

# Homologous Series of Heavier Element Dipnictenes 2,6-Ar<sub>2</sub>H<sub>3</sub>C<sub>6</sub>E=EC<sub>6</sub>H<sub>3</sub>-2,6-Ar<sub>2</sub> (E = P, As, Sb, Bi; Ar = Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>; or Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Pr<sub>3</sub>) Stabilized by *m*-Terphenyl Ligands

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**Abstract:** The synthesis and characterization of several *m*-terphenyl heavier main group 15 (P, As, Sb, or Bi) dihalides, together with their reduction to give a homologous series of double-bonded dipnictenes, are reported. Reaction of LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) or LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Pr<sub>3</sub>) with the appropriate trihalide affords 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>ECl<sub>2</sub> (E = As, **1**; Sb, **2**; Bi, **3**) and 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>ECl<sub>2</sub> (E = P, **4**; As, **5**; Sb, **6**; Bi, **7**). The compounds **1–7** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as by <sup>31</sup>P NMR spectroscopy in the case of **4**. In addition, the structures of **3**, **5**, and **6** were determined. Reduction of the phosphorus species **4** with potassium in hexane gives a mixture of the diphosphene 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P=PC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, **12**, and the phosphafluorene species, 1-(2,4,6-triisopropylphenyl)-5,7-diisopropyl-9-phosphafluorene, **11**. The compound **11**, which results from the insertion of a phosphorus into a C(Ar)–C(*i*-Pr) bond was synthesized in higher yield by the reduction of **4** with magnesium. The simple reduction of **1–4**, **6**, and **7** with potassium, and of **5** with magnesium, yielded the new series of dipnictenes, 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>E=EC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (E = As, **8**; Sb, **9**; Bi, **10**) and 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>E=EC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (E = P, **12**; As, **13**; Sb, **14a**; Bi, **15**), as well as the partially reduced species 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>(Cl)SbSb(Cl)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (**14b**). The compounds, which displayed high thermal stability, were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR and UV–vis spectroscopy. The structures of **8–11**, **13**, **14a**, and **14b** were determined. These compounds constitute the first homologous series of dipnictene structures for all the heavier group 15 elements. The E–E bond shortenings observed for the heaviest antimony or bismuth derivatives lead to the conclusion that  $\pi$  overlap is quite important in the fifth- and sixth-period elements of this group.

## Introduction

The first stable diphosphene that featured an unsupported phosphorus–phosphorus double bond was reported in 1981 by Yoshifuji and co-workers.<sup>1</sup> This compound, Mes\*P=PMes\* (Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Bu<sub>3</sub>), represented a significant landmark in the study of multiple bonding in the heavier main group elements. In the ensuing period, structural data for approximately 20 organo diphosphenes have been published.<sup>2</sup> In addition, there are numerous examples of metalodiphosphenes, in which the organic group at phosphorus is replaced by a transition-metal moiety.<sup>3</sup> Also, there are several related complexes in which an organosubstituted diphosphene with an unsupported phosphorus–phosphorus bond behaves as an end-on, lone-pair electron donor through one or both phosphorus atoms to a transition-metal fragment.<sup>4</sup> In contrast, there are only two published structures of diarsenes,<sup>5</sup> i.e., those of Mes\*AsAsCH(SiMe<sub>3</sub>)<sub>2</sub><sup>5a</sup> and [As{C(SiMe<sub>3</sub>)<sub>3</sub>}]<sub>2</sub> by Cowley and co-workers.<sup>5c</sup> Similarly, there exists just a handful of structurally characterized unsymmetrical species featuring P=As double bonds,<sup>6</sup> e.g., Mes\*PAsCH(SiMe<sub>3</sub>)<sub>2</sub><sup>6a</sup> and  $\{(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\}\{(\text{CO})_5\text{Cr}\}\text{AsPMes}^*$ .<sup>6c</sup> Until

recently, stable-multiple-bonding character in the heaviest elements, antimony and bismuth, was represented only by a few

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transition-metal complexes<sup>7,8</sup> such as {RSb}<sub>2</sub>{W(CO)<sub>5</sub>}<sub>3</sub> (R = 'Bu, Me, Ph)<sup>7a</sup> or {Bi}<sub>2</sub>{W(CO)<sub>5</sub>}<sub>3</sub>,<sup>8a</sup> in which the multiple bond was supported by metal bridging. Apart from the above-mentioned phospharsenes, compounds having double bonding between two different heavier pnictogens were confined to two-solution species featuring phosphorus–antimony double bonds,<sup>2k,6a,9</sup> i.e., Mes\*P=SbCH(SiMe<sub>3</sub>)<sub>2</sub> and Mes\*P=SbN-(SiMe<sub>2</sub>Bu)<sub>2</sub>, which, however, decomposed at room temperature. Nonetheless, Okazaki, Tokitoh, and co-workers have shown that stable examples of distibenes and dibismuthenes with unsupported Sb=Sb or Bi=Bi double bonds can be isolated by using the very crowding -C<sub>6</sub>H<sub>2</sub>-2,4,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub> ligand. A synthetic route which involves deselenation of the six-membered [E(Se)(C<sub>6</sub>H<sub>2</sub>-2,4,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>)]<sub>3</sub> (E = Sb or Bi) precursor was used to isolate these species.<sup>10</sup> Parallel work has demon-

strated that bulky *m*-terphenyl ligands, e.g., -C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>, could be used to stabilize diphosphene derivatives,<sup>11</sup> and recently it has been shown that related *m*-terphenyl ligands can effect the stabilization of unsymmetric dipnictenes such as 2,6-Mes<sub>2</sub>-4-MeH<sub>2</sub>C<sub>6</sub>P=AsC<sub>6</sub>H<sub>2</sub>-2,6-Mes<sub>2</sub>-4-Me<sup>6h</sup> and MesP=EC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, (E = As or Sb; Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>).<sup>12</sup> It is now shown that this type of ligand is generally applicable to the stabilization of the first complete homologous series of double bonds involving all the heavier group 15 elements. Moreover, it is shown that such compounds are accessible in acceptable yields by the simple and straightforward direct reduction of their halide precursors.

## Experimental Section

**General Procedures.** All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N<sub>2</sub> or in a Vacuum Atmospheres HE 553 drybox. All solvents were distilled from a Na/K alloy and degassed twice immediately before use. The compounds LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>,<sup>13a</sup> Et<sub>2</sub>O·LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>,<sup>13b</sup> and KC<sub>8</sub><sup>14</sup> were prepared according to literature procedures. Commercial AsCl<sub>3</sub> and SbCl<sub>3</sub> were distilled before use, and commercial anhydrous BiCl<sub>3</sub> was used as received. <sup>1</sup>H and <sup>13</sup>C NMR data were recorded on a GE 300 MHz instrument and referenced to the deuterated solvent (C<sub>6</sub>D<sub>6</sub>). Infrared spectral data were recorded on a Perkin-Elmer PE-1430 instrument. UV-vis spectral data were recorded on a Hitachi U 2000 instrument.

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>AsCl<sub>2</sub> (1).** A solution of LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (2.30 g, 7.20 mmol) in pentane/Et<sub>2</sub>O (2:1, 60 mL) was added dropwise (10 min) to a stirred solution of AsCl<sub>3</sub> (1.30 g, 7.20 mmol, freshly distilled) in pentane/Et<sub>2</sub>O (2:1, 30 mL) with cooling to ca. -78 °C. The low temperature was maintained for 2 h, and the mixture was allowed to come to room temperature overnight. The solvent was removed under reduced pressure, and the residue was extracted with C<sub>6</sub>H<sub>6</sub> (2 × 100 mL) and filtered (Celite). The solvent was concentrated to approximately 40 mL and reheated to redissolve any precipitate. Cooling to room temperature afforded colorless crystals of **1**. The supernatant liquid was separated, and its volume was reduced further to incipient crystallization; combined yield 1.89 g, 57%; Mp: 206–208 °C; IR  $\nu_{(\text{As-Cl})}$  380, 370 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.10 (s, 12H, *o*-CH<sub>3</sub>), 2.14 (s, 6H, *p*-CH<sub>3</sub>), 6.79 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6.80 (s, 4H, *m*-Mes), 7.09 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.18 (*p*-CH<sub>3</sub>), 21.51 (*o*-CH<sub>3</sub>), 128.61 (*m*-Mes), 130.70 (*m*-C<sub>6</sub>H<sub>3</sub>), 132.53 (*p*-C<sub>6</sub>H<sub>3</sub>), 135.41 (*p*-Mes), 136.89 (*o*-Mes), 138.21 (*i*-Mes), 146.71 (*o*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>SbCl<sub>2</sub> (2).** A solution of LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (2.55 g, 7.96 mmol) in hexane/Et<sub>2</sub>O (1:1, 60 mL) was added dropwise (15 min) to a stirred suspension of SbCl<sub>3</sub> (1.82 g, 7.96 mmol) in hexane/Et<sub>2</sub>O (1:1, 20 mL) at -78 °C. The reaction mixture was kept at ca. -78 °C (3 h) before it was allowed to come to room temperature, whereupon it was stirred for a further 2.5 d. The solvent was then removed under reduced pressure, and the residue was extracted with hexane (60 mL). Filtration at 60 °C through Celite afforded a pale yellow solution. The solvent volume was reduced slightly to incipient crystallization and was cooled to afford the product **2** as pale yellow crystals: 1.72 g, 43%; mp: 163–165 °C; IR  $\nu_{(\text{Sb-Cl})}$  340, 320 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.09 (s, 12H, *o*-CH<sub>3</sub>), 2.14 (s, 6H, *p*-CH<sub>3</sub>), 6.79 (s, 4H, *m*-Mes), 6.87 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 7.13 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.8 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.19 (*p*-CH<sub>3</sub>), 21.51 (*o*-CH<sub>3</sub>), 128.82

