

## Synthesis, Structure, and Redox Properties of the Extremely Crowded Triarylpnictogens: Tris(2,4,6-triisopropylphenyl)phosphine, Arsine, Stibine, and Bismuthine

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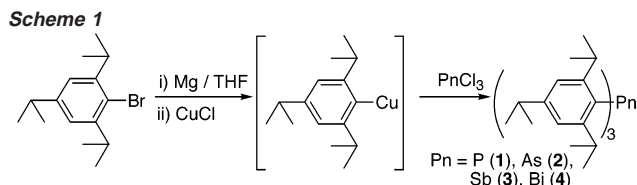
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Crowded triarylpnictogens such as trimesitylphosphine<sup>1,2</sup> and arsine<sup>3,4</sup> have large bond angles and lengths around the pnictogen atoms and are reversibly oxidized to the stable cation radicals at significantly low oxidation potentials due to both structural changes and steric protection by introduction of bulky aryl groups.<sup>5</sup> Recently, we synthesized aminophosphinobenzenes carrying the trimesitylphosphine structure as one of the redox sites.<sup>6</sup> However, the phosphorus redox center was not stable enough to afford a reversible two-step redox system. To construct more stable phosphorus redox center, we pursued the introduction of the more sterically demanding aryl groups on phosphorus, and herein we report the synthesis, structure, and redox properties of some of the most crowded triarylpnictogens, tris(2,4,6-triisopropylphenyl)phosphine (**1**), arsine (**2**), stibine (**3**), and bismuthine (**4**).

Since the reaction of 2,4,6-triisopropylphenylmagnesium bromide with phosphorus trichloride only afforded the corresponding tetraaryldiphosphane<sup>7</sup> unlike the mesityl Grignard reagent,<sup>6,8</sup> aryl copper(I) reagents, which are less reactive as a reducing agent and have been utilized to prepare chlorophosphines<sup>9</sup> and the crowded phosphine ligand,<sup>10</sup> were employed. Phosphine **1** was synthesized by the reaction of 2,4,6-triisopropylphenylcopper(I)<sup>11</sup> with phosphorus trichloride (0.30 equiv) at  $-78$  °C followed by refluxing for 24 h and isolated as colorless prisms (35%) after column chromatography ( $\text{Al}_2\text{O}_3/n$ -hexane) followed by recrystallization from *n*-hexane (Scheme 1).<sup>12</sup> Tris(2,4,6-triisopropylphenyl)arsine (**2**) (75%),<sup>13</sup> stibine (**3**) (58%),<sup>14</sup> and bismuthine (**4**) (3%),<sup>15</sup> were synthesized similarly. These crowded triarylpnictogens except for **4** were stable in air in the solid state.

The <sup>31</sup>P NMR (80 MHz,  $\text{CDCl}_3$ ) chemical shifts of the crowded tris(2,4,6-trialkylphenyl)phosphine showed an upfield shift as the substituents became more sterically demanding from triphenylphosphine ( $\delta$   $-6$ ), and trimesitylphosphine ( $\delta$   $-36$ ) to **1** ( $\delta$   $-53$ ). The <sup>1</sup>H NMR (200 MHz,  $\text{CDCl}_3$ ) and <sup>13</sup>C NMR (50 MHz,  $\text{CDCl}_3$ ) spectra of **1** at 295 K were rather simple and two *o*-CH( $\text{CH}_3$ )<sub>2</sub> protons and four aromatic carbons were observed. On the other hand, four *o*-CH( $\text{CH}_3$ )<sub>2</sub> protons and six aromatic carbons were observed for **2** and **3**. The molecular structures of **1**, **2**, and **3** were further investigated by X-ray crystallography.<sup>16</sup> The triarylpnictogens **1** (Figure 1), **2**, and **3** have a crowded propeller shape and the pnictogen atoms are covered with six ortho isopropyl groups.

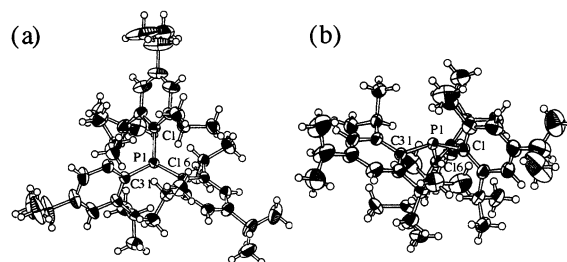
To compare the structure and properties of **1**, **2**, and **3**, with the related compounds, the average bond lengths and angles around pnictogen atoms, and oxidation potentials measured by cyclic voltammetry are summarized in Table 1. The bond lengths and angles become longer and larger as the ortho substituents of the aryl groups become more bulky in these series of compounds, and



