

## When Arsine Makes the Difference: Chelating Phosphino and Bridging Arsinoarylthiolato Gallium Complexes

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The (organo)gallium compounds  $\text{GaCl}\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}_2$  (**1**),  $\text{Ga}\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa\text{S}\}_2$  (**2**),  $\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}$  (**3**),  $\text{Ga}^t\text{Bu}_2\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}$  (**4**),  $\text{Ga}^t\text{Bu}\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa\text{S}\}$  (**5**),  $[\text{GaMe}_2\{(\mu_2\text{-SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}]_2$  (**6**), and  $\text{Ga}^t\text{Bu}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa^2\text{S,As}\}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}$  (**7**) were obtained from the reaction of 2-EPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH (E = P (**PSH**), As (**AsSH**)) with  $\text{GaCl}_3$  (**1**, **2**) or  $\text{GaR}_3$  (R = Me, <sup>t</sup>Bu; **3**–**7**) in different molar ratios and under different reaction conditions. Compound **2** was also obtained from Li(**PS**) and  $\text{GaCl}_3$  (3.5:1). While a monomeric structure with a chelating phosphinoarylthiolato ligand is observed in  $\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPH}_2)\text{-}\kappa^2\text{S,P}\}$  (**3**), a dimeric arsinoarylthiolato-bridged complex  $[\text{GaMe}_2\{(\mu_2\text{-SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}]_2$  (**6**) is obtained with the corresponding **AsS**<sup>−</sup> ligand. B3LYP/6-31G(d) calculations show that although the dimer is thermodynamically favored for both ligands, the formation of **3** is due to the combination of higher stability of the chelate compared with the monodentate phosphorus ligand and a higher barrier for the ring opening of the **PS**<sup>−</sup> than of the **AsS**<sup>−</sup> chelate.

## Introduction

Mixed group 13/15 (Ga, In/P, As) compounds have been under investigation for many years not only due to their wide applications in materials science,<sup>1,2</sup> for fabrication of various

microelectronic devices,<sup>3</sup> or for medical purposes<sup>4,5</sup> but also due to their structural variety.<sup>6</sup> Thus, the number of group 13 metal compounds with tertiary phosphines and arsines<sup>7,12</sup> is continuously growing and is related to both aspects, their applications and their very interesting and rewarding chemistry.

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More complex systems where group 13/15 components are accompanied by other elements such as oxygen or sulfur are barely studied.<sup>13</sup> Phosphinoarylthiols and arsinoarylthiols are excellent heteropolymetallic ligands, and the combination of phosphorus or arsenic with the multiple coordination patterns offered by the presence of sulfur leads to a great variety of structures. While transition metal complexes of 2-PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH have been reported previously<sup>14</sup> derivatives of main group metals, including group 13 elements, are almost unexplored as only some tin<sup>15</sup> and indium<sup>16</sup> complexes have been reported so far. The coordination chemistry of 2-AsPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH is even less explored, the preparation of the free ligand being only recently reported.<sup>17</sup> Here, we report on the synthesis and characterization of the gallium and organogallium complexes GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}<sub>2</sub> (**1**), Ga{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS}<sub>2</sub> (**2**), GaMe<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P} (**3**), Ga'Bu<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P} (**4**), Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS} (**5**), [GaMe<sub>2</sub>{(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS}]<sub>2</sub> (**6**), and Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κ<sup>2</sup>S,As}{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS} (**7**).

## Experimental Section

**General Procedures.** All manipulations were carried out under an inert atmosphere of dry nitrogen. Cyclohexane, *n*-hexane, toluene, diethyl ether, and THF were dried over sodium/benzophenone, distilled under an atmosphere of dry argon, and stored over a potassium mirror. CH<sub>2</sub>Cl<sub>2</sub>, MeOH, and tetramethylethylenediamine (TMEDA) were refluxed over CaH<sub>2</sub>, distilled, and kept under nitrogen. Some deuterated solvents needed for NMR spectroscopy were used as purchased and kept under inert atmosphere over potassium mirror (C<sub>7</sub>D<sub>8</sub>) or molecular sieves (THF-*d*<sub>8</sub>). C<sub>6</sub>D<sub>6</sub> was dried with sodium/potassium alloy, filtered, and kept under inert atmosphere over potassium mirror. CDCl<sub>3</sub> was dried over LiAlH<sub>4</sub>, distilled, and kept over molecular sieves. <sup>n</sup>BuLi (2.2 M in *n*-hexane), <sup>t</sup>BuLi (1.47 M in *n*-pentane), NEt<sub>3</sub>, GaCl<sub>3</sub>, and GaMe<sub>3</sub> were obtained from commercial suppliers. GaCl<sub>3</sub> was freshly sublimed before use. Ga'Bu<sub>3</sub> was synthesized by minor modifications of the standard literature procedure involving the reaction of GaCl<sub>3</sub> with <sup>t</sup>BuLi (1:3).<sup>18,19</sup> The ligands 2-EPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH (E = P (PSH), As (AsSH)) were prepared from thiophenol by *ortho*-lithiation/electrophilic substitution,<sup>17,20</sup> using Schlenk techniques and dry solvents.

Elemental analysis was performed with a Vario EL-Heraeus microanalyzer. IR spectra were recorded using a Perkin-Elmer System 2000 spectrometer in the range 4000–400 cm<sup>−1</sup> and 400–200 cm<sup>−1</sup> using KBr and CsI pellets, respectively. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance DRX-400 instrument, <sup>1</sup>H NMR using TMS as internal standard and <sup>31</sup>P NMR using external 85% H<sub>3</sub>PO<sub>4</sub>.

The mass spectra were recorded on a VG12-520 mass spectrometer (EI-MS, 70 eV, 200 °C), FT ICR MS Bruker Daltonics ESI mass spectrometer (APEX II, 7 T), or a MASPEC II spectrometer (FAB MS, matrix = 3-nitrobenzylalcohol).

The crystallographic data were collected on a Siemens CCD diffractometer (SMART) with  $\omega$  scan rotation, data reduction with SAINT,<sup>21</sup> and empirical absorption correction with SADABS<sup>22</sup> (compounds **2**, **4**, **7**) and on a CCD Oxford Xcalibur S diffractometer in  $\omega$ - and  $\varphi$ -scan mode with data reduction with CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK<sup>23</sup> (compounds **1**, **3**, **5**, **6**). Radiation was Mo K $\alpha$  ( $\lambda$  = 0.71073 Å). Structure refinement was carried out with SHELXL-97.<sup>24</sup> Non-hydrogen atoms, except poorly defined disordered regions, were refined anisotropically, and H atoms were calculated on idealized positions. Structure figures were generated with ORTEP.<sup>25</sup> Thermal ellipsoids are drawn at 50% probability if not otherwise mentioned. The relevant crystallographic data and refinement details are shown in Table 1. For complex **5**, a temperature of 220(2) K was used, because the crystals cracked at lower temperatures. CCDC 688529 (**1**), 688530 (**2**), 688531 (**3**),

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**Table 1.** Summary of Data Collection, Structure Solution and Refinement Details for Compounds 1–7

