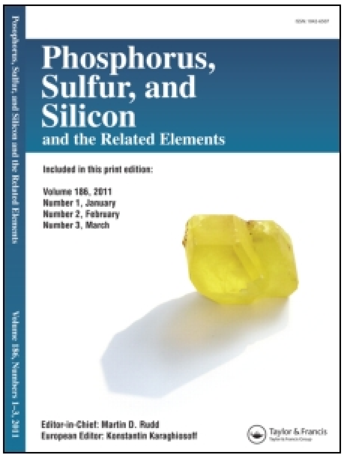
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Study on Synthesis and Structure of Sterically Demanding 6-Phosphafulvenes

Shigekazu Ito[a]; Hideaki Miyake[a]; Masaaki Yoshifuji[a]
[a] Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai, Japan

To cite this Article Ito, Shigekazu , Miyake, Hideaki and Yoshifuji, Masaaki(2009) 'Study on Synthesis and Structure of Sterically Demanding 6-Phosphafulvenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 4, 917 — 927

To link to this Article: DOI: 10.1080/10426500902718240

URL: http://dx.doi.org/10.1080/10426500902718240

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 184:917–927, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902718240

Study on Synthesis and Structure of Sterically Demanding 6-Phosphafulvenes

Shigekazu Ito, Hideaki Miyake, and Masaaki Yoshifuji
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai, Japan

t-Butylcyclopentadienyllithium was allowed to react with (2,4,6-tri-t-butylphenyl)phosphonous dichloride to afford the corresponding chloro-5-cyclopentadienylchlorophosphine as a mixture of diastereomers, the structure of one of which was determined by X-ray crystallography. The mixture of 5-cyclopentadienylchlorophosphine diastereomers was treated with a base to furnish novel 2-t-butyl-6-(2,4,6-tri-t-butylphenyl)-6-phosphafulvenes, and each geometrical isomer of them was fully characterized by X-ray crystallography. The E/Z ratio of the 6-phosphafulvene obtained was considerably dependent on the diastereomeric ratio of the chlorophosphine precursor.

Keywords Chlorophosphines; elimination; fulvenes; phosphaalkenes; steric protection; X-ray crystallography

INTRODUCTION

Chemistry of kinetically stabilized phosphaalkenes [–P=C<] has recently played an important role, not only in fundamental molecular science based on heavier low-coordinated main group elements,[1] but also in several application fields such as synthetic catalysts[2] and optoelectronic functions.[3] Phosphaalkenes show basically similar

Received 30 November 2007; accepted 1 March 2008.

Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

This work was supported in part by Grants-in-Aid for Scientific Research (No. 13304049 and 14044012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

The present affiliation for Shigekazu Ito is Tokyo Institute of Technology, Tokyo, Japan and the present affiliation for Masaaki Yoshifuji is Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama, USA.

Address correspondence to Shigekazu Ito, Department of Applied Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan. E-mail: ito.s.ao@m.titech.ac.jp or Masaaki Yoshifuji, Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, USA. E-mail: myoshifuji@bama.ua.edu

characteristics to their carbon congeners, olefins, and thus it is reasonable to expect that the substituents around the P=C group might modify their physicochemical properties.

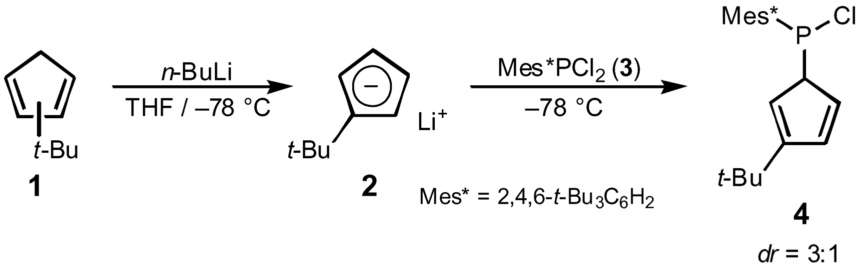
We previously succeeded in preparation and isolation of a kinetically stabilized 1,3,6-triphosphafulvene,[5] and recently we have found its unique electrophilic reactivity providing a number of exotic *P*-heterocyclic compounds.[6–8]

Now we are interested in the chemistry of 6-phosphafulvene bearing a cyclopentadienyl group and an *exo* P=C double bond, which is one of the typical phosphaalkene with an electronically perturbed P=C moiety. Indeed, electrochemistry and reduction generating radical anions have been reported to elucidate the properties of 6-phosphafulvene.[4]

While synthetic procedures for 6-phosphafulvenes have been established,[4a] structural studies on 6-phosphafulvenes as well as chemical modifications leading to a series of novel exotic molecules have been limited so far. Therefore, we needed to synthesize several 6-phosphafulvene derivatives to carry out detailed studies in relation to the 1,3,6-triphosphafulvene, and in this article we present preparation and structural characterization of novel 6-triphosphafulvenes. Some electrophilic properties of the 6-phosphafulvenes are also described.

