

The Phenylthio Group as a New Substituent on the 2-Position of Sterically Protected 1-Phosphaethenes

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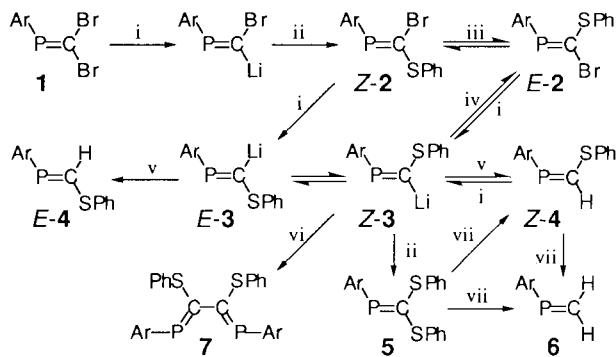
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The phenylthio group was introduced to the sterically protected phosphaethene-system and 1-(phenylthio)-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium was generated. It has been shown that the lithium reagent behaves like a halogen derivative, in terms of elimination, metalation, and coupling reaction, while the *E/Z* isomerization was observed for the phenylthio-derivative, and a 1,4-diphospha-1,3-butadiene as an oxidative coupling product was analyzed by X-ray.

Sterically protected phosphaethenes with the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) are of current interest.¹⁻³ Recently, we have reported on the formation and the utilization of 1-halo-2-phosphaethenyllithiums, which are regarded as phosphanylidene carbenoids, being expected as synthetic building blocks.⁴⁻⁶ We now report on the introduction of the phenylthio group into this system, anticipating that it shows a characteristic substituent effect on the reactions. It might act so as to stabilize α -anions and also act as an eliminating group.⁷

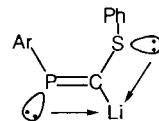
2,2-Dibromo-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (**1**) was lithiated with one equiv. of butyllithium and was allowed to react with diphenyl disulfide to give **Z-2**⁸ in 55% yield from **1**. The reaction of **Z-2** with one equiv. of butyllithium mainly gave **Z-4**⁸ after quenching with methanol. In THF at -100°C , **Z-2** was stirred for 10 min with butyllithium and quenched with methanol to give a mixture of **Z-4** : **E-4** = 10 : 1 in 85% and 8% yields from **Z-2**, respectively. It seemed likely that **Z-3** is formed indirectly, *via* isomerization around the P=C bond of **E-3**. Thus, in ether at -100°C for 30 min, **Z-2** gave a mixture of **Z-4** : **E-4** : **Z-2** = 4 : 10 : 7,⁸ while if this reaction time was elongated to 1 h, a mixture of **Z-4** : **E-4** = 5 : 1 was obtained. These results indicate that **E-3**, if being formed first, is isomerized to **Z-3** during this reaction sequence.



Scheme 1. Reagents and conditions. i) *n*-BuLi; ii) PhSSPh; iii) \hbar ; iv) CBr_4 ; v) MeOH; vi) CuCl_2/O_2 ; vii) 1) $\text{Li}^+[\text{Naph}]^{4-}$, 2) MeOH. Ar = 2,4,6-*t*-Bu₃C₆H₂.

As a transition state of this isomerization, a methylidyne-phosphide anion can be plausible.^{9,10} The reason why the *Z*-

isomer is more favorable than the *E*-isomer, might be due to the interaction between Li and the lone-pair electrons of P and S of **3**, in spite of the steric congestion between the Ar and the PhS groups, as shown in Scheme 2.



Scheme 2. Favorable interaction of P and S with Li in **Z-3**.

Phosphaethene **Z-3** is stable at 25°C : δ_{P} 188.5 (THF/THF-*d*8) and 180.8 (Et₂O/toluene-*d*8). The rate of isomerization in ether was slower than in THF, indicating that the contribution of the separated Li⁺ is smaller than in THF and thus the bond C-Li is stronger in ether than in THF, since an ionic character is stronger in THF than in ether. The observed solvent effect might be caused from the polarity difference between the solvents. When **Z-4** was allowed to react with butyllithium at 25°C , the formation of **Z-3** was observed in the ³¹P NMR; this means that abstraction of proton from **4** easily occurs to give **3**, in contrast to the case of carbon chemistry.⁷ If **Z-3**, generated from **Z-2**, was allowed to react with tetrabromomethane at -78°C to 0°C , **E-2**¹¹ was formed in 72% yield. Thus **E-2** with butyllithium might have afforded **Z-3**, although the NMR signal due to **Z-3** was not observed in ³¹P NMR. The yield of **Z-4** after MeOH-quenching at 25°C was 47% based on **E-2**.