	1	2	3	4	5	6	7
empirical formula	C <sub>40</sub> H <sub>36</sub> ClGaOP <sub>2</sub> S <sub>2</sub>	C <sub>54</sub> H <sub>42</sub> GaP <sub>3</sub> S <sub>3</sub>	C <sub>20</sub> H <sub>20</sub> GaPS	C <sub>26</sub> H <sub>32</sub> GaPS	C <sub>40</sub> H <sub>37</sub> GaP <sub>2</sub> S <sub>2</sub>	C <sub>40</sub> H <sub>40</sub> As <sub>2</sub> Ga <sub>2</sub> S <sub>2</sub>	C <sub>40</sub> H <sub>37</sub> As <sub>2</sub> Ga <sub>2</sub> S <sub>2</sub>
<i>f</i> <sub>w</sub>	763.92	949.69	393.11	477.27	713.48	874.12	801.38
<i>T</i> , K	130(2)	210(2)	130(2)	213(2)	220(2)	180(2)	213(2)
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> na2 <sub>1</sub>	<i>P</i> ca2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.324(5)	26.112(5)	19.7747(2)	14.820(2)	9.4389(5)	12.8578(3)	9.483(1)
<i>b</i> , Å	28.488(5)	17.413(4)	8.5440(1)	11.016(2)	9.9813(5)	9.4095(2)	10.063(2)
<i>c</i> , Å	14.178(5)	10.240(2)	21.7993(2)	16.029(3)	21.8992(9)	15.4085(3)	22.277(3)
$\alpha$ , deg	90	90	90	90	81.212(4)	90	81.227(3)
$\beta$ , deg	106.161(5)	90	90	107.575(2)	79.362(4)	91.582(2)	78.180(3)
$\gamma$ , deg	90	90	90	90	63.086(5)	90	63.959(3)
vol, Å <sup>3</sup>	3617(2)	4656.1(15)	3683.10(7)	2494.6(7)	1802.4(2)	1863.49(7)	1864.8(5)
<i>Z</i>	4	4	8	4	2	2	2
<i>D</i> <sub>calc</sub> , mg/m <sup>3</sup>	1.403	1.355	1.418	1.271	1.315	1.558	1.427
$\mu$ (Mo K $\alpha$ ), mm <sup>−1</sup>	1.070	0.865	1.691	1.260	0.995	3.347	2.637
<i>F</i> (000)	1576	1960	1616	1000	740	880	812
cryst size, mm <sup>3</sup>	0.30 × 0.04 × 0.02	0.30 × 0.10 × 0.10	0.50 × 0.40 × 0.40	0.40 × 0.40 × 0.40	0.20 × 0.10 × 0.10	0.40 × 0.20 × 0.20	0.10 × 0.10 × 0.02
$\theta_{\min}/\theta_{\max}$ , deg	2.61/26.37	2.31/28.56	2.76/30.51	2.34/29.61	2.50/25.51	2.64/28.28	1.87/23.25
no. of reflns collected	60712	24959	94797	14716	17486	19307	8232
no. of independent reflns	7395 [R(int) = 0.0896]	10127 [R(int) = 0.0476]	11227 [R(int) = 0.0245]	6292 [R(int) = 0.0322]	6638 [R(int) = 0.0527]	4614 [R(int) = 0.0341]	5303 [R(int) = 0.0670]
completeness to $\theta_{\max}$ , %	99.9	98.3	99.9	99.2	98.8	99.7	98.9
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0335, <i>wR</i> <sub>2</sub> = 0.0567	<i>R</i> <sub>1</sub> = 0.0399, <i>wR</i> <sub>2</sub> = 0.0675	<i>R</i> <sub>1</sub> = 0.0282, <i>wR</i> <sub>2</sub> = 0.0623	<i>R</i> <sub>1</sub> = 0.0596, <i>wR</i> <sub>2</sub> = 0.1262	<i>R</i> <sub>1</sub> = 0.0373, <i>wR</i> <sub>2</sub> = 0.0545	<i>R</i> <sub>1</sub> = 0.0243, <i>wR</i> <sub>2</sub> = 0.0440	<i>R</i> <sub>1</sub> = 0.0784, <i>wR</i> <sub>2</sub> = 0.1621
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0749, <i>wR</i> <sub>2</sub> = 0.0664	<i>R</i> <sub>1</sub> = 0.0673, <i>wR</i> <sub>2</sub> = 0.0736	<i>R</i> <sub>1</sub> = 0.0396, <i>wR</i> <sub>2</sub> = 0.0742	<i>R</i> <sub>1</sub> = 0.0831, <i>wR</i> <sub>2</sub> = 0.1365	<i>R</i> <sub>1</sub> = 0.0935, <i>wR</i> <sub>2</sub> = 0.0631	<i>R</i> <sub>1</sub> = 0.0465, <i>wR</i> <sub>2</sub> = 0.0495	<i>R</i> <sub>1</sub> = 0.1491, <i>wR</i> <sub>2</sub> = 0.1828
GOF on <i>F</i> <sup>2</sup>	0.877	0.952	1.123	1.173	0.813	0.913	1.105
absolute structure param		0.000(7)	0.790(8) (racemic twin)				
largest diff. peak and hole, e <sup>−</sup> Å <sup>−3</sup>	0.725 and −0.709	0.394 and −0.299	0.933 and −0.908	0.683 and −0.831	0.462 and −0.465	0.351 and −0.348	0.670 and −0.489



688532 (**4**), 688533 (**5**), 688534 (**6**), and 688535 (**7**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44)1223-336-033 or e-mail [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

B3LYP/6-31G(d) full-geometry optimizations were performed on model systems in which both phenyl substituents on phosphorus or arsenic were replaced by hydrogen atoms by using the Spartan 06 package of programs.<sup>26</sup>

**Synthesis of GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}<sub>2</sub> (**1**).** A solution of PSH (0.63 g, 2.14 mmol) and triethylamine (NEt<sub>3</sub>, 0.216 g, 2.14 mmol, 0.3 mL) in methanol (20 mL) was slowly added dropwise to a solution of freshly sublimed GaCl<sub>3</sub> (0.38 g, 2.15 mmol) in 10 mL of methanol. A white precipitate formed immediately. The reaction mixture was stirred at room temperature for 1 h, and then the white precipitate was separated by filtration, washed with methanol, and dried *in vacuo*. The main product was GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}<sub>2</sub> (0.72 g, 1.03 mmol, 96% based on PSH) but a small amount of **2** was also obtained. A 0.5:1 molar ratio (PSH/GaCl<sub>3</sub>) also led to compound **1** (mp 230–234 °C) as the major product, whereas a mixture of **1** and **2** was obtained from the 2:1 reaction. Colorless crystals of **1** were obtained either from dichloromethane solution at 8 °C or from THF/*n*-hexane at room temperature. Both types of crystals were suitable for X-ray measurement, but only the X-ray data of the crystals obtained from THF/*n*-hexane are discussed. Elemental analysis: found C, 59.65; H, 4.08; S, 8.68%; calcd for C<sub>36</sub>H<sub>28</sub>ClGaP<sub>2</sub>S<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub> (M = 734.28) C, 59.70; H, 3.98; S, 8.73%.  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 3052w, 1572m, 1551w, 1481m, 1436s, 1424s, 1308w, 1250s, 1185w, 1130w, 1099s, 1044m, 1027m, 999m, 806w, 744vs, 694vs, 530w, 515m, 503m, 469m, and 400s (Ga–S<sub>as</sub>).  $\nu_{\max}(\text{CsI})/\text{cm}^{-1}$ : 337s (Ga–Cl and Ga–S), 309m, 267m, 238m, and 219w.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 7.58–7.25 (24H, m, aryl-H), 7.05 (2H, t, aryl-H) and 6.94 (2H, t, aryl-H).  $\delta_{\text{P}}$  (161.9 MHz, CDCl<sub>3</sub>): –17.5. *m/z* (<sup>69</sup>Ga) (ESI, in CH<sub>2</sub>Cl<sub>2</sub>) 691.0 (M<sup>+</sup>+1). *m/z* (EI) 293.1 (100%, C<sub>18</sub>H<sub>14</sub>PS<sup>+</sup>).

**Synthesis of Ga{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS}<sub>2</sub> (**2**).** In method a, a solution of PSH (1.45 g, 4.92 mmol) and triethylamine (0.49 g, 4.92 mmol, 0.68 mL) in methanol (40 mL) was added dropwise to a stirred solution of GaCl<sub>3</sub> (0.29 g, 1.64 mmol) in 10 mL of methanol at room temperature (ca. 10 min). Immediately, a white precipitate formed. The reaction mixture was stirred overnight. The white precipitate was isolated by filtration and dried *in vacuo*. Yield of **2**: 1.31 g, 1.38 mmol, 84%. Mp 239–243 °C. A small amount of compound **1** was also obtained.