RESULTS AND DISCUSSION

Compound **1** was lithiated to generate the corresponding cyclopentadienyl anion **2**, and subsequently treated with (2,4,6-tri-*t*-butylphenyl)phosphonous dichloride (Mes*PCl_2; **3**) at −78°C to give chlorophosphine **4** almost quantitatively as a 3:1 diastereomeric [(*R*,*S*)/(*S*,*R*):(*R*,*R*)/(*S*,*S*)] ratio (Scheme 1). Compound **4** is an air stable solid, and one of the diastereomers was successfully recrystallized to give single crystals suitable for X-ray diffraction. Figure 1 shows an ORTEP drawing of the crystallized compound **4**, which turned out to possess the (*R*,*S*) configuration. Steric hindrance around the phosphorus atom causes distortion of the aromatic 6-membered ring to a boat-like form, and correspondingly the *ipso* carbon atom in the Mes* group is slightly pyramidalized [Σ(angles) = 354.1].[9] The molecular structure of **4** in the crystal is comparable to that of **3** showing distortions around the phosphorus atom probably due to steric effects (Figure 2).[10] However, in spite of the considerable steric encumbrance, the *t*-butyl group at the cyclopentadienyl ring is not far from the Mes* moiety. MM2 computations[11] of the most stable conformer for the (*R*,*S*) isomer (based on Figure 1) resulted in a conformation with a dihedral angle of



SCHEME 1 Preparation of chlorophosphine **4** as a mixture of diastereomers.

120 degrees around the P–C1 bond [Θ(C_{ipso}–P–C1–C2)] (Figure 3). This sterically congested form of **4** would be affected by the CH-π interaction between the Mes* and cyclopentadienyl groups[12] and correspond to the chemical shift at higher field of the proton at the C2 position and the *t*-butyl group at the 5-membered ring. Accordingly, the major isomer of **4** could be assigned as the (*R*,*S*) configuration.

The diastereomeric mixture of **4** was allowed to react with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) at −78°C to afford the corresponding

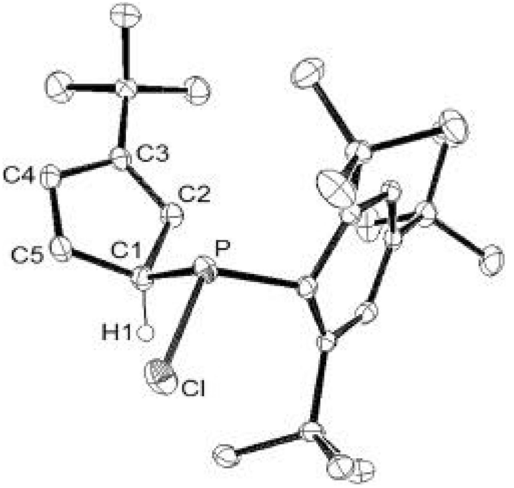


FIGURE 1 Molecular structure of **4** in the crystal; ellipsoids are drawn at 40% probability level. Hydrogen atoms except for H1 are omitted for clarity. Selected distances (Å) and angles (°): P–Cl 2.114(1), P–C1 1.867(3), P–C10 1.844(3), C1–C2 1.499(4), C1–C5 1.495(5), C2–C3 1.342(4), C3–C4 1.475(5), C4–C5 1.339(5), C3–$C_{t\text{-Bu}}$ 1.517(4), P–C10–C11 128.6(2), P–C10–C15 107.2(2), Θ(C10–P–C1–C2) 61.1(2), Θ(C_{meta}–C_{ortho}–C10–P) 131.0(2), 136.7(2).

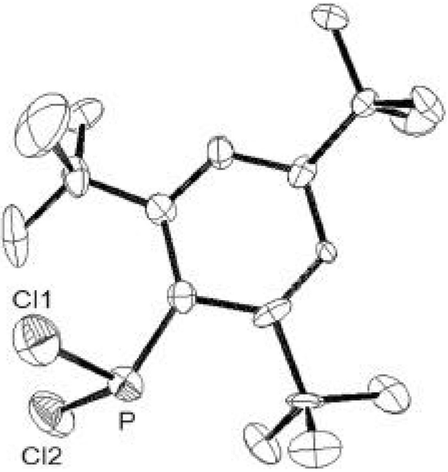


FIGURE 2 Molecular structure of **3** in the crystal; ellipsoids are drawn at 40% probability level. Hydrogen atoms are omitted. Bond angle (°): P–C_{ipso}–C_{ortho} 130.8(9), 111.9(9).

