

## Synthesis and Characterization of the M(II) (M = Ge, Sn, or Pb) Phosphinidene Dimers $\{M(\mu\text{-PAR}')\}_2$ (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr'<sup>i</sup>)<sub>2</sub>)<sub>2</sub>

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Reaction of  $M\{N(\text{SiMe}_3)_2\}_2$  (M = Ge, Sn, or Pb) with the sterically encumbered primary phosphine Ar'PH<sub>2</sub> (**2**), Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr'<sup>i</sup>)<sub>2</sub>, at ca. 200 °C afforded the highly colored phosphinidene dimers  $\{M(\mu\text{-PAR}')\}_2$ , M = Ge(**3**), Sn(**4**), or Pb(**5**), with disilylamine elimination. The compounds were characterized by single-crystal X-ray crystallography and heteronuclear NMR spectroscopy. The structures of **3**, **4**, and **5** featured similar M<sub>2</sub>P<sub>2</sub> ring cores, of which **4** and **5** have 50/50 P atom disorder, consistent with either a planar four-membered M<sub>2</sub>P<sub>2</sub> arrangement with *anti* aryl groups or with an M<sub>2</sub>P<sub>2</sub> ring folded along the M–M axis with *syn* aryl groups. A *syn*-folded structure was resolved for the Ge<sub>2</sub>P<sub>2</sub> ring in compound **3**. The M–P distances resembled those in M(II) phosphido complexes and are consistent with single bonding. The coordination geometries at the phosphorus atoms are pyramidal. DFT calculations on the gas phase models  $\{M(\mu\text{-PMe})\}_2$  (M = Ge, Sn, Pb) agreed with the *syn* (M–M folded) structural interpretation of the X-ray data. The synthesis of the bulky phosphine Ar'PH<sub>2</sub> **2** with the use of the aryl transfer agent Ar'MgBr(THF)<sub>2</sub> is also reported. This route afforded a significantly higher yield of product than that which was obtained using LiAr', which tends to result in aryl halide elimination and the observation of insoluble red phosphorus.

### Introduction

The heavier group 14 elements Ge, Sn, and Pb form numerous oligomeric metal(II) imides which display a wide variety of structures.<sup>1</sup> Their most common formula is  $\{M(\mu\text{-NR})\}_4$  (M = Ge, Sn, or Pb; R = organic or silyl groups), which feature a heterocubane arrangement of group 14 element and nitrogen atoms.<sup>2–13</sup>

A few lower aggregated species that possess the potential for  $\pi$ -bonding between a group 14 empty p-orbital and nitrogen lone pairs are also known. These include the dimers  $\{\text{Ge}(\mu\text{-NR})\}_2$  (R = Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-Bu'<sup>i</sup><sub>3</sub><sup>14</sup> or R = C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub><sup>15</sup>) and the trimeric  $\{\text{Ge}(\mu\text{-NC}_6\text{H}_3\text{-2,6-Pr}'_2)\}_3$ .<sup>16</sup> However, in these compounds,  $\pi$ -bonding is not extensive owing to the considerable electronegativity and size differences between these elements which reduce orbital overlap. Some corresponding derivatives of the heavier pnictogens  $\{M(\mu\text{-ER})\}_n$  (E = P, As, Sb, or Bi; n = 4–7) are also known. The first well-characterized example was the distorted hexagonal prismatic  $\{\text{Sn}(\mu\text{-PSiPr}'_3)\}_6$ , which was reported by Driess in 1997.<sup>17</sup> It was prepared by the reaction of  $\text{Sn}\{C_6H_2\text{-2,4,6-(CF}_3)_3\}_2$  or  $\text{Sn}\{N(\text{SiMe}_3)_2\}_2$  with RPH<sub>2</sub> (R = SiPr'<sup>i</sup><sub>3</sub> or Si(Trip)Pr'<sup>i</sup><sub>2</sub>, Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr'<sup>i</sup><sub>3</sub>), and in the presence of SnCl<sub>2</sub>, the adduct (SnPSi(Trip)Pr'<sup>i</sup><sub>2</sub>)<sub>2</sub>(SnCl<sub>2</sub>) could also be isolated. As a result, it was proposed that the dimeric phosphanediyl (SnPR)<sub>2</sub> was a

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key intermediate which trimerized to form  $\{\text{Sn}(\mu\text{-PR})\}_6$  cage structures. Several other related species with interesting structural arrangements have also been reported. They include the arsenic congener  $\{\text{Sn}(\mu\text{-AsSiPr}^i_3)\}_6$ ,<sup>18</sup> the lead–arsenic hexamer  $\{\text{Pb}(\mu\text{-AsSiPr}^i_3)\}_6$ ,<sup>19</sup> the Sn–P tetramer  $\{\text{Sn}(\mu\text{-PSiBu}^t_3)\}_4$ ,<sup>20</sup> stabilized by the bulkier  $\text{SiBu}^t_3$  substituent, together with the mixed metallic cages such as  $\{(\text{THF})_4\text{Ba}\}_2\text{Sn}_2(\mu\text{-PSiBu}^t_3)_4$ ,<sup>20</sup> the germanium–phosphorus hexamer  $\{\text{Ge}(\mu\text{-PSiPr}^i_3)\}_6$ ,<sup>21</sup> and the unique heptameric  $\{\text{Sn}(\mu\text{-PSiPr}^i_3)\}_7$ .<sup>21</sup> The common feature of these compounds is that they have three-dimensional cage structures in which the pnictogen is four-coordinate, as are the Ge, Sn, or Pb atoms if their lone pairs are considered phantom ligands. No lower-coordinate species, particularly the key dimeric phosphanediides (MPR)<sub>2</sub>, which were proposed as intermediates in their formation, have been characterized. We now report that the use of sterically crowding terphenyl ligand<sup>22,23</sup> ( $\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-}\text{Pr}^i_2)_2$ )<sup>24</sup> as an organic phosphine substituent permits the synthesis of the dimeric phosphanediyls  $\{\text{M}(\mu\text{-PAR}')\}_2$  that were spectroscopically and structurally characterized.

