Stabilisation of an inorganic digallane by the phosphinobisthiolato P,S,S pincer ligand PPh(2-SC_6H_4)$_2$†

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The pincer ligand PPh(2-HSC_6H_4)$_2$ reacts with $GaCl_3$ in the presence of triethylamine to yield the anionic gallium complex [NEt_3H][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (**1**), which undergoes cation exchange with PPh_4Cl to give [PPh_4][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (**2**). Neutral complexes GaR{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*} [R = Me (**3**), ^{t}Bu (**4**)] were obtained by reaction of PPh(2-HSC_6H_4)$_2$ with trialkyl gallium compounds ($GaMe_3$, Ga^tBu_3). Compound **4** is light-sensitive and decomposes in daylight or under UV irradiation. Three decomposition products could be isolated: tetranuclear hydrido-bridged mixed-valent gallium(II)–gallium(III) complex [Ga^{III}\{PPh(2-SC_6H_4)-κ^2*S*,*P*-μ-(2-SC_6H_4)-κ*S*′\}$_2$]$_2$(μ$_3$-H)$_2$$Ga^{II}_2$ (Ga–Ga) (**5**), gallium(II) complex [Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}]$_2$ (Ga–Ga) (**6**), and sulfido-bridged dinuclear complex [Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}]$_2$(μ-S) (**7**). The molecular structures of **2–7** are described.

Introduction

There is considerable current interest in polydentate hetero-donor ligands involving tertiary phosphine groups in combination with nitrogen, oxygen or sulfur donors. Of these, phosphinothiolates derived from thiophenol [PPh_2(2-HSC_6H_4) (**PSH**), PPh(2-HSC_6H_4)$_2$ (**PS_2H_2**) and P(2-HSC_6H_4)$_3$ (**PS_3H_3**)] have been shown to be highly versatile ligands that form stable complexes with a wide range of elements, especially compounds of the heavier transition metals.[1,2]

In particular, the **PS_2H_2** ligand is interesting due to the wide range of potential coordination patterns which result from combinations of phosphorus and sulfur coordination: as P,S,S pincer ligands, as bidentate P,S or S,S ligands, as monodentate S or P ligands, and, additionally, as doubly or triply bridging ligands. Although the chemistry of the **PS_2H_2** ligand with transition metals has been studied to some extent,[1a,2] only a few complexes of main group metals have been reported so far.[3] Until now there have been no reported examples of gallium complexes with this type of ligand.

We now report the reaction of the potentially tridentate **PS_2H_2** ligand with gallium(III) chloride and trialkyl gallium compounds ($GaMe_3$, Ga^tBu_3), which resulted in anionic ([Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}]$^-$) and neutral [GaR{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}; R = Me (**3**), ^{t}Bu (**4**)] gallium(III) complexes. The ^{t}Bu derivative **4** is light-sensitive and decomposed with the formation of a new dimeric dithiolato gallium(II) compound with a Ga–Ga single bond, namely, [Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}]$_2$ (Ga–Ga) (**6**), along with unusual mixed-valent gallium(II)–gallium(III) hydride complex [Ga^{III}\{PPh(2-SC_6H_4)-κ^2*S*,*P*-μ-(2-SC_6H_4)-κ*S*′\}$_2$]$_2$(μ$_3$-H)$_2$$Ga^{II}_2$ (Ga–Ga) (**5**), and sulfido complex [Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}]$_2$(μ-S) (**7**).

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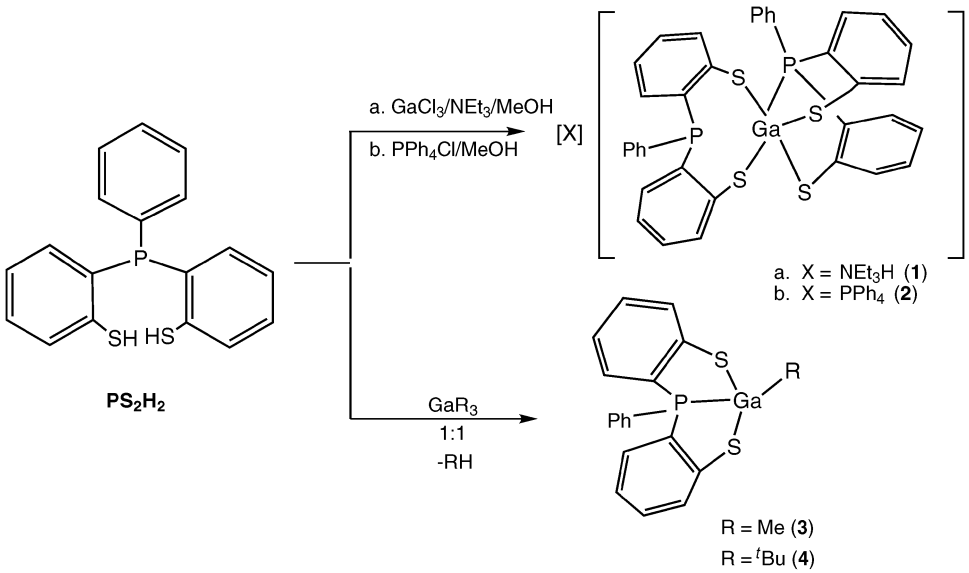
Results and discussion

Gallium(III) chloride reacts with PPh(2-HSC_6H_4)$_2$ (**PS_2H_2**) in the presence of triethylamine with the formation of the anionic gallium complex [NEt_3H][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (**1**). Cation exchange with PPh_4Cl gave the crystalline compound [PPh_4][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (**2**). Neutral complexes GaR{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*} [R = Me (**3**), ^{t}Bu (**4**)] were obtained by the reaction of PPh(2-HSC_6H_4)$_2$ with trialkyl gallium compounds ($GaMe_3$, Ga^tBu_3; Scheme 1). Compounds **1–4** were obtained in good yield and were characterised by ^{1}H, ^{31}P{^{1}H} NMR and IR spectroscopy, mass spectrometry and X-ray crystallography. Complexes **1–3** are stable in solution and in the solid state, whereas **4** decomposes in solution in daylight. The decomposition leads to a mixture of gallium compounds, of which three could be isolated and structurally characterised (*vide infra*).

Anionic complexes, [X][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}-{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] [X = NEt_3H (1), PPh_4 (2)]

The 1 : 1 or 2 : 1 reaction of **PS_2H_2** with $GaCl_3$ in methanol in the presence of triethylamine resulted in the formation of [NEt_3H]-[Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (**1**),



Scheme 1

obtained as a white solid in good yield (84%; Scheme 1). The absence of a ν_{S-H} band in the IR spectrum and the lack of signals associated with the S–H group in the ^{1}H NMR spectrum confirmed the deprotonation of all thiol groups. The presence of a $HNEt_3$ cation was indicated in the IR [2675 cm^{-1} (w, ν_{N-H})] and ^{1}H NMR spectra. The two sets of signals at −23.9 and −26.3 (br) ppm in the $^{31}P\{^1H\}$ NMR spectrum are related to the two non-equivalent phosphorus atoms, as in the product obtained by cation exchange (compound **2**) described below. The gallium complex anion ([M^- − NEt_3H]) peak of compound **1** was observed in the ESI MS (negative) spectrum at m/z 716.96 with the appropriate isotopic distribution. Low-quality crystals were obtained from CH_3CN at room temperature over a few weeks but were unsuitable for X-ray structure determination.

