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

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The (organo)gallium compounds GaCl{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}$_2$ (**1**), Ga{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*}$_2$ (**2**), GaMe$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*} (**3**), Ga^{t}Bu$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*} (**4**), Ga^{t}Bu{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*} (**5**), [GaMe$_2${(μ_2-SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}]$_2$ (**6**), and Ga^{t}Bu{(SC$_6$H$_4$-2-AsPh$_2$)-κ^2*S*,*As*}{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*} (**7**) were obtained from the reaction of 2-EPh$_2$C$_6$H$_4$SH (E = P (**PSH**), As (**AsSH**)) with GaCl$_3$ (**1**, **2**) or GaR$_3$ (R = Me, ^{t}Bu; **3**−**7**) in different molar ratios and under different reaction conditions. Compound **2** was also obtained from Li(**PS**) and GaCl$_3$ (3.5:1). While a monomeric structure with a chelating phosphinoarylthiolato ligand is observed in GaMe$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*} (**3**), a dimeric arsinoarylthiolato-bridged complex [GaMe$_2${(μ_2-SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}]$_2$ (**6**) is obtained with the corresponding **AsS**$^-$ 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**$^-$ than of the **AsS**$^-$ 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,[1,2] for fabrication of various microelectronic devices,[3] or for medical purposes[4,5] but also due to their structural variety.[6] Thus, the number of group 13 metal compounds with tertiary phosphines and arsines[7,12] 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.[13] Phosphinoarylthiols and arsinoarylthiols are excellent heteropolytopic 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-$\text{PPh}_2\text{C}_6\text{H}_4\text{SH}$ have been reported previously[14] derivatives of main group metals, including group 13 elements, are almost unexplored as only some tin[15] and indium[16] complexes have been reported so far. The coordination chemistry of 2-$\text{AsPh}_2\text{C}_6\text{H}_4\text{SH}$ is even less explored, the preparation of the free ligand being only recently reported.[17] Here, we report on the synthesis and characterization of the gallium and organogallium complexes $\text{GaCl}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2 S,P\}_2$ (**1**), $\text{Ga}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2 S,P\}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa S\}_2$ (**2**), $\text{GaMe}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2 S,P\}$ (**3**), $\text{Ga}^t\text{Bu}_2\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2 S,P\}$ (**4**), $\text{Ga}^t\text{Bu}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa^2 S,P\}\{(\text{SC}_6\text{H}_4\text{-2-PPh}_2)\text{-}\kappa S\}$ (**5**), $[\text{GaMe}_2\{(\mu_2\text{-SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa S\}]_2$ (**6**), and $\text{Ga}^t\text{Bu}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa^2 S,As\}\{(\text{SC}_6\text{H}_4\text{-2-AsPh}_2)\text{-}\kappa S\}$ (**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_2Cl_2, MeOH, and tetramethylethylenediamine (TMEDA) were refluxed over CaH_2, 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_7D_8) or molecular sieves (THF-d_8). C_6D_6 was dried with sodium/potassium alloy, filtered, and kept under inert atmosphere over potassium mirror. CDCl_3 was dried over LiAlH_4, distilled, and kept over molecular sieves. ^{n}BuLi (2.2 M in *n*-hexane), ^{t}BuLi (1.47 M in *n*-pentane), NEt_3, GaCl_3, and GaMe_3 were obtained from commercial suppliers. GaCl_3 was freshly sublimed before use. Ga^tBu_3 was synthesized by minor modifications of the standard literature procedure involving the reaction of GaCl_3 with ^{t}BuLi (1:3).[18,19] The ligands 2-$\text{EPh}_2\text{C}_6\text{H}_4$ SH (E = P (**PSH**), As (**AsSH**)) were prepared from thiophenol by *ortho*-lithiation/electrophilic substitution,[17,20] 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^{-1} and 400−200 cm^{-1} using KBr and CsI pellets, respectively. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance DRX-400 instrument, ^{1}H NMR using TMS as internal standard and ^{31}P NMR using external 85% H_3PO_4.