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(*m*-Mes), 130.37 (*m*-C<sub>6</sub>H<sub>3</sub>), 131.98 (*p*-C<sub>6</sub>H<sub>3</sub>), 136.39 (*p*-Mes), 137.14 (*o*-Mes), 138.43 (*i*-Mes), 148.52 (*o*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>BiCl<sub>2</sub> (3).** A solution of LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (2.30 g, 7.20 mmol) in toluene/Et<sub>2</sub>O (1:1, 60 mL) was added dropwise (15 min) to a stirred suspension of BiCl<sub>3</sub> (2.26 g, 7.20 mmol) in toluene/Et<sub>2</sub>O (1:1, 50 mL) at -78 °C. The reaction mixture was kept at ca. -78 °C for 2 h before it was allowed to come to room temperature and stirred overnight. The solvent was then removed under reduced pressure, and the residue was extracted with hot (70 °C) benzene (70 mL) and filtered (Celite) to give a pale yellow solution. The solvent volume was reduced slightly, and cooling at ca. 6 °C overnight yielded pale yellow X-ray diffraction quality crystals of **3**: 2.79 g, 65%; mp 220–224 °C; IR  $\nu_{(\text{Bi-Cl})}$  280, 240 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.13 (s, 12H, *o*-CH<sub>3</sub>), 2.14 (s, 6H, *p*-CH<sub>3</sub>), 6.80 (s, 4H, *m*-Mes), 7.23 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 7.42 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.8 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.17 (*p*-CH<sub>3</sub>), 21.46 (*o*-CH<sub>3</sub>), 128.92 (*m*-Mes), 130.30 (*p*-C<sub>6</sub>H<sub>3</sub>), 135.06 (*m*-C<sub>6</sub>H<sub>3</sub>), 136.13 (*p*-Mes), 137.35 (*o*-Mes), 138.54 (*i*-Mes), 150.13 (*o*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>PcCl<sub>2</sub> (4).** A solution of Et<sub>2</sub>O·LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.00 g, 3.55 mmol) in hexane (50 mL) was added dropwise (15 min) to a stirred solution of freshly distilled PCl<sub>3</sub> (488 mg, 3.55 mmol) in hexane (30 mL) at -78 °C. The mixture was stirred (1 h) and gradually allowed to come to room temperature overnight. The supernatant liquid was filtered (60 °C, Celite), and the solution was concentrated (approximately 40 mL) before cooling in a -20 °C freezer for 20 h. Colorless crystals of **4** were obtained: yield 1.55 g, 75%; mp sweats at 239 °C and melts from 245 to 247 °C; IR  $\nu_{(\text{P-Cl})}$  480, 442 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.08 (d, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.25 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.38 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 2.83 (septet, 6H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 7.04 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.11 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) *J* = 7.35 Hz, 7.2 (s, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  22.64 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.10 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 25.68 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 31.09 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 34.23 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 120.49 (*m*-Trip), 130.57 (*p*-C<sub>6</sub>H<sub>3</sub>), 131.69 (*m*-C<sub>6</sub>H<sub>3</sub>), 133.66 (*J* = 8.3 Hz (*i*-C<sub>6</sub>H<sub>3</sub>), 136.15 (*i*-Trip), 145.09 (*p*-Trip), 146.69 (*o*-Trip), 148.99 (*o*-C<sub>6</sub>H<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  156.47 (referenced to H<sub>3</sub>PO<sub>4</sub>).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>AsCl<sub>2</sub> (5).** A solution of Et<sub>2</sub>O·LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.00 g, 3.55 mmol) in hexane/Et<sub>2</sub>O (2:1, 40 mL) was added dropwise (15 min) to a stirred solution of freshly distilled AsCl<sub>3</sub> (644 mg, 3.55 mmol) in hexane/Et<sub>2</sub>O (2:1, 20 mL) with cooling in a dry ice/acetone bath at ca. -78 °C. Immediate precipitation of LiCl occurred. After the addition, the mixture was kept at -78 °C (3 h) and stirred overnight with gradual warming to room temperature. The solvent was removed under reduced pressure, and the residue was extracted with hexane (3 × 100 mL), heated to 60 °C, and filtered through Celite to give a clear colorless solution. The volume was reduced slightly and upon cooling in a ca. -20 °C freezer, **5** was obtained as X-ray diffraction quality colorless crystals. The supernatant liquid was isolated, and the volume was reduced to incipient crystallization: combined yield 1.65 g, 74%; mp sweats at 241 °C, melts at 259–260 °C; IR  $\nu_{(\text{As-Cl})}$  380, 360 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.07 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.25 (d, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.38 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.84 (septet, 2H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.897 (septet, 4H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 7.14–7.16 (m, 3H, *p*-C<sub>6</sub>H<sub>3</sub>, *m*-C<sub>6</sub>H<sub>3</sub>) 7.198 (s, 4H, *m*-Trip); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  23.01 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.27 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 25.94 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 31.49 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 34.77 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 121.06 (*m*-Trip), 130.25 (*p*-C<sub>6</sub>H<sub>3</sub>), 132.11 (*m*-C<sub>6</sub>H<sub>3</sub>), 133.40 (*i*-Trip), 142.89 (*i*-C<sub>6</sub>H<sub>3</sub>), 145.25 (*p*-Trip), 147.73 (*o*-Trip), 150.14 (*o*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>SbCl<sub>2</sub> (6).** Compound **6** was synthesized using the same procedure outlined above for **2**. A solution of Et<sub>2</sub>O·LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.00 g, 3.55 mmol) in hexane/Et<sub>2</sub>O (2:1, 40 mL) was added dropwise (15 min) to a stirred solution of freshly distilled SbCl<sub>3</sub> (0.81 g, 3.55 mmol) in hexane/Et<sub>2</sub>O (2:1, 20 mL) with cooling in a dry ice/acetone bath at ca. -78 °C. After workup, colorless crystalline X-ray diffraction quality **6** was obtained in a combined yield of 1.68 g, 70%; mp 255–259 °C; IR  $\nu_{(\text{Sb-Cl})}$  345, 330 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.06 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1.25 (d, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.37 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 2.83 (septet, 2H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.94 (septet, 4H,

*o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 7.11 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 7.19 (s, 4H, *m*-Trip), 7.23 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  23.07 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.27 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 26.06 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 31.32 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 34.81 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 121.25 (*m*-Trip), 129.69 (*p*-C<sub>6</sub>H<sub>3</sub>), 131.84 (*m*-C<sub>6</sub>H<sub>3</sub>), 134.51 (*i*-Trip), 146.97 (*p*-Trip), 147.98 (*o*-Trip), 150.46 (*o*-C<sub>6</sub>H<sub>3</sub>), 152.95 (*i*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>BiCl<sub>2</sub> (7).** A solution of Et<sub>2</sub>O·LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.00 g, 3.55 mmol) in Et<sub>2</sub>O (40 mL) was added dropwise (10 min) to a stirred suspension of BiCl<sub>3</sub> (1.12 g, 3.55 mmol) in Et<sub>2</sub>O (30 mL) at ca. -78 °C. The mixture was stirred at ca. -78 °C (1 h) before the solution was allowed to come to room temperature. The solvent was then removed under reduced pressure, and the residue was extracted with toluene (60 mL) and filtered (Celite) to give a clear yellow solution. Reduction of the solvent to ca. 20 mL and cooling in a ca. -20 °C freezer overnight yielded **7** as X-ray quality pale yellow crystals: combined yield 1.91 g, 71%; mp 255–257 °C; IR  $\nu_{(\text{Bi-Cl})}$  310, 295 s, br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.05 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1.25 (d, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1.38 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.83 (septet, 2H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.99 (septet, 4H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 7.21 (s, 4H, *m*-Trip), 7.22 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 7.77 (d, 2H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  22.76 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 23.62 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 25.59 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 30.66 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 34.22 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 120.83 (*m*-Trip), 128.32 (*p*-C<sub>6</sub>H<sub>3</sub>), 133.83 (*i*-Trip), 136.15 (*m*-C<sub>6</sub>H<sub>3</sub>), 147.75 (*o*-Trip), 148.14 (*p*-Trip), 150.01 (*o*-C<sub>6</sub>H<sub>3</sub>), 214.63 (*i*-C<sub>6</sub>H<sub>3</sub>).

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>As=AsC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (8).** A solution of **1** (1.50 g, 3.27 mmol) in hexane (50 mL) was added dropwise (15 min) to a stirred suspension of finely divided potassium (260 mg, 6.53 mmol) in hexane (20 mL) at room temperature. An immediate reaction was observed, and the solution became a pale yellow color. Stirring overnight afforded a deep orange solution with some unreacted potassium. The solution was filtered (medium frit), and the solvent was concentrated to ca. 20 mL. Cooling in a ca. -20 °C freezer overnight yielded X-ray diffraction quality yellow crystals of **8**: yield 0.365 g, 30%; mp 181–186 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.92 (s, 24H, *o*-CH<sub>3</sub>), 2.23 (s, 12H, *p*-CH<sub>3</sub>), 6.74 (s, 8H, *m*-Mes), 6.89 (d, 4H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 7.08 (t, 2H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.17 (*p*-CH<sub>3</sub>), 21.28 (*o*-CH<sub>3</sub>), 128.62 (*m*-Mes), 129.34 (*m*-C<sub>6</sub>H<sub>3</sub>), 130.40 (*p*-C<sub>6</sub>H<sub>3</sub>), 135.64 (*o*-Mes), 136.49 (*p*-Mes), 139.60 (*i*-Mes), 144.97 (*o*-C<sub>6</sub>H<sub>3</sub>); UV-vis (benzene) 462 nm (650), 400 nm (6970).

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Sb=SbC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (9).** A solution of **2** (1.50 g, 2.96 mmol) in pentane (90 mL) was added to a stirred suspension of finely divided potassium (232 mg, 5.93 mmol) in pentane (10 mL). The supernatant liquid developed a dark orange-red color, and a green precipitate appeared. The mixture was stirred (3 d) and the solvent was removed under reduced pressure. The green residue was extracted with C<sub>6</sub>H<sub>6</sub> (100 mL) and filtered at ca. 60 °C through Celite. The resulting dark orange-red solution was concentrated (approximately 40 mL), and on standing overnight at room temperature, X-ray diffraction quality orange crystals of the product **9** were obtained: yield 0.340 g, 26%; mp sweats at 170 °C and melts at 200–210 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.02 (s, 24H, *o*-CH<sub>3</sub>), 2.23 (s, 12H, *p*-CH<sub>3</sub>), 6.74 (s, 8H, *m*-Mes), 6.97 (d, 4H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 7.10 (t, 2H, *p*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  21.34 (*p*-CH<sub>3</sub>), 21.67 (*o*-CH<sub>3</sub>), 127.86 (*p*-C<sub>6</sub>H<sub>3</sub>), 128.27 (*m*-C<sub>6</sub>H<sub>3</sub>), 128.81 (*m*-Mes), 135.46 (*o*-Mes), 136.59 (*p*-Mes), 141.35 (*i*-Mes), 148.36 (*o*-C<sub>6</sub>H<sub>3</sub>); UV-vis (benzene) 451 nm (5450).