Cation exchange of **1** with one equivalent of PPh_4Cl in methanol at room temperature gave the crystalline phosphonium salt [PPh_4][Ga{PPh(2-SC_6H_4)$_2$-κ^3S,S',P}{PPh(2-SC_6H_4)$_2$-κ^2S,S'}] (**2**; Scheme 1). IR and NMR spectra confirm the proposed formula. The $^{31}P\{^1H\}$ NMR spectrum shows the signal of the PPh_4 cation (22.9 ppm) and two singlets in the same range as those of **1**, at −23.9 and −29.3 (br) ppm.

Crystals of **2** suitable for X-ray diffraction were obtained from a saturated diglyme solution at room temperature. Compound **2** crystallises in triclinic space group $P\bar{1}$ with two molecules in the unit cell, which also contains two diglyme molecules, and consists of discrete cations and anions (Fig. 1). The gallium atom is coordinated by one phosphorus and four sulfur atoms in a distorted trigonal-bipyramidal geometry. The atoms P2 and S2 occupy the axial position (P2–Ga1–S2 162.15(2)°; Table 1); the three equatorial sulfur atoms are nearly coplanar with Ga1 [deviations: Ga1 0.321, S1 −0.118, S3 −0.115 and S4 −0.089 Å]. The Ga–S bond lengths (range 2.2970(9)–2.392(1) Å) and S–Ga–S bond angles (87.32(2)–128.65(3)°) agree well with those of similar compounds (Ga–S 2.205–2.446 Å and S–Ga–S 81.80–123.73°).[4,5] Shorter Ga–S bonds were observed in tetrakis-thiolato gallates

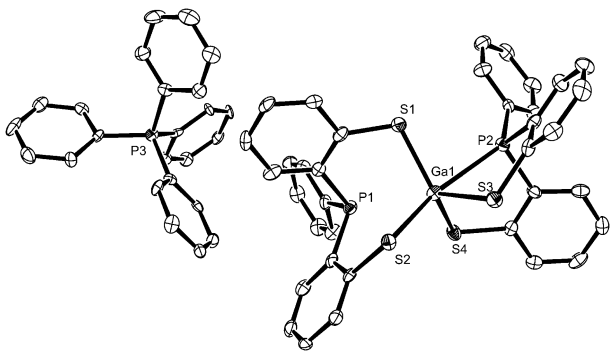


Fig. 1 Molecular structure of [PPh_4][Ga{PPh(2-SC_6H_4)$_2$-κ^3S,S',P}{PPh(2-SC_6H_4)$_2$-κ^2S,S'}] (**2**) with thermal ellipsoids at 50% probability. Hydrogen atoms and the diglyme molecule (solvent) are omitted for clarity.

Table 1 Selected bonds lengths (Å) and angles (°) in **2**

S1–Ga1	2.2970(9)	S1–Ga1–S4	128.65(3)
S2–Ga1	2.3784(8)	S1–Ga1–S2	104.10(4)
S3–Ga1	2.392(1)	S4–Ga1–S2	107.25(3)
S4–Ga1	2.310(1)	S1–Ga1–S3	111.41(2)
P2–Ga1	2.6992(9)	S4–Ga1–S3	109.70(3)
		S2–Ga1–S3	87.32(2)
		S1–Ga1–P2	83.55(3)
		S4–Ga1–P2	78.79(3)
		S2–Ga1–P2	162.15(2)
		S3–Ga1–P2	74.85(2)

[NEt_4][Ga(SPh)$_4$] (2.242(3)–2.260(3) Å), [N^nPr_4][Ga(SEt)$_4$] (2.264(1) Å),[5] [$N^iPr_2H_2$][Ga(S^iPr)$_4$] (2.2541(6)–2.2796(6) Å),[6] and in the five-coordinate compound GaCl{(SC_6H_4-2-PPh_2)-κ^2S,P}$_2$ (2.270(1)–2.295(1) Å).[7] The Ga1–P2 bond length (2.6992(9) Å) greatly exceeds that observed in GaCl{(SC_6H_4-2-PPh_2)-κ^2S,P}$_2$ (Ga–P 2.4927(9) and 2.5872(1) Å). The other phosphorus atom is not coordinated to the gallium atom; however, the Ga1···P1 distance (2.975 Å) is shorter than the sum of the van der Waals radii (3.67 Å),[8] which could be

indicative of some degree of Ga···P interaction. The reason for the non-coordinating P1 atom could be steric hindrance owing to the constraints of the chelate rings and the sterically demanding phosphine groups.

Neutral complexes, GaR{PPh(2-SC$_6$H$_4$)$_2$-κ^3*S*,*S*′,P} [R = Me (3), ^{t}Bu (4)]

The organogallium complexes GaR{PPh(2-SC$_6$H$_4$)$_2$-κ^3*S*,*S*′,*P*} [R = Me (**3**), ^{t}Bu (**4**)] were obtained from the 1 : 1 or 2 : 1 reaction of **PS$_2$H$_2$** with GaR$_3$ (Scheme 1). The IR, ^{1}H and ^{31}P{^{1}H} NMR spectra of **3** and **4** indicate P,S,S coordination of the deprotonated ligand. The signals in the ^{31}P{^{1}H} NMR spectra [0.3 (**3**) and 0.4 ppm (**4**)] are shifted downfield relative to that of the free ligand (−19.3 ppm), as expected for coordination to gallium. The FAB mass spectra show the molecular ion peaks at *m*/*z* 408.9 (100.0%, [M$^+$ + H]) for **3** and 450.9 (47.1%, [M$^+$ + H]) (for **4**) with the appropriate isotopic distributions. The mass spectrum of **4** also exhibits a peak at *m*/*z* 844.8 (4.8%) corresponding to the fragment [2M − ^{t}Bu]$^+$, which suggests formation of a dinuclear complex under MS conditions.

Colourless crystals of **3** and **4** were obtained from Et$_2$O at room temperature. Complex **3** crystallises in orthorhombic space group *Pbca* with eight molecules in the unit cell, and **4** in triclinic space group $P\bar{1}$ with four molecules in the unit cell. Two structurally independent molecules were found in the asymmetric unit of **4**, which differ only slightly in their bond lengths and bond angles (Table 2). The **PS$_2$**$^{2-}$ ligand is coordinated in a pincer-like manner in both compounds, and the coordination sphere is completed by a methyl group in **3** and a *tert*-butyl group in **4** (Fig. 2). The closeness of the S–Ga–P bond angles to 90° indicates distorted square-planar rather than tetrahedral coordination, which is in agreement with the bite angles observed for all complexes containing the **PS$_2$**$^{2-}$ pincer ligand. Thus, the atoms Ga1, C1, S1 and S2 in **4** are nearly coplanar (deviations from the mean plane: Ga1 0.345, S1 −0.104 , S2 −0.110, C1 −0.131 Å).