6-phosphafulvene **5** as an *E*/*Z* isomeric mixture. The *E*/*Z* ratio of **5** at −78°C (1:3) corresponded to the diastereomeric ratio of the employed **4**, and furthermore the *E*/*Z* ratio of **5**, determined by ^{31}P NMR spectroscopy, depended on the reaction temperatures as summarized in Scheme 2.[13] Taking into account the fact that HCl elimination affording **5** generally proceeds in the anti-type manner, the (*R*,*S*) isomer of **4** would afford *E*-**5**. However, our results (Scheme 2) indicate that the

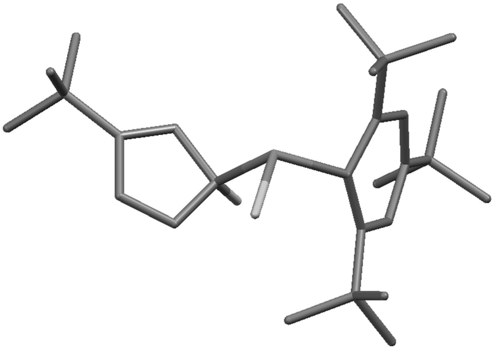
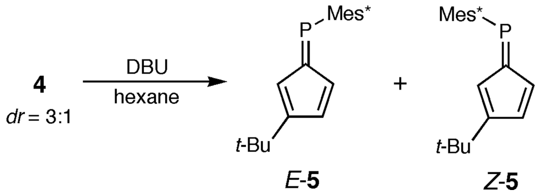


FIGURE 3 Most stable conformation for the (*R*,*S*) isomer of **4a** (optimized by MM2 based on the molecular structure in Figure 1). Hydrogen atoms except for that on the C(sp^3) atom in the 5-membered ring are omitted.



Temp. / °C	*E*/*Z* ratio
–78	1:3
20	1:2
60	1:1

SCHEME 2 Preparation of 6-phosphafulvenes **5**.

(*R*,*S*) isomers afford *Z*-**5** via the syn-type HCl elimination of **4**.[14] Figure 4 displays calculated *anti*- and *syn*-periplanar conformations for **4**, **4b** and **4c**, which were obtained on the basis of the X-ray structure of **4** (Figure 1). It is likely that the reaction in Scheme 2 involves the intermediacy of conformer **4a** permitting the *syn* elimination solely at low temperatures. On the other hand, at higher temperatures, the reaction course may be dependent not only on conformational composition of **4**, but also on changes in elimination rates, and correspondingly the *E*/*Z* ratio would be varied. As for the (*R*,*R*) or (*S*,*S*) isomer of **4**, the syn elimination predominantly affords *E*-**5** at low temperatures.

The geometrical isomerism of **5** corresponds to different melting points. Both the *E* and *Z* isomers of **5** show almost the same relatively low-field δ_P shifts as well as similar ^{13}C NMR data and photoabsorption properties. Alternatively, in the ^{1}H NMR spectrum of *Z*-**5**, the *t*-butyl group at the cyclopentadienyl ring indicates a ring-current effect of the Mes* group, which might correspond to the NMR properties of **4**.

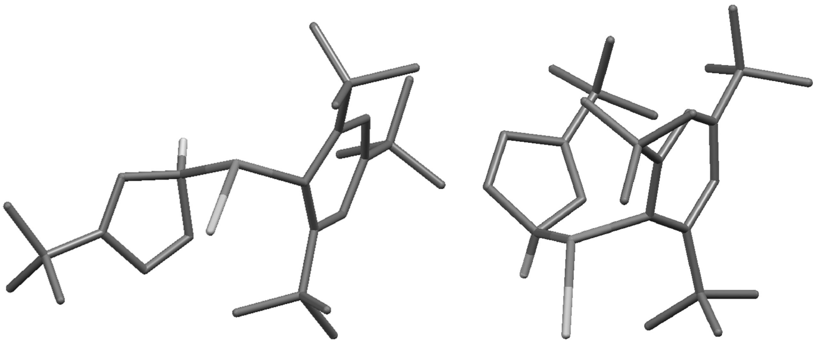


FIGURE 4 *Anti*-periplanar conformation (**4b**, left) and *syn*-periplanar conformation (**4b**, right) for **4** (based on the structure in Figure 1). Hydrogen atoms except for that on the C(sp^3) atom in the 5-membered ring are omitted.

