Pergamon

0277-5387(95)00253-7

Polyhedron Vol. 15, No. 3, pp. 391–402, 1996

0277-5387/96 $9.50+0.00

GALLIUM AND INDIUM COMPOUNDS OF SULPHUR DONOR LIGANDS: PYRIDINE-2-THIOLATES AND DIPHENYLTHIOPHOSPHINATES

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(*Received* 22 *March* 1995; *accepted* 5 *June* 1995)

Abstract—The reaction of GaR_3 (R = ^{t}Bu, Me) with 1, 2, or 3 molar equivalents of 2-mercaptopyridine (HSpy) yielded $Ga(R)_2(Spy)$ [R = ^{t}Bu (**1**), Me(**2**)], $Ga(R)(Spy)_2$ [R = ^{t}Bu (**3**), Me (**4**)], and $Ga(Spy)_3$ (**5**), respectively. Reaction of $GaCl_3$ and HSpy in the presence of NEt_3 does yield $Ga(Spy)_3$ if excess HSpy is employed, otherwise $Ga(Cl)(Spy)_2$ (NEt_3) (**6**) may be isolated. The indium compound, $In(Spy)_3$ (**7**), may be prepared both in an analogous manner to that for compound **5**, but also from the reaction of HSpy with either InCl or $InCl_3$ in the presence of NEt_3. In all the compounds, except compound **3**, the 2-mercaptopyridine acts exclusively as a chelating ligand. Reaction of $Ga(^tBu)_3$ with $Ph_2P(S)(SH)$ yields $[Ph_2P(S)S]_2$ but only traces of the expected product $[(^tBu)_2Ga(\mu\text{-}S_2PPh_2)]_2$ (**8**). In contrast, reaction of $Ga(^tBu)_3$ with $HO(S)PPh_2$ (E = S, O) yields the dimeric compounds $[(^tBu)_2Ga(\mu\text{-}O(E)PPh_2)]_2$, E = S (**9**), O (**10**). Compound **9** exists as a mixture of head-to-head (**9a**, *syn*) and head-to-tail (**9b**, *anti*) isomers due to the asymmetry of the bridging ligand. Reaction of $GaCl_3$ with three molar equivalents of $Na(S_2PR_2)\cdot 2(H_2O)$, R = Me, Et, yields the tris-dithiophosphinate compounds, $Ga(S_2PR_2)_3$, R = Me (**11**), Et (**12**). All new compounds have been characterized by NMR and IR spectroscopy and mass spectrometry. In addition, the molecular structures of compounds **4** and **10** have been determined by X-ray crystallography.

Research in our laboratories has been concerned with the chemistry of the Group 13 elements with Group 16 atom donor ligands.[1–3] Recent work has focused on gallium chalcogenide compounds (in particular those with sulphur donor ligands). To date, we have concentrated on simple sulphide (S^{2-}) and thiolate (RS^-) compounds,[4,5] however, we are interested in determining whether other types of sulphur donor ligand are suitable for stabilizing compounds with unusual structures. In this regard we have investigated the synthesis of group 13 compounds of 2-mercaptopyridine, and thiophosphinates.

A wide variety of industrial applications have been demonstrated for 2-mercaptopyridine (HSpy), including: its use in adhesives (for automobile moldings), batteries, and photographic processing solutions.[6] It has been also used in preparing biological agents for application as analgesics, anticonvulsants, cardiovascular agents, and in the treatment of senile dementia and amnesia,[7] as well as an ingredient in cosmetic effervescent solutions for nail cuticles[8] and as a dandruff control agent.[9] As a ligand 2-mercaptopyridine is equally versatile.

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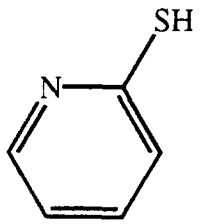
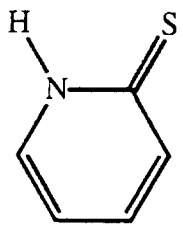
Both the protonated (HSpy) and anionic ($[Spy]^-$) forms can coordinate to metal centres.[10] Reactions with transition metals have shown that several modes of coordination are possible. Although the common name is 2-mercaptopyridine, implying protonation of the sulphur atom (**I**), NMR spectroscopy indicates that the compound exists in the 2(1H)-pyridinethione form (**II**), allowing coordination via either nitrogen or sulphur. While in its anionic form, $[Spy]^-$, it can act as a monodentate or bidentate ligand, as a bridge between two metal centres, or as a capping ligand over three metal centres. The only previous examples of a 2-mercaptopyridine complexes of the group 13 metals (Al, Ga, and In) were the dialkyl aluminium dimers, **III**, reported by Oliver and co-workers.[11]