In method b, Li(PS) was prepared by treating PSH with <sup>n</sup>BuLi (1:1). A solution of GaCl<sub>3</sub> (0.14 g, 0.8 mmol) in toluene (8 mL) was added slowly dropwise to the slurry of Li(PS) (0.84 g, 2.8 mmol) in toluene (20 mL) with continuous stirring. A turbid solution was obtained, which was stirred at room temperature for 40 h. The lithium chloride formed was removed by filtration, and the volatiles were removed *in vacuo* to give compound **2** as a white solid (0.72 g, 0.76 mmol, 95% based on Li(PS)) and a small amount of compound **1**. Colorless crystals of **2** were obtained either from diethyl ether or from tetrahydrofuran solution on cooling at 8 °C. Both types of crystals were measured by X-ray diffraction, but only the data of those obtained from diethyl ether are presented in this paper. Elemental analysis: found C, 67.64; H, 4.71; calcd for C<sub>54</sub>H<sub>42</sub>GaP<sub>3</sub>S<sub>3</sub> (M = 949.69) C, 68.29; H, 4.46%.  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 3052s, 3039m, 1585w, 1570m, 1553w, 1478s, 1435vs, 1422vs, 1332w, 1251m, 1156m, 1101s, 1039s, 1027m, 998w, 864w, 803w,

744vs, 697vs, 535w, 519m, 502vs, 471m, and 456w.  $\nu_{\max}(\text{CsI})/\text{cm}^{-1}$ : 390s (Ga–S<sub>as</sub>), 371w, 336m (Ga–S), 324m, 300s, 260m, 236m, and 215w.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 7.08–7.41 (33H, m, aryl-H), 6.97 (3H, t, aryl-H), 6.90 (3H, t, aryl-H), and 6.64 (3H, d, aryl-H).  $\delta_{\text{P}}$  (161.9 MHz, CDCl<sub>3</sub>): –12.6 (dynamic in solution). *m/z* (EI): 655.1 (100%, M<sup>+</sup> – C<sub>18</sub>H<sub>14</sub>PS) and 293.1 (80%, C<sub>18</sub>H<sub>14</sub>PS<sup>+</sup>).

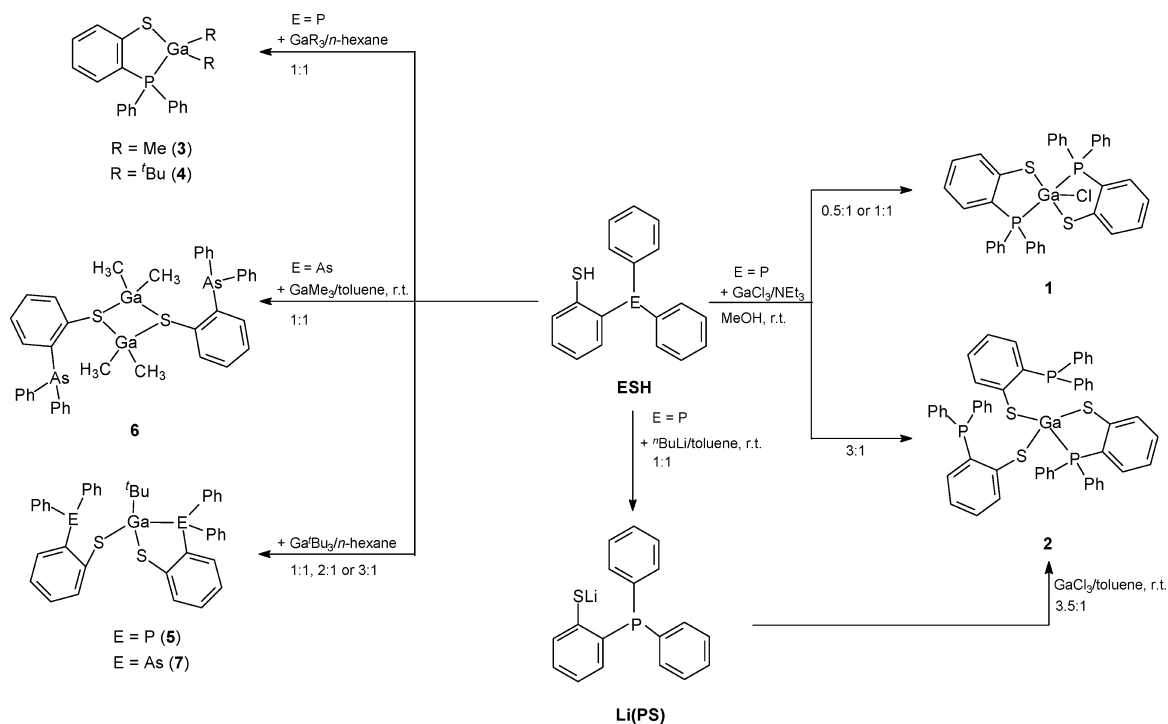
**Synthesis of GaMe<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P} (**3**).** Trimethylgallium (0.445 g, 3.87 mmol, 2.55 mL, 1.52 M in *n*-hexane) was added dropwise to a stirred slurry of PSH (1.14 g, 3.87 mmol) in *n*-hexane (25 mL) at –78 °C (ca. 15 min). During the addition of trimethylgallium, vigorous evolution of gas was observed. The reaction mixture was stirred for a further 3 h, and a white precipitate was formed. The precipitate was isolated by filtration, washed with *n*-hexane and dried *in vacuo* (yield 1.31 g, 3.33 mmol, 86%). Compound **3** could be isolated as the only product even in a 1:1 reaction of **2** with GaMe<sub>3</sub> (yield 96% based on **2**). Colorless crystals of **3** suitable for X-ray studies were obtained from diethyl ether at room temperature (mp 180–188 °C). Elemental analysis: found C, 60.89; H, 5.02%; calcd for C<sub>20</sub>H<sub>20</sub>GaPS (M = 393.11) C, 61.10; H, 5.13%.  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 3057w, 2963w, 1573s, 1480m, 1436vs, 1423s, 1248m, 1181w, 1126m, 1100vs, 1046m, 1026m, 998m, 801w, 754vs, 747vs, 722m, 695vs, 580m, 545w, 530m, 518s, 504s, and 470s.  $\nu_{\max}(\text{CsI})/\text{cm}^{-1}$ : 382s (Ga–S), 292m, 264m, 249w, 229w, 223w, and 209w.  $\delta_{\text{H}}$  (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.84 (1H, t, aryl-H), 7.28 (1H, t, aryl-H), 6.96 (1H, d, aryl-H), 6.86–6.93 (10H, m, aryl-H), 6.64 (1H, t, aryl-H), and 0.26 (6H, s, CH<sub>3</sub>).  $\delta_{\text{P}}$  (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): –1.2. *m/z* (FAB): 393.0 (100%, M<sup>+</sup> + 1) and 293.1 (36%, C<sub>18</sub>H<sub>14</sub>PS<sup>+</sup>).

**Synthesis of Ga'Bu<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P} (**4**).** A slurry of PSH (0.43 g, 1.45 mmol) in *n*-hexane (10 mL) was cooled to –78 °C, and Ga'Bu<sub>3</sub> (0.35 g, 1.45 mmol) was added dropwise. After addition was complete, the reaction mixture was warmed to room temperature and refluxed for 1 h. The volatiles were removed *in vacuo*, and the resulting complex was obtained as a white precipitate (yield 0.65 g, 1.36 mmol, 94%). Colorless crystals of **4** were obtained after crystallization from *n*-hexane solution at 8 °C (mp 132–138 °C). Elemental analysis: found C, 64.01; H, 6.48; S, 6.58%; calcd for C<sub>26</sub>H<sub>32</sub>GaPS (M = 477.27) C, 65.43; H, 6.76; S, 6.72%.  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 3059w, 2928s, 2947s, 2915s, 2866m, 2837vs, 1571m, 1481m, 1465m, 1438s, 1423s, 1359w, 1263m, 1247w, 1159w, 1098s, 1046m, 1027m, 943vw, 866vw, 809m, 747vs, 741vs, 719w, 694s, 533w, 505m, 474m, and 442w.  $\nu_{\max}(\text{CsI})/\text{cm}^{-1}$ : 377s (Ga–S), 297s, 280s, 265m, 248m, 233w, 215m, and 208s.  $\delta_{\text{H}}$  (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.88 (1H, t, aryl-H), 7.49 (1H, t, aryl-H), 6.89–6.97 (11H, m, aryl-H), 6.61 (1H, t, aryl-H), and 1.25 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>).  $\delta_{\text{P}}$  (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): 0.4. *m/z* (EI): 419.0 (100%, M<sup>+</sup> – C<sub>4</sub>H<sub>8</sub>), 363.0 (27%, M<sup>+</sup> – C<sub>8</sub>H<sub>17</sub>), and 293.1 (12%, C<sub>18</sub>H<sub>14</sub>PS<sup>+</sup>).