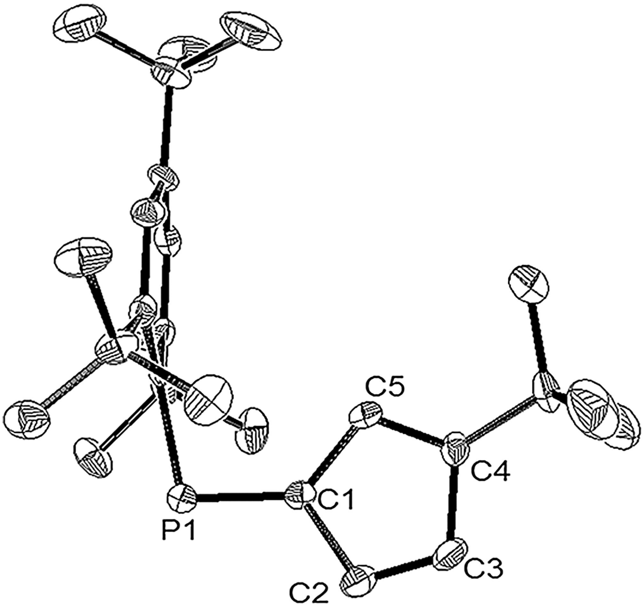


FIGURE 5 Molecular structure of Z-**5** in the crystal; ellipsoids are drawn at 50% probability level. One of the two independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): P1–C1 1.688(5), P1–C_{Mes*} 1.843(5), C1–C2 1.469(7), C1–C5 1.465(7), C2–C3 1.334(7), C3–C4 1.465(7), C4–C5 1.358(7), C4–$C_{t\text{-Bu}}$ 1.510(7), C1–P1–C_{Mes*} 100.2(2).

The *E* and *Z* isomers of **5** show different solubility in hexane, and both of the *E* and *Z* isomers of **5** were successfully purified by recrystallization. The structures were unambiguously determined by X-ray crystallography, and Figures 5 and 6 display the structures of *E*-**5** and *Z*-**5**, respectively. The *E* isomer shows normal P=C bond lengths and Mes*–P–C angle together with an almost planar cyclopentadienyl ring. The Mes* aromatic ring is almost perpendicular to the 6-phosphafulvene plane to minimize steric congestion.

Similarly to fulvene derivatives,[15] Z- and *E*-**5** showed regioselective reactivity to nucleophiles. Both *Z*- and *E*-**5** were allowed to react with reagents such as alkyllithiums and hydrido lithium reagents to generate the corresponding phosphinocyclopentadienyl anions **6** as room-temperature stable species (Scheme 3). According to our previous report on the 1,3,6-triphosphafulvene,[8] we attempted preparation of a phosphorus ylide bearing a P–H bond (**7**). However, the desired compound **7** was not observed in the reaction mixture; instead phosphinocyclopentadiene derivative **8** was observed as a mixture of isomers due to protonation at the cyclopentadienyl group. Less steric

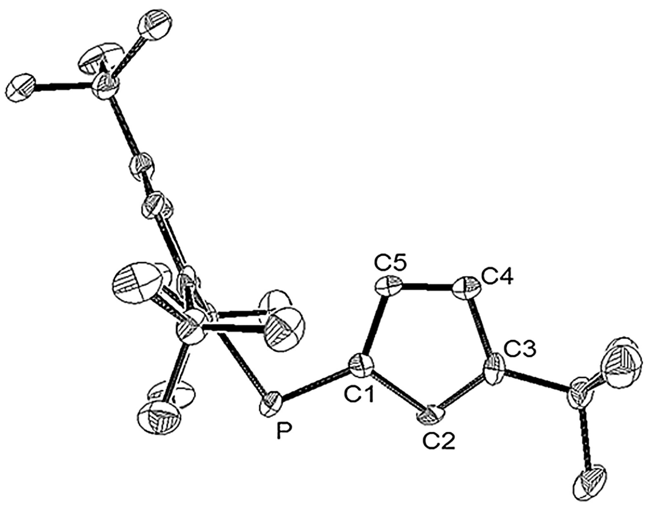
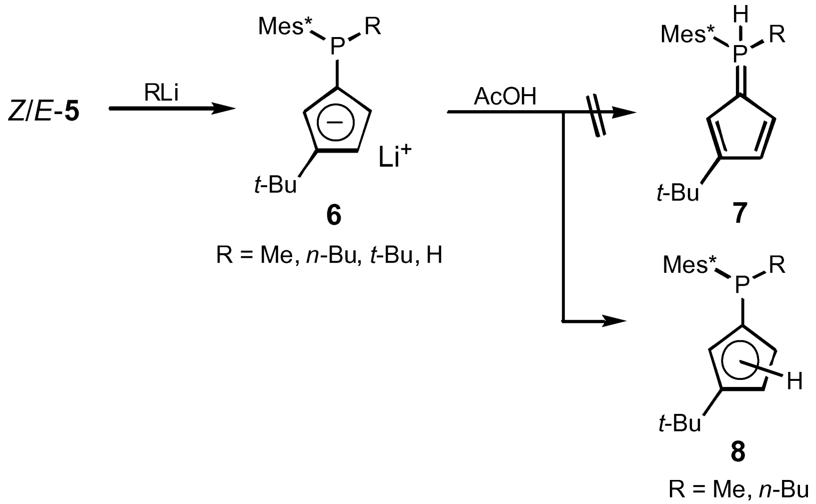