**2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Bi=BiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> (10).** A solution of **3** (1.00 g, 1.77 mmol) in toluene/hexane (3:1, 60 mL) was added dropwise (10 min) to a stirred suspension of finely divided potassium (150 mg, 3.54 mmol) in toluene/hexane (3:1, 10 mL) at ca. -78 °C. The mixture was kept at ca. -78 °C for 6 h before gradual warming to room temperature overnight, during which time the supernatant liquid developed a deep purple color. The mixture was stirred for a further 3 d, and the solvent was removed under reduced pressure. The residue was extracted with C<sub>6</sub>H<sub>6</sub> (60 mL), filtered (fine frit), and concentrated to ca. 20 mL. On standing at room temperature for 0.5 h, red crystals of the product **10** were obtained: yield 0.280 g, 30%; mp darkens at 100 °C and melts at 215–219 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.11 (s, 24H, *o*-CH<sub>3</sub>), 2.29 (s, 12H, *p*-CH<sub>3</sub>), 6.77 (s, 8H, *m*-Mes), 6.92 (t,

2H,  $p\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz, 7.13 (d, 4H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz;  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.198 ( $p\text{-CH}_3$ ), 22.58 ( $o\text{-CH}_3$ ), 126.396 ( $m\text{-C}_6\text{H}_3$ ), 128.306 ( $p\text{-C}_6\text{H}_3$ ), 129.09 ( $m\text{-Mes}$ ), 135.79 ( $o\text{-Mes}$ ), 136.62 ( $p\text{-Mes}$ ), 144.65 ( $i\text{-Mes}$ ), 153.24 ( $o\text{-C}_6\text{H}_3$ ); UV-vis (benzene) 970 nm (27), 505 nm (5012).

**1-(2,4,6-Triisopropylphenyl)-5,7,9-triisopropyl-9-phosphafluorene (11).** THF (50 mL) was added to a mixture of **4** (1.00 g, 1.71 mmol) and Mg (42 mg, 1.71 mmol). There was no apparent reaction, and the solution remained colorless. The mixture was stirred (24 h) during which time it became a bright golden yellow color. After further stirring (12 h) the solution lightened to pale yellow. The solvent was removed under reduced pressure, and the residue was extracted with hexane (60 mL) and filtered (Celite). The solution was concentrated to ca. 15 mL before cooling in a ca.  $-20$  °C freezer. Colorless X-ray diffraction quality crystals of **11** were obtained after 2 d: yield 0.600 g, 68%; mp sweats at 132 °C and melts at 149–152 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.25 (t, 2H,  $\text{PCH}(\text{CH}_3)_2$ ,  $J = 6.6$  Hz), 0.92–1.52 (m, 30H,  $\text{CH}(\text{CH}_3)_2$ ), 1.78 (m, 1H,  $\text{PCH}(\text{CH}_3)_2$ ,  $J_{\text{HH}} = 7$  Hz,  $J_{\text{HP}} = 2.2$  Hz), 2.57 (septet, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 2.696 (septet, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.01 (septet, 2H,  $o\text{-Trip}$   $\text{CH}(\text{CH}_3)_2$ ), 4.07 (septet, 1H,  $o\text{-CH}(\text{CH}_3)_2$ ), 7.10 (d, 1H, H8  $J_{\text{HP}} = 1.8$  Hz), 7.16 (s, 2H,  $m\text{-Trip}$ ), 7.33 (d, 1H, H6  $J_{\text{HP}} = 1.5$  Hz), 7.38 (dd, 1H, H2,  $J = 5.7$ , 1.8 Hz), 7.50 (t, 1H, H3,  $J_{\text{HH}} = 7.5$  Hz), 8.16 (d, 1H, H4,  $J_{\text{HH}} = 8.4$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -3.08.

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P=PC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (12).** A solution of **4** (470 mg, 0.81 mmol) in hexane (50 mL) was added to freshly divided potassium (63 mg, 1.60 mmol). The initially colorless solution rapidly developed a yellow color. The mixture was stirred for 12 h, during which time the color deepened to brown. The supernatant liquid was filtered (fine frit), and the solvent was removed to afford a deep orange residue. NMR analysis of this product showed it to be a mixture of **12** and **11**. The crude product was chromatographed ( $\text{SiO}_2$ , hexane,  $\text{N}_2$  atm), yielding **12** with trace amounts of **11**: yield ca. 0.09 g, 20%; mp sweats at 128 °C and melts at 160–165 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.21 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.36 (d, 24H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6$  Hz, 1.59 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 3.00 (m, 6H,  $o,p\text{-CH}(\text{CH}_3)_2$ ), 3.14 (m, 6H,  $o,p\text{-CH}(\text{CH}_3)_2$ ), 7.34 (s, 8H,  $m\text{-Trip}$ ), 7.44 (d, 4H,  $m\text{-C}_6\text{H}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  23.85 ( $o\text{-CH}(\text{CH}_3)_2$ ), 24.35 ( $p\text{-CH}(\text{CH}_3)_2$ ), 25.68 ( $o\text{-CH}(\text{CH}_3)_2$ ), 31.20 ( $o\text{-CH}(\text{CH}_3)_2$ ), 34.61 ( $p\text{-CH}(\text{CH}_3)_2$ ), 121.54 ( $m\text{-Trip}$ ), 129.07 ( $p\text{-C}_6\text{H}_3$ ), 131.29 ( $m\text{-C}_6\text{H}_3$ ), 137.93 ( $i\text{-Trip}$ ), 144.17 ( $p\text{-Trip}$ ), 146.41 ( $o\text{-Trip}$ ), 148.27 ( $o\text{-C}_6\text{H}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  521.36 (referenced to  $\text{H}_3\text{PO}_4$ ); UV-vis (benzene) 502 nm (570), 393 nm (7270).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>As=AsC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (13).** A mixture of **5** (1.00 g, 1.59 mmol) and magnesium (40 mg, 1.59 mmol) were stirred (2.5 d) in THF (40 mL). The initially colorless solution became deep orange, and all the magnesium was consumed. The solvent was removed under reduced pressure, and the residue was extracted with hexane (60 mL), stirred overnight, and filtered (Celite). The deep orange solution was reduced in volume to ca. 30 mL, and cooling in a  $-20$  °C freezer for several days afforded **13** as X-ray diffraction quality orange crystals: combined yield 0.706 g, 80%; mp 256–260 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.99 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.07 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.32 (d, 24H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 2.79–2.91 (m, 12H,  $o,p\text{-CH}(\text{CH}_3)_2$ ), 6.99–7.02 (m, 6H,  $p\text{-C}_6\text{H}_3$ ,  $m\text{-C}_6\text{H}_3$ ) 7.09 (s, 8H,  $m\text{-Trip}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ) 24.12 ( $o\text{-CH}(\text{CH}_3)_2$ ), 24.32 ( $o\text{-CH}(\text{CH}_3)_2$ ), 25.88 ( $p\text{-CH}(\text{CH}_3)_2$ ), 31.18 ( $o\text{-CH}(\text{CH}_3)_2$ ), 34.55 ( $p\text{-CH}(\text{CH}_3)_2$ ), 121.66 ( $m\text{-Trip}$ ), 127.79 ( $p\text{-C}_6\text{H}_3$ ), 131.07 ( $m\text{-C}_6\text{H}_3$ ), 138.33 ( $i\text{-Trip}$ ), 144.87 ( $p\text{-Trip}$ ), 146.17 ( $o\text{-Trip}$ ), 148.27 ( $o\text{-C}_6\text{H}_3$ ), 151.91 ( $i\text{-C}_6\text{H}_3$ ); UV-vis (hexane) 504 nm (570), 409 nm (4060).

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Sb=SbC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (14a).** Method a. A solution of **6** (0.40 g, 0.59 mmol) in THF (40 mL) was added dropwise (10 min) to a stirred slurry of  $\text{KCl}_3$  (0.16 g, 1.19 mmol) in THF (30 mL) at ca.  $-78$  °C. The solution turned a yellow color immediately. The mixture was stirred at ca.  $-78$  °C for 1.5 h, during which time the solution became orange. After gradual warming to room temperature, the mixture was stirred a further 3.5 d. Filtration, followed by concentration of the orange solution to ca. 30 mL and cooling to ca.  $-25$  °C (2 weeks), gave a mixture of orange and colorless crystals. The orange crystalline product was shown to be a mixture of **14a** (80–

90%) and **2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>(Cl)Sb-Sb(Cl)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, **14b**, by X-ray crystallography. Method b. A solution of **6** (2.40 g, 3.56 mmol) in  $\text{C}_6\text{H}_6$  (100 mL) was added to finely divided potassium (0.278 g, 7.12 mmol). The pale yellow solution immediately darkened to orange. The mixture was stirred (3 d), and the red solution was filtered through Celite. The solvent was removed under reduced pressure, leaving a green residue (**14a**): yield 2.74 g, 81%; mp sweats and darkens at 222 °C and melts at 280–282 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.06 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.08 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6$  Hz, 1.31 (d, 24H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.0$  Hz, 2.83–2.99 (m, 12H,  $o,p\text{-CH}(\text{CH}_3)_2$ ), 7.10 (s, 8H,  $m\text{-Trip}$ ), 7.14–7.16 (m, 6H,  $p\text{-C}_6\text{H}_3$ ,  $m\text{-C}_6\text{H}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  24.28 ( $o\text{-CH}(\text{CH}_3)_2$ ), 26.09 ( $p\text{-CH}(\text{CH}_3)_2$ ), 31.16 ( $o\text{-CH}(\text{CH}_3)_2$ ), 34.53 ( $p\text{-CH}(\text{CH}_3)_2$ ), 121.66 ( $m\text{-Trip}$ ), 127.72 ( $p\text{-C}_6\text{H}_3$ ), 129.94 ( $m\text{-C}_6\text{H}_3$ ), 140.06 ( $i\text{-Trip}$ ), 146.00 ( $o\text{-Trip}$ ), 148.25 ( $p\text{-Trip}$ ), 148.61 ( $o\text{-C}_6\text{H}_3$ ), 150.57 ( $i\text{-C}_6\text{H}_3$ ); UV-vis (hexane) 470 nm (6570).**

**2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Bi=BiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (15).** A solution of **7** (1.00 g, 1.31 mmol) in hexane/toluene (3:1, 80 mL) was added to a stirred suspension of finely divided potassium (103 mg, 2.63 mmol), and the mixture was stirred overnight. The solution developed a deep purple color, and all the potassium was consumed. The solution was filtered (fine frit) and concentrated to ca. 40 mL under reduced pressure. Cooling in a  $-20$  °C freezer overnight afforded deep purple crystalline **15**: yield 0.90 g, 83%; mp  $>250$  °C dec;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.09 (d, 24H,  $p\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6$  Hz, 1.23 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 1.36 (d, 24H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 2.86 (septet, 8H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.9$  Hz, 2.94 (septet, 4H,  $o\text{-CH}(\text{CH}_3)_2$ )  $^3J_{\text{HH}} = 6.6$  Hz, 6.88 (t, 2H,  $p\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz, 7.13 (s, 8H,  $m\text{-Trip}$ ), 7.29 (d, 4H,  $m\text{-C}_6\text{H}_3$ )  $^3J_{\text{HH}} = 7.5$  Hz;  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  24.10 ( $p\text{-CH}(\text{CH}_3)_2$ ), 25.73 ( $o\text{-CH}(\text{CH}_3)_2$ ), 26.03 ( $o\text{-CH}(\text{CH}_3)_2$ ), 30.84 ( $o\text{-CH}(\text{CH}_3)_2$ ), 33.97 ( $p\text{-CH}(\text{CH}_3)_2$ ), 121.04 ( $m\text{-Trip}$ ), 127.51 ( $m\text{-C}_6\text{H}_3$ ), 127.93 ( $p\text{-C}_6\text{H}_3$ ), 142.33 ( $i\text{-Trip}$ ), 146.29 ( $o\text{-Trip}$ ), 148.19 ( $p\text{-Trip}$ ), 153.09 ( $o\text{-C}_6\text{H}_3$ ); UV-vis (hexane) 1025 nm (80), 913 nm (200), 518 nm (6920).