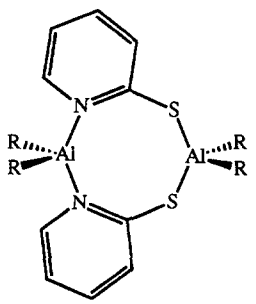
Thio- and dithio-phosphinates potentially represent a class of ligand isoelectronic to 2-mercaptopyridine (cf., **IV**). The first report of group 13 dialkylphosphinate and arsinate compounds was over 30 years ago by Coates and co-workers.[12] Since that time, a number of examples have been prepared (eq. 1).[13] In addition, the diakylphosphinates and arsinates have been prepared by the oxidation of the appropriate dialkylpnictide (eq. 2).[14] Despite these advances and extensive solid-state investigations of the group 13 phosphinates and arsinates, there have been few studies of the thio and dithiophosphinates.



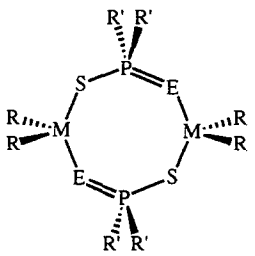
(I)



(II)



(III, R = Me, Et)



(IV, M = Al, Ga, In; E = O, S)

$$MR_3 + HO_2ER'_2 \longrightarrow R_2M(O_2ER'_2) + RH$$
$$M = Ga, In; E = P, As \quad (1)$$

$$R_2M(ER'_2) \xrightarrow{O_2} R_2M(O_2ER'_2)$$
$$M = Ga, E = As; M = In, E = P \quad (2)$$

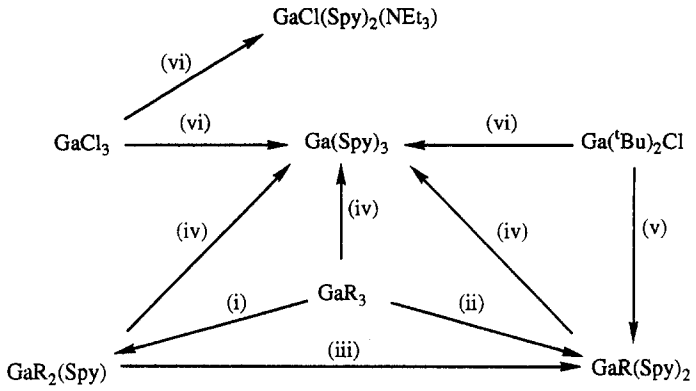
RESULTS AND DISCUSSION

2-Mercaptopyridine

The reaction of $Ga(^tBu)_3$ with 1 molar equivalent of 2-mercaptopyridine yields the dialkyl compound $Ga(^tBu)_2(Spy)$ (**1**), Scheme 1(i). In contrast to the synthesis of compound **1**, the methyl analogue, $GaMe_2(Spy)$ (**2**), is difficult to isolate, and was only obtained in low yield, from the reaction of $GaMe_3(OEt_2)$ with one equivalent of HSpy in hexane. The reaction is clearly dependent on the presence of a coordinating ligand/solvent since in the absence of diethyl ether $GaMe(Spy)_2$ (see below) is the only 2-mercaptopyridine product isolated. Compounds **1** and **2** are highly air sensitive; within seconds of their exposure to air they decompose from off-white crystals to thick yellow oils. Mass spectra of compounds **1** and **2** indicate the presence of monomers in the gas phase. This contrasts with the dimer formation observed for aluminium, i.e. $[R_2Al(\mu\text{-}Spy)]_2$.[11] Unfortunately, the structures of compounds **1** and **2** could not be determined in the solid state due to difficulties in obtaining crystals suitable for X-ray analysis.