FIGURE 6 Molecular structure of *E*-**5** in the crystal; ellipsoids are drawn at 50% probability level. Selected distances (Å) and angles (°): P1–C1 1.693(6), P1–C_{Mes*} 1.858(6), C1–C2 1.462(8), C1–C5 1.453(8), C2–C3 1.348(8), C3–C4 1.462(8), C4–C5 1.333(9), C4–$C_{t\text{-Bu}}$ 1.510(8), C1–P–C_{Mes*} 102.0(3).

encumbrance and stability of the cyclopentadienyl ring compared with the 1,3,6-triphosphafulvene derivative, which bears three Mes* groups and three P=C bonds,[8] might be prone to cause protonation on the cyclopentadienyl ring of **6**.



SCHEME 3 Reaction of **5** with nucleophiles.

In conclusion, we have described the synthesis of novel 6-phosphafulvene derivatives **5** via HCl elimination of chlorophosphine **4**. Structure elucidation of **4** gave information to explain the reaction mechanism from **4** to **5**. The structures of the *Z*- and *E*-isomers of **5** were unambiguously determined by X-ray crystallography, and their electrophilicity affording phosphinocyclopentadienyl anions was characterized.

EXPERIMENTAL

Preparation of 4

To a solution of *t*-butylcyclopentadiene[16] (**1**, 5.6 mmol) in THF (20 mL), butyllithium (5.6 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −78°C was added, and the mixture was stirred for 5 min to furnish **2**. A solution of (2,4,6-tri-*t*-butylphenyl)phosphonous dichloride (**3**, 2.1 g, 6.0 mmol)[17] in THF (20 mL) was added dropwise to the THF solution of **2**, and the mixture was stirred for 5 min. The reaction mixture was allowed to warm up to room temperature, and the volatile materials were removed in vacuo. The residue was washed with acetonitrile to afford 2.2 g of **4** (3:1 mixture of diastereomers, 98% yield) as colorless solid. Single crystals were obtained by recrystallization from dichloromethane at 0°C. Mp 95–97°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): major isomer: $\delta = 7.40$ (s, 2H, Mes*), 6.71 (s, 1H, CH), 6.70 (s, 1H, CH), 4.45 (d, $^2J_{PH} = 15.1$ Hz, 1H, PCH), 3.94 (s, 1H, H-C2), 1.60 (brs, 18H, *o*-*t*-Bu), 1.37 (s, 9H, *p*-*t*-Bu), 0.97 (s, 9H, *t*-Bu); minor isomer: $\delta = 7.40$ (s, 2H, Mes*), 6.43 (s, 1H, CH), 6.27 (s, 1H, CH), 4.47 (s, 1H, H-C2), 4.45 (d, $^2J_{PH} = 14.8$ Hz, 1H, PCH), 1.60 (brs, 18H, *o*-*t*-Bu), 1.37 (s, 9H, *p*-*t*-Bu), 1.16 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): major isomer: $\delta = 160.1$ (d, $^3J_{PC} = 6.0$ Hz, *C**t*-Bu), 157.7 (s, *o*-Mes*), 152.4 (s, *p*-Mes*), 140.0 (d, $^1J_{PC} = 81.1$ Hz, *ipso*-Mes*), 137.2 (d, $^2J_{PC} = 14.3$ Hz, CH), 134.8 (d, $^3J_{PC} = 5.0$ Hz, CH), 122.7 (s, *m*-Mes*), 120.2 (d, $^2J_{PC} = 13.1$ Hz, CH), 59.3 (d, $^1J_{PC} = 43.9$ Hz, PCH), 39.4 (s, *o*-*C*Me$_3$), 34.3 (s, *o*-C*Me*$_3$), 32.1 (s, *p*-*C*Me$_3$), 31.2 (s, *p*-C*Me*$_3$), 29.7 (s, *C*Me$_3$), 29.3 (s, C*Me*$_3$); minor isomer: $\delta = 159.8$ (d, $^3J_{PC} = 6.2$ Hz, *C**t*-Bu), 157.7 (s, *o*-Mes*), 152.3 (s, *p*-Mes*), 139.5 (d, $^1J_{PC} = 81.0$ Hz, *ipso*-Mes*), 135.4 (d, $^3J_{PC} = 4.8$ Hz, CH), 130.6 (d, $^2J_{PC} = 11.9$ Hz, CH), 126.4 (d, $^2J_{PC} = 12.0$ Hz, CH), 122.7 (s, *m*-Mes*), 59.3 (d, $^1J_{PC} = 43.9$ Hz, PCH), 39.4 (s, *o*-*C*Me$_3$), 34.3 (s, *o*-C*Me*$_3$), 32.1 (s, *p*-*C*Me$_3$), 31.2 (s, *p*-C*Me*$_3$), 29.7 (s, *C*Me$_3$), 29.3 (s, C*Me*$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): major isomer: $\delta = 69.2$; minor isomer: $\delta = 72.1$. EI-MS (70 eV) *m/z* (rel. intensity): 432 (M^+, 19 %), 311 (Mes*PCl, 100 %). ESI-MS found: 471.2553, calcd for $C_{27}H_{42}ClP{\cdot}ONa$ 471.2554.