**Synthesis of Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS} (**5**).** Complex **5** was obtained as a minor product from the 1:2 reaction of Ga'Bu<sub>3</sub> (0.20 g, 0.83 mmol) with PSH (0.48 g, 1.65 mmol). Treatment of an *n*-hexane solution of the ligand at –78 °C with Ga'Bu<sub>3</sub> followed by refluxing for 19 h gave a mixture of **4** (ca. 25%), **5** (ca. 20%), **2** (ca. 1%), and unconsumed ligand (ca. 50%), as well as some decomposition products. The products could be separated by crystallization. Slow crystallization from *n*-hexane at room temperature over 3 months afforded a few colorless crystals of **5** (mp 235–239 °C). Elemental analysis: found C, 67.15; H, 5.14; S, 9.04%; calcd for C<sub>40</sub>H<sub>37</sub>GaP<sub>2</sub>S<sub>2</sub> (M = 713.48) C, 67.33; H, 5.23; S, 8.99%.  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 3046m, 2912m, 2836m, 1570m, 1480m, 1434s, 1423s, 1305w, 1261w, 1250m, 1096s, 1040m, 1027s, 998w, 811m, 740vs, 694vs, 529w, 502s, and 471m.  $\nu_{\max}(\text{CsI})/\text{cm}^{-1}$ : 385w (Ga–S), 319w, 285w, 280s, 268m, 249m,

(26) SPARTAN '06, Wavefunction Inc., W.I., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.

Scheme 1. The Synthetic Routes to 1–7



243w, 225m, 212m, and 203s.  $\delta_{\text{H}}$  (400 MHz, C<sub>6</sub>D<sub>6</sub>): 6.69–7.59 (28H, m, aryl-H), and 1.30 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>).  $\delta_{\text{P}}$  (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): –9.6. *m/z* (EI): 655.0 (3%, M<sup>+</sup> – C<sub>4</sub>H<sub>8</sub>) and 293.2 (37%, C<sub>18</sub>H<sub>14</sub>PS<sup>+</sup>).

**Synthesis of [GaMe<sub>2</sub>{(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS}]<sub>2</sub> (6).** Trimethylgallium (0.088 g, 0.77 mmol, 0.50 mL, 1.52 M in *n*-hexane) was added to a stirred solution of AsSH (0.26 g, 0.77 mmol) in toluene (12 mL) at –78 °C. During the addition of trimethylgallium, vigorous evolution of gas was observed. The reaction mixture was stirred at room temperature overnight. The volatiles were removed *in vacuo* to give a white powder (yield 0.31 g, 0.71 mmol, 92%). Colorless crystals of **6** suitable for X-ray studies were obtained from a diethyl ether solution at room temperature in a few hours (mp 157–165 °C). Elemental analysis: found C, 54.58; H, 4.20%; calcd for C<sub>40</sub>H<sub>40</sub>As<sub>2</sub>Ga<sub>2</sub>S<sub>2</sub> (M = 874.12) C, 54.96; H, 4.61%.  $\nu_{\text{max}}$ (KBr)/cm<sup>–1</sup>: 3047m, 2964m, 2905w, 1571w, 1480w, 1434s, 1306m, 1260s, 1186m, 1098s, 1025s, 947w, 866w, 803m, 739vs, 696s, 591w, 537w, 473m, and 446w.  $\nu_{\text{max}}$ (CsI)/cm<sup>–1</sup>: 321w, 303s (Ga–S), 283w, 273w, 253m, 248m, 239w, 227w, and 203m.  $\delta_{\text{H}}$  (400 MHz, C<sub>6</sub>D<sub>6</sub>): 7.66 (2H, d, aryl-H), 7.30 (2H, d, aryl-H), 7.01 (20H, m, aryl-H), 6.89 (2H, t, aryl-H), 6.73 (2H, t, aryl-H) and 0.27 (12H, s, CH<sub>3</sub>). *m/z* (FAB): 437.0 (18%, M/2<sup>+</sup> + 1), 421.0 (34%, M/2<sup>+</sup> – CH<sub>2</sub>), and 337.1 (100%, C<sub>18</sub>H<sub>14</sub>AsS<sup>+</sup>).

**Synthesis of Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κ<sup>2</sup>S,As}{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS} (7).** An *n*-hexane solution of Ga'Bu<sub>3</sub> (0.61 g, 2.53 mmol) was added to AsSH (0.85 g, 2.53 mmol) in *n*-hexane at –78 °C. Evolution of gas was noted upon addition. The colorless solution was stirred for 24 h, the volatiles were removed *in vacuo*, and the oily white residue was washed with small amounts of *n*-hexane, leaving a white powder. A few crystals of compound **7** were obtained from *n*-hexane at room temperature over 2 days. However, the <sup>1</sup>H NMR spectrum showed two sets of signals for the aromatic and aliphatic protons indicating that complex **7** was obtained in a mixture, probably together with Ga'Bu<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κ<sup>2</sup>S,As}. Attempts to separate the compounds were unsuccessful.

## Results and Discussion

The reactivity and the coordination chemistry of the bidentate ligands 2-EPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH (E = P (PSH), As (AsSH)) toward gallium(III) and the influence of different substituents at gallium on these reactions were studied. Seven new gallium and organogallium complexes (Ga(ES)<sub>n</sub>X<sub>3–n</sub>, (**1–7**), *n* = 1–3, Scheme 1) were obtained by reaction of the ligands or their lithium salts with GaX<sub>3</sub> (X = Cl, Me, *t*Bu) in different molar ratios and under different reaction conditions.

Complexes **1–7** were obtained in good yields as white solids (except **5** and **7**, see below) and were fully characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, IR, mass spectrometry, elemental analysis, and X-ray diffraction.

The <sup>1</sup>H NMR spectra for all complexes show the signals due to the aromatic rings and no signal for the S–H proton. The <sup>1</sup>H NMR spectra of **3–7** show additional signals in the aliphatic region due to the corresponding protons of the alkyl groups (methyl or *tert*-butyl) with integrals for the aliphatic and aromatic resonances in the ratio consistent with the presence of one or two alkyl groups per PS<sup>–</sup> or AsS<sup>–</sup> ligand.

The absence of  $\nu_{\text{S–H}}$  and the presence of  $\nu_{\text{Ga–S}}^{27}$  at 400–300 cm<sup>–1</sup> in the IR spectra of **1–6** indicate coordination of the deprotonated thiolato ligands. The assignment of  $\nu_{\text{Ga–C}}$  in the IR spectra of complexes **3–6** is complicated by the number of bands in the expected range of 390–510 cm<sup>–1</sup>.<sup>28</sup>

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(28) (a) Uhl, W.; Spies, T.; Saak, W. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2095–2109. (b) Uhl, W.; Cuypers, L.; Harms, K.; Kaim, W.; Wanner, M.; Winter, R.; Koch, R.; Saak, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 566–568. (c) Uhl, W.; Breher, F.; Haddadpour, S.; Koch, R.; Matar, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1839–1845. (d) Uhl, W.; Fick, A. C.; Spies, T.; Geiseler, G.; Harms, K. *Organometallics* **2004**, *23*, 72–75.

By comparison with other GaCl-containing compounds<sup>29–31</sup> and the calculated normal modes,<sup>32</sup> the band at 337 cm<sup>−1</sup> in the IR spectrum of complex **1** is assigned to  $\nu_{\text{Ga-Cl}}$ .

The molecular-ion peaks were visible in the ESI MS spectrum of **1** and **3** and in the FAB MS spectrum of **6**. The peaks corresponding to the loss of one molecule of ligand are present in the EI MS spectra of **2** and **5**, while the loss of the organic groups attached to gallium was observed in the spectra of **4**, **5**, and **6**.