The Ga–S bond lengths of 2.2794(5)–2.2858(5) Å (**3**) and 2.2943(7)–2.3132(7) Å (**4**) are larger than those found in the three-coordinate compound Ga(S-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_3$ (Ga–S 2.205(6) Å)[9] and the tetracoordinate amine tris-thiolato complex Ga{(SC$_6$H$_4$-2-CH$_2$)$_3$N-κ^4*N*,*S*,*S*′,*S*″} (2.225(2)–2.233(2) Å),[10] but are comparable to those in **2** and in four-coordinate phosphinothiolato complexes.[7]

Table 2 Selected bond lengths (Å) and angles (°) in **3** and **4**[a]

	3		**4**[a]	
Ga1–C19	1.942(2)	Ga1–C1	1.982(2)	[1.982(2)]
Ga1–S1	2.2858(5)	Ga1–S1	2.2943(7)	[2.2828(8)]
Ga1–S2	2.2794(5)	Ga1–S2	2.3132(7)	[2.2876(7)]
Ga1–P1	2.3491(4)	Ga1–P1	2.3602(8)	[2.3680(7)]
C19–Ga1–S1	118.02(7)	C1–Ga1–S1	113.79(7)	[121.42(6)]
C19–Ga1–S2	116.57(7)	C19–Ga1–S2	119.37(7)	[112.88(6)]
S2–Ga1–S1	111.83(2)	S2–Ga1–S1	113.79(3)	[112.31(3)]
C19–Ga1–P1	125.16(7)	C1–Ga1–P1	125.07(6)	[124.05(6)]
S1–Ga1–P1	89.33(2)	S1–Ga1–P1	90.90(3)	[89.90(3)]
S2–Ga1–P1	90.61(2)	S2–Ga1–P1	89.01(3)	[91.03(2)]
C2–S1–Ga1	102.85(5)	C5–S1–Ga1	101.89(7)	[102.90(7)]
C8–S2–Ga1	101.65(5)	C17–S2–Ga1	103.53(7)	[101.41(7)]
C1–P1–Ga1	103.28(5)	C6–P1–Ga1	101.26(6)	[102.70(6)]
C7–P1–Ga1	101.54(5)	C18–P1–Ga1	103.96(6)	[101.05(6)]
C13–P1–Ga1	125.14(5)	C11–P1–Ga1	125.97(7)	[127.81(6)]

[a] Bond lengths and angles of the second independent molecule are given in brackets.

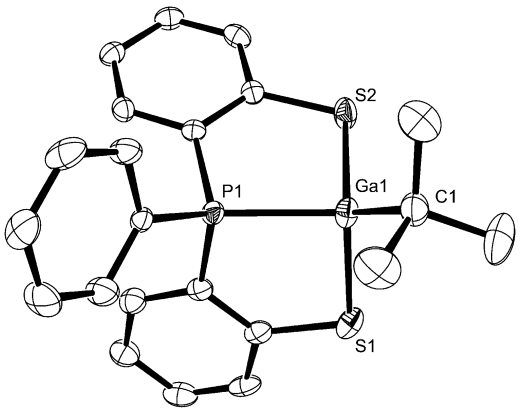


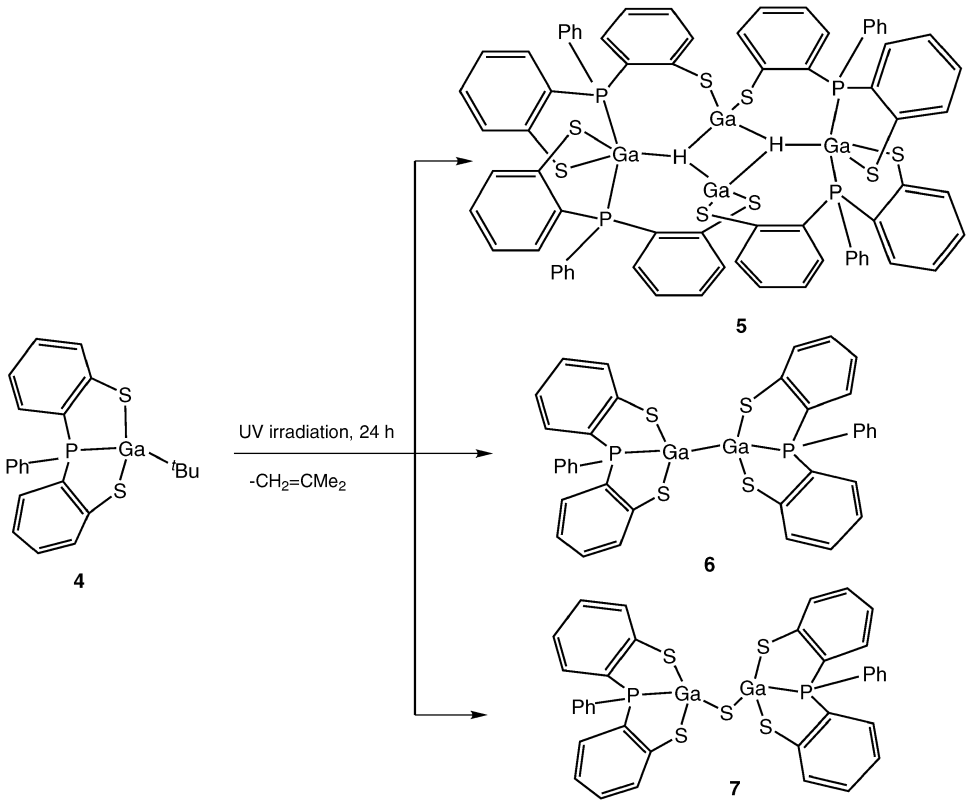
Fig. 2 Molecular structure of Ga^{t}Bu{PPh(2-SC$_6$H$_4$)$_2$-κ^3*S*,*S*′,*P*} (**4**) with thermal ellipsoids at 50% probability (only one of two independent molecules in the asymmetric unit is shown). The hydrogen atoms are omitted for clarity.

The Ga–C bond lengths [1.942(2) Å (**3**), 1.982(2) Å (**4**)] are slightly shorter than the Ga–C$_{trisyl}$ distance in GaMe$_2${C(SiMe$_3$)$_3$}(THF) (2.046(2) Å)[11] due to the higher effective positive charge of the gallium atoms caused by the electronegative sulfur atoms. However, the Ga–C distances are comparable to those observed for previously reported related gallium complexes (GaR$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}, R = Me: 1.958(3)–1.959(4) Å, ^{t}Bu: 2.005(4)–2.017(4) Å; Ga^{t}Bu{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{SC$_6$H$_4$-2-PPh$_2$)-κ*S*} 1.977(3) Å)[7] and in other organogallium compounds.[12]

The Ga–P bond lengths [2.3491(4) Å (**3**), 2.3602(8) Å (**4**)] are in the expected range for gallium phosphine complexes, *e.g.*, GaCl$_3$(PMe$_3$) 2.353(2) Å,[13] GaCl$_3${P(SiMe$_3$)$_3$} 2.379(5) Å,[14] Ga{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*}$_2$ 2.3923(8) Å.[7] However, the Ga–P distances are shorter than in [Me$_2$GaPPh$_2$]$_3$ 2.433(1) Å,[15] GaClMe$_2${CH$_2$(PPh$_2$)$_2$-κ*P*} 2.535(2) Å[16] or GaMe$_2${(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S*,*P*} 2.4602(8).[7] The shorter Ga–P bond lengths in **3** and **4** compared with other tetracoordinate organogallium complexes are probably a result of the pincer-like coordination of the ligand.