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 ω scan rotation, data reduction with SAINT,[21] and empirical absorption correction with SADABS[22] (compounds **2**, **4**, **7**) and on a CCD Oxford Xcalibur S diffractometer in ω- and φ-scan mode with data reduction with CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK[23] (compounds **1**, **3**, **5**, **6**). Radiation was Mo Kα (λ = 0.71073 Å). Structure refinement was carried out with SHELXL-97.[24] 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.[25] 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	$C_{40}H_{36}ClGaOP_2S_2$	$C_{54}H_{42}GaP_3S_3$	$C_{20}H_{20}GaPS$	$C_{26}H_{32}GaPS$	$C_{40}H_{37}GaP_2S_2$	$C_{40}H_{40}As_2Ga_2S_2$	$C_{40}H_{37}As_2GaS_2$
fw	763.92	949.69	393.11	477.27	713.48	874.12	801.38
T, 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	$P2_1/n$	$Pna2_1$	$Pca2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	9.324(5)	26.112(5)	19.7747(2)	14.820(2)	9.4389(5)	12.8578(3)	9.483(1)
b, Å	28.488(5)	17.413(4)	8.5440(1)	11.016(2)	9.9813(5)	9.4095(2)	10.063(2)
c, Å	14.178(5)	10.240(2)	21.7993(2)	16.029(3)	21.8992(9)	15.4085(3)	22.277(3)
α, deg	90	90	90	90	81.212(4)	90	81.227(3)
β, deg	106.161(5)	90	90	107.575(2)	79.362(4)	91.582(2)	78.180(3)
γ, deg	90	90	90	90	63.086(5)	90	63.959(3)
vol, Å^3	3617(2)	4656.1(15)	3683.10(7)	2494.6(7)	1802.4(2)	1863.49(7)	1864.8(5)
Z	4	4	8	4	2	2	2
D_{calcd}, mg/m^3	1.403	1.355	1.418	1.271	1.315	1.558	1.427
μ (Mo Kα), mm^{-1}	1.070	0.865	1.691	1.260	0.995	3.347	2.637
$F(000)$	1576	1960	1616	1000	740	880	812
cryst size, mm^3	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 θ_{max}, %	99.9	98.3	99.9	99.2	98.8	99.7	98.9
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0567$	$R_1 = 0.0399$, $wR_2 = 0.0675$	$R_1 = 0.0282$, $wR_2 = 0.0623$	$R_1 = 0.0596$,$wR_2 = 0.1262$	$R_1 = 0.0373$, $wR_2 = 0.0545$	$R_1 = 0.0243$, $wR_2 = 0.0440$	$R_1 = 0.0784$, $wR_2 = 0.1621$
R indices (all data)	$R_1 = 0.0749$, $wR_2 = 0.0664$	$R_1 = 0.0673$, $wR_2 = 0.0736$	$R_1 = 0.0396$, $wR_2 = 0.0742$	$R_1 = 0.0831$, $wR_2 = 0.1365$	$R_1 = 0.0935$ $wR_2 = 0.0631$	$R_1 = 0.0465$, $wR_2 = 0.0495$	$R_1 = 0.1491$, $wR_2 = 0.1828$
GOF on F^2	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·Å^{-3}	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 (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.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.[26]

Synthesis of GaCl{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}$_2$ (1). A solution of PSH (0.63 g, 2.14 mmol) and triethylamine (NEt_3, 0.216 g, 2.14 mmol, 0.3 mL) in methanol (20 mL) was slowly added dropwise to a solution of freshly sublimed $GaCl_3$ (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$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}$_2$ (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/$GaCl_3$) 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 $C_{36}H_{28}ClGaP_2S_2\cdot 1/2CH_2Cl_2$ (M = 734.28) C, 59.70; H, 3.98; S, 8.73%. ν_{max}(KBr)/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$_{as}$). ν_{max}(CsI)/cm^{-1}: 337s (Ga−Cl and Ga−S), 309m, 267m, 238m, and 219w. δ_H (400 MHz, $CDCl_3$): 7.58−7.25 (24H, m, aryl-H), 7.05 (2H, t, aryl-H) and 6.94 (2H, t, aryl-H). δ_P (161.9 MHz, $CDCl_3$): −17.5. *m/z* (^{69}Ga) (ESI, in CH_2Cl_2) 691.0 (M$^+$+1). *m/z* (EI) 293.1 (100%, $C_{18}H_{14}PS^+$).