**Table 1.** Average C–Pn Bond Lengths, C–Pn–C Bond Angles, and Oxidation Potentials of the Crowded Triarylphosphine, Arsine, Stibine, and Related Compounds.

compounds	bond lengths/Å	bond angles/deg	$E_{1/2}/\text{V}^a$
triphenylphosphine	1.828 <sup>b</sup>	103.0 <sup>b</sup>	1.03 <sup>c</sup>
trimesitylphosphine	1.837 <sup>d</sup>	109.7 <sup>d</sup>	0.41
<b>1</b>	1.845	111.5	0.16
triphenylarsine	1.949 <sup>e</sup>	99.8 <sup>e</sup>	1.18 <sup>c</sup>
trimesitylarsine	1.976 <sup>f</sup>	107.6 <sup>f</sup>	0.73
<b>2</b>	1.986	109.2	0.50
triphenylstibine	(2.141) <sup>g</sup>	(97.3) <sup>g</sup>	1.05 <sup>c</sup>
trimesitylstibine	2.183 <sup>h</sup>	105.3 <sup>h</sup>	0.76 <sup>c</sup>
<b>3</b>	2.197	106.7	0.57

<sup>a</sup> Reversible unless otherwise stated, V vs  $\text{Ag}/\text{Ag}^+$  in dichloromethane with 0.10 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>, scan rate: 30 mVs<sup>-1</sup>. <sup>b</sup> Reference 22. <sup>c</sup> Irreversible, peak potential. <sup>d</sup> Reference 1. <sup>e</sup> Reference 23. <sup>f</sup> Reference 3. <sup>g</sup> Tris(4-methylphenyl)stibine, ref 24. <sup>h</sup> Reference 25.



**Figure 1.** ORTEP drawing of tris(2,4,6-triisopropylphenyl)phosphine (**1**) with 50% thermal ellipsoids, (a) top view, (b) side view.

the tris(2,4,6-triisopropylphenyl)pnictogens have the longest bond length and largest bond angle for each element. Steric repulsion among the bulky substituents was revealed by elongation of the bond lengths and expansion of the bond angles around the pnictogen atoms. Similar trend was recently reported for trisilylphosphines with enhanced planarity around pnictogens.<sup>17</sup> The bond angles and length of **1** are slightly larger than those of tris(9-anthracenyl)phosphine<sup>18</sup> (1.839 Å, 110.4°), which is one of the most crowded triarylphosphines known to exist. The oxidation potentials of the triarylphosphines become lower as the molecules become more crowded since the energy level of the lone pair (HOMO) is raised by enhanced planarity of the pnictogen atoms induced by steric congestion<sup>5</sup> as well as the electron donation by the alkyl groups.

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The 2,4,6-triisopropylphenyl derivatives have the lowest potentials, especially, that of **1** was comparable to ferrocene. The dichloromethane solution of the phosphine **1** and arsine **2** can be oxidized by silver perchlorate and afforded a purple ( $\lambda_{\max} = 528$  and 516 nm for **1**<sup>+</sup> and **2**<sup>+</sup>, respectively) solution of the corresponding cation radical, which were also characterized by the EPR parameters<sup>19</sup> similar to those of the trimesityl derivatives.<sup>3,5</sup> A similar reaction of trimesitylphosphine was reported to lead to the metal complex formation.<sup>20</sup> Although **1** and **2** were inert to hydrogen peroxide or elemental sulfur, **1**<sup>+</sup> and **2**<sup>+</sup> reacted slowly with oxygen to result in incorporation of oxygen. Interestingly, not only **1** and **2**, but also stibine **3** displayed a reversible redox wave with the ratio of anodic and cathodic peaks as unity at the 30 mVs<sup>-1</sup> scanning rate at 293 K, which suggests considerable stability of the corresponding cation radical.<sup>21</sup> A detailed study of the cation radicals and application of these structures to the multistep redox systems is in progress.