## Experimental Section

**General Procedures.** All manipulations were performed with the use of modified Schlenk techniques under argon or in a Vacuum Atmospheres drybox under  $\text{N}_2$ . Solvents were dried and collected using a Grubbs-type solvent purification system (Glass Contour)<sup>25</sup> and were degassed immediately prior to use by sparging with dry Ar or  $\text{N}_2$  for 10 min. Unless otherwise noted, all chemicals were obtained from commercial sources and used without further purification.  $\text{PCl}_3$  was obtained from Aldrich and distilled onto 4 Å molecular sieves prior to use.  $\text{GeCl}_2$  (dioxane) was synthesized according to the literature procedure<sup>26</sup> using  $\text{GeCl}_4$  and  $\text{Bu}^n_3\text{SnH}$ .  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$  ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ) was prepared by literature procedures<sup>27</sup> from the corresponding lithium amide and  $\text{GeCl}_2$  (dioxane),  $\text{SnCl}_2$ , or  $\text{PbCl}_2$ .  $\text{Ar}'\text{MgBr}(\text{THF})_2$  was prepared as described previously.<sup>28</sup>

All physical measurements were obtained under strictly anaerobic and anhydrous conditions.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired on a Varian Mercury 300 MHz instrument and referenced internally either to residual protiobenzene or trace silicone vacuum grease,  $\delta$  0.29 ppm in  $\text{C}_6\text{D}_6$ .  $^{31}\text{P}$  NMR spectra were recorded on a Varian Mercury 300 MHz instrument and referenced externally to 85%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$ .  $^{119}\text{Sn}$  NMR spectra were acquired a Varian Inova 600 MHz (at 223.7 MHz) instrument and were referenced externally to  $\text{Bu}^n_4\text{Sn}$  in  $\text{C}_6\text{D}_6$  ( $\delta$  –11.7 ppm).  $^{207}\text{Pb}$  NMR spectra were recorded on a Bruker 500 MHz instrument (at 105.3 MHz), externally referenced to  $\text{Pb}(\text{NO}_3)_2$  in  $\text{D}_2\text{O}$  ( $\delta$  –2984.4 ppm). IR spectra were recorded as

Nujol mulls between CsI plates on a Perkin-Elmer 1430 spectrophotometer. UV–visible spectra were recorded as dilute hexane solutions in 3.5 mL quartz cuvettes using a HP 8452 diode array spectrophotometer. Melting points were determined on a Meltemp II apparatus using glass capillaries sealed with vacuum grease and are uncorrected.

**$\text{Ar}'\text{PX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) (1).**  $\text{Ar}'\text{MgBr}(\text{THF})_2$  (12.92 g, 20 mmol) in ca. 150 mL of  $\text{Et}_2\text{O}$  and 100 mL of THF was added dropwise to  $\text{PCl}_3$  (2.75 g, 20 mmol) in ca. 50 mL of  $\text{Et}_2\text{O}$  at 0 °C, affording a yellow solution. The reaction mixture was stirred for 4 days to yield a white precipitate, whereupon the solvents were removed under reduced pressure. Benzene (200 mL), along with ca. 30 mL of 1,4-dioxane, was added to effect  $\text{MgX}_2$  precipitation. The solution was filtered via filter cannula, and the solvents were removed to afford a pale yellow solid. This was dissolved in hot hexane and concentrated to incipient crystallization to give two crops of light yellow crystalline material identified by  $^{31}\text{P}$  NMR as a mixture of halogenated species  $\text{Ar}'\text{PX}_2$  ( $\text{X} = \text{Cl}$  and/or  $\text{Br}$ ). Yield 7.0 g, 65% based on the average weight of the halogens.  $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy showed that the product was a mixture of  $\text{Ar}'\text{PCl}_2$ ,  $\text{Ar}'\text{P}(\text{Cl})\text{Br}$ , and  $\text{Ar}'\text{PBr}_2$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  158.77 ( $\text{Ar}'\text{PCl}_2$ , ca. 50%), 153.97 ( $\text{Ar}'\text{P}(\text{Cl})\text{Br}$ , ca. 40%), 146.30 ( $\text{Ar}'\text{PBr}_2$ , ca. 10%).

**$\text{Ar}'\text{PH}_2$  (2).** To  $\text{LiAlH}_4$  (2.0 g, 53 mmol) in ca. 100 mL of  $\text{Et}_2\text{O}$  at 0 °C was added  $\text{Ar}'\text{PX}_2$  (7.0 g, ca. 13 mmol) in ca. 150 mL of  $\text{Et}_2\text{O}$ . The mixture was stirred overnight, whereupon the solvent was removed under reduced pressure. The residue was extracted with ca. 150 mL of benzene and filtered over a Celite padded frit. Removal of the solvent afforded an off-white analytically pure powder in 87% yield (4.85 g), mp 105 °C. Anal. Calcd for  $\text{C}_{30}\text{H}_{39}\text{P}$ : C, 83.68; H, 9.13. Found: C, 83.11; H 9.41. IR 2300  $\nu(\text{P-H})$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  1.08 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 1.29 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 2.78 (sept, 2H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 7.2$  Hz), 3.27 (d, 2H,  $\text{ArPH}_2$ ,  $^1J_{\text{HP}} = 212$  Hz), 7.07 (m, 6H,  $m$ - and  $p$ -Dipp), 7.19 (d, 2H,  $m\text{-C}_6\text{H}_3$ ,  $^3J_{\text{HH}} = 8.4$  Hz), 7.32 (t, 1H,  $p\text{-C}_6\text{H}_3$ ,  $^3J_{\text{HH}} = 8.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  23.68, 25.23 ( $\text{CH}(\text{CH}_3)_2$ ), 31.07 ( $\text{CH}(\text{CH}_3)_2$ ), 122.86, 123.50, 127.16, 128.73, 128.95, 139.58, 144.69, 146.47 ( $\text{Ar-C}$ ).  $^{31}\text{P}$  NMR (121.4 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  –139.4 (t,  $\text{Ar}'\text{PH}_2$ ,  $^1J_{\text{PH}} = 212$  Hz).