Reaction of GaR_3 with two equivalents of 2-mercaptopyridine yields the expected mono-alkyl compounds $GaR(Spy)_2$ [R = ^{t}Bu (**3**), Me (**4**)], Scheme 1(ii). As noted above, compound **4** is also formed upon addition of only 1 molar equivalent of 2-mercaptopyridine to $GaMe_3$ in toluene (see Experimental). This would suggest that the dimethyl compound, **2**, is unstable and disproportionates to compound **4** and $GaMe_3$, i.e. Scheme 1(iii). We have previously reported similar disproportionation reactions for 1,2-diphenyltriazenide compounds of indium,[15] and 1,2-di-*tert*-butyl-4-methyl phenoxide compounds of aluminium.[16]

The molecular structure of compound **4** is shown in Fig. 1; selected bond lengths and angles are given in Table 1. The compound is monomeric with no close intermolecular contacts. The gallium centre is in a distorted trigonal bipyramidal coordination environment [N(1)—Ga(1)—N(2) = 156.8(2)°]. The equatorial positions are occupied by the alkyl group and the sulphur atoms, as would be expected based upon the relative *trans*-influences and ligand



Scheme 1. Synthesis of 2-mercaptopyridine compounds of gallium. (i) HSpy, R = 'Bu, toluene; R = Me, hexane/Et_2O. (ii) 2 HSpy, toluene. (iii) hexane, Δ. (iv) HSpy, toluene, Δ. (v) HSpy, NEt_3. (vi) HSpy, NEt_3, Δ.

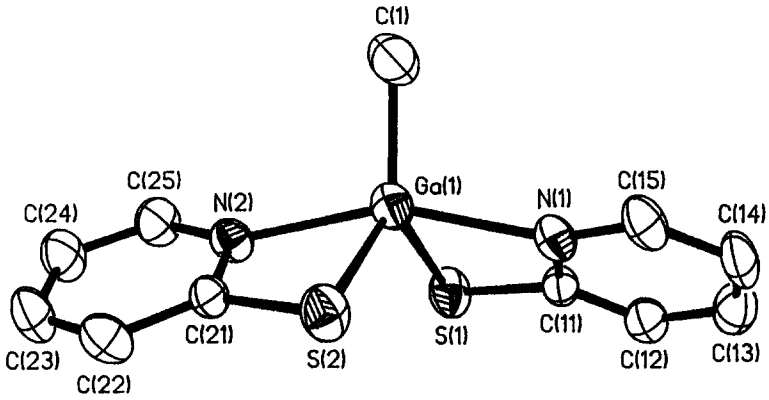


Fig. 1. Molecular structure of $GaMe(Spy)_2$ (**4**). Thermal ellipsoids shown at the 30% level, and all hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) in $GaMe(SPy)_2$ (**4**)

Ga(1)—C(1)	1.933(7)	Ga(1)—S(1)	2.333(2)
Ga(1)—S(2)	2.333(2)	Ga(1)—N(1)	2.186(6)
Ga(1)—N(2)	2.201(6)	S(1)—C(11)	1.756(7)
S(2)—C(21)	1.767(7)		
C(1)—Ga(1)—S(1)	122.5(2)	C(1)—Ga(1)—S(2)	123.5(2)
C(1)—Ga(1)—N(1)	100.3(3)	C(1)—Ga(1)—N(2)	102.9(3)
S(1)—Ga(1)—S(2)	114.0(1)	S(1)—Ga(1)—N(1)	69.6(2)
S(1)—Ga(1)—N(2)	97.0(2)	S(2)—Ga(1)—N(1)	97.0(2)
S(2)—Ga(1)—N(2)	96.9(4)	N(1)—Ga(1)—N(2)	156.8(2)

basicities.[17] The Ga—C and Ga—S bond distances are within previously recorded ranges, however, the axial Ga—N bond distances [2.184(6) and 2.201(6) Å] are longer than observed for tetrahedral gallium. The lengthening of the axial Ga—N bonds would be expected, based on the relative *p*-character of the tetrahedral (sp^3) versus axial trigonal pyramidal (*p*) coordination.[18] The overall structure of compound **4** is similar to that reported for the monomeric aluminium compound, MeAl[O=C(OMe)C_6H_4-*o*-OH].[19]

Attempts to obtain X-ray structural data on Ga ('Bu)$(Spy)_2$ (**3**) were frustrated by the poor quality of the data and possible disorder, however, a partial solution[20] was sufficient to determine that the overall structure was essentially identical to that