In benzene, **E-2** and **Z-2** became a 1 : 1 equilibrium mixture after 10-h irradiation with a medium-pressure Hg lamp. However, upon longer irradiation the mixture gradually gave decomposition products, probably due to elimination of Br atom.

When **Z-3** was allowed to react with diphenyl disulfide at -78°C to 0°C , **5**⁸ was obtained in 51% yield from **Z-2**. The reaction of **5** with lithium naphthalenide at -78°C gave **Z-4** after quenching with methanol in 39% yield from **5**. Phosphaethene **Z-4** reacted with lithium naphthalenide to afford **6** (15% yield) together with **Z-4** (60% recovery) after quenching with methanol, indicating that the PhS group can be regarded as a leaving group.⁷ Among the reaction products of this reaction, there was observed a trace amount of phosphaalkyne, ArC≡P, due to [1,2] rearrangement,^{12,13} was observed in the ³¹P NMR.

Furthermore, a coupling reaction of **Z-3** took place in the presence of Cu(II) chloride under an atmosphere of oxygen at -78°C to give **7**⁸ in 84% yield from **Z-2**, similarly to 1-halo-1-phosphaethenyllithium.⁴ The structure of **7** was confirmed by X-ray analysis, as shown in Fig. 1,¹⁴ to indicate to take *Z,Z*-conformation with *s-cis* conformation. In contrast to that of the dichloro-derivative **8**,⁴ the 1,4-diphospha-1,3-butadiene system in **7** is not planar; the plane [P(1),C(1),C(2),S(1)] makes an angle of 38.4(6) $^{\circ}$ with the plane [P(2),C(2),C(1),S(2)].

Table 1. Redox properties of phosphaethenes **2** and **4** — **10**

Compound	$E_p^{\text{ox}}/\text{Va}$	$E_p^{\text{red}}/\text{Va}$	
Z-2	+1.55	-0.86	
E-2	+1.54	-0.86 (sh)	
Z-4	+1.49	-0.76	
5	+1.23, +1.55 (sh)	-0.91 (sh)	
6	+1.76	-0.87	
$\text{Ar}-\text{P}=\text{C}-\text{X}$	7 (X = SPh)	+1.20	-0.80, -1.57
	8 (X = Cl)	+1.55	-0.92, -1.31
	9 (X = Br)	+1.00	-0.82(sh), -1.08
$\text{X}-\text{Ar}$	10 (X = H)	+1.35	-0.87

^a CV conditions: 1 mM in CH_2Cl_2 ; 0.1 M $n\text{-Bu}_4\text{NClO}_4$; Scan rate, 50 mV s⁻¹; 25 °C; Counter electrode, Pt; Working electrode, glassy carbon; Reference electrode, Ag/AgCl.

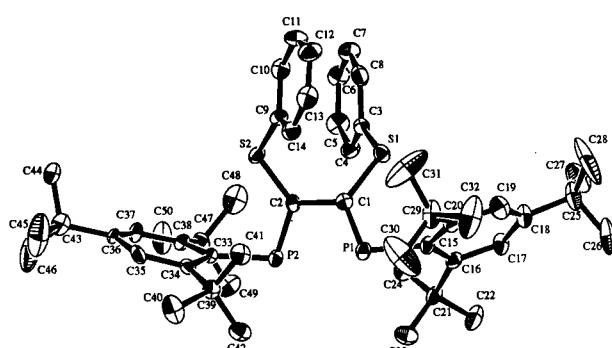


Figure 1. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. Some important bond lengths (Å) and angles (°): P(1)–C(1), 1.70(1); C(1)–S(1), 1.76(1); P(1)–C(15), 1.82(1); P(2)–C(2), 1.72(1); C(2)–S(2), 1.72(1); P(2)–C(33), 1.85(1); C(1)–C(2), 1.49(2); C(1)–P(1)–C(15), 103.3(7); C(2)–P(2)–C(33), 103.2(6); S(1)–C(1)–P(1), 122.3(8); S(1)–C(1)–C(2), 124.5(10); P(1)–C(1)–C(2), 113.1(10); S(2)–C(2)–P(2), 123.8(7); S(2)–C(2)–C(1), 124.7(10); P(2)–C(2)–C(1), 111.3(9).

