

Transmetallation Reaction of 1-Phenylthio- or 1-Tolylthio-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium with Copper(II) and Mercury(II)

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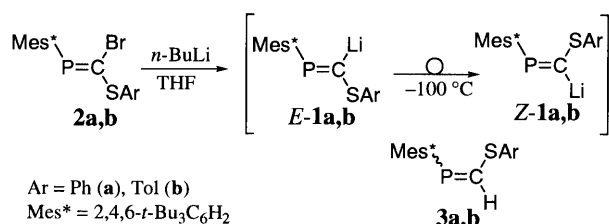
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Transmetallation of bulky 1-arylthio-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithiums with copper(II) and mercury(II) afforded the corresponding 1,4-diphospha-1,3-butadiene derivatives as homocoupled products and organomercury compounds, respectively, which were analyzed by X-ray crystallography.

Kinetic stabilization with bulky substituent(s) has been widely used for study on multiple bonds of heavier main group elements, and various types of unsaturated bonds containing phosphorus have been reported.¹ We have been interested in the compounds containing phosphorus-carbon multiple bond(s) kinetically stabilized with the 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to the Mes*) group(s).² Previously, we have reported the preparation and some reactions of 1-phenylthio-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (**1a**) as one of the phosphanylidene carbenoids^{2,3} to show the effects of sulfur atom on the stability of *Z*-isomer.⁴

In the course of our study, we found that the transmetallation reaction of phosphanylidene carbenoids with copper through the oxidative coupling is a powerful method to construct a conjugated system with phosphorus-carbon double bonds.⁵ Thus transmetallation is useful not only for preparation of organometallic compounds but also for organic synthesis. Here we report the transmetallation of 1-arylthio-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (**1**; aryl = Ph, Tol) with copper(II) and mercury(II) giving the corresponding coupling products and organomercury compounds.



Scheme 1.

2-Arylthio-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethenes **2**, prepared from 1-bromo-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium and diaryl disulfides, were allowed to react with butyllithium to afford the corresponding phosphoethenyllithiums **1**. During the process of preparation of **1**, the *E/Z* isomerization was observed even at -100°C in THF, and the *Z*-isomers (**Z-1**) were predominantly formed to afford phosphoethenes **Z-3** after quenching of the reaction mixture with methanol (ca. *E:Z* = 1:10; Scheme 1). The phosphoethenyl-lithiums **1** are stable at 25°C due to carbanion-stabilizing effect of the thio groups. In the ^{31}P NMR spectra, the higher chemical shifts were observed for **1** compared to phosphoethenes **3** [δ_{p} = 188.5 (**1a**), 185.6 (**1b**); 218.8 (**Z-3a**), 221.7

(**Z-3b**) in THF].⁶ The interaction between Li and the lone-pair electrons of P and S in **1** has been discussed for the stability of *Z*-isomers.⁴ The structure of **Z-3a** was confirmed by X-ray crystallography,⁷ and Figure 1 displays a drawing of the molecular structure of **Z-3a** indicating the P=C skeleton [1.655(4) Å] in *Z*-configuration and the repelled phenylthio group from the Mes* group [P1-C1-S1 129.4(3)°].

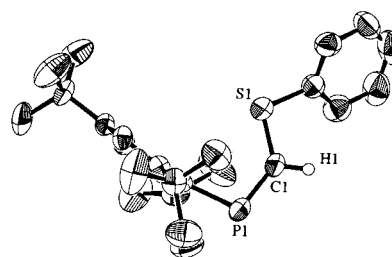


Figure 1. An ORTEP drawing of **Z-3a** with 50% probability ellipsoids. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths (Å) and angles (°): P1-C1 1.655(4), C1-S1 1.724(4), P1-C_{ipso}(Mes*) 1.844(4), S1-C_{ipso}(Ph) 1.776(4), C1-P1-C_{ipso}(Mes*) 102.1(2), P1-C1-S1 129.4(3), C1-S1-C_{ipso}(Ph) 102.2(2).