Synthesis of Ga{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*}$_2$ (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 $GaCl_3$ (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 ^{n}BuLi (1:1). A solution of $GaCl_3$ (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 $C_{54}H_{42}GaP_3S_3$ (M = 949.69) C, 68.29; H, 4.46%. ν_{max}(KBr)/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. ν_{max}(CsI)/cm^{-1}: 390s (Ga−S$_{as.}$), 371w, 336m (Ga−S), 324m, 300s, 260m, 236m, and 215w. δ_H (400 MHz, $CDCl_3$): 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). δ_P (161.9 MHz, $CDCl_3$): −12.6 (dynamic in solution). *m/z* (EI): 655.1 (100%, M$^+$ − $C_{18}H_{14}PS$) and 293.1 (80%, $C_{18}H_{14}PS^+$).

Synthesis of GaMe$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*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 $GaMe_3$ (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 $C_{20}H_{20}GaPS$ (M = 393.11) C, 61.10; H, 5.13%. ν_{max}(KBr)/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. ν_{max}(CsI)/cm^{-1}: 382s (Ga−S), 292m, 264m, 249w, 229w, 223w, and 209w. δ_H (400 MHz, C_6D_6): 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_3). δ_P (161.9 MHz, C_6D_6): −1.2. *m/z* (FAB): 393.0 (100%, M$^+$ + 1) and 293.1 (36%, $C_{18}H_{14}PS^+$).

Synthesis of Ga^{t}Bu$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*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^{t}Bu$_3$ (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 $C_{26}H_{32}GaPS$ (M = 477.27) C, 65.43; H, 6.76; S, 6.72%. ν_{max}(KBr)/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. ν_{max}(CsI)/cm^{-1}: 377s (Ga−S), 297s, 280s, 265m, 248m, 233w, 215m, and 208s. δ_H (400 MHz, C_6D_6): 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_3)$_3$). δ_P (161.9 MHz, C_6D_6): 0.4. *m/z* (EI): 419.0 (100%, M$^+$ − C_4H_8), 363.0 (27%, M$^+$ − C_8H_{17}), and 293.1 (12%, $C_{18}H_{14}PS^+$).

Synthesis of Ga^{t}Bu{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*} (5). Complex **5** was obtained as a minor product from the 1:2 reaction of Ga^{t}Bu$_3$ (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^{t}Bu$_3$ 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 $C_{40}H_{37}GaP_2S_2$ (M = 713.48) C, 67.33; H, 5.23; S, 8.99%. ν_{max}(KBr)/cm^{-1}: 3046m, 2912m, 2836m, 1570m, 1480m, 1434s, 1423s, 1305w, 1261w, 1250m, 1096s, 1040m, 1027s, 998w, 811m, 740vs, 694vs, 529w, 502s, and 471m. ν_{max}(CsI)/cm^{-1}: 385w (Ga−S), 319w, 285w, 280s, 268m, 249m,

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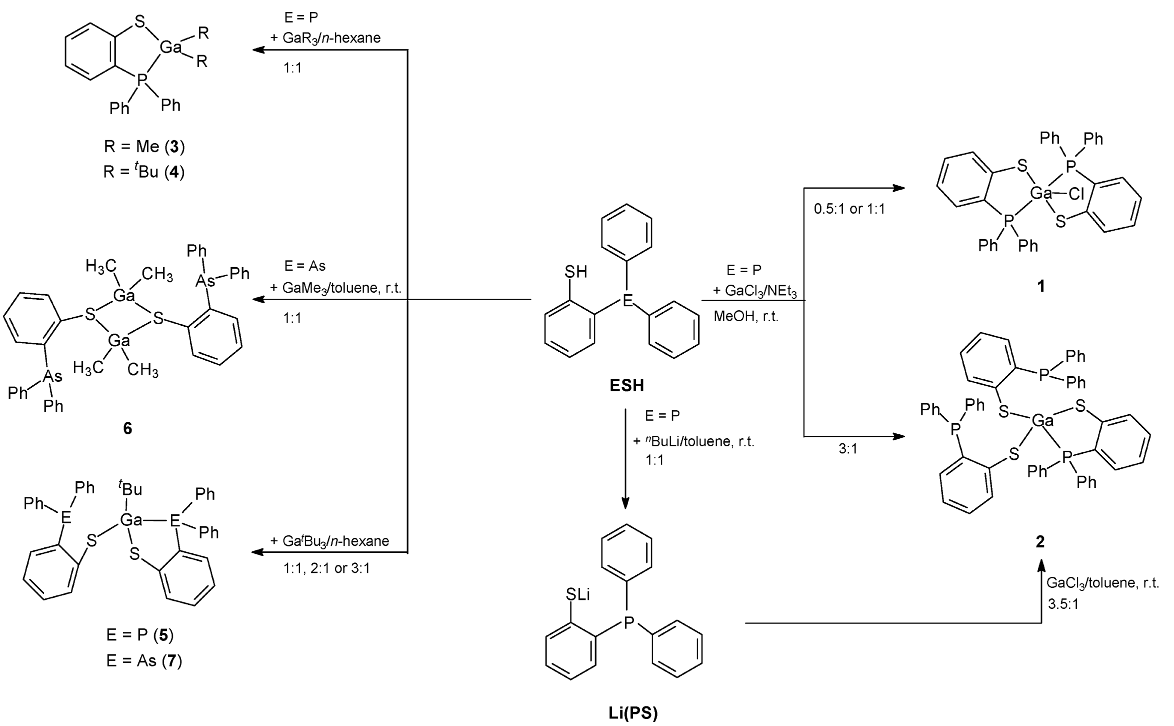
Scheme 1. The Synthetic Routes to **1**−**7**