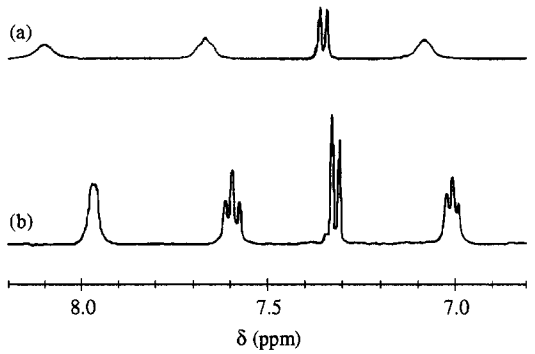


Fig. 2. ^{1}H NMR spectra of Ga(^{t}Bu)(Spy)$_2$ (**3**) in d_3-MeCN at 25°C (a), and d_6-DMSO at 25°C (b).

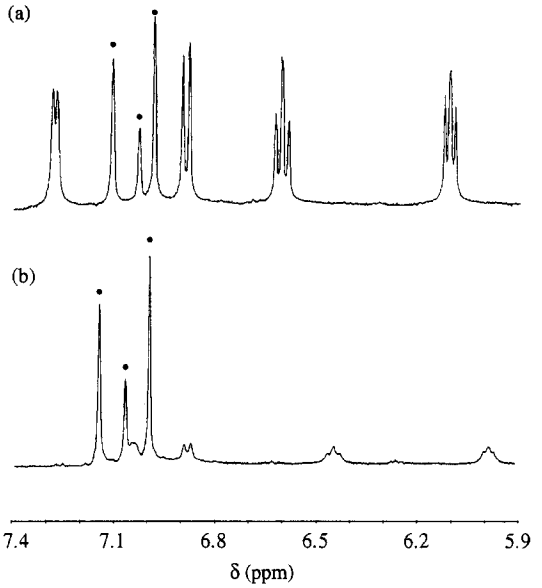
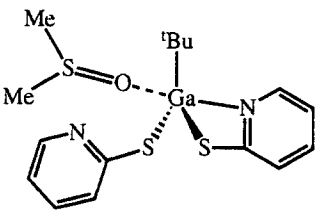


Fig. 3. ^{1}H NMR spectra of Ga(^{t}Bu)(Spy)$_2$ (**3**) in toluene at (a) 20°C, and (b) −40°C. Peaks marked with (●) are due to toluene.

observed for GaMe(Spy)$_2$, i.e. monomeric with a five-coordinate trigonal bipyramidal coordination geometry. In contrast to the structure observed in the solid state, and unlike GaMe(Spy)$_2$, compound **3** shows peaks in the mass spectrum consistent with a dimer, i.e. 637 ($2M^+ - {}^t$Bu, 15), 584 ($2M^+ -$ Spy, 8). Furthermore, Ga(^{t}Bu)(Spy)$_2$ appears to exhibit an interesting fluxionality in solution.

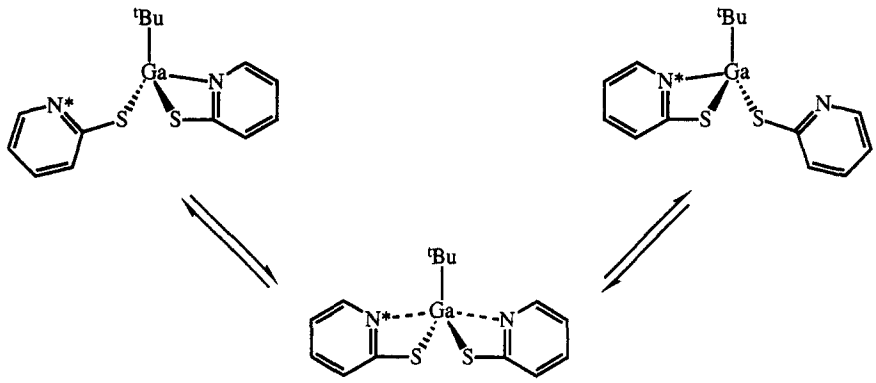
Compared to all the other compounds reported herein, Ga(^{t}Bu)(Spy)$_2$ is the only one whose ^{1}H NMR did not show a well-resolved four line pattern for the 2-mercaptopyridine ligand. Instead, the room temperature ^{1}H NMR spectrum of Ga(^{t}Bu)(Spy)$_2$ consists of broad signals for the protons at the 6, 5, and 4 ring positions and a doublet for the proton at the 3-position (see Fig. 2a), typical of the slow exchange region of a fluxional process. Heating to 50°C results in significant sharpening (Fig. 2b), i.e. the ligands are truly equivalent on the NMR time scale. Conversely, cooling the NMR sample should cause the four broad peaks observed at room temperature to separate out into signals for two different 2-mercaptopyridine ligand environments. However, the high melting point of DMSO (m.p. 18°C) requires that toluene be used for the low temperature NMR (Fig. 3). The room temperature spectrum for Ga(^{t}Bu)(Spy)$_2$ in d_8-toluene is sharper than that observed in DMSO. As the NMR of sample of Ga(^{t}Bu)(Spy)$_2$ is cooled below room temperature, the signal for the ring protons broaden, decrease in intensity, and by −50°C (Fig. 3b), new peaks are just beginning to appear. However, the increase viscosity of the solution, and precipitation of Ga(^{t}Bu)(Spy)$_2$, precludes studies of the ^{1}H NMR spectra at lower temperatures.