Next we performed the transmetallation for the thio-derived phosphoethenyllithiums **1** with copper(II). Phosphoethenyllithiums **1**, derived from **2** and butyllithium, were allowed to react with copper(II) chloride and oxygen at -78°C in THF to afford the 1,4-diphospha-1,3-butadienes **4** in the yields of 84% (**4a**) and 38% (**4b**), respectively, as yellow crystals indicating the extended π -conjugation (Scheme 2).⁸ The *s-cis* conformation in **4a**⁴ and **4b**⁹ has been confirmed by X-ray crystallographic analyses. Figure 2 displays the structure of **4b**.^{9,10} The P=C-C=P planes are twisted with the torsion angles of 38.5° (**4a**) and 38.3° (**4b**), respectively. On the contrary, 2,3-dichloro-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene was planar with *s-trans* conformation.^{5a} We expect the intramolecular electronic interaction between the σ -orbital of C-S bond and the σ^* -orbital of P-C bond for the reason for taking the *s-cis* conformation.¹¹ The twisted conformation of **4** might be due to the repulsion of the lone pairs of phosphorus atoms. A similar "screw-type" structure was reported for 2-trimethylsilyl-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene, indicating the stereoelectronic effect between the σ -orbital of C-Si or C-H bond and the σ^* -orbital of P-C bond.¹²

Moreover we examined the transmetallation of phosphoethenyllithiums **1a** and **1b** with mercury(II). Phosphoethenyllithiums **1** were treated with 0.5 equivalent amount of mercury(II) chloride in THF to afford the corresponding organomercury compounds **5a** (79% yield) and **5b** (60% yield), respectively, as colorless crystals (Scheme 2).⁸ The structures of **5** were characterized by means of spectroscopic data. Large $^1J_{\text{HgP}}$ values are similar to those of the hydrogen-derivative (*E,E*-mercuriobis[methylene(2,4,6-tri-*t*-butylphenyl)phosphane])

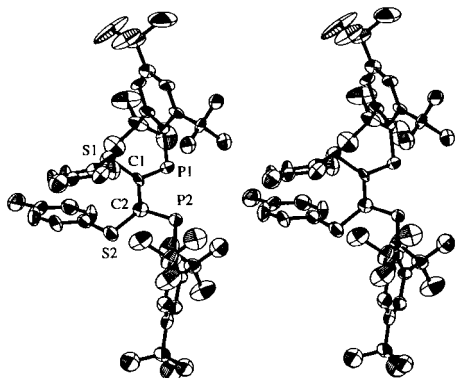
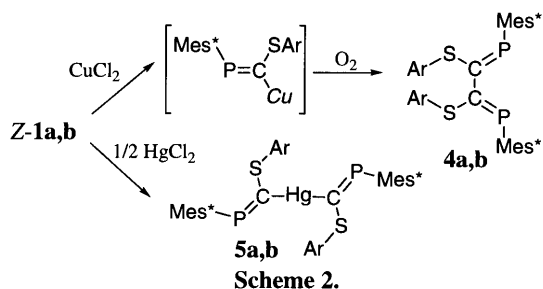


Figure 2. An ORTEP drawing (stereoview) of **4b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The *p*-*t*-butyl group of Mes* at P2 is disordered, and the atoms with the predominant occupancy factors (0.60), which are refined isotropically, are shown. Selected bond lengths (Å) and angles (°): P1–C1 1.74(2), P2–C2 1.71(1), C1–C2 1.44(2), C1–S1 1.74(1), C2–S2 1.75(2), P1–C_{ipso} 1.84(1), P2–C_{ipso} 1.86(2), P1–C1–C2 112(1), P1–C1–S1 122.3(9), S1–C1–C2 124(1), P2–C2–C1 113(1), P2–C2–S2 121.4(8), S2–C2–C1 124(1), C1–P1–C_{ipso} 101.7(7), C2–P2–C_{ipso} 105.8(7).



[(*E,E*)-**5H**].¹³ Gratifyingly, compound **5a** afforded a suitable crystal for X-ray analysis and the molecular structure is displayed in Figure 3.⁹ The straight skeleton (C–Hg–C) is characteristic for a mercury(II) compound, and all of the aryl moieties locate perpendicularly to the plane [P–C(–S)–Hg–C(–S)–P]. The C–Hg length is 2.058(4) Å, which is similar to (*Z,Z*)-**5H** (2.042 and 2.079 Å).¹³ The P=C length is 1.680(5) Å, which is slightly longer than that for (*Z,Z*)-**5H** (1.644 and 1.643 Å),¹³ probably due to electronic effect of sulfur atoms. There are no remarkable interactions between the lone pairs of sulfur or phosphorus and mercury. On the other hand, non-covalent interaction between the aromatic rings of phenylthio groups and mercury was observed. That is, the phenyl ring locates above