Decomposition of 4: [Ga^{III}{PPh(2-SC$_6$H$_4$)-κ^2*S*,*P*-μ-(2-SC$_6$H$_4$)-κ*S*′}$_2$]$_2$(μ$_3$-H)$_2$Ga$^{II}_2$ (Ga–Ga) (5), [Ga{PPh(2-SC$_6$H$_4$)$_2$-κ^3*S*,*S*′,*P*}]$_2$ (Ga–Ga) (6), and [Ga{PPh(2-SC$_6$H$_4$)$_2$-κ^3*S*,*S*′,*P*}]$_2$(μ-S) (7)

When a toluene–*n*-hexane solution of **4** was kept at room temperature in daylight a few very small colourless crystals formed after more than three weeks. The ^{31}P{^{1}H} NMR spectrum of the crystals exhibited two signals of almost equal intensity at −15.8 and −16.5 ppm, assigned, on the basis of X-ray single-crystal molecular structure determinations, to compounds **5** and **6** (*vide infra*). There were no changes in the ^{31}P{^{1}H} NMR spectra (C$_7$D$_8$) of a solution of **4** kept in the dark for more than 60 days or recorded after several hours of refluxing in toluene, but the formation of a small amount of **5**



Scheme 2

and **6** was observed when the solution was exposed to daylight for more than 20 days. Total decomposition of **4** was found after an additional month (*ca.* 40 days) in daylight (signals at −15.8, −16.6 ppm and a low intensity signal at *ca.* −24.0 ppm).

The ^{1}H NMR spectra of a solution (C_6D_6) of **4** exposed to daylight for three months in a sealed NMR tube showed additional signals at 4.74 (septet, CH_2═) and 1.60 (t, CH_3) ppm assigned to isobutene and at 0.85 ppm (d) corresponding to isobutane,[17] both formed, most probably, by recombination of *tert*-butyl radicals,[18] as shown before for other *tert*-butyl containing organometallics.[19]

Complete decomposition of **4** was observed on irradiation for 24 h with a UV lamp at 366 nm in toluene–*n*-hexane–C_6D_6 solution (Scheme 2, details in the ESI†). Besides **5** and **6**, at least 19 other products were formed, as indicated by the ^{31}P{^{1}H} NMR spectrum. From the clear solution, on standing, only a few crystals were formed which were identified as [Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}]$_2$(μ-S) (**7**; Scheme 2).

Efforts to isolate and fully characterise compounds **5** and **6** spectroscopically were unsuccessful; only a mixture of products was obtained in all cases.

Gas-phase geometry optimisation of **4** at the B3LYP/6-31G(d)[20] level of theory reproduced fairly well the main features of the observed structure (see ESI†). The electronic spectrum of **4** was calculated (TD-DFT using the Spartan'06 package) in order to understand the nature of the absorbance transitions. The experimental and calculated spectra, the excitation energies for the first 10 singlet states and the shapes of the main orbitals involved are available as the ESI†. The HOMO−1 and HOMO−2 orbitals (Fig. 3) have Ga−C bonding character, so any transitions from these levels should weaken this bond, as was observed experimentally. The lability of the Ga−C bond might also be associated with the high electrostatic positive charges on these atoms (Ga + 0.603, C + 0.552).

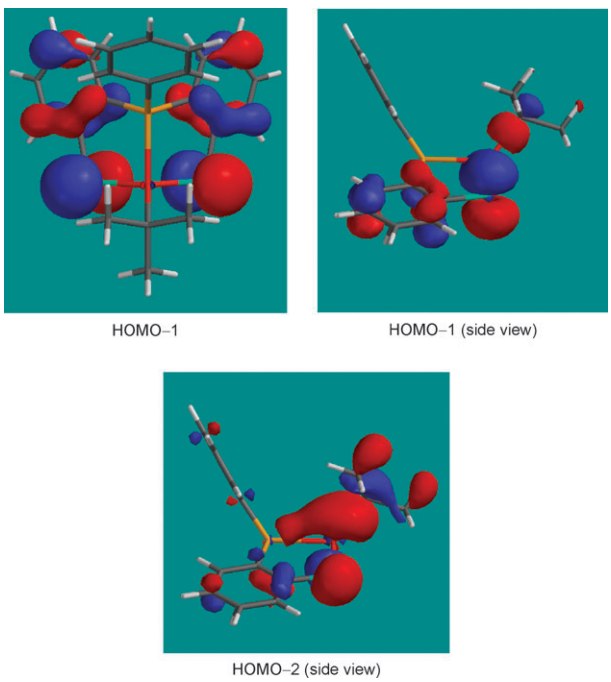


Fig. 3 The shape of the HOMO orbitals of **4**.

Based on the theoretical studies, the first step in the formation of **5**, **6** and **7** can be described as homolytic cleavage of the Ga–C bond in **4**. The gallium(II) intermediates thus formed may dimerise through Ga–Ga and Ga–H (**5**), Ga–Ga (**6**) or Ga–S (**7**) bond formation. A similar mechanism was proposed for formation of the organo-digallane $(Bu^tGaGaBu^t)_2(\mu\text{-}H)_2[\mu\text{-}H_2Ga(Bu^t)_2]_2$.[21] During the last few decades many organo-digallanes[22] have been synthesised by various methods and with diverse structures, and their reactivity has also been investigated.[23] Inorganic digallane chemistry is mainly represented by adducts of gallium(II) halides,[24] other inorganic digallanes reported so far being the tetra(amido)digallane $[Ga\{(NSiMe_3CH_2)_2CMe_2\}]_2$ (obtained from the reaction of $(LiNSiMe_3CH_2)_2CMe_2$ with $Ga_2Cl_4(dioxane)_2$) and tetraalkoxy-substituted digallane $[Ga_2(O^tBu)_2(\mu\text{-}O^tBu)_2]_2$ (*Ga–Ga*).[25] Thus, the inorganic dithiolato framework in the structure of **6** is unprecedented.