Preparation of 5

To a solution of **4** (3:1 mixture of diastereomers, 2.2 g, 5.5 mmol) in hexane (30 mL), DBU (8.4 mmol) was added, and the mixture was stirred for 0.5 h. The reaction mixture was monitored by ^{31}P NMR spectroscopy, and both *Z*-**5** and *E*-**5** were observed in a 3:1 ratio. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (hexane) to afford a mixture of *Z*-**5** and *E*-**5** as deep red solids. Recrystallization from hexane afforded pure *E*-**5** at first and *Z*-**5** subsequently. *Z*-**5**: 770 mg (35%). Mp 104–106°C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$ (s, 2H, Mes*), 6.45 (s, 2H, H3 and H4), 4.49 (s, 1H, H1), 1.43 (s, 18H, *o*-*t*-Bu), 1.38 (s, 9H, *p*-*t*-Bu), 0.99 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): $\delta = 182.3$ (d, $^{1}J_{\mathrm{PC}} = 40.2$ Hz, P=C), 156.9 (d, $^{3}J_{\mathrm{PC}} = 22.0$ Hz, C2), 155.3 (s, *o*-Mes*), 150.8 (s, *p*-Mes*), 137.8 (d, $^{1}J_{\mathrm{PC}} = 55.7$ Hz, *ipso*-Mes*), 130.5 (d, $^{3}J_{\mathrm{PC}} = 25.3$ Hz, C3), 127.6 (d, $^{2}J_{\mathrm{PC}} = 37.0$ Hz, C4), 121.3 (s, *m*-Mes*), 113.0 (d, $^{2}J_{\mathrm{PC}} =$ 11.4 Hz, C1) 38.5 (s, *o*-*C*Me$_3$), 35.5 (s, *p*-*C*Me$_3$), 34.3 (d, $^{4}J_{\mathrm{PC}} = 7.2$ Hz, *o*-C*Me*$_3$), 32.3 (s, *C*Me$_3$), 31.9 (s, *p*-C*Me*$_3$), 29.9 (s, C*Me*$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = 296.0$. UV (hexane) $\lambda_{\max}$ (ε x 10^{-3} $M^{-1}cm^{-1}$): 380 (2.0), 324 (21.0), 237 (10.0) nm. EA Calcd for $C_{27}H_{41}P$: C 81.77, H 10.42; found: C 81.42, H 10.44. *E*-**5**: 370 mg (17%). Mp 179–181°C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$ (s, 2H, Mes*), 6.36 (s, 1H, H3), 6.23 (s, 1H, H4), 4.98 (s, 1H, H1), 1.53 (s, 18H, *o*-*t*-Bu), 1.42 (s, 9H, *p*-*t*-Bu), 1.25 (s, 9H, *t*-Bu). ^{13}C^{1}H NMR (151 MHz, $CDCl_3$) $\delta = 182.3$ (d, $^{1}J_{\mathrm{PC}} =$ 40.2 Hz, P=C), 157.3 (d, $^{3}J_{\mathrm{PC}} = 27.0$ Hz, C2), 155.1 (s, *o*-Mes*), 150.7 (s, *p*-Mes*), 137.3 (d, $^{1}J_{\mathrm{PC}} = 97.2$ Hz, *ipso*-Mes*), 130.6 (d, $^{3}J_{\mathrm{PC}} = 18.7$ Hz, C3), 121.2 (s, *m*-Mes*) 121.0 (d, $^{2}J_{\mathrm{PC}} = 7.0$ Hz, C4), 118.1 (d, $^{2}J_{\mathrm{PC}} =$ 34.1 Hz, C1) 38.5 (s, *o*-*C*Me$_3$), 35.5 (s, *p*-*C*Me$_3$), 34.3 (d, $^{4}J_{\mathrm{PC}} = 7.0$ Hz, *o*-C*Me*$_3$), 32.6 (s, *C*Me$_3$), 31.9 (s, *p*-C*Me*$_3$), 30.1 (s, C*Me*$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = 295.0$. UV (hexane) $\lambda_{\max}$ (ε x 10^{-3} $M^{-1}cm^{-1}$): 380 (2.2), 323 (22.0), 236 (11.0) nm. EA Calcd. for $C_{27}H_{41}P$: C 81.77, H 10.42; found: C 81.82, H 10.34.