**$\{\text{Ge}(\mu\text{-PAR}')\}_2$  (3).**  $\text{Ar}'\text{PH}_2$  (0.861 g, 2 mmol) and  $\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_2$  (0.865 g, 2.2 mmol) were combined in a Schlenk flask and heated at 170 °C in an oil bath with stirring. A deep red melt resulted, and the evolution of vapor was observed. Heating was continued over ca. 30 min, up to a temperature of 230 °C, with intermittent reduced pressure applied, to afford a deep red solid. All volatile materials were removed by distillation. The residue was extracted with 30 mL of hexanes, and the solution was filtered via cannula. Concentration and storage at 7 °C afforded deep red, diamond-shaped X-ray quality crystals of **3n**-hexane (0.240 g, 21% based on Ge), mp 310 °C. UV–vis, nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 368 (1650), 518 (7100).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  0.89 (t, 8H,  $n$ -hexane  $\text{CH}_3$ ), 1.00 (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 1.10 (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 1.24 (m, 8H,  $n$ -hexane  $\text{CH}_2$ ), 2.84 (sept, 8H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{HH}} = 7.2$  Hz), 7.11–7.29 (m, 18H,  $\text{ArH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 70 °C):  $\delta$  14.18 ( $n$ -hexane  $\text{CH}_3$ ), 22.98 ( $n$ -hexane  $\text{CH}_2$ ), 23.78 ( $\text{CH}(\text{CH}_3)_2$ ), 25.54 ( $\text{CH}(\text{CH}_3)_2$ ), 31.25 ( $\text{CH}(\text{CH}_3)_2$ ), 31.93 ( $n$ -hexane  $\text{CH}_2$ ), 124.14, 126.00, 129.14, 129.49, 141.42, 142.63, 143.98, 147.63 ( $\text{Ar-C}$ ).  $^{31}\text{P}$  NMR (121.4 MHz,  $\text{C}_6\text{D}_6$ , 70 °C)  $\delta$  +270.2 (singlet/quintet,  $\text{Ar}'\text{PGe}$ ,  $^1J_{31\text{P}-73\text{Ge}} = 553$  Hz).

**$\{\text{Sn}(\mu\text{-PAR}')\}_2$  (4).**  $\text{Ar}'\text{PH}_2$  (0.861 g, 2 mmol) and  $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$  (0.967 g, 2.2 mmol) were combined in a Schlenk flask and heated from 170 °C up to 220 °C in an oil bath with stirring. A deep violet melt resulted, and the evolution of vapor was observed. Heating was continued over ca. 5 min, with intermittent reduced pressure applied, to yield a violet solid. All volatile materials were removed by distillation. The crude solid product was extracted with 35 mL of hexanes, which was

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heated to a brief reflux and filtered. The solution was concentrated to ca. 25 mL and stored at 7 °C, which yielded deep violet, block-shaped X-ray quality crystals of **4***n*-hexane in two crops. Yield: 0.354 g, 32% based on Sn, mp 332 °C. UV-vis, nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 402 (5114), 548 (5525). IR, cm<sup>-1</sup>: 460, 390, 330  $\nu$ (P-Sn). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  0.89 (t, 6H, *n*-hexane CH<sub>3</sub>), 1.10 (overlapped d's, 48H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.24 (m, 8H, *n*-hexane CH<sub>2</sub>), 2.89 (sept, 8H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 3.27 (d, 2H, ArPH<sub>2</sub>, <sup>1</sup>J<sub>HP</sub> = 212 Hz), 7.05–7.27 (m, 18H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 70 °C):  $\delta$  14.18 (*n*-hexane CH<sub>3</sub>), 22.97 (*n*-hexane CH<sub>2</sub>), 24.28 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.44 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.23 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.92 (*n*-hexane CH<sub>2</sub>), 124.44, 124.75, 128.55, 129.33, 129.47, 142.70, 142.81, 147.21 (Ar-C). <sup>31</sup>P NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  +255.61 (s/d, Ar'PSn, <sup>1</sup>J<sub>31P-117/119Sn</sub> = 1463 Hz). <sup>119</sup>Sn{<sup>1</sup>H} NMR (223.7 MHz, C<sub>6</sub>D<sub>6</sub>, 70 °C)  $\delta$  +966.6 (t, ArPSn, <sup>1</sup>J<sub>31P-119Sn</sub> = 1464 Hz).

{Pb( $\mu$ -PAR')}<sub>2</sub> (**5**). Ar'PH<sub>2</sub> (0.861 g, 2 mmol) and Pb{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (1.161 g, 2.2 mmol) were reacted in a similar manner to that described for **3** and **4** combined in a Schlenk flask and heated from 190 °C up to 210 °C in an oil bath with stirring. The crude solid product was extracted with 35 mL of hexanes, and the resultant solution was heated to a brief reflux and filtered. The solution was concentrated to ca. 25 mL and stored at 7 °C to afford dark violet, block-shaped X-ray quality crystals of **5***n*-hexane in two crops (0.450 g, 31% based on Pb), mp 274 °C. UV-vis, nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 406 sh (2500), 518 (3300), 650 (1500). IR, cm<sup>-1</sup>: 460, 390, 270  $\nu$ (P-Pb). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 70 °C)  $\delta$  0.88 (t, 6H, *n*-hexane CH<sub>3</sub>), 1.09 (overlapped d's, 48H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.25 (m, 8H, *n*-hexane CH<sub>2</sub>), 2.88 (sept, 8H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 3.27 (d, 2H, ArPH<sub>2</sub>, <sup>1</sup>J<sub>HP</sub> = 212 Hz), 6.77–7.41 (m, 18H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 70 °C):  $\delta$  13.89 (*n*-hexane CH<sub>3</sub>), 23.38 (*n*-hexane CH<sub>2</sub>), 24.72 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.00 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.23 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.64 (*n*-hexane CH<sub>2</sub>), 123.25, 124.04, 124.92, 128.41, 141.86, 146.40, 147.45, 148.59 (Ar-C). <sup>31</sup>P NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>, 70 °C), +302.48 (s, d, Ar'PPb, <sup>1</sup>J<sub>31P-207Pb</sub> = 2070 Hz). <sup>207</sup>Pb NMR (105.28 MHz, C<sub>6</sub>D<sub>6</sub>, 70 °C):  $\delta$  +6150 (t, Ar'PPb, <sup>1</sup>J<sub>Pb-P</sub> = 2068 Hz).