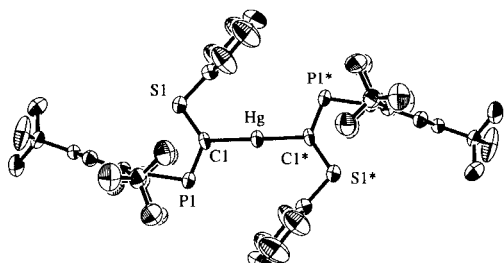


Figure 3. An ORTEP drawing of **5a** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg–C1 2.058(4), P1–C1 1.680(5), P1–C_{ipso} 1.847(7), C1–S1 1.731(5), C1–Hg–C1* 180.0, C1–P1–C_{ipso} 103.6(2), P1–C1–S1 123.8(3), P1–C1–Hg 114.1(3), S1–C1–Hg 122.1(3).

the mercury atom, with the shortest distance to C-*ipso* [3.242(5) Å] and its ortho carbons [3.56(1) and 3.85(1) Å]. A similar coordination was also observed for (*Z,Z*)-**5H**, where the Mes* rings interact with the mercury atom.¹⁴ In contrast to **4**, influential electronic effect is not obvious on the molecular structure, and each substituent locates to avoid steric congestion.

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References and Notes

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- Selected NMR data: **Z-3b**: ¹H NMR (200 MHz, CDCl₃) δ = 7.80 (1H, d, ²J_{PH} = 35.3 Hz, P=CH); ³¹P NMR (81 MHz, CDCl₃) δ = 221.7 (²J_{PH} = 35.3 Hz); **E-3b**: ¹H NMR (200 MHz, CDCl₃) δ = 7.81 (1H, d, ²J_{PH} = 22.0 Hz, P=CH); ³¹P NMR (81 MHz, CDCl₃) δ = 233.1 (²J_{PH} = 22.0 Hz).
- Crystal data: **Z-3a**: C₂₅H₃₅PS, fw = 398.59, orthorhombic, P2₁2₁ (#19), a = 10.682(2), b = 23.699(10), c = 9.485(2) Å, V = 2401(1) Å³, Z = 4, d_{calc} = 1.103 g·cm⁻³, temperature 288 K. R = 0.040 for 1740 independent reflections [θ < 25.07, I > 3.00σ(I)], S = 1.11 for 280 parameters (CCDC 151316).
- Selected physical data: **4a**: mp 200–203 °C (decomp); ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 173.4 (dd, ¹J_{PC} = 12.8 Hz, ²J_{PC} = 7.8 Hz, P=C); ³¹P{¹H} NMR (81 MHz, CDCl₃) δ = 238.6; UV (hexane) λ_{max} (log ε) 255 (4.39), 336 (4.31), and 424 nm (3.84); **4b**: mp 207–208 °C (decomp); ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 174.0 (dd, ¹J_{PC} = 12.6 Hz, ²J_{PC} = 8.8 Hz, P=C); ³¹P{¹H} NMR (81 MHz, CDCl₃) δ = 237.6; UV (hexane) λ_{max} (log ε) 336 (4.28) and 419 nm (3.81); **5a**: mp 178–180 °C; ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 211.1 (dd, ¹J_{PC} = 84.3 Hz, ³J_{PC} = 5.0 Hz, P=C); ³¹P{¹H} NMR (81 MHz, CDCl₃) δ = 231.2 (¹J_{HgP} = 866 Hz); **5b**: mp 165–167 °C; ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 211.6 (dd, ¹J_{PC} = 84.7 Hz, ³J_{PC} = 5.0 Hz, P=C); ³¹P{¹H} NMR (81 MHz, CDCl₃) δ = 230.0 (¹J_{HgP} = 870 Hz).
- Crystal data: **4b**: C₅₂H₇₂P₂S₂, fw = 823.21, triclinic, P $\bar{1}$ (#2), a = 16.191(5), b = 17.18(2), c = 9.791(5) Å, α = 97.78(7), β = 95.90(4), γ = 68.60(6)°, V = 2507(3) Å³, Z = 2, d_{calc} = 1.090 g·cm⁻³, temperature 288 K. R = 0.085 for 2304 independent reflections [θ < 25.08, I > 3.00σ(I)], S = 1.98 for 503 parameters (CCDC 151317). **5a**: C₅₀H₆₈HgP₂S₂, fw = 995.74, triclinic, P $\bar{1}$ (#2), a = 10.097(2), b = 16.318(4), c = 8.351(8) Å, α = 99.64(4), β = 114.11(4), γ = 79.38(2)°, V = 1227(1) Å³, Z = 2, d_{calc} = 2.693 g·cm⁻³, temperature 288 K. R = 0.043 for 3958 independent reflections [θ < 25.13, I > 3.00σ(I)], S = 1.56 for 250 parameters (CCDC 151318).
- An X-ray structure determination of **4b** at low temperature (150 K) failed to give better results.
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