Based on the variable temperature ^{1}H NMR spectra of compound Ga(^{t}Bu)(Spy)$_2$, two possible fluxional processes may be proposed. First, if Ga(^{t}Bu)(Spy)$_2$ is monomeric in solution, as is observed in the solid state, then the gallium centre may be four-coordinate: with one of the two 2-mercaptopyridine ligands monodentate the other bidendate-chelating, which undergo exchange, as shown in Scheme 2. Interestingly, room temperature ^{1}H NMR data recorded for Ga(^{t}Bu)(Spy)$_2$ in acetonitrile and toluene show the sharp doublets and triplets expected for the ring protons of a 2-mercaptopyridine complex, suggesting that the rate of fluxionality is solvent dependent. Given the coordinating nature of DMSO it is possible that the four-coordinate compounds are stabilized by complexation to gallium, i.e. **V**, slowing the exchange at a given temperature with respect to that in non- or weakly-coordinating solvents.



(**V**)

The second possible process involving the fluxionality of the 2-mercaptopyridine ligands would result if, as is suggested by gas phase mass spectrometry (see above and Experimental), Ga(^{t}Bu)(Spy)$_2$ is a dimer, [(^{t}Bu)(pyS)Ga(μ-Spy)]$_2$, in which terminal and bridging 2-mercaptopyridine ligands are exchanging.



Scheme 2. Proposed fluxionality of Ga(ᵗBu)(Spy)$_2$ (**3**).

It is interesting to note that the ^{1}H NMR spectra of GaMe(Spy)$_2$ do not show any variation over the temperature range −50 to 60°C. This suggests that the 2-mercaptopyridine ligands in the methyl derivative are either not fluxional or have a lower barrier to exchange. The former would be consistent with the monodentate–bidentate exchange in Scheme 2, due to the lower steric hindrance and σ-donor ability of methyl versus *tert*-butyl.

The thermogravimetric/differential thermal analysis (TG/DTA) of Ga(ᵗBu)(Spy)$_2$ is consistent with its complete sublimation under nitrogen at 220°C, suggesting that Ga(ᵗBu)(Spy)$_2$ would be suitable as a precursor for the chemical vapour deposition of gallium sulphide thin films. The methyl compound, GaMe(Spy)$_2$, decomposes near 300°C (Fig. 4). The decomposition observed in the TGA is numerically consistent with the formation of GaS (calculated = 66.7%, observed = 70.1%). Energy dispersive X-ray (EDX) analysis confirms the formation of GaS.

There are a wide variety of routes to the *tris*-2-mercaptopyridine compound Ga(Spy)$_3$ (**5**). For example, any of the di- or mono-alkyl compounds, **1**–**4**, may be converted to Ga(Spy)$_3$ by reacting with the correct number of equivalents of HSpy, in refluxing toluene. Although the gallium alkyl compounds are the best synthons for the synthesis of compound Ga(Spy)$_3$, due to the volatile, and hence, readily separable side products, i.e. MeH and ᵗBuH, the *tris*-2-mercaptopyridine compound may also be obtained from the reaction of either GaCl$_3$ or Ga(ᵗBu)$_2$Cl with excess HSpy in the presence of NEt$_3$, Scheme 1(iv, vi). However, significant difficulty in separating Ga(Spy)$_3$ pure from the [HNEt$_3$]Cl containing reaction mixture, make these routes impractical. Furthermore, if an excess of HSpy is not used the chloro compound, GaCl(Spy)$_2$