**X-ray Crystallographic Studies.** The crystals were removed from the Schlenk tube under a stream of  $\text{N}_2$  and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.<sup>15a</sup> All data were collected near 130 K using the following instruments: a Siemens R3 (Mo  $\text{K}\alpha$  radiation, **5**, **8**, and **10**), a Syntex P2<sub>1</sub> (Cu  $\text{K}\alpha$  radiation, **3b**, **11**, and **13**), a Siemens P4-R4 (Cu  $\text{K}\alpha$  radiation, **14**), and a Siemens SMART system (Mo  $\text{K}\alpha$  radiation and a CCD area detector, **3a**, **6**, and **9**). In the case of **3b**, **5**, **8–11**, **13**, and **14**, the diffractometers were equipped with a locally modified Enraf-Nonius universal low-temperature device for low-temperature work. The SHELXTL version 5.03 program package was used for the structure solutions and refinements.<sup>15b</sup> An absorption correction was applied using the program XABS2.<sup>15c</sup> For **3a** and **9** the programs SIR92<sup>16a</sup> and teXsan,<sup>16b</sup> respectively, were used for solution and refinement. An absorption correction was applied using XPREP.<sup>16c</sup> SHELXTL, version 5.03 was used for the refinement of **6**, and an absorption correction was applied using SADABS.<sup>16d</sup> The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, except those involved in disorder or in **3b** (due to absorption effects) which were maintained isotropic. Hydrogen atoms in **3b**, **5**, **6**, **8–11**, **13**, and **14** were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Some hydrogen atoms in **3a** and **9** were located on the Fourier difference maps; the rest were placed in calculated positions and were not refined. The structures of **5**, **6**, and

(15) (a) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1. (b) SHELXTL PC, version 5.03; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994. (c) Parkin, S. R.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(16) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1993**, *26*, 343. (b) teXsan: Crystal Structure Analysis Package; Molecular Structure Corporation: 1985 and 1992. (c) XPREP, version 5.03, part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI 1995. (d) SADABS (Siemens Area Detector Absorption correction program); George Sheldrick 1996.

**Table 1.** Selected Crystallographic Data for **3a**·0.5C<sub>6</sub>H<sub>6</sub>, **3b**·Et<sub>2</sub>O, **5**, **6**, **8–11**, **13**·0.5n-C<sub>6</sub>H<sub>14</sub>, and **14**·n-C<sub>6</sub>H<sub>14</sub>

	<b>3a</b> ·0.5C <sub>6</sub> H <sub>6</sub>	<b>3b</b> ·Et <sub>2</sub> O	<b>5</b>	<b>6</b>
formula	C <sub>27</sub> H <sub>28</sub> BiCl <sub>2</sub>	C <sub>52</sub> H <sub>60</sub> Bi <sub>2</sub> OCl <sub>4</sub>	C <sub>36</sub> H <sub>49</sub> AsCl <sub>2</sub>	C <sub>36</sub> H <sub>49</sub> SbCl <sub>2</sub>
fw	632.405	1260.76	627.57	674.40
color, habit	pale yellow, brick	colorless, parallelepiped	colorless, parallelepiped	colorless, parallelepiped
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pnma</i>
<i>a</i> , Å	11.0928(3)	10.474(2)	11.063(4)	25.651(5)
<i>b</i> , Å	16.5753(5)	17.278(4)	12.079(4)	11.110(5)
<i>c</i> , Å	13.7509(4)	13.870(3)	25.634(8)	12.087(5)
α, deg				
β, deg	95.344(1)	92.04(3)	90.03(3)	
γ, deg				
<i>V</i> , Å <sup>3</sup>	2517.3(1)	2508.5(9)	3425(2)	3445(2)
<i>Z</i>	4	2	4	4
cryst dim, mm	0.16 × 0.18 × 0.25	0.40 × 0.30 × 0.20	0.30 × 0.10 × 0.10	0.27 × 0.18 × 0.07
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.565	1.669	1.217	1.300
μ, mm <sup>-1</sup>	7.209	15.832	1.170	0.978
no. of refln	4651	3517	7862	15 954
no. of obsd refln	3511 (I > 3σ(I))	3328 (I > 2σ(I))	6277 (I > 2σ(I))	3334 (I > 2σ(I))
<i>R</i> <sub>1</sub> obsd refln	0.024	0.0605	0.0599	0.0455
w <i>R</i> <sub>2</sub> all		0.1530	0.1524	0.0959
	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>
formula	C <sub>48</sub> H <sub>50</sub> As <sub>2</sub>	C <sub>48</sub> H <sub>50</sub> Sb <sub>2</sub>	C <sub>48</sub> H <sub>50</sub> Bi <sub>2</sub>	C <sub>36</sub> H <sub>49</sub> P
fw	776.72	870.42	1044.84	512.72
color, habit	pale yellow, parallelepiped	orange, brick	red, hexagonal	colorless, parallelepiped
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> 1̄
<i>a</i> , Å	9.821(2)	9.9691(3)	10.052(2)	9.877(3)
<i>b</i> , Å	23.018(5)	22.8395(5)	22.784(5)	13.185(6)
<i>c</i> , Å	8.7090(17)	8.7017(3)	8.7387(17)	13.560(4)
α, deg				62.54(3)
β, deg	101.16(3)	99.6250(1)	99.00(3)	77.13(3)
γ, deg				83.66(3)
<i>V</i> , Å <sup>3</sup>	1931.5(7)	1953.39(8)	1976.7(7)	1527.5(9)
<i>Z</i>	2	2	2	2
cryst dim, mm	0.20 × 0.10 × 0.04	0.10 × 0.16 × 0.21	0.22 × 0.12 × 0.10	0.38 × 0.25 × 0.25
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.335	1.48	1.755	1.115
μ, mm <sup>-1</sup>	1.763	1.413	8.922	0.936
no. of refln	1755	3560	1811	4055
no. of obsd refln	1032 (I > 2σ(I))	1628 (I > 3σ(I))	1459 (I > 2σ(I))	2954 (I > 2σ(I))
<i>R</i> <sub>1</sub> obsd refln	0.0967	0.023	0.0527	0.0756
w <i>R</i> <sub>2</sub> all	0.2475		0.1297	0.2252
		<b>13</b> ·0.5n-C <sub>6</sub> H <sub>14</sub>		<b>14</b> ·n-C <sub>6</sub> H <sub>14</sub>
formula		C <sub>75</sub> H <sub>105</sub> As <sub>2</sub>		C <sub>78</sub> H <sub>110</sub> Cl <sub>0.42</sub> Sb <sub>2</sub>
fw		1156.44		1307.89
color, habit		bright orange, parallelepiped		red, parallelepiped
cryst syst		monoclinic		monoclinic
space group		<i>P</i> 2 <sub>1</sub> / <i>n</i>		<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å		15.097(18)		13.129(11)
<i>b</i> , Å		12.420(13)		15.969(6)
<i>c</i> , Å		20.424(12)		17.397(5)
α, deg				
β, deg		90.61(7)		104.06(5)
γ, deg				
<i>V</i> , Å <sup>3</sup>		3829(6)		3538(3)
<i>Z</i>		2		2
cryst dim, mm		0.40 × 0.40 × 0.30		0.26 × 0.22 × 0.04
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>		1.003		1.228
μ, mm <sup>-1</sup>		1.326		6.482
no. of refln		6168		4461
no. of obsd refln		4532 (I > 2σ(I))		3338 (I > 2σ(I))
<i>R</i> <sub>1</sub> obsd refln		0.1417		0.0908
w <i>R</i> <sub>2</sub> all		0.4211		0.2386

**13** were subject to disorder which could be modeled successfully using partial occupancies for the disordered atoms as described in the Supporting Information. The structure of **14** displays partial occupancy of 2 species, the distibene 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Sb=SbC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, **14a**, with Sb occupancies of 79%, and the partially reduced 1,2-dichloro-distibane 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>(Cl)Sb–Sb(Cl)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>, **14b**, with Sb and Cl occupancies of 21%. Some details of the data collection and

refinement are given in Table 1. Further details are provided in the Supporting Information.