Molecular structures of complexes 5, 6 and 7

The crystal structures of **5**, **6** and **7** were determined by X-ray structure analysis. The molecular structure of **5** is of only low accuracy due to limited crystal data. Complex **5** is a tetranuclear compound with two types of gallium atoms: two are connected *via* a Ga–Ga single bond (Ga^{II}_2), and two Ga^{III} atoms which are connected with the Ga_2 group by two bridging hydrogen atoms through 3c–2e bonds. Since the hydrogen atom could not be unambiguously located in the X-ray structure analysis, an IR spectrum of the mixture of crystals of **5** and **6** was recorded, which showed a Ga–H vibration at 1603 cm^{-1} (*cf.* Ga–H 1638 cm^{-1} in $(Bu^tGaGaBu^t)_2(\mu\text{-}H)_2[\mu\text{-}H_2Ga(Bu^t)_2]_2$),[21] supporting the proposed structure of compound **5**.

Compound **6** crystallises in the triclinic space group $P\bar{1}$ with four molecules of the dimeric gallium(II) complex and five toluene molecules in the unit cell (Fig. 4, Table 3). Two structurally independent molecules were found in the asymmetric unit of **6**. Complex **6** is a dinuclear gallium(II) compound in which each Ga atom is coordinated by a $\mathbf{PS_2}^{2-}$ ligand in a pincer-like manner resulting in a highly distorted tetrahedral arrangement for both gallium atoms, in which Ga1, Ga2, S1 and S2 are virtually coplanar with deviations of about 0.23, 0.08, 0.07 and 0.07 Å from the mean plane, respectively. The distortion of the tetrahedral geometry in Ga1 and Ga2 is apparent from P–Ga–S angles of 84.26(2) to 90.20(2)° and S–Ga–Ga angles of 120.56(2) to 128.54(2)°.

The Ga–Ga distance of 2.3832(4) Å is not significantly shorter than the sum of covalent radii (2.44 Å)[26] or the gallium–gallium distance in elemental gallium (2.442 Å) and is comparable to those found in other inorganic digallanes: $Ga_2Cl_4(dioxane)_2$ (Ga–Ga 2.406(1) Å),[24a] $Ga_2I_4(NH_3)_2$ (Ga–Ga 2.498(7) Å),[24d] $Ga_2I_4(AsEt_3)_2$ (Ga–Ga 2.428(7) Å),[24g] $Ga_2I_4(PEt_3)_2$ (Ga–Ga 2.444(2) Å),[24h] $Ga_2I_2L_2$ (where L = NH_2Cy, Ga–Ga 2.429(1) Å; L = $NH_2{}^tBu$, Ga–Ga 2.4243(9) Å, L = $PHCy_2$, Ga–Ga 2.437(2) Å, L = PH^tBu_2, Ga–Ga 2.4448(9) Å),[24i] $Ga_2[Ga_2I_6]$ (Ga–Ga 2.388(5) Å)[24j] or $[Ga\{(NSiMe_3CH_2)_2CMe_2\}]_2$ (Ga–Ga 2.385(1) Å)[25] and related compounds with a Ga–Ga single bond,[27] but longer than the shortest Ga–Ga bond known to date (2.343(2) Å), observed in $[Li([12]crown\text{-}4)_2][\{Ga(Trip)_2\}_2]$ (Trip = C_6H_2-2,4,6-^{i}Pr$_3$).[28]

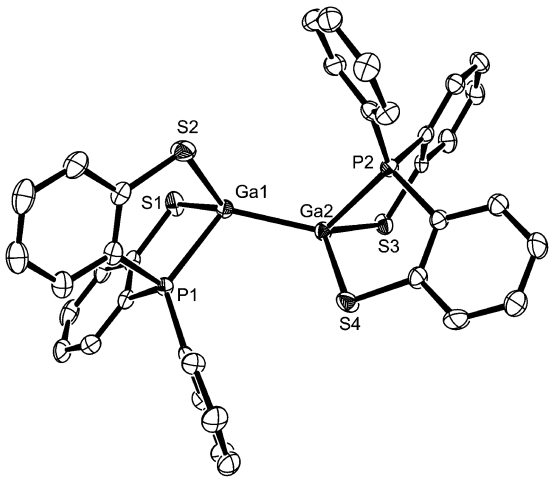


Fig. 4 Molecular structure of **6** with thermal ellipsoids at 50% probability (only one of two independent molecules found in the asymmetric unit is shown). The solvent molecules and hydrogen atoms are omitted for clarity.

Table 3 Selected bonds lengths (Å) and bond angles (°) in **6**[a]

Ga1–Ga2	2.3832(4)	[2.3935(4)]	S1–Ga1–S2	110.08(3)	[111.41(3)]
Ga1–S1	2.3155(6)	[2.2891(7)]	S3–Ga2–S4	114.20(3)	[108.51(2)]
Ga1–S2	2.2902(8)	[2.3219(7)]	S1–Ga1–Ga2	123.87(2)	[112.86(2)]
Ga2–S3	2.3272(7)	[2.2945(6)]	S2–Ga1–Ga2	120.56(2)	[123.67(2)]
Ga2–S4	2.3037(6)	[2.3142(6)]	S3–Ga2–Ga1	128.54(2)	[122.51(2)]
Ga1–P1	2.3783(6)	[2.3969(6)]	S4–Ga2–Ga1	121.15(2)	[121.99(2)]
Ga2–P2	2.3870(6)	[2.3832(7)]	P1–Ga1–Ga2	113.54(2)	[126.18(2)]
			Ga1–Ga2–P2	118.59(2)	[115.84(2)]
			S1–Ga1–P1	87.53(2)	[89.66(2)]
			S2–Ga1–P1	90.20(2)	[86.50(2)]
			S3–Ga2–P2	84.26(2)	[89.38(2)]
			S4–Ga2–P2	88.03(2)	[88.48(2)]

[a] Bond lengths and angles of the second independent molecule are given in brackets.

The Ga–S bond lengths are in the same range as those found in complex **4** (2.2902(8)–2.3272(7) Å), but they are shorter than those found in $[Ga\{CH(SiMe_3)_2\}\{(SPPh_2NPPh_2S)\text{-}\kappa^2S,S\}]_2$ (2.4047(8)–2.4450(8) Å).[22b] The Ga–P bond lengths (av. 2.3826 Å) are slightly shorter than those in the gallium(II) compounds $[GaCl_2(PEt_3)]_2$ (2.4269(5) Å),[24e] $[GaI_2(PHCy_2)]_2$ (2.424(2) Å), $[GaI_2(PH^tBu_2)]_2$ (2.446(1) Å)[24i] and $GaI_2(PEt_3)$–$GaI(PEt_3)$–$GaI_2(PEt_3)$ (2.404(3)–2.427(3) Å).[24h] However, the Ga–P distances are slightly longer than those observed in the previously mentioned gallium(III) compounds, which indicates the influence of the oxidation state of the metal atom. The S–Ga–P bond angles of the pincer ligand are similar to those of the starting material **4**.

The two independent molecules in the asymmetric unit differ only slightly in their respective Ga–Ga, Ga–S and Ga–P bond lengths.