Redox properties of the series of the phenylthio-substituted phosphaethenes were measured by cyclic voltammetry. The results are listed in Table 1, together with the results of phosphaethene **6** and 1,4-diphosphabutadienes **8**, **9**, and **10** (X = H¹⁷). Phosphaethenes are electrochemically amphoteric and show irreversible or quasi-reversible redox potentials.^{15,16} The introduction of the PhS group decreased the oxidation potential E_p^{ox} , suggesting that the group has an electron donating character. E_p^{red} does not change that much compared with that of a plain phosphaethene **6**. Furthermore, **7** showed two reduction potentials, whereas **10** showed one reduction potential. A similar successive reduction has been observed for **8** and **9**. These results indicate that the first reduction in **7** — **10** occurs in the P=C—C=P system and the second one at the C—X group. The first reduction potential for **8** is lower than those for others, indicating a strong interaction of chlorine upon the system. The second reduction potential for **7** is lower than those for **8** and **9**, because the leaving ability of the PhS group is poorer than that of the Br or Cl atom. As a result, **8** and **9** reacted with lithium naphthalenide to afford 1,4-diphosphabutatriene, whereas **7** was unreactive under the similar conditions. The E_p^{ox} value of **9** shows the lowest among those, indicating some electron donating character of the Br atom to P=C bonding of **9**, contrary to the case of **2**. Thus chemical oxidation of **7** seems to afford stable cationic species, which might suggest intramolecular interaction between P and S.¹⁸