**X-ray Crystallography.** Crystals of appropriate quality for X-ray diffraction studies were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen (90(2) K).<sup>29</sup> Data for all compounds were obtained on a Bruker SMART 1000 or SMART APEX instrument using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) in conjunction with a CCD detector. The collected reflections were corrected for Lorentz and polarization effects by using Blessing's method as incorporated into the program SADABS.<sup>30a,b</sup> The structures were solved by direct methods and refined with the SHELXTL v.6.1 software package.<sup>31a,b</sup> Refinement was by full-matrix least-squares procedures with all carbon-bound hydrogen atoms included in calculated positions and treated as riding atoms. A summary of crystallographic and data collection parameters for **3**–**5** is given in Table 1.

**Theoretical Methods.** The model compounds {M( $\mu$ -PAR')}<sub>2</sub> (**3**'–**5**') were calculated as gas phase dimers at the B3LYP/6-31G\* level for M = Ge and at the B3LYP/cc-pVTZ-PP level for M = Sn or Pb. All calculated structures represent true minima. DFT calculations were performed with the Gaussian 03

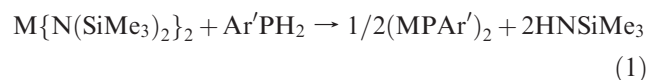
Table 1. Selected Crystallographic Data for Compounds **3**–**5**

compound	<b>3</b> <i>n</i> -C <sub>6</sub> H <sub>14</sub>	<b>4</b> <i>n</i> -C <sub>6</sub> H <sub>14</sub>	<b>5</b> <i>n</i> -C <sub>6</sub> H <sub>14</sub>
formula	C <sub>66</sub> H <sub>88</sub> P <sub>2</sub> Ge <sub>2</sub>	C <sub>66</sub> H <sub>88</sub> P <sub>2</sub> Sn <sub>2</sub>	C <sub>66</sub> H <sub>88</sub> P <sub>2</sub> Pb <sub>2</sub>
fw	1088.48	1180.68	1357.68
color, habit	red, rod	violet, rod	deep violet, block
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>I</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>I</i> 2/ <i>m</i>
<i>a</i> , Å	12.0005(5)	16.0315(16)	11.846(3)
<i>b</i> , Å	19.9995(8)	20.514(2)	20.612(7)
<i>c</i> , Å	12.7349(5)	11.8910(12)	12.737(3)
$\alpha$ , deg	90	90	90
$\beta$ , deg	98.9790(10)	128.261(2)	98.466(4)
$\gamma$ , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	3019.09(2)	3070.6(5)	3076.2(15)
<i>Z</i>	2	2	2
crystal dimension, mm	0.40 × 0.35 × 0.13	0.40 × 0.20 × 0.20	0.40 × 0.38 × 0.33
<i>T</i> , K	90(2)	90(2)	90(2)
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.197	1.277	1.466
abs. coefficient $\mu$ , mm <sup>-1</sup>	1.086	0.902	5.555
$\theta$ range, deg	1.91 to 27.50	1.90 to 28.70	1.89 to 27.50
reflections collected	3565	21241	16047
obs reflections [I > 2 $\sigma$ (I)]	2943	3041	2587
data/restraints/parameters	3565/0/183	4084/0/174	3598/0/175
<i>R</i> <sub>1</sub> , observed reflections	0.0394	0.0574	0.0904
w <i>R</i> <sub>2</sub> , all	0.1055	0.1178	0.2027

package,<sup>32a</sup> and the geometries were generated with the Chemcraft program.<sup>32b</sup>

## Results and Discussion

**Synthesis.** The phosphinidene compounds **3**–**5** were synthesized by amine elimination reactions between the silylamides M{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (M = Ge, Sn, or Pb) and Ar'PH<sub>2</sub> (**2**) (eq 1).



The primary phosphine Ar'PH<sub>2</sub> was prepared by a modified route involving the reaction of the Grignard reagent Ar'MgBr(THF)<sub>2</sub><sup>28</sup> with PCl<sub>3</sub> to give **1** and the subsequent reduction of **1** with LiAlH<sub>4</sub> to afford **2**. We had observed previously that the synthetic approach to bulky terphenyl phosphine derivatives using LiAr<sup>#</sup> (Ar<sup>#</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)<sup>23</sup> or LiAr\* (Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sub>3</sub>)<sub>2</sub>)<sup>33</sup> as terphenyl transfer agents led to undesirable side products and low yields. The direct reaction of LiAr' and PCl<sub>3</sub> gave an approximate 50/50 mixture of the desired Ar'PCL<sub>2</sub> and Ar'Cl, which co-crystallized from hexane or ether extracts. An unidentified insoluble red material was also observed. These results had similarities to those reported by Hey-Hawkins and co-workers for the LiMes\* (Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-Bu<sup>t</sup><sub>3</sub>)-based synthesis of Mes\*PCL<sub>2</sub>.<sup>34</sup> However, the use of the Ar'MgBr(THF)<sub>2</sub> transfer agent instead of LiAr' afforded "Ar'PX<sub>2</sub>" exclusively and in good yield with essentially no aryl halide elimination.

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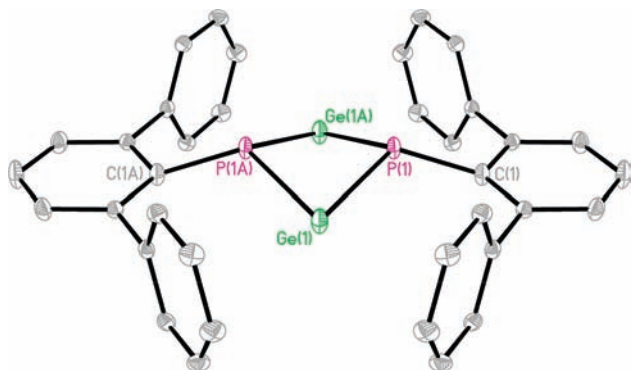
(30) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38. (b) Sheldrick, G. M. *SADABS*; Universität Göttingen: Göttingen, Germany, 2008.

(31) (a) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker AXS Inc.: Madison, WI, 2002. (b) Sheldrick, G. M. *SHELXS97 and SHELXL97*; Universität Göttingen: Göttingen, Germany, 1997.