## Results and Discussion

The synthesis and structural characterization of the stable dipnictene compounds [EC<sub>6</sub>H<sub>2</sub>-2,4,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>3</sub><sub>2</sub> (E =



Sb<sup>10a</sup> or Bi<sup>10b</sup>), which have Sb=Sb and Bi=Bi double bonded distances of 2.642(1) and 2.8208(8) Å (cf. Sb–Sb and Bi–Bi single bond, distances of 2.837 and 2.990(2) Å, respectively, in E<sub>2</sub>Ph<sub>4</sub> (E = Sb<sup>17a</sup> or Bi<sup>17b</sup>) molecules), have added new vigor to the study of multiple bonding of the heavier pnictogen elements. Unlike related heavier main group 13 and 14 analogues of alkenes or alkynes, these compounds bear considerable structural similarity to their lighter, congeneric diimines, diphosphenes, and diarsenes.<sup>10,18</sup> For example, they generally have a trans geometry featuring an essentially planar C–E–E–C array as well as bond lengths that are ca. 6–7% shorter than single bonds (cf. ca. 7–10% shortening in diphosphenes and diarsenes). These parameters suggest that, although  $\pi$  bonding is weakened with increasing atomic number, it remains quite appreciable in strength even in the fifth and sixth periods. The only notable structural change going down the group is that the angle at the pnictogen atom in dipnictenes narrows from ca. 113.6(2)° in PhNNPh<sup>19</sup> to 102.8(9)° in Mes\*PPMes\*<sup>1</sup> and 100.5(2)° in 2,4,6-{(Me<sub>3</sub>Si)<sub>2</sub>CH}<sub>3</sub>H<sub>2</sub>C<sub>6</sub>Bi=BiC<sub>6</sub>H<sub>2</sub>-2,4,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>.<sup>10a</sup> As a result it has been proposed<sup>10,20</sup> that the s-orbital character of the lone pairs also increases with increasing atomic number such that at antimony or bismuth the lone pairs have mostly s-orbital character. Accordingly, the  $\sigma$  and  $\pi$  bonds comprising the Sb=Sb and Bi=Bi double bonds are mostly composed from p-orbitals. It is noteworthy that the existence of significant  $\pi$ -orbital overlap between the heaviest group members (at least in the group 15 elements) is contrary to one of the major justifications of the so-called “double bond rule” which accounted for the weakness of heavier main group multiple bonds in terms of greatly diminished p overlap upon descending the group.<sup>21</sup>

The synthesis of the Sb=Sb and Bi=Bi double-bonded dipnictenes also highlights the fact that even though there exists a fair amount of structural data for diimines and diphosphenes, data for the rest of the heavier main group 15 elements analogues are quite scant. The literature shows that, besides the above-mentioned Sb=Sb and Bi=Bi species, the structures of only two diarsenes,<sup>5a,5c</sup> one phospharsene,<sup>6a</sup> one metallaphospharsene,<sup>6e</sup> and the recently reported pair of unsymmetric species MesPEC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (E = As or Sb)<sup>12</sup> are known at present. To study the dipnictene series further, it was thought desirable to have one or more complete series of heavier element dipnictenes in which the stabilizing ligand remains unchanged throughout the group. In addition, a simple synthetic route (preferably with the use of one step and beginning with the easily synthesized halide precursors) to the heaviest antimony and bismuth derivatives would enable convenient accessibility to these compounds as well as promote the study of their chemistry. It was found that the use of the terphenyl ligands –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> and –C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> adequately enables the first of these objectives to be achieved.

Oddly, terphenyl or related ligands such as –C<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub> have rarely been used in association with the group 15 elements. Although the nitro and amine derivatives O<sub>2</sub>NC<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub> or H<sub>2</sub>NC<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub> have been known since 1957,<sup>22</sup> heavier

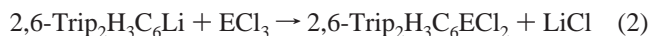
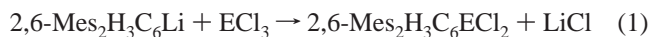
**Table 2.** Selected Spectroscopic Data for Compounds 1–7

	compound	mp (°C)	IR $\nu_{(E-Cl)}$ (cm <sup>-1</sup> )	C <sub>ipso</sub> (ppm)
1	2,6-Mes <sub>2</sub> H <sub>3</sub> C <sub>6</sub> AsCl <sub>2</sub>	206–208	380, 370	n.o.
2	2,6-Mes <sub>2</sub> H <sub>3</sub> C <sub>6</sub> SbCl <sub>2</sub>	263–265	340, 320	n.o.
3	2,6-Mes <sub>2</sub> H <sub>3</sub> C <sub>6</sub> BiCl <sub>2</sub>	220–224	280, 240	n.o.
4	2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> PCL <sub>2</sub>	245–247	480, 442	133.66 <i>J</i> = 8.3 Hz
5	2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> AsCl <sub>2</sub>	259–260	380, 360	142.89
6	2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> SbCl <sub>2</sub>	255–259	345, 330	152.95
7	2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> BiCl <sub>2</sub>	255–257	310, 295	214.63

<sup>a</sup> n.o. = not observed.

element terphenyl compounds were reported only recently. The compound 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>PCL<sub>2</sub> was synthesized by the reaction of the organolithium reagent with PCl<sub>3</sub>, and hydrolysis affords the phosphinic acid derivative 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P(O)(OH)H.<sup>11a</sup> Reduction of the dihalide by magnesium with sonication affords the diphosphene 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P=PC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> which has a remarkably short PP distance of 1.985(2) Å. The phosphine dihalide and diphosphene derivatives of –C<sub>6</sub>H<sub>2</sub>-2,6-Mes<sub>2</sub>-4-Me and –C<sub>6</sub>H<sub>3</sub>-2,6-{C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>}<sub>2</sub> have also been synthesized and spectroscopically characterized in order to study their reduction potentials.<sup>11b</sup> For the heavier elements the arsenic compound 2,6-Mes<sub>2</sub>-4-Me-H<sub>2</sub>C<sub>6</sub>AsCl<sub>2</sub> has been reported,<sup>6h</sup> and the phospharsene 2,6-Mes<sub>2</sub>-4-Me-H<sub>2</sub>C<sub>6</sub>As=PC<sub>6</sub>H<sub>2</sub>-2,6-Mes<sub>2</sub>-4-Me and the corresponding radical anion were generated, although no structures were determined owing to disorder and instability problems. Unusually, the attempted synthesis of the corresponding diarsene was also unsuccessful.<sup>6h</sup> Some related bismuth derivatives have also been studied. Reaction of LiC<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub> with BiCl<sub>3</sub> in a 2:1 or 3:1 ratio affords (2,4,6-Ph<sub>3</sub>H<sub>2</sub>C<sub>6</sub>)<sub>2</sub>-BiCl or Bi(C<sub>6</sub>H<sub>3</sub>-2,4,6-Ph<sub>3</sub>)<sub>3</sub>. The monoaryl 2,4,6-Ph<sub>3</sub>H<sub>2</sub>C<sub>6</sub>BiCl<sub>2</sub> could be synthesized by the reaction of BiCl<sub>3</sub> with the triaryl- or diarylbismuth halide in the appropriate ratio.<sup>23a</sup> However, direct reaction of BiCl<sub>3</sub> with LiC<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub> in a 1:1 ratio gave only a low yield (20%) of the monosubstituted species. The monoaryl 2,4,6-Ph<sub>3</sub>H<sub>2</sub>C<sub>6</sub>BiCl<sub>2</sub> is a dimer in the solid with Bi–Cl distances of 3.074(1) Å (bridging) and 2.532(1) Å (terminal) and a Bi–C distance of 2.226(4) Å.<sup>23b</sup>

**Aryldihalopnictogen Synthesis.** In the systems studied in this paper it was found that the reaction of LiC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> with ECl<sub>3</sub> (E = As, Sb, or Bi) or LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> with ECl<sub>3</sub> (E = P, As, Sb, or Bi) yields the monosubstituted products 1–7 in accordance with eqs 1 and 2.



The products 1–7 were obtained in moderate to good yield (usually 50–80%) by the dropwise addition of an ether solution of the lithium reagent to a cooled ether solution or suspension of the pnictogen trihalide. All the products 1–7 are colorless or pale yellow crystals and are air- and moisture-sensitive. They possess excellent thermal stability and display no sign of an orthometalation reaction such as that observed in some Mes\*-As derivatives.<sup>2k,6a</sup> For example, the compounds 4–7 melt without decomposition within the temperature range 245–260 °C. Selected spectroscopic data for 1–7 are given in Table 2. It can be seen that two IR absorptions are observed for the

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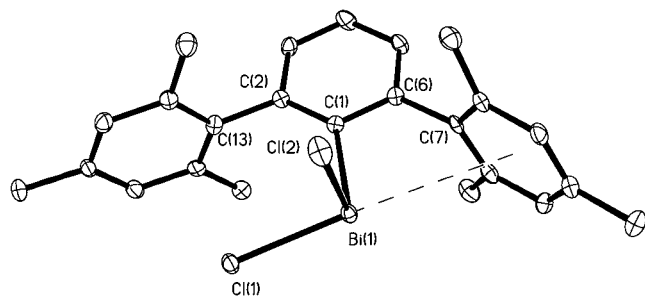
(18) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939.

(19) Brown, C. J. *Acta Crystallogr.* **1966**, 21, 146.

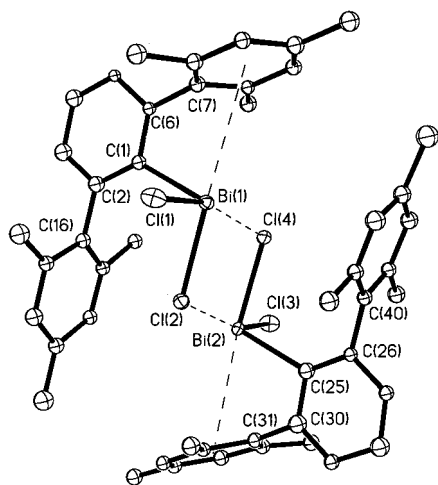
(20) Nagase, S.; Suzuki, S.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1724.

(21) For short critical discussions see: (a) Dasent, W. E. *Nonexistent Compounds*; Marcel Dekker: New York, 1965, Chapter 4. (b) Norman, N. C. *Polyhedron* **1993**, 12, 2431.

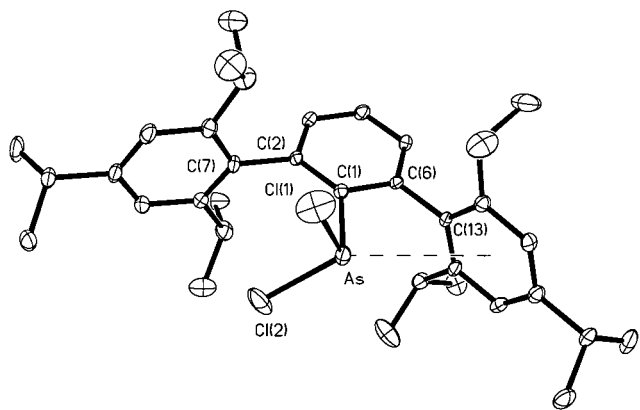
(22) Dimroth, K.; Brauning, G.; Neubauer, G. *Chem. Ber.* **1957**, 90, 1634.