Reaction of *Z/E*-5 with Alkyllithiums: Typical Procedures

To a solution of *Z*-**5** (10 mg, 2.5 μmol) in THF (0.5 mL), methyllithium (5.0 μmol) at -78°C was added and was monitored by ^{31}P NMR spectroscopy after warming up to room temperature. The corresponding anion **6** was observed at δ_{P} –40 (R = Me) or –26 (R = *n*-Bu). The reaction solution was treated with acetic acid to give **8** as a mixture of diastereomers at δ_P –38, –39, and –42 (R = Me) or δ_{P} –24, –25, and –28 (R = *n*-Bu). Almost the same results were obtained in the reaction of *E*-**5**.

X-Ray Crystallography

3: $C_{18}H_{29}Cl_2P$: $M = 347.31$, monoclinic, $P2_1/a$ (No. 14), $a = 16.707(2)$, $b = 11.678(2)$, $c = 9.780(2)$ Å, $\beta = 90.511(4)^\circ$, $V = 1908.1(5)$ Å^3, $Z = 4$, $T = 143$ K, $\rho_{\text{calcd}} = 1.209\ \text{g cm}^{-3}$, $\mu(\text{MoK}_\alpha) = 0.417\ \text{mm}^{-1}$, $2\theta_{\max} = 55.0^\circ$, 13538 observed reflections, 13031 unique reflections ($R_{int} = 0.067$), $R1 = 0.250$ ($I > 2\sigma(I)$), $R_{\text{w}} = 0.530$ (all data) (CCDC-668729). The high R value might be due to the crystal of low quality. **4**: $C_{27}H_{42}ClP$: $M = 433.06$, monoclinic, $P2_1/n$ (No. 14), $a = 8.9814(3)$, $b = 17.6217(5)$, $c = 16.5341(5)$ Å, $\beta = 93.331(1)^\circ$, $V = 2612.4(1)$ Å^3, $Z = 4$, $T = 140$ K, $\rho_{\text{calcd}} = 1.101\ \text{g cm}^{-3}$, $\mu(\text{MoK}_\alpha) = 0.218\ \text{mm}^{-1}$, $2\theta_{\max} = 55.0^\circ$, 21012 observed reflections, 12116 unique reflections ($R_{\text{int}} = 0.050$), $R1 = 0.056$ ($I > 2\sigma(I)$), $R_w = 0.068$ (all data) (CCDC-667900). *Z*-**5**: $C_{27}H_{41}P$: $M = 396.59$, monoclinic, $P2_1/c$ (No. 14), $a = 16.369(1)$, $b = 16.3314(5)$, $c = 19.3928(5)$ Å, $\beta = 91.235(2)^\circ$, $V = 5142.1(4)$ Å^3, $Z = 8$, $T = 153$ K, $\rho_{\text{calcd}} = 1.025$ g cm^{-3}, $\mu(\text{MoK}_\alpha) = 0.116\ \text{mm}^{-1}$, $2\theta_{\max} = 55.0^\circ$, 38939 observed reflections, 13891 unique reflections ($R_{\text{int}} = 0.124$), $R1 = 0.105$ ($I > 2\sigma(I)$), $R_w = 0.194$ (all data) (CCDC-667901). *E*-**5**: $C_{27}H_{41}P$: $M = 396.59$, monoclinic, $P-1$ (No. 2), $a = 11.387(3)$, $b = 11.533(3)$, $c = 9.558(2)$ Å, $\alpha = 88.20(2)$, $\beta = 90.28(2)$, $\gamma = 88.75(1)^\circ$, $V = 1254.2(5)$ Å^3, $Z = 2$, $T = 143$ K, $\rho_{\text{calcd}} = 1.050$ g cm^{-3}, $\mu(\text{MoK}_\alpha) = 0.119\ \text{mm}^{-1}$, $2\theta_{\max} = 55.0^\circ$, 8189 observed reflections, 3525 unique reflections ($R_{\text{int}} = 0.078$), $R1 = 0.138$ ($I > 2\sigma(I)$), $R_w = 0.288$ (all data) (CCDC-667902).