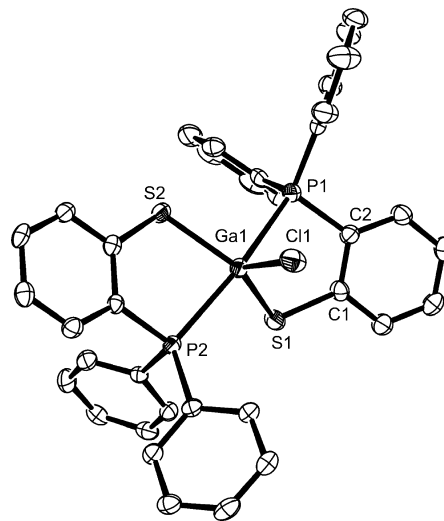
From the reaction of PSH with GaCl<sub>3</sub> in the presence of NEt<sub>3</sub> in both 0.5:1 or 1:1 molar ratio GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P}<sub>2</sub> (**1**) was obtained (Scheme 1). No GaCl<sub>2</sub>(PS) was observed irrespective of the molar ratio used. The reaction of PSH with GaCl<sub>3</sub> in the molar ratio 3:1 led to Ga{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa$ S}<sub>2</sub> (**2**). Compound **2** could be also synthesized in higher yield by treating the lithium salt of the ligand Li(PS) with GaCl<sub>3</sub> in a 3.5:1 molar ratio. Li(PS) was prepared from PSH and <sup>n</sup>BuLi in toluene (Scheme 1). In the solid state, compounds **1** and **2** are air-stable for at least 2 days.

The <sup>31</sup>P NMR spectrum of complex **1** shows one signal at −17.5 ppm, which is shifted to high field relative to the free ligand (−12.6 ppm), indicating the coordination of the phosphorus atoms. Both, the room-temperature and the low-temperature (173 K, THF-*d*<sub>8</sub>) <sup>31</sup>P NMR spectra of **2** exhibit signals in the range of the free ligand, suggesting noncoordinating phosphine groups in solution.

The organogallium complexes GaMe<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P} (**3**) and Ga'Bu<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P} (**4**) were obtained by reaction of PSH with GaMe<sub>3</sub> and Ga'Bu<sub>3</sub> (ratio 1:1), respectively (Scheme 1). Compound **3** was also obtained in excellent yield (96%) from **2** and GaMe<sub>3</sub> in toluene at room temperature. Compound **3** is an air-stable compound that sublimates at 200 °C (under dynamic vacuum, 3 × 10<sup>−3</sup> mbar) giving colorless crystals. In the <sup>31</sup>P NMR spectra of compounds **3** and **4**, only one signal at −1.2 (**3**) and 0.4 ppm (**4**), respectively, is observed, consistent with the coordination of the phosphine group.

Attempts to replace more than one alkyl group in GaR<sub>3</sub> by phosphinoarylthiol were unsuccessful in case of GaMe<sub>3</sub>. Compound **3** was the only product even when a 2:1 or 3:1 (PSH/GaMe<sub>3</sub>) molar ratio was used. When PSH was treated with Ga'Bu<sub>3</sub> in a 2:1 or 3:1 molar ratio either at room temperature or in boiling *n*-hexane (19 h), a mixture of products was obtained.

The 2:1 reaction led (according to the <sup>31</sup>P NMR spectra) to a mixture of **4** (ca. 25%), Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa$ S} (**5**; ca. 20%), unconsumed PSH (ca. 50%), and small amounts of **2** (ca. 1%), as well as some decomposition products. Attempts to obtain **5** as a major product by a 3:1 reaction of PSH with Ga'Bu<sub>3</sub> using different refluxing times or by a 1:1 reaction of **1** with <sup>n</sup>BuLi or the equimolar reaction of complex **4** with PSH (ca. 20 h reflux)



**Figure 1.** Molecular structure of GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P}<sub>2</sub> (**1**). Hydrogen atoms are omitted for clarity.

were unsuccessful. The <sup>31</sup>P NMR spectra of **5** recorded at room temperature and at low temperature (193 K, C<sub>7</sub>D<sub>8</sub>) show a single signal shifted only by ca. 3 ppm to lower field relative to the signal of the free ligand and suggest a symmetrical weak phosphorus–gallium interaction of both phosphinoarylthiolato ligands.

The reaction of AsSH with GaCl<sub>3</sub> (in the presence of NEt<sub>3</sub> as base) in different molar ratios and reaction conditions led to white solids with very low solubility, which could not be characterized. The equimolar reaction of AsSH with GaMe<sub>3</sub> in toluene led to [GaMe<sub>2</sub>{(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)- $\kappa$ S}]<sub>2</sub> (**6**; Scheme 1). Attempts to replace more methyl groups were unsuccessful. Like **3**, **6** was also obtained as major product in the 2:1 or 3:1 reaction (AsSH/GaMe<sub>3</sub>) and under different reaction conditions (room temperature or refluxing toluene).

For the preparation of Ga'Bu{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)- $\kappa^2$ S,As}{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)- $\kappa$ S} (**7**; Scheme 1) a similar procedure as for **5** was employed. The <sup>1</sup>H NMR spectrum of the reaction product showed two sets of signals for the aromatic and aliphatic protons, assigned to complex **7** and probably Ga'Bu<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)- $\kappa$ S,As}. Attempts to reproduce and isolate **7** always led to a mixture of products. However a few crystals of compound **7** were obtained from an *n*-hexane solution of this mixture at room temperature over 2 days.

**Molecular Structures of Complexes 1–7.** GaCl{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)- $\kappa^2$ S,P}<sub>2</sub> (**1**). The gallium atom in **1** is coordinated by the chlorine atom and two chelating ligands in a trigonal-bipyramidal geometry (Figure 1). The two phosphorus atoms occupy the axial positions [P(1)–Ga(1)–P(2) 165.58(3)°] (Table 2). The chlorine and the two sulfur atoms are in the equatorial plane. The angles involving the chlorine atom [S(1)–Ga(1)–Cl(1) 115.76(3)° and S(2)–Ga(1)–Cl(1) 114.40(3)°] are smaller than the S(2)–Ga(1)–S(1) bond angle 129.48(4)°, a difference that is probably imposed by the structure of the ligand.

The angles formed between equatorial and axial ligands range from 80.27(3)° to 99.74(4)°. The Ga(1)–Cl(1) bond length of 2.2161(9) Å is similar to those in related trigonal-bipyramidal complexes: 2.193(3) Å for GaCl{PhC-

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**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) in Compound **1**

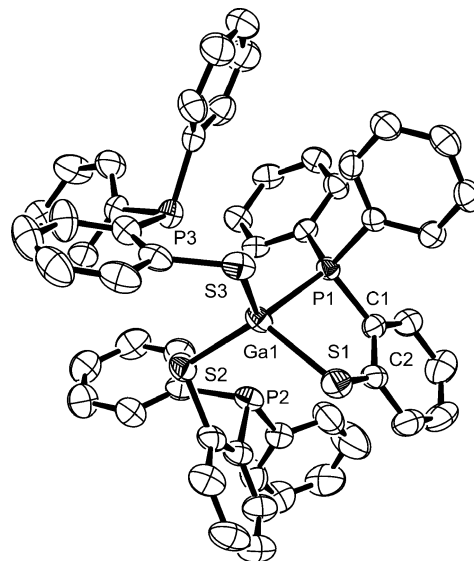
Ga(1)–Cl(1)	2.2161(9)	Cl(1)–Ga(1)–S(1)	115.76(3)
Ga(1)–S(1)	2.295(1)	Cl(1)–Ga(1)–S(2)	114.40(3)
Ga(1)–S(2)	2.270(1)	S(2)–Ga(1)–S(1)	129.48(4)
Ga(1)–P(1)	2.5872(1)	Cl(1)–Ga(1)–P(1)	94.67(4)
Ga(1)–P(2)	2.4927(9)	Cl(1)–Ga(1)–P(2)	99.74(4)
		S(1)–Ga(1)–P(2)	93.23(3)
		S(2)–Ga(1)–P(2)	84.05(3)
		S(1)–Ga(1)–P(1)	80.27(3)
		S(2)–Ga(1)–P(1)	90.17(3)
		P(2)–Ga(1)–P(1)	165.58(3)