**Figure 1.** Thermal ellipsoid plot (30%) of **3a**. H atoms are omitted for clarity.



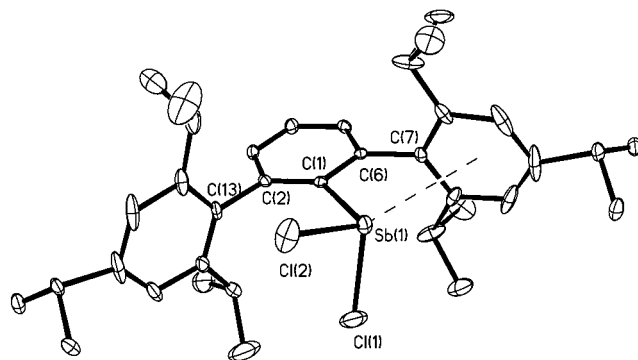
**Figure 2.** Thermal ellipsoid plot (30%) of **3b**. H atoms are omitted for clarity.



**Figure 3.** Thermal ellipsoid plot (30%) of **5**. H atoms are omitted for clarity.

pnictogen halide stretching vibrations. The  $^{13}\text{C}$  chemical shift of the *ipso*-C atom moves to lower field with increasing atomic number of the pnictogen. The  $^{31}\text{P}$  NMR chemical shift (156.47 ppm) of **4** is almost identical to that observed for 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>-PCl<sub>2</sub> (160.4 ppm).<sup>11a</sup>

The structures of **3a**, **3b**, **5**, and **6** were also determined, and these are illustrated in Figures 1–4. Selected structural parameters are given in Table 3. The bismuth dihalide **3** can be crystallized in either a monomeric form (**3a**) from benzene or as a weakly associated dimer (**3b**) from Et<sub>2</sub>O. The dimeric form has a structure similar to that of {2,4,6-Ph<sub>3</sub>H<sub>2</sub>C<sub>6</sub>BiCl<sub>2</sub>}<sub>2</sub><sup>23a</sup> with the terminal and one of the bridging Bi–Cl distances averaging about 2.52 Å in both compounds. The “long” bridging Bi–Cl distances in **3b**, 3.104(6) and 3.138(6) Å, are just marginally longer than those seen in {2,4,6-Ph<sub>3</sub>H<sub>2</sub>C<sub>6</sub>BiCl<sub>2</sub>}<sub>2</sub>, 3.009(5) and 3.078(12) Å, perhaps as a result of the greater steric congestion



**Figure 4.** Thermal ellipsoid plot (30%) of **6**. H atoms are omitted for clarity.

in **3b**. When it is crystallized from benzene, **3a** is obtained as a monomer with Bi–C and terminal Bi–Cl distances that are essentially the same as those seen in the weakly dimerized form. The most unusual feature of **3** (both structures) is the existence of a Menshutkin interaction<sup>24</sup> between the bismuth and one of the ortho aromatic rings. The strength of this interaction can be expressed as a difference in the C(2)–C(1)–Bi(1) and the C(6)–C(1)–Bi(1) angles at the ipso carbon which in **3a** is 23.4°. The distance from the C(7) ring centroid to bismuth is 3.472 Å. The arsenic and antimony compounds **5** and **6**, which are derivatives of the –C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> rather than the –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> ligand, display very similar structures to the monomeric bismuth species **3a** and feature a strongly pyramidalized geometry at the pnictogen atom. The monomeric structure of the antimony compound, in particular, may be contrasted with those of other organoantimony dihalide species which display a tendency to associate, even in the presence of bulky substituents such as –CH(SiMe<sub>3</sub>)<sub>2</sub>, as in the compound (Me<sub>3</sub>Si)<sub>2</sub>HCSbCl<sub>2</sub>.<sup>25</sup> The structure of **6** is also characterized by the existence of a plane of symmetry that incorporates the plane of the central C(1) ring. There is also a strong Menshutkin interaction as evidenced by a difference of 22.5° in the C(2)–C(1)–Sb and C(6)–C(1)–Sb angles and an antimony–C(7) ring centroid distance of 3.474 Å. The Sb–Cl distance 2.365(av) Å is comparable to those observed in other organoantimony dihalides and the Sb–C distance, 2.187(5) Å, is within the experimentally known range of ca. 2.13–2.20 Å.<sup>25</sup> The arsenic compound **5** has a structure that is very similar to that of its antimony analogue. A strong Menshutkin interaction is also observed, as evidenced by the As–C(7) ring centroid distance of 3.43 (av) Å and a difference in the C(2)–C(1)–As and C(6)–C(1)–As angles of 23.3°. The As–C and As–Cl distances are normal. The Menshutkin interactions observed for these group 15 aryldihalides are, apparently, a common feature of heavier main group terphenyl derivatives, and similar interactions have already been observed for germanium and tin derivatives of these ligands.<sup>27</sup>

**Reduction of the Aryl Pnictogen Dihalides.** Reduction of the halide derivatives **1**–**7** always produces a doubly bonded

(24) For example, see 23(b) and the following: (a) Mootz, D.; Handler, V. Z. *Anorg. Allg. Chem.* **1986**, 533, 23 and references therein. (b) Menshutkin, B. N. *Zh. Russ. Fiz. Khim. Ova.* **1911**, 43, 1298, 1785.

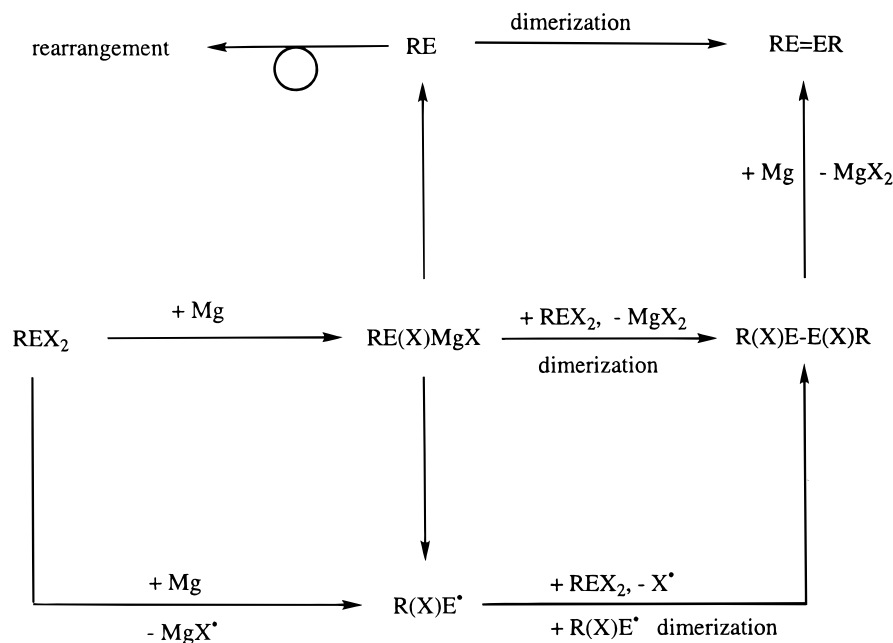
(25) (Me<sub>3</sub>Si)<sub>2</sub>HCSbCl<sub>2</sub> crystallizes as a monomer<sup>25a</sup> from hexane but as a dimer<sup>25b</sup> from the melt: (a) Cowley, A. H.; Norman, N. C.; Pakulski, M.; Bricker, D. L.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, 107, 8211. (b) Mohammed, M. A.; Ebert, K. E.; Breunig, H. Z. *Naturforsch., B: Chem. Sci.* **1996**, 51, 149.

(26) Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Oxford: 1982; Vol. 2, Chapter 13. *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Davies, A. W., Eds.; Pergamon-Elsevier: Oxford, 1995; Vol. 2, Chapter 8.

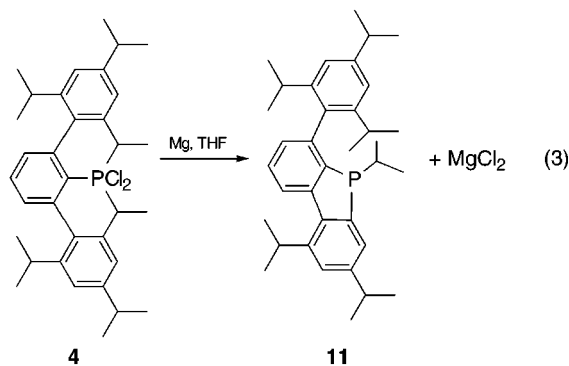
(27) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, 16, 1920.

**Table 3.** Selected Structural Parameters for **3a**, **3b**, **5**, **6**, **11**, and **14a**

Compound	E–C(1) (Å)	E–X (Å)	E–Cent <sup>a</sup> (Å)	C(2)–C(1)–E (deg)	C(6)–C(1)–E (deg)	C(1)–E–X (deg)	X–E–X (deg)
9-phosphafluorene, <b>11</b> (X = C)	1.805(11)	1.817(4) 1.867(5)		112.8(3)	126.1(3)	89.4(2) 104.2(2)	101.56(19)
2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> AsCl <sub>2</sub> , <b>5</b> (X = Cl)	2.005(av)	2.164(av) 2.131(av)	3.43(av)	137.8(av)	103.2(av)	101.9(av) 100.1(av)	105.9(av)
2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> SbCl <sub>2</sub> , <b>6</b> (X = Cl)	2.187(5)	2.384(3) 2.346(2)	3.474	131.5(4)	109.0(4)	97.40(8) 103.04(13)	94.43(12)
[2,6-Trip <sub>2</sub> H <sub>3</sub> C <sub>6</sub> (Cl)Sb] <sub>2</sub> , <b>14b</b> (X = Cl)	2.172(10)	2.427(16)	3.613	141.8(7)	100.8(6)	101.0(5)	
2,6-Mes <sub>2</sub> H <sub>3</sub> C <sub>6</sub> BiCl <sub>2</sub> , <b>3a</b> (X = Cl)	2.267(5)	2.539(1) 2.501(1)	3.472	131.7(3)	108.3(3)	102.3(1) 94.3(1)	88.20(5)
{2,6-Mes <sub>2</sub> H <sub>3</sub> C <sub>6</sub> BiCl <sub>2</sub> } <sub>2</sub> , <b>3b</b> (X = Cl)	2.29(2)	2.496(6) 2.544(5)	3.485	130.7(16)	110.9(15)	94.3(6)	88.78(19)
	2.21(2)	2.516(6) 2.531(5)	3.584	132.2(17)	108.5(17)	96.7(6)	88.87(19)

<sup>a</sup> Cent = Centroid.**Scheme 1.** Possible Reduction Pathways of REX<sub>2</sub> (E = P, As, Sb, or Bi; X = Halogen) with Magnesium

dipnictene species among the products. However, the type of reductant used may influence the product obtained, and the reduction of **4** illustrates this point. If **4** is treated with magnesium in THF, the cyclized phosphafluorene **11** is produced in ca. 70% yield as illustrated in eq 3.