(32) (a) Frisch, M. J., et al. *Gaussian 03*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003 (full reference can be found in the Supporting Information).

(b) Zhurko, G. A. *Chemcraft*.





**Figure 1.** Thermal ellipsoid (30%) drawing of **3**. Hydrogen atoms, isopropyl groups, and disordered and minor twin component core atoms are not shown. Ge···Ge 3.392 Å; Ge–P 2.313 Å (average); P(1)–Ge(1)–P(1A) 85.67°.

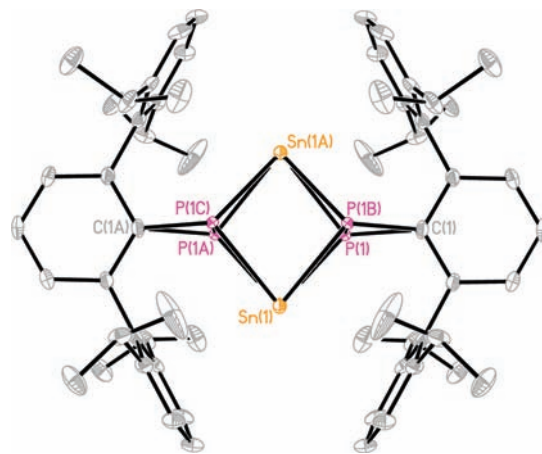
This material proved suitable for reduction to the arylphosphine  $\text{Ar}'\text{PH}_2$  by reaction with an excess of  $\text{LiAlH}_4$ .

When the reactions were carried out with 2 equiv of  $\text{H}_2\text{PAr}'$  per  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$ , the corresponding phosphinidenes **3**, **4**, or **5** were also the only pure products isolated from solution. It is possible that any " $\text{M}\{\text{P}(\text{H})\text{Ar}'\}_2$ " formed in this reaction readily eliminates  $\text{H}_2\text{PAr}'$  to form the phosphinidene dimer (eq 2).

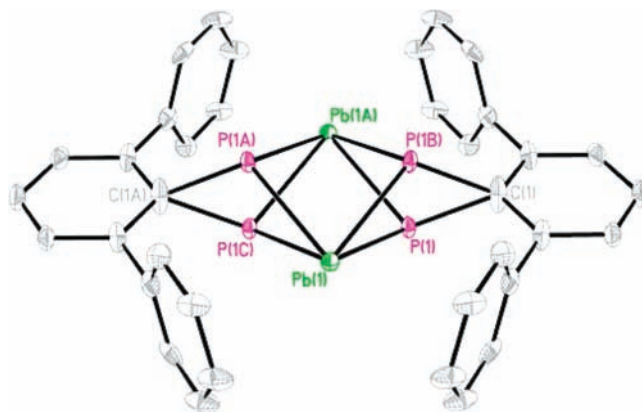


Other attempts to synthesize diphosphides  $\text{M}\{\text{P}(\text{H})\text{Ar}'\}_2$  ( $\text{M} = \text{Sn}, \text{Pb}$ ) by the reaction of 2 equiv of  $\text{LiP}(\text{H})\text{Ar}'$  with  $\text{SnCl}_2$  or  $\text{PbBr}_2$  at  $-78^\circ\text{C}$  resulted in grey precipitates and weakly colored solutions upon warming to room temperature. Treatment of  $\text{GeCl}_2$  (dioxane) with 2 equiv of  $\text{LiP}(\text{H})\text{Ar}'$  did not afford isolable quantities of  $\text{Ge}\{\text{P}(\text{H})\text{Ar}'\}_2$ .

**Structures.** Each of the phosphinidenes **3–5** crystallized with one-quarter of the dimer comprising the asymmetric unit (crystallographic data collection parameters are given in Table 1). The structures (Figures 1–3) have similar  $\text{M}_2\text{P}_2$  ring cores, which in the case of **4** and **5** have 50/50 disorder of the pyramidally coordinated phosphorus atoms over two positions, consistent with either a planar four-membered ring with aryl P-substituents that are *anti* with respect to each other or with an  $\text{M}_2\text{P}_2$  ring folded along the  $\text{M}\cdots\text{M}$  vector with *syn*-disposed aryl P-substituents. Such disorder was resolved, however, in **3** (see Supporting Information), which has a  $\text{Ge}_2\text{P}_2$  core folded along the  $\text{Ge}\cdots\text{Ge}$  axis and clearly *syn*-oriented aryl substituents. The folding between the two  $\text{M}_2\text{P}$  planes in the *syn* structures increased in the order  $\mathbf{3} < \mathbf{4} < \mathbf{5}$  ( $45.4^\circ$  for Ge,  $59.7^\circ$  for Sn, and  $63.0^\circ$  for Pb, cf. Table 2), which may be steric in origin. The internal ring angles at the metals average  $85.67(5)^\circ$  (**3**),  $87.20^\circ$  (**4**), and  $86.40^\circ$  (**5**), and those at phosphorus average  $94.33^\circ$  (**3**),  $92.78^\circ$  (**4**), and  $89.86^\circ$  (**5**). The Ge–P and Sn–P bond lengths are considerably shorter than those observed in the three-dimensional cage species or phosphide derivatives. The M–P distances average  $2.312(10)$  Å in **3** and  $2.466(18)$  Å in **4**; cf.  $2.416(2)$  to  $2.487(2)$  Å in the germanium–phosphinidene cage  $\{\text{Ge}(\mu\text{-PSiPr}_3)\}_6$ ,<sup>21</sup>  $2.490$  Å in  $\{\text{Ge}(\text{Br})\text{PBu}'_2\}_2$ ,<sup>35</sup> and  $2.626(3)$  to  $2.665(3)$  Å in the tin species  $\{\text{Sn}(\mu\text{-PSiPr}_3)\}_6$ ,<sup>17</sup>  $2.567(1)$  Å in  $\text{Sn}\{\text{P}(\text{SiPr}_3)\}\{\text{Si}$



**Figure 2.** Thermal ellipsoid (30%) drawing of **4**. Hydrogen atoms are not shown. Phosphorus atoms have 50% occupancies for the P(1)/P(1A) or P(1B)/P(1C) positions. Sn···Sn 3.572 Å; Sn–P 2.466 Å (average); P(1)–Sn(1)–P(1A)  $87.20^\circ$ .