A small amount of compound **7** was obtained as thin colourless needles from a toluene–*n*-hexane–C_6D_6 solution of **4** which was irradiated with UV light at room temperature for 24 h. The compound crystallises in the monoclinic space group $C2/c$ with four molecules of **7** and four C_6D_6 molecules in the

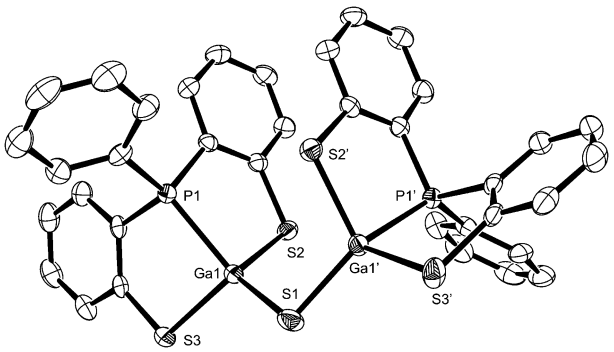


Fig. 5 Molecular structure of **7** with thermal ellipsoids at 50% probability. The solvent molecules and hydrogen atoms are omitted for clarity. S1 atom is located on a twofold axis. Symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 1/2$.

unit cell. Compound **7** is a dinuclear complex which contains two almost identical Ga(**PS_2**) fragments linked by a sulfido bridge (Fig. 5, Table 4).

In **7**, each gallium atom is surrounded in a distorted tetrahedral fashion by three sulfur atoms (two thiolato groups and one bridging sulfido group) and one phosphorus atom, with S–Ga–S bond angles between 109.23(3) and 116.59(3)°. Moreover, the large S1–Ga1–P1 bond angle of 137.22(2)° is compensated by the small S3–Ga1–P1 and S2–Ga1–P1 bond angles of 91.86(3) and 88.78(3)°, respectively. The Ga1–S2 and Ga1–S3 bonds of the gallium thiolato groups (2.2757(8) and 2.2513(8) Å) are slightly shorter than those observed in compounds **4** and **6**, and this could be attributed to less steric hindrance. As expected, the Ga1–S1 bond length of the bridging sulfido group (2.1876(7) Å) is smaller than the Ga–$S_{thiolate}$ distances. In the trimer, [Ga^{t}Bu(py)(μ-S)]$_3$, a longer Ga–S_{bridge} bond is observed (2.231(3)–2.253(3) Å).[12b] No significant differences between the Ga–P distances of **7** and **4** and **6** were observed.

The Ga1···Ga1′ distance (3.308 Å) is shorter than the sum of the van der Waals radii (3.74 Å),[8] which could be indicative of some degree of Ga···Ga interaction, as reported for $[NEt_4]_2[Ga_2S_2(SPh)_4]$ (2.943 Å).[5]

Experimental

General procedures

All manipulations were carried out under an inert atmosphere of dry nitrogen. ^{n}BuLi (2.2 M in *n*-hexane), ^{t}BuLi (1.47 M in *n*-pentane), PPh_4Cl, NEt_3, $GaCl_3$ and $GaMe_3$ are commercially available. $GaCl_3$ was freshly sublimed before use. The synthesis of Ga^{t}Bu$_3$ was carried out with minor modification of the standard literature procedure involving the 1 : 3 reaction of $GaCl_3$ with ^{t}BuLi.[29] PPh(2-HSC_6H_4)$_2$ (**PS_2H_2**) was prepared from thiophenol by *ortho*-lithiation/electrophilic substitution by using Schlenk techniques and dry solvents.[30] Toluene, *n*-hexane, dimethoxydiethyl ether (diglyme), diethyl ether and tetrahydrofuran (THF) were dried over sodium–benzophenone, distilled under an atmosphere of dry argon and stored over potassium mirror. CH_3OH and CH_3CN were refluxed over CaH_2, distilled and kept under nitrogen. C_7D_8 for NMR spectroscopy was used as purchased and kept under inert atmosphere over potassium mirror. C_6D_6 was dried over sodium–potassium alloy, filtered and kept under an inert atmosphere over potassium mirror. $CDCl_3$ was dried over $LiAlH_4$, distilled and kept over molecular sieves.

Table 4 Selected bonds lengths (Å) and bond angles (°) in **7**

Ga1···Ga1′	3.308	Ga1–S1–Ga1′	98.24(4)
Ga1–S1	2.1876(7)	S1–Ga1–S2	112.10(3)
Ga1–S2	2.2757(8)	S1–Ga1–S3	109.23(3)
Ga1–S3	2.2513(8)	S3–Ga1–S2	116.59(3)
Ga1–P1	2.3688(7)	S1–Ga1–P1	137.22(2)
		S2–Ga1–P1	88.78(3)
		S3–Ga1–P1	91.86(3)

Elemental analysis was performed with a Vario EL-Heraeus microanalyzer. IR spectra were recorded with a Perkin-Elmer System 2000 spectrometer in the range 4000–400 cm^{-1} and 400–200 cm^{-1} on KBr and CsI pellets, respectively. ^{1}H (TMS internal standard) and ^{31}P (85% H_3PO_4 external standard) NMR spectra were recorded on a Bruker Avance DRX-400 instrument. 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-nitrobenzyl alcohol). A Perkin-Elmer UV-Vis spectrophotometer with 1.0 cm quartz cells was used for absorbance studies.

B3LYP/6-31G(d) full geometry optimisations were performed on model systems in which two phenyl substituents on phosphorus and arsenic were replaced by hydrogen atoms, by using the Spartan 06 package of programs (SPARTAN '06 Wavefunction inc.).[31] TD-DFT/TDA calculations were carried out with the same package of programs.

The crystallographic data were collected on a CCD Oxford Xcalibur S diffractometer, radiation MoKα (λ = 0.71073 Å), ω- and φ-scan mode. Data reduction was carried out with CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK.[32] The structure refinement was carried out by direct methods with SHELXS-97[33] and was refined using SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically and H atoms were calculated on idealised positions. Structure figures were generated with ORTEP.[35] A summary of data collection, structure solution and refinement details for compounds **2–4**, **6** and **7** is given in Table 5.

Synthesis of [NEt_3H][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}-{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (1)

Both the 1 : 1 and 2 : 1 reactions of **PS_2H_2** with $GaCl_3$ in the presence of NEt_3 gave **1**. At room temperature a solution of **PS_2H_2** (1.27 g, 3.895 mmol) and NEt_3 (0.791 g, 7.835 mmol, 1.09 ml) in methanol (48 ml) was slowly added dropwise to a solution of freshly sublimed $GaCl_3$ (0.35 g, 1.983 mmol) in methanol (15 ml). The white precipitate that formed immediately turned pale yellow during the reaction. The reaction mixture was stirred at room temperature for 22 h, and the precipitate was separated by filtration, washed with *n*-hexane and dried *in vacuo* (yield 1.37 g, 1.671 mmol, 84% based on $GaCl_3$). Very small colourless crystals were obtained from a MeCN solution at room temperature over a few weeks but were unsuitable for

Table 5 Summary of data collections, structure solution and refinement details for compounds **2–4**, **6** and **7**