When **4** is reduced with potassium, however, the diphosphene **12** is produced together with a minor amount of **11**. The exact mechanism of the reduction pathway of organophosphorus dihalides by magnesium is unknown. However, the observation of **11** in addition to partially reduced dipnictanes such as Mes<sup>\*</sup>-

(Cl)P–P(Cl)Mes<sup>\*</sup><sup>28a</sup> and **14b** (vide infra) suggests that one of the two initial reduction pathways illustrated by Scheme 1 may exist. One pathway involves insertion of magnesium into the E–X bond to give RE(X)MgX which may then, either eliminate MgX<sub>2</sub> to generate a phosphanediyl(phosphinidene), or react further with REX<sub>2</sub> to give the 1,2-dihalodipnictane R(X)E–E(X)R. The alternate radical pathway has received strong support from EPR studies.<sup>28b</sup> Cyclized products related to **11** have also been observed in the reduction of 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>BX<sub>2</sub> (X = Cl or Br) species.<sup>29</sup>

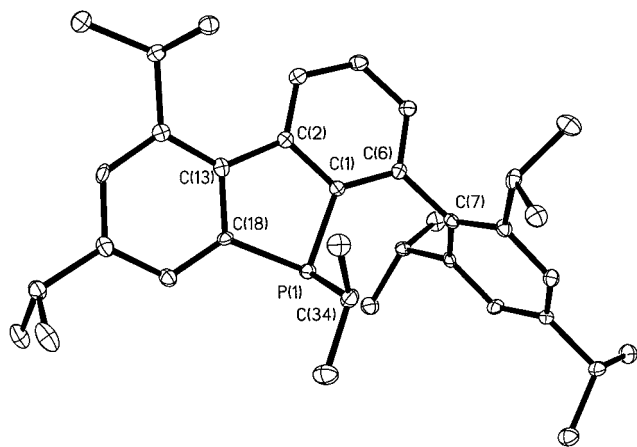
The crystal structure of **11** (Figure 5) shows that phosphorus center has quite pyramidal coordination, Σ°P = 295.2°, suggesting little delocalization of the phosphorus lone pair in the five-membered ring, at least in the ground state.<sup>30</sup> However, it is notable that the P(1)–C(1) and P(1)–C(18) distances (Table 3) are significantly, ca. 0.05–0.06 Å, shorter than the P(1)–C(34) distance. The difference in the P–C bond lengths may be partially due to the approximate sp<sup>2</sup> hybridization of the

(28) (a) Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L.; Lappert, M. F.; Smith, S. J. *J. Organomet. Chem.* **1986**, *310*, 21. (b) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609.

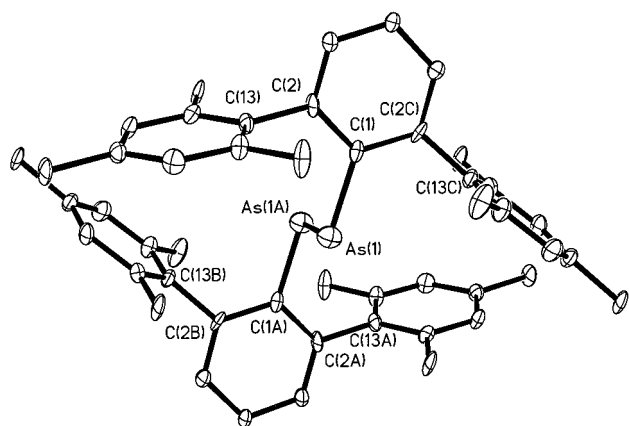
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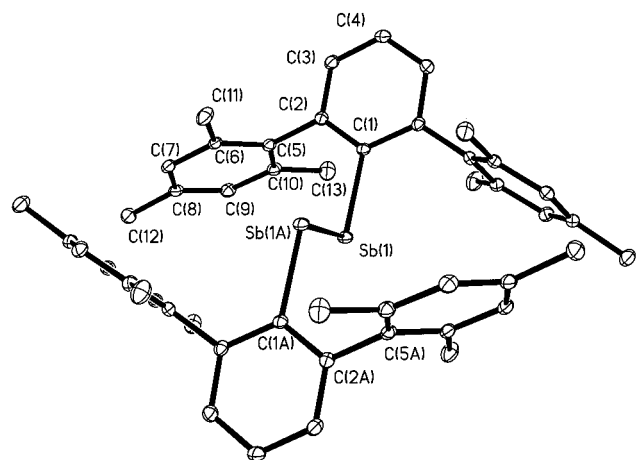




**Figure 5.** Thermal ellipsoid plot (30%) of **11**. H atoms are omitted for clarity.



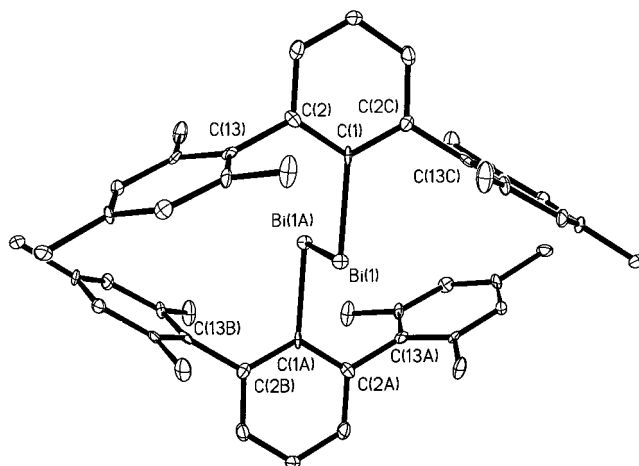
**Figure 6.** Thermal ellipsoid plot (30%) of **8**. H atoms are omitted for clarity.



**Figure 7.** Thermal ellipsoid plot (30%) of **9**. H atoms are omitted for clarity.

$\sigma$ -bonding orbitals of the C(1) and C(18) carbons (cf. approximate  $sp^3$  hybridization for C(34)), but it may also be a reflection of the incipient delocalization of the phosphorus lone pair in a 6  $\pi$  electron aromatic ring in the transition state for the inversion of the phosphorus the geometry.

The structure of the diphosphene species **12** is probably very similar to that of the diphosphene 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P=PC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> reported by Protasiewicz and co-workers.<sup>11a</sup> The related diarsene **8** (Figure 6), distibene **9** (Figure 7), and dibismuthene **10** (Figure 8) were synthesized in ca. 30% yield by reduction of the corresponding dihalide. Selected structural data for the

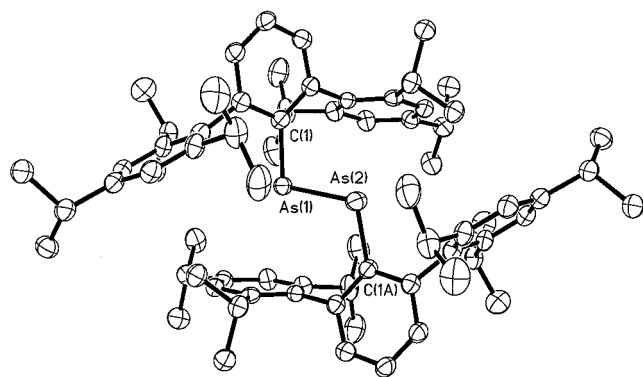
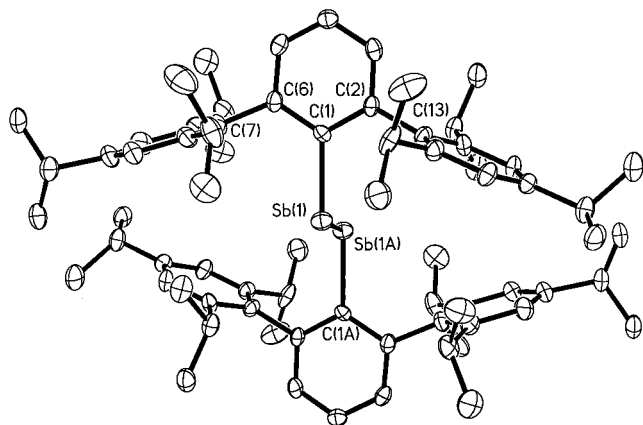


**Figure 8.** Thermal ellipsoid plot (30%) of **10**. H atoms are omitted for clarity.

phosphorus compound,<sup>11a</sup> in addition to the arsenic, antimony, and bismuth analogues, are presented in Table 4. The two main features of interest in these molecules are the E–E bond distance and the E–E–C bond angle. In the diphosphene two different P–P–C angles, 97.5(1) and 109.8(1) (average 103.7°), together with a P–P distance of 1.985(2) Å (the shortest P–P distance in a diphosphene) are observed. The reason for the differing P–P–C angles is probably steric. It appears that the size of the –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> ligand does not allow a parallel alignment of central C<sub>6</sub>H<sub>3</sub> rings. In fact, these rings are almost perpendicular to each other in the diphosphene, and a wider angle at one of the phosphorus centers is due to steric conflict between one of the ortho mesityl groups and the P=P double bond. Crystals of the arsenic, antimony, and bismuth compounds are isomorphous with each other and have a different space group from that of the phosphorus species.<sup>11a</sup> The structures of **8**, **9**, and **10** all have a center of symmetry in the middle of the E–E bond, and thus, the planar C<sub>6</sub>H<sub>3</sub> rings in each –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> substituent are parallel. This configuration is permitted by the steric relaxation caused by the larger central atom size. In addition, the two E–E–C angles are identical and decrease from 98.5(4)° in the diarsene, to 94.1(1)° in the distibene, and finally to 92.5(4)° in the dibismuthene (Table 4). The As–As distance in **8**, 2.276(3) Å is somewhat longer than the average distance of 2.244(1) Å in (Me<sub>3</sub>Si)<sub>3</sub>CAs=AsC(SiMe<sub>3</sub>)<sub>3</sub><sup>5c</sup> (As–As–C = 106.4(2)°) and 2.224(2) Å in Mes\*As=AsCH(SiMe<sub>3</sub>)<sub>2</sub><sup>5a</sup> (As–As–C(Mes\*) = 93.6(3)°; As–As–CH(SiMe<sub>3</sub>)<sub>2</sub> = 99.9(3)°). In addition, the Sb–Sb (2.6558(5) Å) and Bi–Bi (2.8327(14) Å) distances in **9** and **10** are slightly longer than the 2.642(1) and 2.8208(8) Å in the recently reported 2,4,6-{Me<sub>3</sub>Si<sub>2</sub>CH}<sub>3</sub>H<sub>2</sub>C<sub>6</sub>E=EC<sub>6</sub>H<sub>3</sub>-2,4,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub> (E = Sb<sup>10a</sup> or Bi<sup>10b</sup>, respectively) species. These compounds have Sb–Sb–C and Bi–Bi–C angles of 101.4(1) and 100.5(2)°, respectively. The variety of ligand sizes and paucity in numbers of these previously known compounds make angular trends more difficult to assess. However, it is clear from the data in Table 4 that the E–E–C angles decrease in the sequence 103.7°(P) > 98.5(4)°(As) > 94.1(1)°(Sb) > 92.5(4)°(Bi). The angles measured in the antimony and bismuth compounds **9** and **10** are in quite good agreement with the 93.0 and 91.8° values calculated<sup>20</sup> for the hypothetical hydrogen derivatives HSb=SbH and HBi=BiH. The experimental angles in the known diphosphenes and diarsenes are significantly wider than those calculated for the hydrogen derivatives, however. This is probably a result of the greater steric congestion in the smaller, lighter congeners. In contrast, the calculated P=P and As=As double-bonded di-