243w, 225m, 212m, and 203s. δ_H (400 MHz, C_6D_6): 6.69−7.59 (28H, m, aryl-H), and 1.30 (9H, s, $C(CH_3)_3$). δ_P (161.9 MHz, C_6D_6): −9.6. *m/z* (EI): 655.0 (3%, $M^+ - C_4H_8$) and 293.2 (37%, $C_{18}H_{14}PS^+$).

Synthesis of [GaMe$_2${(μ_2-SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}]$_2$ (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 $C_{40}H_{40}As_2Ga_2S_2$ (M = 874.12) C, 54.96; H, 4.61%. ν_{max}(KBr)/cm^{-1}: 3047m, 2964m, 2905w, 1571w, 1480w, 1434s, 1306m, 1260s, 1186m, 1098s, 1025s, 947w, 866w, 803m, 739vs, 696s, 591w, 537w, 473m, and 446w. ν_{max}(CsI)/cm^{-1}: 321w, 303s (Ga−S), 283w, 273w, 253m, 248m, 239w, 227w, and 203m. δ_H (400 MHz, C_6D_6): 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_3). *m/z* (FAB): 437.0 (18%, $M/2^+ + 1$), 421.0 (34%, $M/2^+ - CH_2$), and 337.1 (100%, $C_{18}H_{14}AsS^+$).

Synthesis of GaᵗBu{(SC$_6$H$_4$-2-AsPh$_2$)-κ^2*S,As*}{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*} (7). An *n*-hexane solution of GaᵗBu$_3$ (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 ^{1}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 GaᵗBu$_2${(SC$_6$H$_4$-2-AsPh$_2$)-κ^2*S,As*}. Attempts to separate the compounds were unsuccessful.

Results and Discussion

The reactivity and the coordination chemistry of the bidentate ligands 2-EPh$_2$C$_6$H$_4$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)$_n$X$_{3-n}$, (**1**−**7**), $n = 1-3$, Scheme 1) were obtained by reaction of the ligands or their lithium salts with GaX$_3$ (X = Cl, Me, ᵗBu) 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 ^{1}H and ^{31}P NMR spectroscopy, IR, mass spectrometry, elemental analysis, and X-ray diffraction.

The ^{1}H NMR spectra for all complexes show the signals due to the aromatic rings and no signal for the S−H proton. The ^{1}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$^-$ or AsS$^-$ ligand.

The absence of ν_{S-H} and the presence of ν_{Ga-S}[27] at 400−300 cm^{-1} in the IR spectra of **1**−**6** indicate coordination of the deprotonated thiolato ligands. The assignment of ν_{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^{-1}.[28]

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By comparison with other GaCl-containing compounds[29-31] and the calculated normal modes,[32] the band at 337 cm^{-1} in the IR spectrum of complex **1** is assigned to ν_{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 $GaCl_3$ in the presence of NEt_3 in both 0.5:1 or 1:1 molar ratio $GaCl\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2$ (**1**) was obtained (Scheme 1). No $GaCl_2(PS)$ was observed irrespective of the molar ratio used. The reaction of PSH with $GaCl_3$ in the molar ratio 3:1 led to $Ga\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa S\}_2$ (**2**). Compound **2** could be also synthesized in higher yield by treating the lithium salt of the ligand Li(PS) with $GaCl_3$ in a 3.5:1 molar ratio. Li(PS) was prepared from PSH and ^{n}BuLi in toluene (Scheme 1). In the solid state, compounds **1** and **2** are air-stable for at least 2 days.