(S)CHC(O)Ph)<sub>2</sub><sup>29</sup> and 2.195(1) Å for {H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>GaCl (pz = pyrazolyl).<sup>33</sup> The Ga–S bond lengths of 2.270(1) and 2.295(1) Å are similar to those described for other five-coordinate complexes (e.g., GaCl{PhC(S)CHC(O)Ph}<sub>2</sub> 2.274(2) Å).<sup>29</sup> The gallium–phosphorus bond lengths are well within the normal range associated with such bonds [2.4–2.7 Å].<sup>7,8,34,35</sup> The Ga(1)–P(1) bond length [2.5872(1) Å] exceeds the Ga(1)–P(2) bond length [2.4927(9) Å]. However, the average Ga–P bond length [avg 2.54 Å] greatly exceeds those observed in the tetracoordinate gallium(III) phosphine complexes GaCl<sub>3</sub>(PMe<sub>3</sub>) [2.353(2) Å]<sup>36</sup> or GaCl<sub>3</sub>{P(SiMe<sub>3</sub>)<sub>3</sub>} [2.379(5) Å]<sup>37</sup> but is smaller than the Ga–P bond length observed in Ga(CH<sub>2</sub>/Bu)<sub>3</sub>(PPh<sub>2</sub>) [2.683(5) Å].<sup>35</sup> Comparable Ga–P bond lengths were found in GaMe<sub>3</sub>(dppe) (dppe = bis(diphenylphosphino)ethane) [2.563(3) Å],<sup>38</sup> GaClPh<sub>2</sub>{P(SiMe<sub>3</sub>)<sub>3</sub>} [2.459(2) Å], GaPh<sub>3</sub>–{P(SiMe<sub>3</sub>)<sub>3</sub>} [2.539(6) Å],<sup>8</sup> [Ga(CH<sub>2</sub>/Bu)(PPh<sub>2</sub>)<sub>2</sub>]<sub>2</sub> [Ga–P<sub>br</sub> 2.4689(9) Å],<sup>39</sup> [GaMe<sub>2</sub>(PPh<sub>2</sub>)<sub>3</sub>] [2.433(1) Å],<sup>40</sup> or GaClMe<sub>2</sub>–(dppm-κP) (dppm = bis(diphenylphosphino)methane) [2.535(2) Å].<sup>41</sup>

**Ga{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS}<sub>2</sub> (**2**).** The structure of **2** (Figure 2, Table 3) consists of discrete molecules with the gallium atom in a distorted tetrahedral environment, coordinated by three 2-(diphenylphosphino)benzenethiolato ligands.

One of the ligands is chelating while the other two are coordinated only through their sulfur atoms, probably because of steric hindrance. The S–Ga–S bond angles range from 107.10(3) to 116.73(3)°, and the S–Ga–P bond angles range from 85.79(3) (bite angle of the chelating ligand) to 121.27(3)°.

The mean Ga–S bond length of 2.283(1) Å is close to those found in gallium complex **1** and [HNet<sub>3</sub>][Ga{SC(O)Ph}<sub>4</sub>].

**Figure 2.** Molecular structure of Ga{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P}{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κS}<sub>2</sub> (**2**). Hydrogen atoms are omitted for clarity.**Table 3.** Selected Bond Lengths (Å) and Bond Angles (deg) in Compound **2**

Ga(1)–S(1)	2.294(1)	S(2)–Ga(1)–S(3)	116.73(3)
Ga(1)–S(2)	2.2579(9)	S(2)–Ga(1)–S(1)	110.78(3)
Ga(1)–S(3)	2.2696(9)	S(3)–Ga(1)–S(1)	107.10(3)
Ga(1)–P(1)	2.3923(8)	S(2)–Ga(1)–P(1)	121.27(3)
Ga(1)••P(2)	3.241	S(3)–Ga(1)–P(1)	110.12(3)
Ga(1)••P(3)	4.468	S(1)–Ga(1)–P(1)	85.79(3)

**Table 4.** Selected Bond Lengths (Å) and Bond Angles (deg) in Compounds **3** and **4**

<b>3</b>		<b>4</b>	
Ga(1)–C(19)	1.958(3)	Ga(1)–C(23)	2.005(4)
Ga(1)–C(20)	1.959(4)	Ga(1)–C(19)	2.017(4)
Ga(1)–S(1)	2.3109(9)	Ga(1)–S(1)	2.343(1)
Ga(1)–P(1)	2.4602(8)	Ga(1)–P(1)	2.5003(9)
C(19)–Ga(1)–C(20)	124.0(2)	C(23)–Ga(1)–C(19)	122.2(2)
C(19)–Ga(1)–S(1)	109.1(1)	C(23)–Ga(1)–S(1)	111.1(1)
C(20)–Ga(1)–S(1)	112.1(1)	C(19)–Ga(1)–S(1)	110.0(1)
C(19)–Ga(1)–P(1)	114.7(1)	C(23)–Ga(1)–P(1)	112.8(1)
C(20)–Ga(1)–P(1)	106.8(1)	C(19)–Ga(1)–P(1)	111.1(1)
S(1)–Ga(1)–P(1)	82.73(3)	S(1)–Ga(1)–P(1)	82.72(3)

H<sub>2</sub>O.<sup>42</sup> On the other hand, the Ga(1)–P(1) bond length [2.3923(8) Å] is comparable to the shortest reported gallium–phosphorus bond of 2.353(2) Å found in GaCl<sub>3</sub>(PMe<sub>3</sub>)<sup>36</sup> and significantly shorter than that for the five-coordinate complex **1** [avg Ga–P 2.54 Å], as expected. This distance, indicative of the Lewis acidic nature of the metal center, is approximately the sum of the covalent radii [ca. 2.30 Å].<sup>38</sup> The other phosphorus atoms are not coordinated to gallium, but the Ga(1)••P(2) distance of 3.241 Å is shorter than the sum of the van der Waals radii [3.67 Å],<sup>43</sup> which could be indicative of some degree of Ga••P interaction.

A different behavior was observed for **2** in solution compared with the solid state: the <sup>31</sup>P NMR spectra suggest noncoordinating phosphine groups, while in the solid state one of the three phosphorus atoms is coordinated to gallium.

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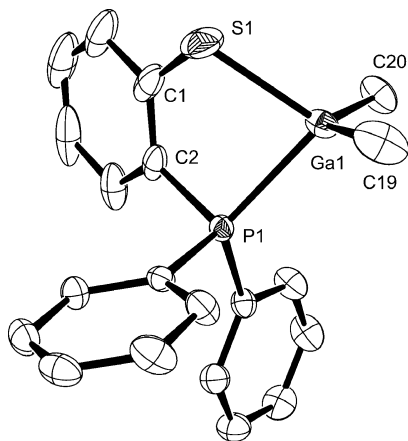
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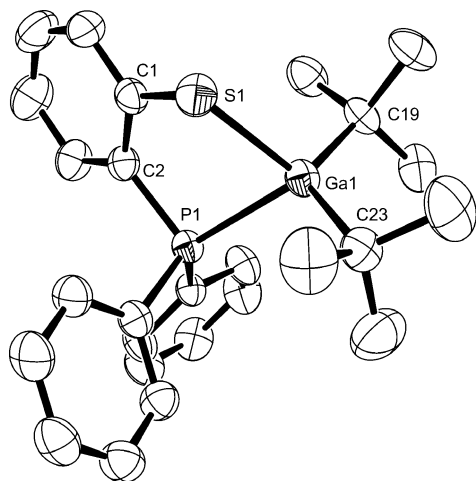
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**Figure 3.** Molecular structure of  $\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}$  (**3**). Only one of two independent molecules found in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.