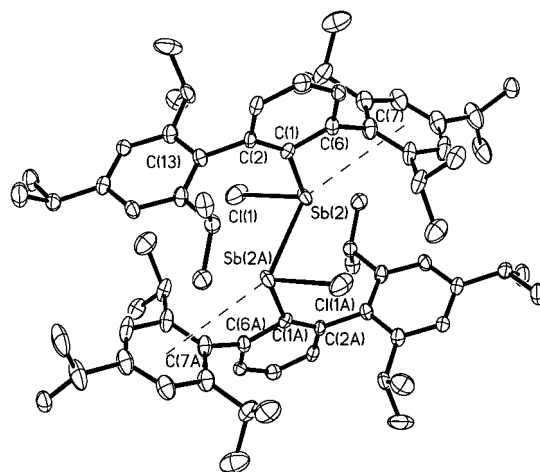
**Table 4.** Selected Structural Parameters for **8–10**, **13**, and **14a**

Compound	E–C (Å)	E–E (Å)	E–E–C (deg)	C–E–E–C (deg)
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> P=PC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> <sup>a</sup>	1.842(3)	1.985(2)	109.8(1)	177.1(2)
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> As=AsC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>8</b>	1.840(3)	2.276(3)	97.5(1)	180
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> As=AsC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>13</b>	1.963(13)	2.285(3)	98.5(4)	180
	1.986(7)		96.4(2)	176.6
	1.980(7)		107.8(2)	
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Sb=SbC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>9</b>	2.169(4)	2.6558(5)	94.1(1)	180
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Sb=SbC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>14a</b>	2.190(9)	2.668(2)	98.9(2)	180
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Bi=BiC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>10</b>	2.257(17)	2.8327(14)	92.5(4)	180

<sup>a</sup> Reference 11a.**Figure 9.** Thermal ellipsoid plot (30%) of **13**. H atoms are omitted for clarity.**Figure 10.** Thermal ellipsoid plot (30%) of **14a**. H atoms are omitted for clarity.

tances are in good agreement with experimentally measured values, whereas the Sb=Sb and Bi=Bi experimental distances are 0.04–0.11 Å longer than the calculated values.

Reduction of the bulkier 2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>ECl<sub>2</sub> (E = As, **5**; Sb, **6**; Bi, **7**) dihalides affords the dipnictenes **13–15** in 80–90% yield. The almost quantitative yields of these products may be due to the greater steric crowding which may prevent side reactions leading to other products. The structures of the diarsene and distibene **13** (Figure 9) and **14a** (Figure 10) have slightly longer (0.01 Å) As–As and Sb–Sb distances than in their less sterically crowded –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> counterparts. The average As–As–C (102.1°) and Sb–Sb–C (99.0(2)°) angles in **13** and **14a** are wider than the corresponding ones in **8** and **9** for the same reason. The structures of **14a** and the partially reduced 1,2-dihalodipnictane species **14b** (Figure 11), which have similar degrees of steric crowding since they have the same aryl substituents, provide a further gauge of the shortening caused by reduction to a double bond. A difference of 0.223 Å or 7.7% was observed in the Sb–Sb bond lengths (Sb–Sb: 2.668(2) Å, **14a**; 2.892(8) Å, **14b**). It is notable that the diarsene **13** has

**Figure 11.** Thermal ellipsoid plot (30%) of **14b**. H atoms are omitted for clarity.

two different As–As–C angles of 96.4(2) and 107.8(2)°. These values are very close to the two different P–P–C angles observed in 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>PPC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>.<sup>11a</sup> The cause of the difference in **13** is probably the same as that argued earlier for the phosphorus compound. The good agreement between the three experimentally determined Sb=Sb double-bonded distances and the two Bi=Bi double-bonded distances demonstrates beyond doubt that the amount of the shortening in these bonds, in comparison to the single bond lengths in Ph<sub>2</sub>EEPPh<sub>2</sub> (E = Sb<sup>17a</sup> or Bi<sup>17b</sup>), is both consistent and significant. Furthermore, calculations have shown that rotational barriers of the order of 12–15 kcal mol<sup>–1</sup> can be expected for the Sb=Sb and Bi=Bi double bonds.<sup>20</sup> These values are in reasonable agreement with the π-bond strengths expected from spectroscopic measurements and data extrapolation.<sup>18</sup> The experimental results together with the theoretical data provide strong evidence that p–p orbital overlap to give π bonding is important even in the heaviest elements—at least those in group 15. It has often been suggested that side-on p–p π-orbital overlap diminishes at a much more rapid rate than head-to-head orbital overlap in σ bonding.<sup>31</sup> The presently available data suggest that the difference in the rates at which σ- and π-bonds decrease in strength is not as great as was once thought.

The arsenic and antimony species **13** and **14a** are isoelectronic with the recently synthesized germanium and tin species Na<sub>2</sub>{2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>Ge=GeC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>} and K<sub>2</sub>{2,6-Trip<sub>2</sub>H<sub>3</sub>C<sub>6</sub>-Sn=SnC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>}, which have Ge=Ge and Sn=Sn double-bonded distances of 2.394(1) and 2.7763(9) Å.<sup>32</sup> These distances are 0.1 Å longer than those in **13** and **14a**, and some of this increase can be attributed to the slightly larger covalent radius

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**Table 5.** UV-vis Spectroscopic Data for Dipnictenes

Compound	$\lambda_1$ (nm, $\epsilon$ )	$\lambda_2$ (nm, $\epsilon$ )	$\lambda_3$ (nm, $\epsilon$ )
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> P=PC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> <sup>a</sup>	371, 8000	455, 501	
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> P=PC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>12</b>	393, 7270	502, 570	
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> As=AsC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>8</b>	400, 6970	462, 650	
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> As=AsC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>13</b>	409, 4060	504, 120	
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Sb=SbC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>9</b>	451, 5450		
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Sb=SbC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>14a</b>	470, 6570		
2,6-Mes <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Bi=BiC <sub>6</sub> H <sub>3</sub> -2,6-Mes <sub>2</sub> , <b>10</b>	505, 5010	970, 30	
2,6-Trip <sub>2</sub> -H <sub>3</sub> C <sub>6</sub> Bi=BiC <sub>6</sub> H <sub>3</sub> -2,6-Trip <sub>2</sub> , <b>15</b>	518, 6920	913, 200	1025, 80

<sup>a</sup> Reference 11a.

of germanium in comparison to arsenic (1.22 vs 1.21 Å).<sup>33</sup> However, the covalent radii of tin and antimony are very similar,<sup>33</sup> and it seems likely that the primary reason for the longer distances in the tin and germanium species is the presence of a double negative charge located mainly at the Ge=Ge and Sn=Sn moieties. This causes an increase in interelectronic repulsion, and hence, a lengthening of the Ge–Ge and Sn–Sn bonds. This phenomenon has also been observed in single bonds. For example, the Sb–Sb single bond distance in Ph<sub>2</sub>Sb–SbPh<sub>2</sub> (Sb–Sb = 2.837 Å)<sup>17a</sup> is shorter than the corresponding Sn–Sn distance (2.905(3) Å) in the isoelectronic dianion [Ph<sub>2</sub>Sn–SnPh<sub>2</sub>]<sup>2-</sup>.<sup>34</sup>

The dipnictene compounds **8–10** and **12–15** are intensely colored. Their color ranges from yellow or orange yellow in the phosphorus and arsenic species to deep red (purple solution) in the case of the bismuth derivative **15**. The color arises from chromophores (usually two) in the visible region. The UV–vis data are summarized in Table 5; also included are data for the phosphorus species 2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>P=PC<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>. Generally speaking, the two absorption maxima are thought to correspond to the  $\pi$ – $\pi^*$  (symmetry allowed) and  $n$ – $\pi^*$  (symmetry forbidden) electronic transitions. The  $\pi$ – $\pi^*$  absorption maxima are thus significantly more intense ( $\epsilon$  value is usually several

thousand). It can be seen that, for the  $\pi$ – $\pi^*$  absorptions of the –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> derivatives, there is a shift to longer wavelength (cf. 371 nm (P), 400 (As), 451 (Sb), 505 (Bi)) as the group is descended. Very similar maxima are observed for the  $\pi$ – $\pi^*$  transitions for the –C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> derivatives **12**, **13**, **14a**, and **15** which are all at slightly longer (by 9–19 nm) wavelength (i.e., lower energy) than their –C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub> substituted counterparts. Longer wavelengths were also reported for the  $\pi$ – $\pi^*$  absorption in the 2,4,6-[(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>3</sub>H<sub>2</sub>C<sub>6</sub>E=EC<sub>6</sub>H<sub>2</sub>-2,4,6-[(CH(SiMe<sub>3</sub>)<sub>2</sub>)]<sub>3</sub> derivatives. The wavelengths measured for these compounds, Sb (466 nm) and Bi (525 nm), are within 4 and 7 nm, respectively, of those measured for **14a** and **15**. These trends are consistent with a weakening of the  $\pi$  bond as the group is descended and consistent with calculations on these systems.

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**Supporting Information Available:** Tables of data-collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters and hydrogen coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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