The ^{31}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_8) ^{31}P NMR spectra of **2** exhibit signals in the range of the free ligand, suggesting noncoordinating phosphine groups in solution.

The organogallium complexes $GaMe_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}$ (**3**) and $Ga^tBu_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}$ (**4**) were obtained by reaction of PSH with $GaMe_3$ and Ga^tBu_3 (ratio 1:1), respectively (Scheme 1). Compound **3** was also obtained in excellent yield (96%) from **2** and $GaMe_3$ in toluene at room temperature. Compound **3** is an air-stable compound that sublimes at 200 °C (under dynamic vacuum, 3×10^{-3} mbar) giving colorless crystals. In the ^{31}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_3 by phosphinoarylthiol were unsuccessful in case of $GaMe_3$. Compound **3** was the only product even when a 2:1 or 3:1 ($PSH/GaMe_3$) molar ratio was used. When PSH was treated with Ga^tBu_3 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 ^{31}P NMR spectra) to a mixture of **4** (ca. 25%), $Ga^tBu\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa S\}$ (**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^tBu_3 using different refluxing times or by a 1:1 reaction of **1** with ^{t}BuLi or the equimolar reaction of complex **4** with PSH (ca. 20 h reflux) were unsuccessful. The ^{31}P NMR spectra of **5** recorded at room temperature and at low temperature (193 K, C_7D_8) 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.

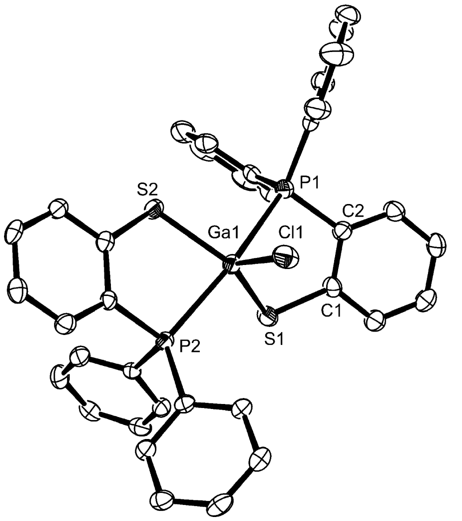

Figure 1. Molecular structure of $GaCl\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2$ (**1**). Hydrogen atoms are omitted for clarity.

The reaction of AsSH with $GaCl_3$ (in the presence of NEt_3 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 $GaMe_3$ in toluene led to $[GaMe_2\{(\mu_2\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}]_2$ (**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 ($AsSH/GaMe_3$) and under different reaction conditions (room temperature or refluxing toluene).

For the preparation of $Ga^tBu\{(SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa^2S,As\}\{(SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}$ (**7**; Scheme 1) a similar procedure as for **5** was employed. The ^{1}H NMR spectrum of the reaction product showed two sets of signals for the aromatic and aliphatic protons, assigned to complex **7** and probably $Ga^tBu_2\{(SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S,As\}$. 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. $GaCl\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2$ (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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(32) Calculations performed at the B3LYP/6-31G(d) level of theory.

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}$_2$[29] and 2.195(1) Å for {$H_2B(pz)_2$}$_2$GaCl (pz = pyrazolyl).[33] 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}$_2$ 2.274(2) Å).[29] The gallium−phosphorus bond lengths are well within the normal range associated with such bonds [2.4−2.7 Å].[7,8,34,35] 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 $GaCl_3(PMe_3)$ [2.353(2) Å][36] or $GaCl_3${$P(SiMe_3)_3$} [2.379(5) Å][37] but is smaller than the Ga−P bond length observed in $Ga(CH_2{}^tBu)_3(PHPh_2)$ [2.683(5) Å].[35] Comparable Ga−P bond lengths were found in $GaMe_3$(dppe) (dppe = bis(diphenylphosphino)ethane) [2.563(3) Å],[38] $GaClPh_2${$P(SiMe_3)_3$} [2.459(2) Å], $GaPh_3${$P(SiMe_3)_3$} [2.539(6) Å],[8] [$Ga(CH_2{}^tBu)(PPh_2)_2$]$_2$ [Ga−P_{br} 2.4689(9) Å],[39] [$GaMe_2(PPh_2)$]$_3$ [2.433(1) Å],[40] or $GaClMe_2$(dppm-*κP*) (dppm = bis(diphenylphosphino)methane) [2.535(2) Å].[41]

Ga{(SC_6H_4-2-PPh_2)-κ^2S,P}{(SC_6H_4-2-PPh_2)-κS}$_2$ (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)°.

