline{C}(CH_3)_3$), 38.1 (s, *o*-$\underline{C}(CH_3)_3$), 122.9 (s, *m*-Ph), 128.3 (s, *o*-Ph), 130.0 (d, $^3J_{PC}$=5.2 Hz, *m*-Ar), 132.2 (s, *p*-Ph), 133.8 (d, $^1J_{PC}$=56.2 Hz, *ipso*-Ar), 140.0 (s, *ipso*-Ph), 152.0 (s, *p*-Ar), 153.9 (s, *o*-Ar), 167.4 (d, $^1J_{PC}$=72.3 Hz, P=C), and 190.2 (d, $^2J_{PC}$=29.8 Hz, C=O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ=334.4; IR (KBr) 1651 cm^{-1}; UV (hexane) 235 (log ε 4.28), 304 (3.54), and 372 nm (2.36); MS *m/z* (rel intensity) 428 (M^+; 2), 393 (M^+−Cl; 30), 373 (M^+−*t*-Bu+2; 20), 371 (M^+−*t*-Bu; 50), and 57 (*t*-Bu^+; 100). Found: *m/z* 428.2036. Calcd for $C_{26}H_{34}{}^{35}ClOP$: M, 428.2036.

Isomerization of (*E*)-2-Chloro-1-phenyl-3-(2,4,6-tri-*t*-butylphenyl)-3-phospha-2-propen-1-one (*E*-4e). To a THF (5 mL) solution of **2** (60.0 mg, 0.185 mmol) at −78 °C were successively added butyllithium (0.188 mmol) and benzoyl chloride (30 μL, 0.24 mmol). After being stirred for 30 min at −78 °C, an aliquot of the reaction mixture was removed by a syringe and a small amount of THF-d_8 was added to this sample for signal locking. ^{31}P NMR measurement at room temperature of the sample solution showed the formation of ***E*-4e** (δ_P=263.7) as a major product. Then the reaction mixture was warmed to room temperature. The ^{31}P NMR spectrum of the resulting solution indicated that ***E*-4e** disappeared at room temperature within 0.5 h and ***Z*-4e** (δ_P=323.7) appeared as a major product together with **2** (δ_P=251.7) and some unidentified peaks (δ_P=228.0 and 231.0). Silica-gel column chromatographic treatment (hexane/CH_2Cl_2, 1:1) gave ***Z*-4e** (40.0 mg, 50%).

(*Z*)-2-Chloro-4,4-dimethyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1-penten-3-one (*Z*-4f): Similarly to the case of ***Z*-4a**, starting from **1** (119.5 mg, 0.333 mmol), butyllithium (0.333 mmol), and pivaloyl chloride (58 μL, 0.500 mmol), ***Z*-4f** (100.0 mg) was obtained in 74% yield.

***Z*-4f:** Yellow crystals, mp 120—123 °C; ^1H NMR (200 MHz $CDCl_3$) δ=1.33 (9H, s, *p*-*t*-Bu), 1.43 (9H, s, *t*-BuCO), 1.47 (18H, s, *o*-*t*-Bu), and 7.44 (2H, d, $^4J_{PH}$=1.7 Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=28.2 (d, $^4J_{PC}$=6.9 Hz, CO–C($\underline{C}H_3)_3$), 31.2 (s, *p*-C($\underline{C}H_3)_3$), 32.6 (d, $^4J_{PC}$=6.6 Hz, *o*-C($\underline{C}H_3)_3$), 35.0 (s, *p*-$\underline{C}(CH_3)_3$), 37.7 (s, *o*-$\underline{C}(CH_3)_3$), 44.4 (s, CO–$\underline{C}(CH_3)_3$), 122.3 (d, $^3J_{PC}$=1.1 Hz, *m*-Ar), 132.7 (d, $^1J_{PC}$=56.1 Hz, *ipso*-Ar), 151.4 (s, *p*-Ar), 153.3 (d, $^2J_{PC}$=2.7 Hz, *o*-Ar), 163.6 (d, $^1J_{PC}$=70.1 Hz, P=C), and 202.4 (d, $^2J_{PC}$=21.0 Hz, C=O); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ=304.1; IR (KBr) 1643 cm^{-1}; UV (hexane) 239 (log ε 4.19) and 298 nm (3.82); MS *m/z* (rel intensity) 409 (M^++1; 2), 373 (M^+−Cl; 5), 371 (M^+−Cl−2; 70), 353 (M^+−*t*-Bu; 21), 275 (ArP^+−1; 100), and 57 (*t*-Bu^+; 77). Found: *m/z* 408.2348. Calcd for $C_{24}H_{38}{}^{35}ClOP$: M, 408.2349.