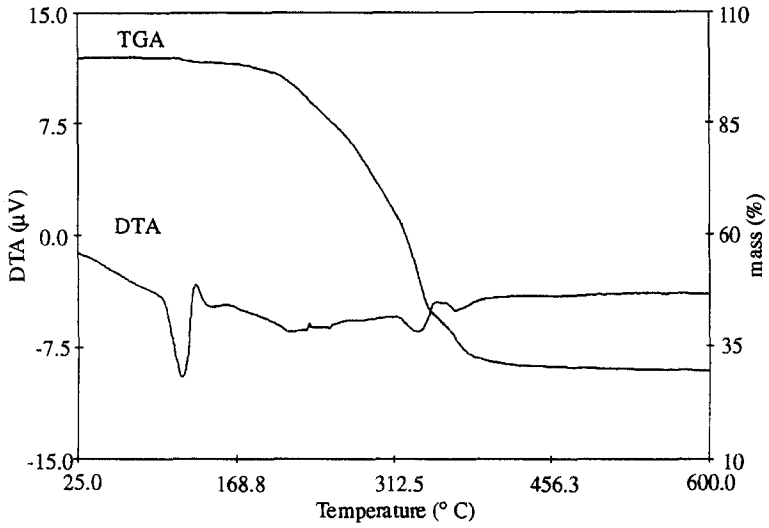
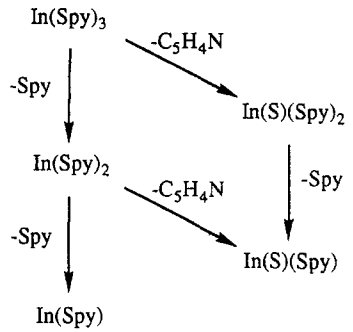


Fig. 4. Thermogravimetric/differential thermal (TG/DTA) analysis of GaMe(Spy)$_2$ (**4**).



Scheme 3. Partial fragmentation pattern for $In(Spy)_3$ (**7**).

(NEt_3) (**6**) is formed, see Experimental. The indium analogue of compound **5**, i.e. $In(Spy)_3$ (**7**), may be prepared from either $InCl_3$ (eq. 3) or $InMe_3$ as for compound **5** (see Experimental). In addition, the reaction of indium(I) chloride with 2-mercaptopyridine in the presence of NEt_3 also yields compound **5** (eq. 4).

$$InCl_3 + 3HSpy + 3NEt_3 \longrightarrow In(Spy)_3 + 3[HNEt_3]Cl \quad (3)$$

$$InCl + 3HSpy + NEt_3 \longrightarrow In(Spy)_3 + [HNEt_3]Cl + H_2 \quad (4)$$

Mass spectral data indicate the monomeric structure of $M(Spy)_3$ (M = Ga, In). While $Ga(Spy)_3$ only shows fragmentation due to the successive loss of 2-mercaptopyridine the mass spectrum of $In(Spy)_3$ is consistent with the fragmentation of the 2-mercaptopyridine, Scheme 3. Both compounds yield GaS and InS, respectively, with low carbon contamination.[21]

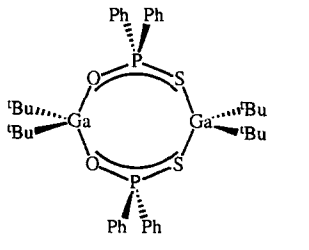
Diphenylthiophosphinate

The reaction of $Ga(^tBu)_3$ with diphenyldithiophosphinic acid gives only trace quantities of the expected dimeric product $[(^tBu)_2Ga(\mu\text{-}S_2Ph_2)]_2$ (**8**). Compound **8** was not isolated, but characterized by ^1H NMR spectroscopy and mass spectrometry (see Experimental). The main product isolated was as a result of sulphur–sulphur coupling of dithiophosphinate, i.e. $[Ph_2P(S)S]_2$. We have also observed that the reaction of group 13 alkyls with 2-mercaptopyridine often yields to the formation of the coupled compound [pySSpy] as an impurity.[21]