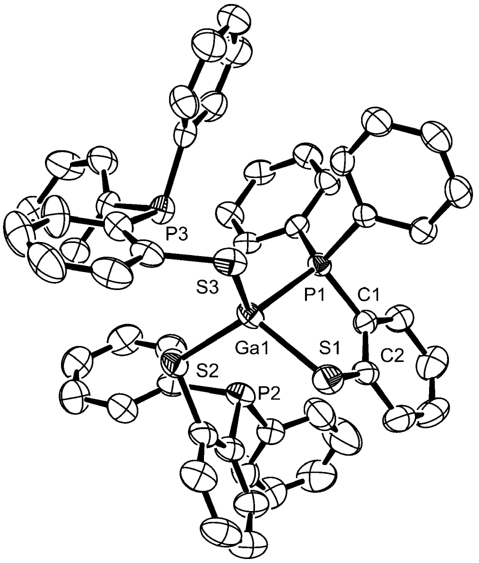

Figure 2. Molecular structure of Ga{(SC_6H_4-2-PPh_2)-κ^2S,P}{(SC_6H_4-2-PPh_2)-κS}$_2$ (**2**). Hydrogen atoms are omitted for clarity.

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**

3		4	
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)

The mean Ga−S bond length of 2.283(1) Å is close to those found in gallium complex **1** and [$HNEt_3$][Ga{SC(O)Ph}$_4$]·H_2O.[42] 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 $GaCl_3(PMe_3)$[36] 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].[38] 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],[43] 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 ^{31}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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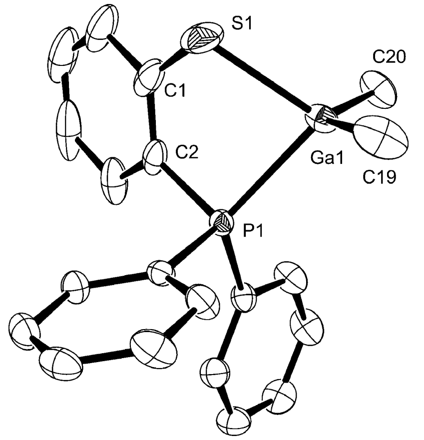

Figure 3. Molecular structure of $\mathrm{GaMe_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}$ (**3**). Only one of two independent molecules found in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.

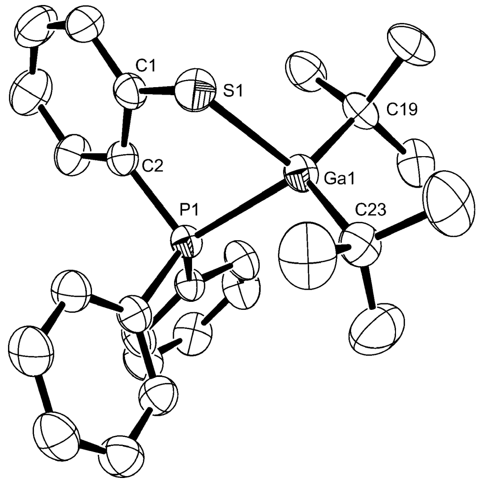

Figure 4. Molecular structure of $\mathrm{Ga^tBu_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}$ (**4**). Hydrogen atoms are omitted for clarity.

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

$\mathrm{GaMe_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}$ (3) and $\mathrm{Ga^tBu_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}$ (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.[44−47] The Ga−P bond lengths are slightly different [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**.

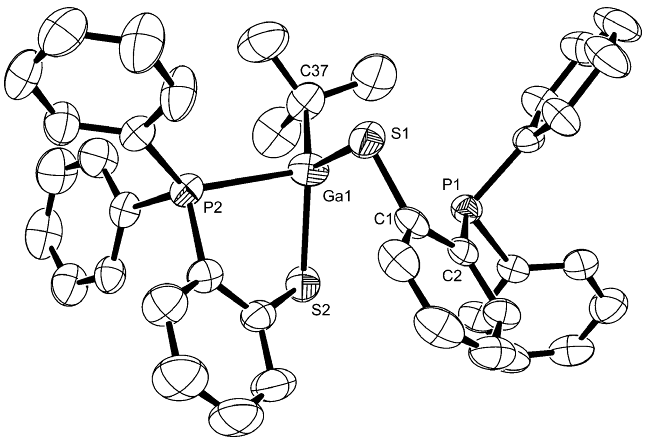

Figure 5. Molecular structure of $\mathrm{Ga^tBu\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}\{\mathrm{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa S\}$ (**5**). Hydrogen atoms are omitted for clarity. Complex **7** is isostructural.