(*E*)-2-Chloro-4,4-dimethyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1-penten-3-one (*E*-4f): Similarly to the case of ***E*-4a**, starting from **2** (128.5 mg, 0.396 mmol),

butyllithium (0.398 mmol), and pivaloyl chloride (70 μL, 0.594 mmol), ***E*-4f** (113.6 mg) was obtained in 70% yield.

***E*-4f:** Yellow oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.94 (9H, s, *t*-BuCO), 1.29 (9H, s, *p*-*t*-Bu), 1.50 (18H, s, *o*-*t*-Bu), and 7.31 (2H, d, $^4J_{PH}$=1.7 Hz, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=27.2 (s, CO–C($\underline{C}H_3)_3$), 31.2 (s, *p*-C($\underline{C}H_3)_3$), 34.1 (d, $^4J_{PC}$=7.2 Hz, *o*-C($\underline{C}H_3)_3$), 34.8 (s, *p*-$\underline{C}(CH_3)_3$), 38.5 (d, $^3J_{PC}$=0.7 Hz, *o*-$\underline{C}(CH_3)_3$), 43.4 (s, CO–$\underline{C}(CH_3)_3$), 121.8 (d, $^3J_{PC}$=1.1 Hz, *m*-Ar), 129.3 (d, $^1J_{PC}$=58.1 Hz, *ipso*-Ar), 150.9 (s, *p*-Ar), 155.1 (d, $^2J_{PC}$=2.6 Hz, *o*-Ar), 161.0 (d, $^1J_{PC}$=57.6 Hz, P=C), and 202.0 (s, C=O); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=258.7; IR (neat) 1712 and 1684 cm^{-1}; UV (hexane) 270 nm (sh, log ε 3.5); MS *m*/*z* (rel intensity) 407 (M^+-1; 0.2), 373 (10), 372 (20), 371 (60), 353 (25), 275 (66), and 57 (100). Found: *m*/*z* 408.2350. Calcd for $C_{24}H_{38}{}^{35}ClOP$: M, 408.2349.

X-Ray Crystallographic Analysis of *Z*-5. Compound ***Z*-5** was recrystallized from hexane to give yellow prisms. $C_{33}H_{39}N_2O_2P$, molecular weight, 546.66. Crystal data: triclinic, space group $P\bar{1}$, with cell dimensions, a=11.131(3), b=13.608(3), c=11.016(2) Å, α=103.50(2)°, β=98.06(2)°, γ=67.21(2)°, V=1493.6(6) Å^3; Z=2. Diffracted intensities were recorded at 296 K on a Rigaku AFC-7S diffractometer (ω–2θ scan, $2\theta_{max}$=50.0°, Mo $K\alpha$, λ=0.71069 Å), graphite monochromated. Number of reflections measured, total, 5535, unique 5242; No. observations ($I>3.00\sigma(I)$), 2794. The structure was solved by a direct method (MULTAN88)[12] and expanded Fourier technique (DIRDIF92).[13] The structure was refined by a full-matrix least-squares refinement. The *p*-*t*-butyl group was disordered. The non-hydrogen atoms were refined anisotropically, except for the disordered carbon atoms (C31–C33). Hydrogen atoms were included but not refined. The R factor and R_w factor were 0.073 and 0.081, respectively. All calculations were performed using the TEXSAN[14] crystallographic software package of Molecular Structure Corporation. Further details concerning the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (U.K.). The complete F_o-F_c data are also deposited as Document No. 68016 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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