	2·Diglyme	**3**	**4**	**6**	**7**
Empirical formula	$C_{66}H_{60}GaO_3P_3S_4$	$C_{19}H_{16}GaPS_2$	$C_{22}H_{22}GaPS_2$	$C_{44.75}H_{36}Ga_2P_2S_4$	$C_{42}H_{32}Ga_2P_2S_5$
FW	1192.01	409.13	451.21	903.36	898.36
T/K	130(2)	130(2)	130(2)	130(2)	130(2)
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	12.142(5)	15.8418(1)	11.064(2)	12.439(1)	21.4599(8)
b/Å	14.078(5)	14.3993(1)	12.605(3)	13.867(3)	10.1678(4)
c/Å	18.389(5)	15.8970(1)	15.919(3)	24.722(1)	18.2790(7)
α/°	97.013(5)	90	93.73(2)	83.400(9)	90
β/°	109.103(5)	90	102.65(2)	83.011(6)	95.722(3)
γ/°	99.798(5)	90	99.97(2)	73.18(1)	90
Volume/Å^3	2873.1(17)	3626.28(4)	2121.1(7)	4037.1(9)	3968.6(3)
Z	2	8	4	4	4
D_{calc}/Mg m^{-3}	1.378	1.499	1.413	1.486	1.504
μ (MoKα)/mm^{-1}	0.755	1.832	1.573	1.653	1.732
F(000)	1240	1664	928	1842	1824
Crystal size/mm^3	0.3 × 0.12 × 0.08	0.4 × 0.4 × 0.2	0.4 × 0.2 × 0.2	0.4 × 0.3 × 0.3	0.3 × 0.02 × 0.02
$\theta_{Min}/\theta_{Max}$/°	2.56/26.02	2.83/30.50	2.57/28.28	2.73/28.28	2.79/28.27
No. of reflns collected	46 215	94 604	38 133	104 559	50 091
No. of indep. reflns	11 299 [R_{int} = 0.0608]	5538 [R_{int} = 0.0213]	10 517 [R_{int} = 0.0378]	19 952 [R_{int} = 0.0437]	4922 [R_{int} = 0.0634]
Completeness to θ_{Max}(%)	99.9	99.9	99.9	99.6	99.9
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0325, wR_2 = 0.0429	R_1 = 0.0262, wR_2 = 0.0588	R_1 = 0.0280, wR_2 = 0.0565	R_1 = 0.0293, wR_2 = 0.0549	R_1 = 0.0377, wR_2 = 0.0808
R indices (all data)	R_1 = 0.0698, wR_2 = 0.0483	R_1 = 0.0354, wR_2 = 0.0686	R_1 = 0.0504, wR_2 = 0.0618	R_1 = 0.0554, wR_2 = 0.0627	R_1 = 0.0662, wR_2 = 0.0914
Goodness-of-fit on F^2	0.950	1.228	0.919	1.027	1.031
Largest diff. peak/e·Å^{-3}	0.313 and −0.342	0.441 and −0.372	0.590 and −0.307	0.459 and −0.365	1.339 and −0.783

X-ray structure determination. Compound **1** is a pale yellow solid, mp 223–240 °C, with low solubility in common solvents: *n*-hexane, THF, CH_2Cl_2, Et_2O, CH_3CN.

^{1}H NMR (δ, $CDCl_3$, ppm): 7.52–6.91 (m, 26H, phenyl), 3.04 (q, 6H, $HN(CH_2CH_3)_3$), 1.35 (t, 9H, $HN(CH_2CH_3)_3$), N–H proton was not observed. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, ppm): −23.9, −26.3 (br). Anal. calcd for $C_{42}H_{42}GaNP_2S_4$ (M = 820.71): C 61.47, H 5.16, S 15.63, N 1.71%; found: C 60.97, H 5.20, S 15.54, N 1.67%. IR (KBr, cm^{-1}): 3044 (m), 2965 (m), 2675 (w, ν_{N-H}), 1571 (s), 1542 (w), 1480 (w), 1442 (s), 1420 (vs), 1263 (m), 1245 (m), 1155 (w), 1097 (s), 1047 (s), 1027 (s), 804 (w), 736 (vs), 720 (w), 694 (m), 659 (w), 535 (w), 519 (w), 473 (m), 456 (w), 492 (w). IR (CsI, cm^{-1}): 385 (m, ν_{Ga-S}), 336 (w, ν_{Ga-S}), 306 (w), 286 (w), 277 (m), 256 (m), 248 (m), 227 (s), 221 (m), 204 (w). ESI MS (negative, $CHCl_3$–CH_3CN (1 : 1)), m/z: 716.96 ([M$^-$ − NEt_3H]).

Synthesis of [PPh_4][Ga{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*}-{PPh(2-SC_6H_4)$_2$-κ^2*S*,*S*′}] (2)

A solution of PPh_4Cl (0.124 g, 0.331 mmol) in methanol (6 ml) was added dropwise over 20 min to a suspension of **1** (0.273 g, 0.333 mmol) in the same solvent (18 ml). The suspension was heated to reflux for 1 h and then stirred overnight at room temperature; the precipitate was isolated by filtration and dried *in vacuo*. The product, identified as compound **2** (yield: 0.21 g, 0.198 mmol, *ca.* 60% based on **1**), is a white-cream solid with mp 189–205 °C, slightly soluble in THF, dichloromethane and diglyme but insoluble in diethyl ether and *n*-hexane. However, **2** decomposes in THF in a few weeks. A few colourless crystals suitable for X-ray diffraction were obtained from a concentrated solution of **2** in diglyme at room temperature in 3 days.

^{1}H NMR (δ, $CDCl_3$, ppm): 7.86–7.62 (m, 20H, phenyl), 7.43–6.80 (m, 26H, aryl). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, ppm): 22.9 (PPh_4), −23.9, −29.3 (br). Anal. calcd for $C_{66}H_{60}GaO_3P_3S_4$ (M = 1192.01): C 66.50, H 5.07%; found: C 66.12, H 5.18%. IR (KBr, cm^{-1}): 3051 (m), 2962 (w), 1911 (w), 1572 (s), 1545 (w), 1482 (m), 1436 (vs), 1420 (s), 1338 (w), 1315 (w), 1263 (m), 1245 (m), 1187 (w), 1159 (w), 1130 (m), 1109 (vs), 1049 (s), 1027 (s), 998 (w), 806 (w), 744 (vs), 723 (vs), 690 (s), 660 (w), 527 (vs), 475 (m), 453 (w), 409 (w). IR (CsI, cm^{-1}): 377 (s, ν_{Ga-S}), 360 (s), 337 (m, ν_{Ga-S}), 304 (s), 283 (w), 265 (m), 253 (m), 221 (m). ESI MS (negative, $CHCl_3$–CH_3OH (1 : 1)), m/z: 1036.6, 732.9, 683.1, 464.9; no assignment possible. ESI MS (positive, $CHCl_3$–CH_3OH (1 : 1)), m/z: 339.1 ([PPh_4]$^+$).