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

	5 (E = P)	**7** (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)

$\mathrm{Ga^tBu\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa^2 S,P\}\{\mathrm{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}}\kappa S\}$ (5) and $\mathrm{Ga^tBu\{(SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}}\kappa^2 S,As\}\{\mathrm{(SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}}\kappa S\}$ (7). X-ray structure analysis revealed the isostructural complexes $\mathrm{Ga^tBu\{(SC_6H_4\text{-}2\text{-}EPh_2)\text{-}}\kappa^2 S,E\}\{\mathrm{(SC_6H_4\text{-}2\text{-}EPh_2)\text{-}}\kappa S\}$ (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 $\mathrm{PS^-}$ or $\mathrm{AsS^-}$ 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 $\mathrm{GaI_3(AsPh_3)}$ [2.489(2) Å][9] or covalent bonds in $\mathrm{Ga\{As(C_6H_2Me_3)_2\}_3}$ [2.470(1)−2.508(1) Å],[48] $\mathrm{[GaPh_2\{As(CH_2SiMe_3)_2\}]_2}$ [2.518(1)−2.530(1) Å],[49] $\mathrm{[GaMe_2(As^tBu_2)]_2}$ [2.541(1)−2.558(1) Å],[50] $\mathrm{Ga^tBu_2(As^tBu_2)}$ [2.446(3) Å],[18] $\mathrm{Ga^tBu_2\{As(SiPh_3)CH(SiMe_3)_2\}}$ [2.458(1) Å],[51]

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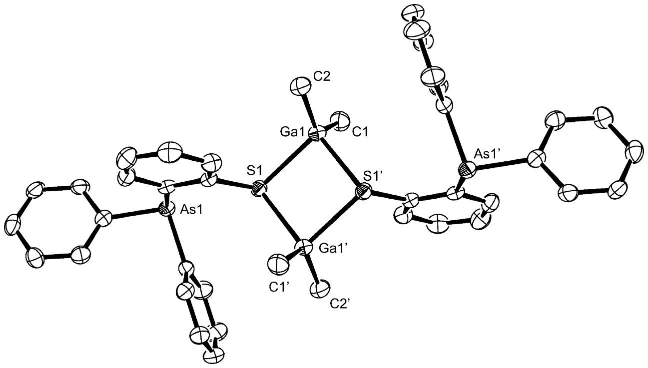


Figure 6. Molecular structure of $[GaMe_2\{(\mu_2\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}]_2$ (**6**). Hydrogen atoms are omitted for clarity.

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

Ga(1)$\cdots$Ga(1)′	3.418	C(1)−Ga(1)−C(2)	125.9(1)
Ga(1)$\cdots$As(1)	4.951	C(1)−Ga(1)−S(1)	110.04(7)
S(1)$\cdots$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 $[(Cl_3Ga)\{Me_2AsCH_2C(Me)(CH_2AsMe_2)_2\}GaCl_2][GaCl_4]$ [2.435(1)−2.465(2) Å].[52] The reason could be steric hindrance in compound **7**.

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

$[GaMe_2\{(\mu_2\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}]_2$ (6). Compound **6** (Figure 6 and Table 6) consists of a dimer with a central planar almost rectangular four-membered Ga_2S_2 ring [Ga(1)−S(1)−Ga(1)′ 89.74(2)°, S(1)−Ga(1)−S(1)′ 90.26(2)°]. Planar Ga_2S_2 rings were also found in $[GaI_2(\mu\text{-}SMe)]_2$[44] and $[GaPh_2(\mu\text{-}SEt)]_2$.[45]

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 $[NEt_4]_2[Ga_2S_2(SPh)_4]$ [2.264(1) to 2.288(1) Å][53] but comparable with those found in other four-membered Ga_2S_2 rings, $[Ga^tBu_2(\mu\text{-}SPh)]_2$ [2.421(2)−2.445(2) Å][46] and $[GaMe_2(\mu\text{-}SC_6F_5)]_2$ [2.436(3)−2.460(2) Å].[54] 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 AsS^- acts as a monodentate ligand, unlike PS^- in **3**, for which bidentate coordination was found.