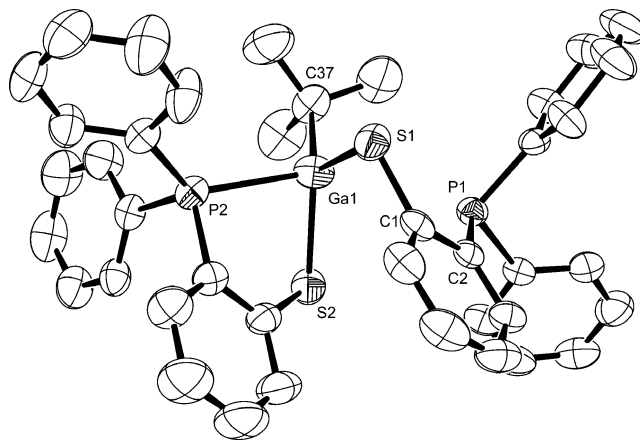


**Figure 4.** Molecular structure of  $\text{Ga'Bu}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}$  (**4**). Hydrogen atoms are omitted for clarity.

Exchange between the hemilabile ligand and the solvent or just hemilability of the ligand may account for the structure in solution.

**$\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}$  (**3**) and  $\text{Ga'Bu}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}$  (**4**).** Two structurally independent molecules were found in the asymmetric unit of **3** (no significant differences in bond lengths and angles between the molecules were observed). Selected bond lengths and angles are given in Table 4.

In **3** (Figure 3) and **4** (Figure 4), the gallium atom is coordinated in a distorted tetrahedral fashion by one sulfur atom, one phosphorus atom, and two alkyl (methyl or *tert*-butyl) groups. The Ga–S and Ga–C bond lengths in **3** are slightly smaller than those found in **4** but lie in the same range as those found in the literature for similar complexes.<sup>44–47</sup> The Ga–P bond lengths are slightly different



**Figure 5.** Molecular structure of  $\text{Ga'Bu}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa\text{S}\}$  (**5**). Hydrogen atoms are omitted for clarity. Complex **7** is isostructural.

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) in Compounds **5** and **7**

	<b>5</b> (E = P)	<b>7</b> (E = As)
Ga(1)–C(37)	1.977(3)	1.98(1)
Ga(1)–S(1)	2.2726(7)	2.277(3)
Ga(1)–S(2)	2.2777(8)	2.268(3)
Ga(1)–E(2)	2.5182(9)	2.689(2)
Ga(1)⋯E(1)	3.191	3.029
C(37)–Ga(1)–S(1)	117.1(1)	119.8(4)
C(37)–Ga(1)–S(2)	125.1(1)	125.2(4)
S(2)–Ga(1)–S(1)	112.90(3)	113.4(1)
C(37)–Ga(1)–E(2)	110.6(1)	107.1(3)
S(1)–Ga(1)–E(2)	98.69(3)	94.2(1)
S(2)–Ga(1)–E(2)	81.95(3)	80.4(1)

[2.4602(8) Å (**3**) and 2.5003(9) Å (**4**)], and they are longer than that found in tetra-coordinate compound **2** but shorter than those observed in five-coordinate complex **1**.

**$\text{Ga'Bu}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa\text{S}\}$  (**5**) and  $\text{Ga'Bu}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa^2\text{S,As}\}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}$  (**7**).** X-ray structure analysis revealed the isostructural complexes  $\text{Ga'Bu}\{(\text{SC}_6\text{H}_4\text{-2-EPh}_2)\text{-}\kappa^2\text{S,E}\}\{(\text{SC}_6\text{H}_4\text{-2-EPh}_2)\text{-}\kappa\text{S}\}$  (E = P (**5**), As (**7**)) (Figure 5, Table 5). In both compounds, the gallium atom is coordinated in a distorted tetrahedral fashion by two sulfur atoms and one phosphorus or arsenic atom from two  $\text{PS}^-$  or  $\text{AsS}^-$  ligands, and one *tert*-butyl group.

The Ga–S, Ga–C, and Ga–P bond lengths for compounds **5** and **7** are in the same range as those in **1–4**. The Ga(1)–As(2) bond length of 2.689(2) Å in **7** exceeds that observed for known Ga–As bonds, for example, in the adduct  $\text{GaI}_3(\text{AsPh}_3)$  [2.489(2) Å]<sup>9</sup> or covalent bonds in  $\text{Ga}\{\text{As}(\text{C}_6\text{H}_2\text{Me}_3)_2\}_3$  [2.470(1)–2.508(1) Å],<sup>48</sup>  $[\text{GaPh}_2\{\text{As}(\text{CH}_2\text{SiMe}_3)_2\}]_2$  [2.518(1)–2.530(1) Å],<sup>49</sup>  $[\text{GaMe}_2(\text{As'Bu}_2)]_2$  [2.541(1)–2.558(1) Å],<sup>50</sup>  $\text{Ga'Bu}_2(\text{As'Bu}_2)$  [2.446(3) Å],<sup>18</sup>  $\text{Ga'Bu}_2\{\text{As}(\text{SiPh}_3)\text{CH}(\text{SiMe}_3)_2\}$  [2.458(1) Å],<sup>51</sup>

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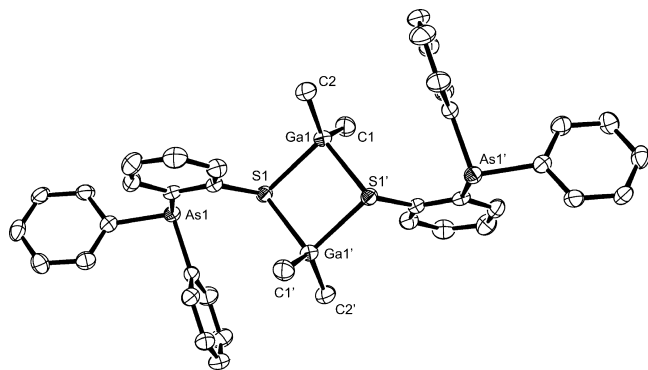
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**Figure 6.** Molecular structure of  $[\text{GaMe}_2\{(\mu_2\text{-SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}]_2$  (**6**). Hydrogen atoms are omitted for clarity.

**Table 6.** Selected Bond Lengths (Å) and Bond Angles (deg) in Compound **6**

Ga(1)···Ga(1)′	3.418	C(1)–Ga(1)–C(2)	125.9(1)
Ga(1)···As(1)	4.951	C(1)–Ga(1)–S(1)	110.04(7)
S(1)···S(1)′	3.434	C(1)–Ga(1)–S(1)′	102.71(7)
C(1)–Ga(1)	1.946(2)	C(2)–Ga(1)–S(1)	107.86(8)
C(2)–Ga(1)	1.948(2)	C(2)–Ga(1)–S(1)′	114.31(7)
S(1)–Ga(1)	2.4075(6)	C(3)–S(1)–Ga(1)	107.68(7)
S(1)–Ga(1)′	2.4372(6)	C(3)–S(1)–Ga(1)′	110.37(7)
		Ga(1)–S(1)–Ga(1)′	89.74(2)
		S(1)–Ga(1)–S(1)′	90.26(2)

or  $[(\text{Cl}_3\text{Ga})\{\text{Me}_2\text{AsCH}_2\text{C}(\text{Me})(\text{CH}_2\text{AsMe}_2)_2\}\text{GaCl}_2][\text{GaCl}_4]$  [2.435(1)–2.465(2) Å].<sup>52</sup> The reason could be steric hindrance in compound **7**.

The other phosphorus or arsenic atom is not bonded to the gallium atom. However, the  $\text{Ga}\cdots\text{E}$  distances [3.191(5) and 3.029(7) Å] are shorter than the sum of the van der Waals radii ( $\Sigma\text{Ga}\cdots\text{P} = 3.67$  Å,  $\Sigma\text{Ga}\cdots\text{As} = 3.72$  Å)<sup>43</sup> and suggest interaction between the gallium and phosphorus or arsenic atoms.

