

# Synthesis of Bis(2,6-dimesityl-4-methylphenyl)phosphaarsene and EPR of its Radical Anion

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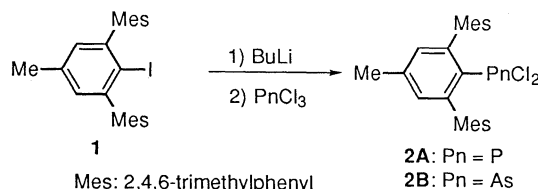
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Novel bis(2,6-dimesityl-4-methylphenyl)phosphaarsene was synthesized by the coupling reaction of 2,6-dimesityl-4-methylphenylphosphine with dichloro(2,6-dimesityl-4-methylphenyl)arsine in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and isolated as stable crystals. The radical anion generated by the sodium metal reduction of the phosphaarsene was investigated by X-band EPR.

The compounds possessing double bonds between the group 15 elements have received considerable attention<sup>1</sup> and the chemistry of low-coordinated phosphorus compounds has been developed by utilizing the sterically bulky substituents such as the 2,4,6-tri-*t*-butylphenyl group. During the course of our investigation on the low-coordinated group 15 compounds, we needed to develop sterically bulky aromatic auxiliaries of comparable bulkiness to that of the 2,4,6-tri-*t*-butylphenyl group, because even dichloro(2,4,6-tri-*t*-butylphenyl)arsine has to be handled at low temperature to avoid intramolecular reaction with the ortho *t*-butyl group to give an arsaindan derivative.<sup>2</sup> Thus we started investigation on the group 15 compounds carrying 2,6-diarylphenyl substituents, which can be easily synthesized by the Hart reaction<sup>3</sup> and have been successfully used as protecting groups for low coordinated main-group element as well as transition metal compounds by Power *et al.*<sup>4</sup> We wish to report on the synthesis of stable dichloro(2,6-dimesityl-4-methylphenyl)arsine and its application to the synthesis of a stable phosphaarsene. We were also successful in EPR observation of the phosphaarsene radical anion for the first time.

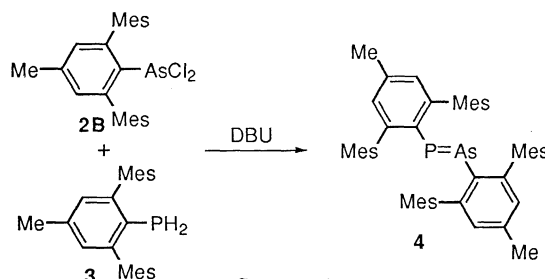
Dichlorophosphine **2A** and dichloroarsine **2B** carrying the 2,6-dimesityl-4-methylphenyl group were prepared as follows. 2,6-Dimesityl-4-methylphenyliodobenzene (**1**), which was prepared in moderate yield by the Hart reaction<sup>3</sup> of 2,6-dibromo-4-methyliodobenzene with the mesityl Grignard reagent followed by quenching with iodine, was lithiated with butyllithium in tetrahydrofuran at  $-78^{\circ}\text{C}$ . 2,6-Dimesityl-4-methylphenyllithium thus obtained was allowed to react with phosphorus trichloride to give **2A**<sup>5</sup> in quantitative yield. Although **2B** was obtained by addition of arsenic trichloride to the corresponding lithium reagent under the same conditions, it was contaminated with inseparable impurity, but the reaction in ether afforded **2B** as stable crystals almost quantitatively (Scheme 1).<sup>6</sup>



Scheme 1.

Reductive coupling between **2A** and **2B** in the presence of magnesium metal gave an orange mixture and the formation of bis(2,6-dimesityl-4-methylphenyl)diphosphene (**5**)<sup>7</sup> and bis(2,6-dimesityl-4-methylphenyl)phosphaarsene (**4**) was confirmed by

the  $^{31}\text{P}$  NMR signals at  $\delta = 492$  and 536, respectively. However, phosphaarsene **4** could not be separated from **5** by either chromatographic separation or recrystallization. On the other hand, the coupling between dichloroarsine **2B** and 2,6-dimesityl-4-methylphenylphosphine (**3**), which was prepared by the lithium aluminum hydride reduction of **2A**, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave phosphaarsene **4** as orange air-stable crystals in 23% yield (Scheme 2).<sup>8</sup>



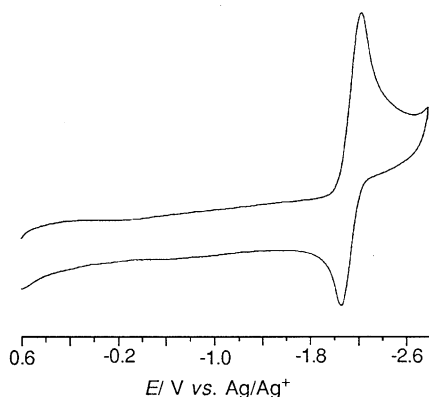
Scheme 2.

$^{31}\text{P}$  NMR chemical shift and UV-vis spectrum of **4** were in the range of known phosphaarsenes<sup>1,2,9</sup> and the structure was further confirmed by  $^{13}\text{C}$  NMR, MS, and elemental analysis. Taking extremely bulky 2,6-dimesityl-4-methylphenyl substituent on both phosphorus and arsenic atoms and the  $^{31}\text{P}$  NMR chemical shift into account it is suggested that **4** takes the *E*-form. However, attempted X-ray crystal analysis of **4**<sup>10</sup> failed due to disorder of the phosphorus and arsenic atoms.