The high R values for *Z*- and *E*-**5** might be due to the presence of unsolved molecular structures. Attempts to solve the structures with either lower symmetrical space groups or larger crystal lattices failed.

REFERENCES

[1] (a) M. Yoshifuji and S. Ito, *Top. Curr. Chem.*, **223,** 67 (2003); (b) M. Regitz and O. J. Scherer, Eds., *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Thieme, Stuttgart, 1990); (c) K. B. Dillon, F. Mathey, and J. F. Nixon, *Phosphorus: The Carbon Copy*, (Wiley, Chichester, 1998).

[2] F. Ozawa and M. Yoshifuji, *Dalton Trans.*, 4987 (2006).

[3] T. Baumgartner and R. Réau, *Chem. Rev.*, **106,** 4681 (2006).

[4] (a) G. Märkl and K. M. Raab, *Tetrahedron Lett.*, **30,** 1077 (1989); (b) A. Al Badri, M. Chentit, M. Geoffroy, and A. Jouaiti, *J. Chem. Soc.*, *Faraday Trans.*, **93,** 3631 (1997).

[5] S. Ito, H. Sugiyama, and M. Yoshifuji, *Angew. Chem.*, *Int. Ed.*, **39,** 2781 (2000).

[6] S. Ito, H. Miyake, H. Sugiyama, and M. Yoshifuji, *Tetrahedron Lett.*, **45,** 7019 (2004).

[7] S. Ito, H. Miyake, H. Sugiyama, and M. Yoshifuji, *Heterocycles*, **63,** 2591 (2004).

[8] S. Ito, H. Miyake, M. Yoshifuji, T. Höltzl, and T. Veszprémi, *Chem. Eur. J.*, **11,** 5960 (2005).

[9] (a) M. Yoshifuji, I. Shima, N. Inamoto, and T. Aoyama, *Tetrahedron Lett.*, **32,** 3057 (1981); (b) M. Freytag, P. G. Jones, R. Schmutzler, and M. Yoshifuji, *Heteroatom*

Chem., **12,** 300 (2001); **12,** 457 (2001); (c) S. Ito and M. Yoshifuji, *Sci. Rep. Tohoku University Ser. 1*, **79,** 9 (2002); (d) M. Unno, Y. Kawai, and H. Matsumoto, *Heteroatom Chem.*, **12,** 238 (2001).

[10] (a) R. J. Wehmschulte, M. A. Khan, and S. I. Hossain, *Inorg. Chem.*, **40,** 2756 (2001); (b) C. Overländer, J. J. Tirrée, M. Nieger, E. Niecke, C. Moser, S. Spirk, and R. Pietschnig, *Adv. Organometal. Chem.*, **21,** 46 (2007).

[11] J.-H. Lii, S. Gallion, C. Bender, H. Wikstrom, N. L. Allinger, K. M. Flurchick, and M. M. Teeter, *J. Comp. Chem.*, **10,** 503 (1989).

[12] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Am. Chem. Soc.*, **122,** 3746 (2000).

[13] No *E*/*Z* isomerization of **5** was observed upon heating.

[14] R. W. Carling and A. B. Holmes, *J. Chem. Soc.*, *Chem. Commun.*, 325 (1986).

[15] K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Liebigs Ann. Chem.*, **589,** 91 (1954).

[16] (a) D. L. Compton and T. B. Rauchfuss, *Organometallics*, **13,** 4367 (1994); (b) D. Tews and P. E. Gaede, *Tetrahedron Lett.*, **45,** 9029 (2004).

[17] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103,** 4587 (1981).