**Figure 3.** Thermal ellipsoid (30%) drawing of **5**. Hydrogen atoms, isopropyl groups, and disordered Pb atom positions (above and below Pb(1) and Pb(1A), respectively) are not shown. Phosphorus atoms have 50% occupancies for the P(1)/P(1C) or P(1A)/P(1B) positions. Pb···Pb 3.487(3) Å; Pb–P 2.621(3) Å (average); P(1)–Pb(1)–P(1C)  $86.40^\circ$ .

(Trip)(Bu')F<sub>2</sub>],<sup>36</sup> as well as  $2.738$  Å in  $\text{Sn}\{\text{P}(\text{C}_4\text{Et}_4)\}_2$ .<sup>37</sup> The most relevant structurally characterized molecular lead(II) phosphorus compounds are the phosphido derivatives  $\text{Pb}\{\text{P}(\text{SiPr}_3)\}\{\text{Si}(\text{Trip})(\text{Bu}')\text{F}\}_2$  (Pb–P  $2.654(4)$  Å)<sup>36</sup> and  $[\text{Pb}\{\mu\text{-P}(\text{SiMe}_3)_2\}\text{P}(\text{SiMe}_3)_2]_2$  (Pb–P  $2.696(7)$ , terminal, to  $2.796(7)$  Å, bridging),<sup>38</sup> which have average Pb–P distances that are longer than the  $2.621(3)$  Å found for **5**. Overall, the M–P bond lengths in **3–5** are consistent with single bond distances predicted from the sums of the single bond radii: Ge–P ( $2.32$  Å), Sn–P ( $2.51$  Å), and Pb–P ( $2.55$  Å).<sup>39</sup>

The  $\text{M}_2\text{P}_2$  cores of **3–5**, which have two-coordinate metal atoms, are unprecedented and are comparable only with the less sterically encumbered congeneric imido germanium compounds  $\{\text{Ge}(\mu\text{-NMe}_3^*)\}_2$ <sup>14</sup> and  $\{\text{Ge}(\mu\text{-N}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-}(\text{CF}_3)_3)\}_2$ .<sup>15</sup> Although the M–P distances

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**Table 2.** Selected Interatomic Distances (Å) and Angles (deg) for Compounds **3**, **4**, and **5**. Calculated Values for the Corresponding Model Compounds  $\{M(\mu\text{-PMe})\}_2$ , M = Ge (**3'**), Sn (**4'**), Pb (**5'**) Are Shown in Brackets

$\{\text{Ge}(\mu\text{-PAr}')\}_2$ ( <b>3</b> )			
Ge(1)···Ge(1A)	3.392	P(1)–Ge(1)–P(1A)	85.67 [81.6]
Ge(1)–P(1)	2.3104(10) [2.354]	Ge(1)–P(1)–Ge(1A)	94.33 [78.5]
Ge(1A)–P(1)	2.3153(9) [2.354]	C(1)–P(1)–Ge(1)	120.40 [111.1]
P(1)···P(1A)	2.902	P(1)–C(1)–C(4)	161.03
P(1)–C(1)	1.865(2) [1.886]	Ge <sub>2</sub> P <sub>2</sub> dihedral angle	134.63 [115.1]
		Σ angles at P(1)	335.38
$\{\text{Sn}(\mu\text{-PAr}')\}_2$ ( <b>4</b> )			
Sn(1)···Sn(1A)	3.572	P(1)–Sn(1)–P(1A)	87.20 [77.8]
Sn(1)–P(1)	2.4134(18) [2.562]	Sn(1)–P(1)–Sn(1A)	92.78 [84.2]
Sn(1A)–P(1)	2.5192(17) [2.562]	C(1)–P(1)–Sn(1)	120.82 [114.3]
P(1)···P(1B)	1.424	P(1)–C(1)–C(4)	158.10
P(1)···P(1A)	3.091	Sn <sub>2</sub> P <sub>2</sub> dihedral angle	130.26 [115.7]
P(1)–C(1)	1.908(5) [1.884]	Σ angles at P(1)	329.49
$\{\text{Pb}(\mu\text{-PAr}')\}_2$ ( <b>5</b> )			
Pb(1)···Pb(1A)	3.487	P(1)–Pb(1)–P(1C)	86.40 [77.5]
Pb(1)–P(1)	2.616(3) [2.653]	Pb(1)–P(1)–Pb(1A)	89.86 [84.2]
Pb(1A)–P(1)	2.625(3)	C(1)–P(1)–Pb(1)	111.8 [114.4]
P(1)···P(1B)	1.482(8)	P(1)–C(1)–C(4)	157.13
P(1)···P(1C)	3.166(10)	Pb <sub>2</sub> P <sub>2</sub> dihedral angle	117.03 [115.1]
P(1)–C(1)	1.905(10) [1.887]	Σ angles at P(1)	318.79

in **3–5** are consistent with single bonding, with little  $\pi$ -donation from P to M,<sup>16,38</sup> it is noteworthy that the coordination geometry at phosphorus becomes increasingly flattened with decreasing atomic number of M:  $\Sigma^\circ P$  (Ge > Sn > Pb) = 335.38° (**3**), 329.49° (**4**), and 318.79° (**5**). A similar trend can be seen in the X-ray structures of  $[M\{\text{P}(\text{SiMe}_3)_2\}_2]_2$  (M = Zn, Cd, Hg, Sn, Pb), where the degree of pyramidalization at the terminal phosphido ligand can also be correlated with increasing atomic number of M.<sup>38</sup>