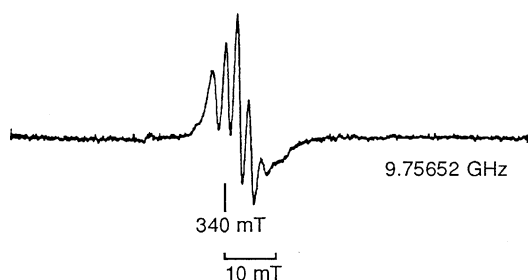
On the other hand, two different paths of photolysis are known for bis(2,4,6-tri-*t*-butylphenyl)diphosphene. One is *E/Z* isomerization by visible light irradiation at low temperature,<sup>11,12</sup> and the other is formation of phosphaindan derivative by UV irradiation.<sup>12</sup> However, attempted irradiation of **4** with a 500-W Xe lamp ( $\lambda > 490 \text{ nm}$  or  $\lambda > 300 \text{ nm}$ ) at  $-78^{\circ}\text{C}$  being monitored by  $^{31}\text{P}$  NMR resulted in neither *E/Z* isomerization nor decomposition of **4**. The reason for the inertness toward photolysis is not clear at present. Furthermore, irradiation of diphosphene **5** under the same condition as above also gave no  $^{31}\text{P}$  NMR signals due to the *Z* form or any other products. Steric bulkiness or other photochemical process of 2,6-dimesityl-4-methylphenyl moiety appears to cause low photo-reactivity.

Cyclic voltammogram of **4** (Figure 1) shows a quasi-reversible redox wave at  $-2.16 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$  which was the same value as the reduction potential of **5** ( $-2.16 \text{ V}$ ) and could be attributed to one electron reduction to the relatively unstable radical anion.

Formation of the radical anion was further confirmed by EPR study: *i. e.*, reduction of **4** by sodium or potassium mirror was monitored by X-band EPR. The color of a tetrahydrofuran solution of **4** changed from orange to brown after contact with sodium mirror and the EPR spectrum was observed as shown in Figure 2. The spectrum was regarded as a pseudo-sextet due to  $a_{\text{As}} = 2.3 \text{ mT}$  and  $a_{\text{P}} = 4.8 \text{ mT}$  at  $g = 2.027$ , which is consistent with the structure of phosphaarsene radical anion, and the line



**Figure 1.** Cyclic voltammogram of **4**. Solvent: tetrahydrofuran with 0.1 M  $n\text{-Bu}_4\text{NClO}_4$  as a supporting electrolyte. Working electrode, glassy carbon. Counter electrode, Pt wire. Reference electrode, Ag / 0.01 M  $\text{AgNO}_3$  / 0.1 M  $n\text{-Bu}_4\text{NClO}_4$  /  $\text{CH}_3\text{CN}$  ( $E_{1/2}(\text{Ferrocene} / \text{Ferricinium}) = 0.17$  V). Scan rate, 100 mV/sec.



**Figure 2.** EPR spectrum of  $4^{\bullet+}$  generated by the sodium metal reduction of **4** in tetrahydrofuran at 293 K.

shape would reflect the large anisotropy of hyperfine coupling typical of phosphorus centered radicals such as diphosphene radical anions.<sup>13</sup> The large  $g$  value implies a significant distribution of unpaired electron on the arsenic as well as the phosphorus atom. The spin density on the arsenic and phosphorus atoms was roughly estimated from the hyperfine coupling to be 35 and 65%, respectively, on the assumption that the ratio of spin density among  $s$  and  $p$  orbitals are the same for the arsenic and phosphorus atoms. On the other hand, reddish purple solution, obtained after reduction of **4** by potassium mirror, was EPR silent, probably due to the further reduction to the closed shell species such as  $4^{2-}$ .

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- 2A**:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.04 (12H, s), 2.34 (6H, s), 2.41 (3H, s), 6.92 (4H+2H, s);  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ )  $\delta$  = 161.2.
- 2B**:  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 2.02 (3H, s), 2.19 (12H, s), 2.23 (6H, s), 6.71 (2H, s), 6.89 (4H, s); MS (EI, 70 eV)  $m/z$  474 ( $\text{M}^+ + 2$ , 10%), 472 ( $\text{M}^+$ , 15), 326 ( $\text{M}^+ - \text{AsCl}_2 + 1$ , 100).
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- 4**: Orange needles (hexane-benzene), mp 206.0–208.0 °C (decomp.);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.69 (12H, s), 1.71 (12H, s), 2.27 (3H, s), 2.28 (3H, s), 2.30 (6H, s), 2.32 (6H, s), 6.70 (4H, br.s), 6.72 (4H, br.s), 6.75 (2H, br.d,  $J$  = 0.5 Hz), 6.76 (2H, br.d,  $J$  = 0.6 Hz);  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ )  $\delta$  = 537.0; UV-vis (hexane)  $\lambda$  (log  $\epsilon$ ) 267 (sh, 4.30), 327 (sh, 3.61), 385 (3.98), 463 (2.94) nm; MS (FAB)  $m/z$  761 ( $\text{M}^+ + 1$ , 84%), 760 ( $\text{M}^+$ , 100), 433 (39), 401 (40), 387 (55), 357 (31); Found: C, 78.63; H, 7.04%. Calcd for  $\text{C}_{50}\text{H}_{54}\text{AsP}$ : C, 78.93; H, 7.15%.
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- Crystal data of **4**: orthorhombic,  $P_{bcn}$ ,  $Z$  = 4,  $a$  = 21.970(4),  $b$  = 8.29(1),  $c$  = 23.329(5) Å,  $V$  = 4246(5) Å<sup>3</sup>.
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