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**Supporting Information Available:** Experimental procedures and spectroscopic data of **1**, **2**, **3**, and **4**, EPR spectra of **1**<sup>+</sup>, **2**<sup>+</sup>, and **3**<sup>+</sup> (PDF), and crystallographic data for **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- 1**: colorless prisms, mp 165–166 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  6.88 (6H, d,  $J = 3.12$  Hz), 3.48 (6H, m,  $J = 6.70, 5.43$  Hz), 2.82 (3H, sept,  $J = 6.89$  Hz), 1.21 (18H, d,  $J = 6.90$  Hz), 1.14 (18H, d,  $J = 6.70$  Hz), 0.66 (18H, d,  $J = 6.65$  Hz); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  152.89 (d,  $J = 18.02$  Hz), 148.99 (s), 132.20 (d,  $J = 24.01$  Hz), 121.85 (d,  $J = 4.56$  Hz), 34.04 (s), 31.92 (d,  $J = 17.98$  Hz), 24.52 (s), 23.94 (s), 23.00 (s); <sup>31</sup>P NMR (80 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  -52.4 (s).
- 2**: colorless prisms, mp 145–146 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  6.90 (6H, s), 3.39 (3H, sept,  $J = 6.71$  Hz), 3.32 (3H, sept,  $J = 6.72$  Hz), 2.83 (3H, sept,  $J = 6.69$  Hz), 1.26 (9H, d,  $J = 6.68$  Hz), 1.21 (18H, d,  $J = 6.91$  Hz), 1.07 (9H, d,  $J = 6.79$  Hz), 1.01 (9H, d,  $J = 6.74$  Hz), 0.45 (9H, d,  $J = 6.57$  Hz); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 293 K)  $\delta$  153.08, 152.83, 148.70, 136.36, 122.76, 120.86, 34.01, 33.43, 32.67, 25.37, 24.22, 24.02, 24.00, 23.91, 22.78.
- 3**: colorless prisms, mp 145–146 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 294 K)  $\delta$  6.93 (6H, s), 3.32 (6H, sept,  $J = 6.46$  Hz), 2.84 (3H, sept,  $J = 7.04$  Hz), 1.32 (9H, d,  $J = 6.54$  Hz), 1.22 (18H, d,  $J = 6.99$  Hz), 1.08 (18H, m), 0.49 (9H, d,  $J = 6.32$  Hz); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 294 K)  $\delta$  154.85, 154.78, 148.92, 137.70, 122.52, 120.97, 36.81, 35.97, 34.02, 25.92, 24.85, 24.44, 24.03, 23.91, 23.26.
- 4**: colorless prisms, mp 149–150 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 330 K)  $\delta$  7.09 (6H, s), 3.18 (6H, sept,  $J = 6.46$  Hz), 2.84 (3H, sept,  $J = 6.85$  Hz), 1.24 (18H, d,  $J = 6.90$  Hz), 1.03 (36H, brs); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 330 K)  $\delta$  159.36, 155.92, 148.44, 122.54, 39.54, 34.17, 24.97, 24.00.
- 1**: C<sub>45</sub>H<sub>69</sub>P,  $M = 641.01$ , colorless prism, 0.75 × 0.75 × 0.40 mm<sup>3</sup>, triclinic,  $P\bar{1}$  (no. 2),  $a = 11.492(2)$  Å,  $b = 18.212(7)$  Å,  $c = 10.496(2)$  Å,  $\alpha = 100.96(2)^\circ$ ,  $\beta = 91.82(1)^\circ$ ,  $\gamma = 96.24(2)^\circ$ ,  $V = 2140.8(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 0.994$  gcm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.091$  mm<sup>-1</sup>,  $T = 200$  K,  $R_1; R_w = 0.081; 0.084$ ; 0.166, GOF = 1.66. **2**: C<sub>45</sub>H<sub>69</sub>As,  $M = 684.94$ , colorless prism, 0.55 × 0.25 × 0.15 mm<sup>3</sup>, triclinic,  $P\bar{1}$  (no. 2),  $a = 17.686(2)$  Å,  $b = 18.44(1)$  Å,  $c = 14.890(2)$  Å,  $\alpha = 99.54(1)^\circ$ ,  $\beta = 110.68(1)^\circ$ ,  $\gamma = 107.37(2)^\circ$ ,  $V = 4130(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.101$  gcm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.850$  mm<sup>-1</sup>,  $T = 123$  K,  $R_1; R_w = 0.047; 0.066; 0.064$ , GOF = 1.65. **3**: C<sub>45</sub>H<sub>69</sub>Sb,  $M = 731.79$ , colorless prism, 0.25 × 0.20 × 0.20 mm<sup>3</sup>, monoclinic,  $P2_1/c$  (no. 14),  $a = 19.757(2)$  Å,  $b = 18.344(2)$  Å,  $c = 24.842(4)$  Å,  $\beta = 111.049(3)^\circ$ ,  $V = 8402(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calc}} = 1.157$  gcm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.683$  mm<sup>-1</sup>,  $T = 115$  K,  $R_1; R_w = 0.034; 0.041; 0.048$ , GOF = 1.34.
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- 1**<sup>+</sup>:  $g = 2.007$ ,  $a(\text{P}) = 23.7$  mT;  $g_{\parallel} = 2.002$ ,  $a_{\parallel} = 41.7$  mT,  $g_{\perp} = 2.009$ ,  $a_{\perp} = 13.0$  mT. **2**<sup>+</sup>:  $g = 2.042$ ,  $a(\text{As}) = 26.4$  mT;  $g_{\parallel} = 2.002$ ,  $a_{\parallel} = 48.3$  mT,  $g_{\perp} = 2.020$ ,  $a_{\perp} = 19.5$  mT.
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