**NMR and Electronic Spectroscopy.** The <sup>31</sup>P NMR chemical shifts observed at +270.2 and +255.6 ppm for **3** and **4** differed by only ca. 15 ppm. The <sup>31</sup>P signal for the lead compound **5** was observed somewhat further downfield than these at +302.5 ppm. The +255.6 ppm shift for the Ge derivative **3** is considerably downfield of the +13.8 and –36.8 ppm chemical shifts reported for the terminal and bridging P atoms in the three-coordinate Ge phosphido compound  $\{\text{Ge}(\text{PPr}^i_2)\mu\text{-PPr}^i_2\}_2$ .<sup>40</sup> The <sup>31</sup>P signal of the tin derivative **4** is well downfield of the +0.1 ppm reported for the dark green tin phosphide  $\text{Sn}\{\text{P}(\text{Ph})\text{Ar}^\#_2\}_2$  (Ar<sup>#</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>).<sup>41</sup> The <sup>31</sup>P NMR chemical shift of the lead compound **5** (+302.5 ppm) is also downfield of the few chemical shifts that have been reported for Pb–P bonded compounds, –88.8 (terminal P) and –95.6 ppm (bridging P) in  $\text{Pb}[\text{P}(\text{SiPr}^i_3)\{\text{Si}(\text{Trip})(\text{Bu}^t)\text{F}\}_2]_2$ <sup>36</sup> (see Table 3). In general, these downfield shifts are typical for metalated derivatives relative to the upfield shifts of their parent phosphines (cf. Ar'<sup>#</sup>PH<sub>2</sub> <sup>31</sup>P NMR  $\delta$  = –139.4 ppm). The <sup>31</sup>P NMR spectra of compounds **3–5** also displayed marked <sup>1</sup>J coupling to the group 14 element spin-active nuclei. The coupling constants are <sup>1</sup>J<sub>31P–73Ge</sub> = 553 Hz, <sup>1</sup>J<sub>31P–119Sn</sub> = 1464 Hz, and <sup>1</sup>J<sub>31P–207Pb</sub> = 2068 Hz. The value obtained for coupling to <sup>73</sup>Ge ( $I = 9/2$ ,

7.8%) is apparently unique, and it cannot be compared to other values at present. The couplings to the tin and lead nuclei are discussed further below.

Although a <sup>73</sup>Ge NMR spectrum was not observed, <sup>119</sup>Sn and <sup>207</sup>Pb NMR spectroscopy afforded signals that display coupling to the phosphorus nuclei. Initially, we were unable to find a <sup>119</sup>Sn NMR signal for **4** in C<sub>6</sub>D<sub>6</sub> in the region deemed most probable on the basis of scarce published <sup>119</sup>Sn NMR data for Sn(II)–P compounds,<sup>42</sup> some of which are shown for comparison in Table 3. However, at elevated temperature (70 °C), sufficient solubility of **4** in C<sub>6</sub>D<sub>6</sub> was achieved and a signal with a 1:2:1 intensity pattern due to coupling to two equivalent <sup>31</sup>P nuclei ( $J_{119\text{Sn}-31\text{P}} = 1465$  Hz) was observed at +966.6 ppm. This signal is farther downfield than the  $\delta = +499.5$  ppm observed for the Sn–P doubly bonded species  $\text{Trip}_2\text{Sn}=\text{PMes}^*$  (Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup><sub>3</sub>, Mes\* = C<sub>6</sub>H<sub>3</sub>-2,4,6-Bu<sup>t</sup><sub>3</sub>), a phosphinidene Sn(IV) derivative,<sup>43</sup> although it is upfield of the +1101 ppm reported for the sterically encumbered Sn(II) phosphide  $\text{Sn}\{\text{P}(\text{Ph})\text{Ar}^\#_2\}_2$  (Ar<sup>#</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>).<sup>41</sup> The chemical shift of **4** lies further downfield than the +738.9 ppm observed for the related species  $\{\text{Sn}(\mu\text{-NAr}^\#_2)\}_2$ ,<sup>44</sup> which is the opposite of what is expected on the basis of  $\sigma$ -inductive effects. However, the  $\{\text{Sn}(\mu\text{-NAr}^\#_2)\}_2$  displays closer average aryl(centroid)···Sn approaches than those in **4** (ca. 3.17 vs 3.32 Å) and may be responsible for the shift differences. The <sup>1</sup>J<sub>119Sn–31P</sub> coupling found that **4** is essentially the same as that determined from the <sup>31</sup>P NMR spectrum and is almost twice that found for the hexameric tin triisopropylsilylphosphanedide of Driess and co-workers.<sup>17</sup>

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**Table 3.** Selected NMR Parameters for Some Ge–P, Sn–P, and Pb–P Bonded Compounds

compound	M $\delta$ , ppm	$^{31}\text{P}$ $\delta$ , ppm	$J_{\text{P-M}}$ , Hz	reference
<b>3</b> {Ge(PPr <sup><i>t</i></sup> ) $\mu$ -PPr <sup><i>t</i></sup> )} <sub>2</sub>		+270.2 +13.8 <sup><i>t</i></sup> , –36.8 <sup><i>br</i></sup>	553	this work 40
<b>4</b> Li(THF) <sub>4</sub> - {Sn <sub>2</sub> ( $\mu_3$ -PC <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> } <sub>2</sub> {Sn( $\mu$ -PSiPr <sup><i>t</i></sup> ) <sub>3</sub> } <sub>6</sub> Sn{[P(SiPr <sup><i>t</i></sup> )- {Si(Trip) <sub>2</sub> F}] <sub>2</sub> } <sup><i>†</i></sup>	+996.6 –139.5	+255.6 –184.2	1464 550	this work 9
Sn{P(Ph)Ar <sup><i>#</i></sup> } <sub>2</sub> Trip <sub>2</sub> Sn=PMe <sup><i>s</i></sup> * <sup><i>a,b</i></sup>	+1551	–475.2 –102.5	708 1682	17 36
<b>5</b> Pb{P(SiPr <sup><i>t</i></sup> )- {Si(Trip)(Bu <sup><i>t</i></sup> )F}] <sub>2</sub> Li(THF){PbPBu <sup><i>t</i></sup> )} <sub>2</sub> {Pb(PBu <sup><i>t</i></sup> ) $\mu$ -PBu <sup><i>t</i></sup> )} <sub>2</sub>	+1101 +499.5 +6150	+0.1 +170.7 +302.5 –88.8, –95.6 +71.5 +90.8 <sup><i>t</i></sup> , +65.3 <sup><i>br</i></sup>	891 2208 2068 1995, 1979	39 42 this work 36
			1770 2452, 1100	48 49

<sup>*a*</sup> Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>*t*</sup><sub>3</sub>, Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-Bu<sup>*t*</sup><sub>3</sub>. <sup>*b*</sup> Sn(IV). <sup>*t*</sup> Terminal. <sup>*br*</sup> Bridging.