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- Z-2:** Colorless needles (MeOH), mp 74 — 75 °C (decomp); ¹H NMR (200 MHz, CDCl_3) δ = 1.32 (9H, s, *p*-*t*-Bu), 1.52 (18H, s, *o*-*t*-Bu), 7.2 — 7.5 (5H, m, Ph), and 7.40 (2H, d, $^4J_{\text{PH}}$ = 1.5 Hz, *m*-Ar); ¹³C{¹H} NMR (50 MHz, CDCl_3) δ = 152.8 (d, $^1J_{\text{PC}}$ = 70.1 Hz, P=C); ³¹P{¹H} NMR (81 MHz, CDCl_3) δ = 272.8; MS (70 eV, EI) *m/z* 476 (M^+). Found 476.1288; Calcd for $\text{C}_{25}\text{H}_{34}\text{BrPS}$: 476.1302. **E-2:** Colorless prisms (MeOH), mp 104 — 106 °C (decomp); ¹H NMR δ = 1.34 (9H, s, *p*-*t*-Bu), 1.59 (18H, s, *o*-*t*-Bu), 7.2 — 7.4 (5H, m, Ph), and 7.44 (2H, d, $^4J_{\text{PH}}$ = 1.4 Hz, *m*-Ar); ¹³C{¹H} NMR δ = 155.9 (d, $^1J_{\text{PC}}$ = 7.5 Hz, P=C); ³¹P{¹H} NMR δ = 244.0; MS *m/z* 476 (M^+). **Z-4:** Colorless needles (MeOH), mp 130 — 131 °C (decomp); ¹H NMR δ = 1.36 (9H, s, *p*-*t*-Bu), 1.58 (18H, s, *o*-*t*-Bu), 7.2 — 7.5 (5H, m, Ph), 7.45 (2H, d, $^4J_{\text{PH}}$ = 1.3 Hz, *m*-Ar), and 7.84 (1H, d, $^2J_{\text{PH}}$ = 35.1 Hz, P=CH); ¹³C{¹H} NMR δ = 162.9 (d, $^1J_{\text{PC}}$ = 53.7 Hz, P=C); ³¹P{¹H} NMR δ = 224.8 (d, $^2J_{\text{PH}}$ = 35.1 Hz); MS *m/z* 398 (M^+). Found 398.2204; Calcd for $\text{C}_{25}\text{H}_{35}\text{PS}$: 398.2197. **E-4:** Colorless oil (crude); ¹H NMR δ = 1.33 (9H, s, *p*-*t*-Bu), 1.53 (18H, s, *o*-*t*-Bu), 7.2 — 7.8 (5H, m, Ph), 7.42 (2H, d, $^4J_{\text{PH}}$ = 1.4 Hz, *m*-Ar), and 7.84 (1H, d, $^2J_{\text{PH}}$ = 21.0 Hz, P=CH); ³¹P{¹H} NMR δ = 239.0 (d, $^2J_{\text{PH}}$ = 21.0 Hz). **5:** Pale yellow prisms (MeOH), mp 128 — 129 °C (decomp); ¹H NMR δ = 1.32 (9H, s, *p*-*t*-Bu), 1.63 (18H, s, *o*-*t*-Bu), 6.9 — 7.2 (10H, m, Ph), and 7.43 (2H, d, $^4J_{\text{PH}}$ = 1.3 Hz, *m*-Ar); ³¹P{¹H} NMR δ = 235.9; MS *m/z* 506 (M^+). Found 506.2242; Calcd for $\text{C}_{31}\text{H}_{39}\text{PS}_2$: 506.2231. **7:** Yellow prisms (MeOH), mp 200 — 203 °C (decomp); ¹H NMR δ = 1.32 (18H, s, *p*-*t*-Bu), 1.59 (36H, s, *o*-*t*-Bu), 6.9 — 7.1 (10H, m, Ph), and 7.31 (4H, m, *m*-Ar); ³¹P{¹H} NMR δ = 238.6; UV (hexane) λ_{max} (log ϵ) 255 (4.39), 336 (4.31), and 424 nm (3.84); FAB-MS *m/z* 793 (M^+); Anal. Found: C, 75.39; H, 8.67%; Calcd for $\text{C}_{50}\text{H}_{68}\text{P}_2\text{S}_2$: C, 75.53; H, 8.62%. **9:** Similar isomerization has been described in 2-(2,4,6-tri-*t*-butylphenyl)-1-(trimethylsilyl)-2-phosphaethenyllithium; M. van der Sluis, Dissertation, Vrije University (1997). **10:** Soleilhavoup, M.; Baceiredo, A.; Treutler, R.; Ahlrichs, M.; Nieger, M.; Bertrand, G. *J. Am. Chem. Soc.*, **114**, 10959 (1992). **11:** The structure of **E-2** was confirmed by X-ray analysis and the detailed descriptions will be published elsewhere. **12:** Yoshifuji, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.*, **1988**, 1733. **13:** Appel, R.; Immenkappel, Z. *Anorg. Allg. Chem.*, **553**, 7 (1987). **14:** Crystal Data for **7:** Recrystallized from MeOH. $\text{C}_{50}\text{H}_{68}\text{P}_2\text{S}_2$, M_r = 795.15, monoclinic, a = 18.972(4) Å, b = 27.922(5) Å, c = 21.408(4) Å, β = 116.08(1)°, V = 10186(3) Å³, $C2/c$ (#15), Z = 8, T = 296 K, R = 0.089, R_w = 0.118; 3492 unique reflections with $I > 3\sigma(I)$. The structure was solved with SHELXS86; G. M. Sheldrick, *SHELXS86, Programs for the Automatic Solution of Crystal Structures*, University of Göttingen, Germany (1986). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ (UK). **15:** Schoeller, W. W.; Niemann, J.; Thiele, R.; Haug, W. *Chem. Ber.*, **124**, 417 (1991). **16:** Jouaiti, A.; Al Badri, M.; Geoffroy, M.; Bernardinelli, G. *Organometal. Chem.*, **529**, 143 (1997). **17:** Appel, R.; Hünerbein, J.; Siabalis, N. *Angew. Chem., Int. Ed. Engl.*, **26**, 779 (1987). **18:** Fujihara, H.; J.-J. Chiu, and N. Furukawa, *Chem. Lett.*, **1990**, 2217.