**[GaMe<sub>2</sub>{(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS}]<sub>2</sub> (**6**).** Compound **6** (Figure 6 and Table 6) consists of a dimer with a central planar almost rectangular four-membered Ga<sub>2</sub>S<sub>2</sub> ring [Ga(1)–S(1)–Ga(1)′ 89.74(2)°, S(1)–Ga(1)–S(1)′ 90.26(2)°]. Planar Ga<sub>2</sub>S<sub>2</sub> rings were also found in  $[\text{GaI}_2(\mu\text{-SMe})_2]$ <sup>44</sup> and  $[\text{GaPh}_2(\mu\text{-SEt})_2]$ .<sup>45</sup>

The gallium atoms are coordinated in a distorted tetrahedral fashion by two thiolato and two methyl groups. The Ga–S bond lengths [2.4075(6) and 2.4372(6) Å] are larger than those in **3** and  $[\text{NET}_4]_2[\text{Ga}_2\text{S}_2(\text{SPh})_4]$  [2.264(1) to 2.288(1) Å]<sup>53</sup> but comparable with those found in other four-membered Ga<sub>2</sub>S<sub>2</sub> rings,  $[\text{Ga}^t\text{Bu}_2(\mu\text{-SPh})_2]$  [2.421(2)–2.445(2) Å]<sup>46</sup> and  $[\text{GaMe}_2(\mu\text{-SC}_6\text{F}_5)_2]$  [2.436(3)–2.460(2) Å].<sup>54</sup> The

Ga–C bond lengths [1.946(2) and 1.948(2) Å] are within the expected range. Unexpectedly, the arsenic atom of the ligand is not coordinated to gallium, and  $\text{AsS}^-$  acts as a monodentate ligand, unlike  $\text{PS}^-$  in **3**, for which bidentate coordination was found.

The intramolecular S(1)···S(1)′ (3.434 Å) and Ga(1)···Ga(1)′ [3.418 Å] distances are shorter than the sum of the van der Waals radii of the atoms involved, which could be indicative of some degree of S···S and Ga···Ga interactions ( $\Sigma\text{Ga}\cdots\text{Ga} = 3.74$  Å,  $\Sigma\text{S}\cdots\text{S} = 3.6$  Å).<sup>43</sup> Similar Ga···Ga distances were observed in  $[\text{GaMe}_2(\mu\text{-SC}_6\text{F}_5)_2]$  [3.397 Å],<sup>54</sup> longer distances in  $[\text{GaPh}_2(\mu\text{-SEt})_2]$  [3.257 Å]<sup>45</sup> and  $[\text{NET}_4]_2[\text{Ga}_2\text{S}_2(\mu\text{-SPh})_4]$  [2.943 Å],<sup>53</sup> and shorter ones in  $[\text{Ga}^t\text{Bu}_2(\mu\text{-SPh})_2]$  [3.663 Å].<sup>46</sup>

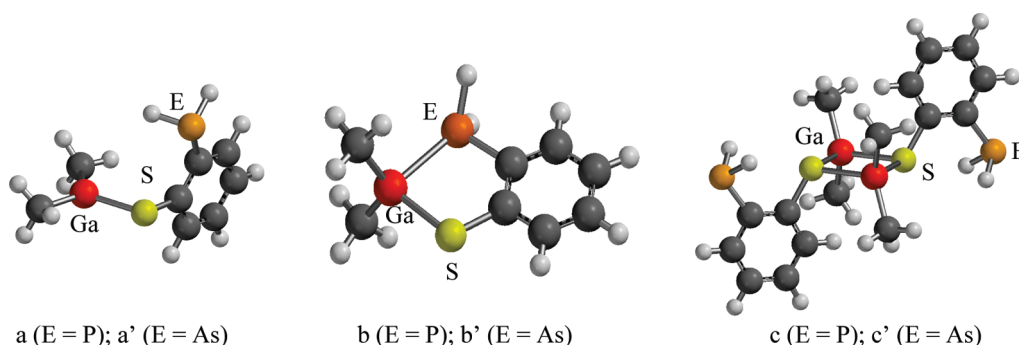
The packing diagram of **6** shows the molecules arranged in columns along the crystallographic *b* axis, connected through H(phenyl)–π interactions [ $\pi$  stacking avg H(Ph)···Ph 2.785 Å and H(Ph)···S 2.924 Å interactions].

**Chelate or Bridging Ligands in 3 and 6.** Complexes **3** and **6** represent relatively rare examples<sup>31</sup> of different coordination behavior of the two very similar ligands PSH and AsSH toward the same metal complex fragment, GaMe<sub>2</sub>. While a monomeric structure with a chelating phosphanyl-arylthiolato ligand is observed in  $\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2\text{S,P}\}$  (**3**), a dimeric arsanylarlythiolato-bridged complex  $[\text{GaMe}_2\{(\mu_2\text{-SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa\text{S}\}]_2$  (**6**) is obtained with the corresponding AsS ligand. In order to understand this difference in the behavior of the  $\text{PS}^-$  and  $\text{AsS}^-$  ligand in **3** and **6**, molecular orbital calculations on models H–PS and H–AsS, in which the substituents on phosphorus or arsenic are replaced by hydrogen, and their complexes with GaMe<sub>2</sub> (Scheme 2) were performed at the B3LYP/6-31G(d)<sup>55</sup> level of theory. The results for GaMe<sub>2</sub>(H–PS) and GaMe<sub>2</sub>(H–AsS) with varying coordination of the ligand, monodentate through sulfur (a, a′), bidentate (chelate) (b, b′), and thiolato-bridged to form dimers (c, c′), are summarized in Table 7.

## Summary

(Organo)gallium compounds were obtained by treating 2-EPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>SH (E = P, As) with GaCl<sub>3</sub> or GaR<sub>3</sub> (R = Me, <sup>t</sup>Bu) in different molar ratios and under different reaction conditions. With the exception of compounds **5** and **7**, all complexes were obtained in high yield. In complexes **2**–**7**,

**Scheme 2.** Computed Models of  $\text{GaMe}_2\{\text{SC}_6\text{H}_4\text{-2EPh}_2\}$  (E = P, As)



**Table 7.** Total (au) and Relative (kcal/mol) Energies of the Monomeric Monodentate or Chelate Complexes and Dimers of the Model Systems GaMe<sub>2</sub>(H-ES) (E = P, As)

	total energy (au)	$2(E(\text{chelate}) - E(\text{dimer}))$ (kcal/mol)	chelate/monodentate relative energy (kcal/mol)	$2(E(\text{monodentate}) - E(\text{dimer}))$ (kcal/mol)
a (E = P) monodentate H-PS	-2976.283 958 5		+5.12	+17.19
b (E = P) chelate H-PS	-2976.292 115 1	+6.95	0.0	
c (E = P) dimer Ga <sub>2</sub> S <sub>2</sub> [GaMe <sub>2</sub> (μ <sub>2</sub> -H-PS-κS)] <sub>2</sub>	-5952.595 310 4	0.0		0.0
a' (E = As) monodentate H-AsS	-4870.562 673 9		0.0	+15.90
b' (E = As) chelate H-AsS	-4870.562 596 9	+16.00	+0.05	
c' (E = As) dimer Ga <sub>2</sub> S <sub>2</sub> [GaMe <sub>2</sub> (μ <sub>2</sub> -H-AsS-κS)] <sub>2</sub>	-9741.150 688 9	0.0		0.0

the gallium atom is tetracoordinate, whereas chloro complex **1** has a coordination number of five and trigonal-bipyramidal geometry.

Although, similar phosphorus and arsenic ligands usually exhibit the same coordination behavior toward the same metal complex fragment, different structures are observed here: a monomeric structure with a chelating phosphinoarylthiolato ligand in GaMe<sub>2</sub>{(SC<sub>6</sub>H<sub>4</sub>-2-PPh<sub>2</sub>)-κ<sup>2</sup>S,P} (**3**)

and a dimeric arsinoarylthiolato-bridged complex [GaMe<sub>2</sub>{(μ<sub>2</sub>-SC<sub>6</sub>H<sub>4</sub>-2-AsPh<sub>2</sub>)-κS}]<sub>2</sub> (**6**). B3LYP/6-31G(d) calculations show that although the dimer is thermodynamically favored for both ligands, the formation of **3** is due to the combination of higher stability of the chelate compared with the monodentate phosphorus ligand and a higher barrier for the ring opening of the PS- than of the AsS-chelate.

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