The intramolecular S(1)$\cdots$S(1)′ (3.434 Å) and Ga(1)$\cdots$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$\cdots$S and Ga$\cdots$Ga interactions ($\sum$Ga$\cdots$Ga = 3.74 Å, $\sum$S$\cdots$S = 3.6 Å).[43] Similar Ga$\cdots$Ga distances were observed in $[GaMe_2(\mu\text{-}SC_6F_5)]_2$ [3.397 Å],[54] longer distances in $[GaPh_2(\mu\text{-}SEt_2)]_2$ [3.257 Å][45] and $[NEt_4]_2[Ga_2S_2(\mu\text{-}SPh)_4]$ [2.943 Å],[53] and shorter ones in $[Ga^tBu_2(\mu\text{-}SPh)]_2$ [3.663 Å].[46]

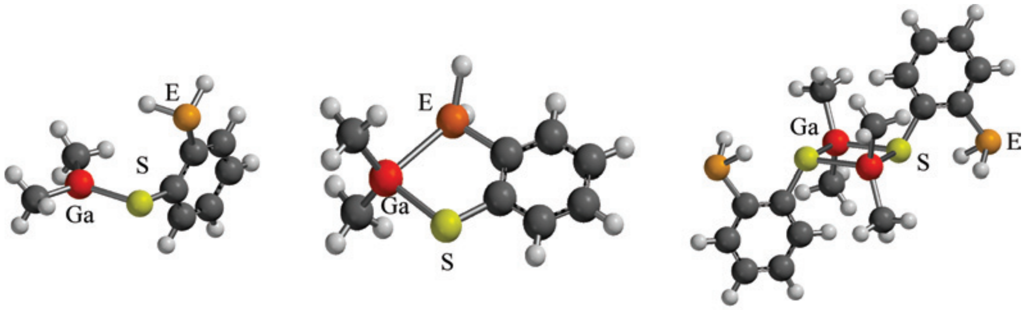
The packing diagram of **6** shows the molecules arranged in columns along the crystallographic *b* axis, connected through H(phenyl)−π interactions [π stacking avg H(Ph)$\cdots$Ph 2.785 Å and H(Ph)$\cdots$S 2.924 Å interactions].

Chelate or Bridging Ligands in 3 and 6. Complexes **3** and **6** represent relatively rare examples[31] of different coordination behavior of the two very similar ligands PSH and AsSH toward the same metal complex fragment, $GaMe_2$. While a monomeric structure with a chelating phosphanylarylthiolato ligand is observed in $GaMe_2\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}$ (**3**), a dimeric arsanylarylthiolato-bridged complex $[GaMe_2\{(\mu_2\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}]_2$ (**6**) is obtained with the corresponding AsS ligand. In order to understand this difference in the behavior of the PS^- and 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 $GaMe_2$ (Scheme 2) were performed at the B3LYP/6-31G(d)[55] level of theory. The results for $GaMe_2$(H−PS) and $GaMe_2$(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 $2\text{-}EPh_2\text{-}C_6H_4SH$ (E = P, As) with $GaCl_3$ or GaR_3 (R = Me, ^{t}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 $GaMe_2\{SC_6H_4\text{-}2EPh_2\}$ (E = P, As)



a (E = P); a' (E = As) b (E = P); b' (E = As) c (E = P); c' (E = As)

Table 7. Total (au) and Relative (kcal/mol) Energies of the Monomeric Monodentate or Chelate Complexes and Dimers of the Model Systems $GaMe_2(H-ES)$ (E = P, As)

	total energy (au)	2(*E*(chelate) − *E*(dimer)) (kcal/mol)	chelate/monodentate relative energy (kcal/mol)	2(*E*(monodentate) − *E*(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_2S_2 $[GaMe_2(\mu_2\text{-H}-\text{PS-}\kappa S)]_2$	−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_2S_2 $[GaMe_2(\mu_2\text{-H}-\text{AsS-}\kappa S)]_2$	−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 $GaMe_2\{(SC_6H_4\text{-2-}PPh_2)\text{-}\kappa^2 S,P\}$ (**3**) and a dimeric arsinoarylthiolato-bridged complex $[GaMe_2\{(\mu_2\text{-}SC_6H_4\text{-2-}AsPh_2)\text{-}\kappa S\}]_2$ (**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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