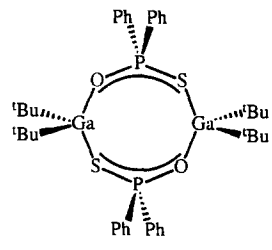
In contrast to the dithiophosphinate, the reaction of $Ga(^tBu)_3$ with one equivalent of $HO(S)PPh_2$ or HO_2PPh_2 allows for the isolation of the appropriate dimeric compounds $[(^tBu)_2Ga(\mu\text{-}OP(S)Ph_2)]_2$ (**9**) and $[(^tBu)_2Ga(\mu\text{-}O_2PPh_2)]_2$ (**10**) as white crystalline solids, in essentially quantitative yield. The dimeric nature of compounds **9** and **10** was confirmed in the gas phase by the observation of a parent ion in the mass spectrum. However, based upon ^1H and ^{13}C NMR spectroscopy compound **9** exists as two isomers: a head-to-head (**9a**, *syn*) and a head-to-tail (**9b**, *anti*) isomer. In the reaction mixture the isomers are present in a 4:1 ratio, **9a**:**9b**, respectively, however, the two isomers are separated by repeated recrystallization.

Interestingly, in the EI mass spectrum of **9b**, M^+ is major fragment observed as a consequence of the symmetrical cleavage of a centro-symmetrical dimer. In contrast, the mass spectrum of **9a** shows in addition to M^+ a *bis*-thiophosphinate fragment, $[(^tBu)_2Ga\{O(S)PPh_2\}_2]^+$, as a product from the asymmetric cleavage of **9a**, i.e. two Ga—S bonds. Since the phosphinates show no cleavage under equivalent mass spectral conditions, the cleavage of **9a** and **9b** in the mass spectrometer occurs at the weaker sulphide bridge, as opposed to the oxide. The formation of asymmetric group 13 dimers $[R_2M(\mu\text{-}L)]_2$ formed from a bi-functional bridging ligand was first reported by Oliver and co-workers for the aluminium 2-mercaptopyridine compound, **III**.[11]

While crystals of compounds **8** and **9** suitable for X-ray crystallography could not be obtained, the structure of compound **10** was determined. The molecular structure of compound **10** is shown in Fig. 5; selected bond length and angles are given in Table 2. The structure consists of a centro-symmetric dimer of two $(^tBu)_2Ga$ units bridged by two diphenylphosphinate groups. The resulting $Ga_2O_2P_2$ cycle is a rare example of an eight-membered ring containing a group 13 metal.[22] While the Ga—O [1.950(8), 1.969(7) Å] distances are similar to that observed for $(^tBu)_2Ga[(O)PPh_2CHP(O)Ph_2]$, the P—O distances [1.485(8), 1.497(8) Å] are slightly shorter [1.935(2)–1.948(2) Å and 1.530(2)–1.534(2) Å, respectively].[23] The P—O bond distances are equivalent [1.485(8) and 1.497(8) Å], indicating that the bridging phosphate unit is delocalized, i.e. [O⋯P⋯O]. However, the Ga—O—P angles are distinct



(**9a**)



(**9b**)

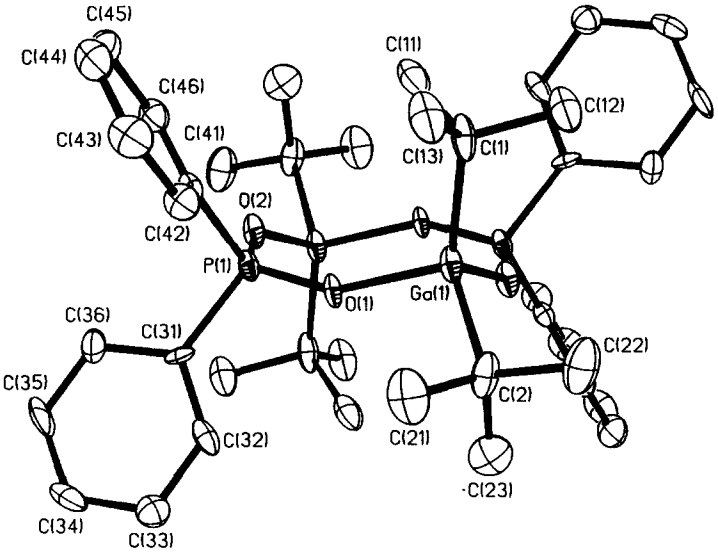
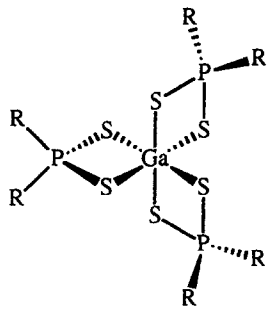