Synthesis of GaMe{PPh(2-SC_6H_4)$_2$-κ^3*S*,*S*′,*P*} (3)

Compound **3** was obtained by treating **PS_2H_2** with $GaMe_3$ (1 : 1 or 2 : 1). Trimethylgallium (0.20 ml, 1.52 M in *n*-hexane, 0.05 g, 0.307 mmol) was added dropwise to a stirred solution of **PS_2H_2** (0.10 g, 0.307 mmol) in toluene (6 ml) at −78 °C. During the addition of trimethylgallium vigorous evolution of gas was observed. After addition was complete, the reaction mixture was warmed to room temperature and stirred for another 24 h. The volatiles were removed *in vacuo* resulting in a white solid (yield: 0.05 g, 0.122 mmol, *ca.* 40% based on **PS_2H_2**). The 2 : 1 reaction occurred with 80% yield of **3** based on **PS_2H_2**. Colourless crystalline rods of **3** were obtained on recrystallisation from Et_2O at room temperature. Mp 210–215 °C.

^{1}H NMR (δ, C_6D_6, ppm): 7.66 (t, 2H, phenyl), 7.07 (t, 2H, aryl), 6.98–6.77 (m, 7H, aryl), 6.60 (t, 2H, aryl), 0.31 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (δ, C_6D_6, ppm): 0.3. Anal. calcd for $C_{19}H_{16}GaPS_2$ (M = 409.13): C 55.78, H 3.94, S 15.67; found:

C 55.45, H 3.39, S 16.04%. IR (KBr, cm^{-1}): 3050 (w), 2964 (w), 1577 (s), 1547 (w), 1482 (w), 1447 (s), 1437 (s), 1422 (s), 1310 (w), 1251 (s), 1185 (w), 1131 (s), 1102 (s), 1046 (s), 1026 (m), 999 (w), 804 (m), 762 (s), 744 (vs), 706 (m), 690 (m), 582 (w), 542 (w), 523 (m), 513 (w), 475 (s), 450 (w), 434 (w). IR (CsI, cm^{-1}): 398 (m, ν_{Ga-S}), 354 (m, ν_{Ga-S}), 302 (s), 278 (s), 268 (m), 227 (s), 222 (s). FAB MS, *m*/*z*: 408.9 (100.0%, $[M^+ + H]$), 392.9 (79.0%, $[M^+ - Me]$), 325.0 (10.8%, $[\mathbf{PS_2}^+]$).

Synthesis of $Ga^tBu\{PPh(2\text{-}SC_6H_4)_2\text{-}\kappa^3S,S',P\}$ (4)

A slurry of $\mathbf{PS_2H_2}$ (1.2 g, 3.681 mmol) in *n*-hexane (20 ml) was cooled to −78 °C and Ga^tBu_3 (0.88 g, 3.651 mmol) was added dropwise (over *ca.* 20 min). After addition was complete, the reaction mixture was warmed to room temperature (a white precipitate was observed) and stirred overnight. The white precipitate was isolated by filtration and dried *in vacuo* (yield: 1.31 g, 2.905 mmol, 79% based on $\mathbf{PS_2H_2}$). Colourless crystals of **4** were obtained on recrystallisation from Et_2O at room temperature. Mp 186–193 °C.

^1H NMR (δ, C_6D_6, ppm): 7.67 (t, 2H, phenyl), 7.17–6.84 (m, 7H, phenyl), 6.79 (t, 2H, phenyl), 6.61 (t, 2H, phenyl), 1.25 (s, 9H, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (δ, C_6D_6, ppm): 0.4. Anal. calcd for $C_{22}H_{22}GaPS_2$ (M = 451.21): C 58.56, H 4.91, S 14.21; found: C 58.06, H 5.69, S 14.23%. IR (KBr, cm^{-1}): 3049 (w), 2945 (m), 2914 (m), 2869 (m), 2843 (s), 2708 (w), 1963 (w), 1811 (w), 1577 (s), 1548 (w), 1482 (w), 1448 (s), 1422 (s), 1362 (w), 1333 (w), 1252 (s), 1176 (w), 1162 (w), 1133 (m), 1101 (s), 1046 (s), 1029 (m), 999 (w), 944 (w), 866 (w), 812 (w), 756 (s), 743 (vs), 718 (m), 704 (m), 690 (m), 522 (m), 512 (m), 474 (s), 450 (m), 431 (w). IR (CsI, cm^{-1}): 392 (s, ν_{Ga-S}), 353 (w, ν_{Ga-S}), 304 (s), 274 (s), 237 (m), 214 (w), 208 (w).

FAB MS, *m*/*z*: 844.8 (4.8%, $[2M^+ - {}^tBu]$), 450.9 (47.1%, $[M^+ + H]$), 392.9 (100.0%, $[M^+ - {}^tBu]$), 325.0 (2.9%, $[\mathbf{PS_2}^+]$).

Conclusions

The coordination chemistry of potentially tridentate ligand $PPh(2\text{-}HSC_6H_4)_2$ ($\mathbf{PS_2H_2}$) toward gallium has been investigated. Treatment of GaR_3 (R = Cl, Me, ^{t}Bu) with $\mathbf{PS_2H_2}$ gives anionic and neutral complexes, $[Ga(\mathbf{PS_2})_2]^-$ and $GaR(\mathbf{PS_2})$, respectively. Crystals could be obtained only when the bulky cation $[PPh_4]^+$ was employed as the counterion. The gallium atom of the anion in **2** is coordinated in a distorted trigonal-bipyramidal fashion resulting from unsymmetrical coordination of the two $\mathbf{PS_2}^{2-}$ ligands. In the neutral complexes **3** and **4**, the Ga atom is coordinated in a distorted tetrahedral fashion by one alkyl group and one pincer-like $\mathbf{PS_2}^{2-}$ ligand. Irradiation of $Ga^tBu(\mathbf{PS_2})$ (**4**) leads to decomposition, the mechanism of which can be described as homolytic cleavage of the Ga–C bond based on TD-DFT calculations using the Spartan'06 package. Three of the products which were formed could be isolated, albeit only in small amounts, and structurally characterised: tetranuclear hydrido-bridged mixed-valent gallium(II)–gallium(III) complex $[Ga^{III}\{PPh(2\text{-}SC_6H_4)\text{-}\kappa^2S,P\text{-}\mu\text{-}(2\text{-}SC_6H_4)\text{-}\kappa S'\}_2]_2(\mu_3\text{-}H)_2Ga^{II}{}_2$ (Ga–Ga) (**5**), gallium(II) complex $[Ga\{PPh(2\text{-}SC_6H_4)_2\text{-}\kappa^3S,S',P\}]_2$ (Ga–Ga) (**6**) and sulfido-bridged dinuclear complex $[Ga\{PPh(2\text{-}SC_6H_4)_2\text{-}\kappa^3S,S',P\}]_2(\mu\text{-}S)$ (**7**). The Ga–Ga bond (2.3832(4) Å) in **6** is slightly shorter than observed for the majority of digallane complexes, which could be due to steric and electronic effects of the pincer ligand.

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