The <sup>207</sup>Pb NMR signal for **5** was also initially difficult to locate in the region expected for a two-coordinate Pb(II) species (ca. 2000–5000 ppm).<sup>46a,b</sup> Upon repeated data collections in a variety of spectral windows, and reduction of the relaxation, or recycle, delay time to the minimum allowed by the instrument, a well-resolved <sup>31</sup>P-coupled triplet (<sup>1</sup> $J_{207\text{Pb}-31\text{P}} = 2025$  Hz) was observed at 6150 ppm<sup>47</sup> (cf.  $\delta = +5019$  ppm for Pb( $\mu$ -NAr<sup>*#*</sup>)<sub>2</sub>.<sup>44</sup> <sup>1</sup> $J_{207\text{Pb}-31\text{P}}$  coupling constants are rare for Pb(II)–P compounds.<sup>46</sup> Some examples are given in Table 3. These include the “ate” complex Li(THF){PbPBu<sup>*t*</sup>)}<sub>2</sub><sup>48</sup> (<sup>1</sup> $J_{\text{Pb-P}} = 1770$  Hz) and the lead *tert*-butylphosphanediide {Pb( $\mu$ -PBu<sup>*t*</sup>)<sub>2</sub>}<sub>2</sub> (no  $\delta$  <sup>207</sup>Pb reported).<sup>49</sup> The 2068 Hz <sup>1</sup> $J_{\text{Pb-P}}$  found for **5** lies between the 2452 Hz reported for the bridging PBu<sup>*t*</sup> groups in {Pb( $\mu$ -PBu<sup>*t*</sup>)<sub>2</sub>}<sub>2</sub> and about twice that assigned to its terminal PBu<sup>*t*</sup> groups (1100 Hz).

The UV–visible spectra of **3–5** in hexane solution reveal  $\lambda_{\text{max}}$  absorptions similar to the metal lone pair to empty p-orbital ( $n \rightarrow p$ ) transitions reported for V-shaped monomeric amido germynes, -stannylenes, and -plumbylenes.<sup>50</sup> The absorption maxima attributable to these ( $n \rightarrow p$ ) transitions were observed at 518 nm (**3**), 548 nm (**4**), and 650 nm (**5**). These absorptions are all at lower energies than the corresponding ( $n \rightarrow p$ )-related maxima recorded for the nitrogen-containing ring congeners {M( $\mu$ -NAr<sup>*#*</sup>)<sub>2</sub>} (M = Ge, Sn, Pb; Ar<sup>*#*</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>).<sup>44</sup> This bathochromic shift is to be expected given the lower electronegativity of P versus N which results in a higher energy for the lone pair orbital as a result of the weaker  $\sigma$ -withdrawing P ligands. As expected, the energy of this HOMO  $\rightarrow$  LUMO transition decreases in the sequence Ge > Sn > Pb for the series **3–5**.

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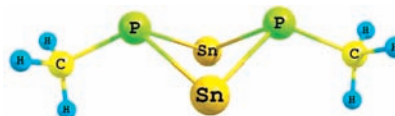
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**Figure 4.** Calculated structure of the P-methyl gas-phase model **5**.

**Density Functional Theory Results.** Structural parameters for the gas-phase model dimers {M( $\mu$ -PMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub> (M = Ge (**3'**), Sn (**4'**), Pb (**5'**)) were calculated at the B3LYP/cc-pVTZ-PP (**4'**, **5'**) and B3LYP/6-31G\* levels (**3'**). As observed in the experimental crystal structures, the geometries calculated for the model compounds displayed folding along their M···M axes (Sn model shown in Figure 4). However, in these much less hindered MeP-bridged models of all three elements Ge, Sn, and Pb, the calculated dihedral angle was found to be similar (ca. 115°) in **3'–5'**. This is in contrast to the experimental values from the crystal structures of **3–5**, {134.6° (**3**), 130.3° (**4**), and 117.0° (**5**)}. This difference can be attributed to ligand–ligand opposing steric pressure in the real compounds which forces open their M···M “hinge” in comparison to the simple P–Me models which experience no such interligand opposition. As observed in the sequence of fold angles for the real compounds **3–5**, this steric pressure effect is more pronounced in the order Ge > Sn > Pb—the smaller the metal, the closer the interligand approach. The calculated bond lengths and angles for the {M( $\mu$ -PMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub> models **3'–5'** are shown in brackets for comparison in Table 2.

Although the *syn* structure of the M<sub>2</sub>P<sub>2</sub> core was resolved for the Ge compound **3** (Figure 1), 50/50 up/down P atom disorder seen in the crystal structures determined for **4** and **5** (Figures 2 and 3) prohibits crystallographic distinction between a (M···M) folded (*syn*) or flat M<sub>2</sub>P<sub>2</sub> (*anti*) core structure. However the DFT-calculated geometries for **4'** and **5'** featuring a folded rhomboid M<sub>2</sub>P<sub>2</sub> core (PMe groups *syn*-disposed) suggest that this geometry is preferred in single molecules **4** and **5** in the crystalline state, rather than a planar (PAr<sup>*r*</sup> groups *anti*-disposed) configuration.

## Conclusions

Compounds **3–5** are dimers of the putative monomeric “Ar<sup>*r*</sup>P=M:” (M = Ge, Sn, Pb) fragments which remain unknown as stable species. The large size of the Ar<sup>*r*</sup> ligand has allowed the stabilization of a stable homologous series of dimeric heavier group 14 phosphinidenes that are preceded only by congeneric M<sub>2</sub>N<sub>2</sub> rings in the compounds {M( $\mu$ -NR)}<sub>2</sub> (M = Ge, R = Mes\*,<sup>14</sup> or C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>;<sup>15</sup> M = Ge, Sn, Pb, R = Ar<sup>*#*</sup>). Furthermore, <sup>31</sup>P, <sup>119</sup>Sn, and <sup>207</sup>Pb NMR spectroscopy has allowed rare heteronuclear shifts and  $J_{\text{P-M}}$  coupling constants to be recorded. The data indicate that there is minimal delocalization of the phosphorus lone pair into the valence p-orbitals of the tetrel atoms.

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**Supporting Information Available:** Crystallographic information files (CIF) for **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.