Fig. 5. Molecular structure of $[(^tBu)_2Ga(\mu\text{-}O_2PPh_2)]_2$ (**10**). Thermal ellipsoids shown at the 40% level, and all hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) in $[(^tBu)_2Ga(\mu\text{-}O_2PPh_2)]_2$ (**10**)

Ga(1)—O(1)	1.950(8)	Ga(1)—O(2a)	1.969(7)
Ga(1)—C(1)	1.96(1)	Ga(1)—C(2)	1.97(1)
P(1)—O(1)	1.485(8)	P(1)—O(2)	1.497(8)
P(1)—C(31)	1.76(1)	P(1)—C(41)	1.79(1)
O(1)—Ga(1)—O(2a)	96.8(3)	O(1)—Ga(1)—C(1)	112.4(5)
O(1)—Ga(1)—C(2)	103.1(5)	C(1)—Ga(1)—O(2a)	109.5(5)
C(1)—Ga(1)—C(2)	125.8(5)	O(1)—P(1)—O(2)	116.1(5)
O(1)—P(1)—C(31)	108.6(6)	O(1)—P(1)—C(41)	109.5(5)
C(31)—P(1)—C(41)	103.8(6)	Ga(1)—O(1)—P(1)	152.9(6)
P(1)—O(2)—Ga(1a)	139.5(6)		



(**VI**)

[152.9(6) and 139.5(6)°]. A dimethyl gallium analogue of compound **10**, i.e. $[Me_2Ga(\mu\text{-}O_2PPh_2)]_2$ has been recently investigated by X-ray diffraction.[24]

The reaction of $GaCl_3$ with sodium dialkyldithiophosphinates, $Na(S_2PR_2)\cdot 2(H_2O)$, gives the expected *tris*-chelate products $Ga(S_2PR_2)_3$, R = Me (**11**), Et (**12**), in essentially quantitative (85–95%) yield. Based upon the IR and NMR spectroscopic characterization the structures of compounds **11** and **12** are proposed to be similar to that previously reported for $M(S_2PR_2)_3$, M = Ga, In, i.e. **VI**.

EXPERIMENTAL

Unless otherwise stated, all manipulations were carried out under either prepurified nitrogen or argon. All solvents were distilled from sodium-benzophenone ketyl solution and degassed immediately before use. $GaMe_3$ and $InMe_3$ were donated by Morton International; $GaMe_3$ was used as a 0.854 M solution in pentane while $InMe_3$ was used as received. 2-Mercaptopyridine was purchased from Aldrich and was used as received. $Ga(^tBu)_3$, $Ga(^tBu)_2Cl$, $GaMe_3(OEt_2)$, HS_2PPh_2, $HOP(S)Ph_2$,

HO_2PPh_2, $NaS_2PMe_2 \cdot 2(H_2O)$, and $NaS_2PEt_2 \cdot 2(H_2O)$ were all prepared as previously described.[25,26]

Melting points were determined in sealed capillaries and are uncorrected. Mass spectra were obtained by using a JEOL AX-505H mass spectrometer and associated data system. An electron beam energy of 70 eV was used for EI mass spectra. Thermogravimetric analyses were obtained on a Seiko 200 TG/DTA instrument using an argon carrier gas. IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet DX-5 FTIR spectrometer as Nujol mulls. ^1H and ^{13}C NMR spectra were obtained on Bruker AM-250 and Bruker AM-400 spectrometers, and chemical shifts are reported in ppm relative to $SiMe_4$. EDX analyses studies of the products from the TG/DTA experiments were performed on a JEOL JSM-35 scanning microscope. A small amount of the material was attached to an aluminium stub with graphite paint.

$Ga(^tBu)_2(Spy)$ (1)

To a suspension of HSpy (1.39 g, 12.50 mmol) in hexane (50 cm^3) was added $Ga(^tBu)_3$ (3.00 g, 12.46 mmol) via syringe, with no evidence of gas evolution. After stirring overnight, the pale yellow solution was concentrated to one-fifth of its original volume and cooled to −10°C for 3 days, during which time pale yellow needles formed. Yield 2.64 g, 72%. M.p.: 43–45°C. MS (EI, *m/z*:, %) 293 (M^+, 7), 236 ($M^+ - {}^t$Bu, 100), 180 ($M^+ - 2{}^t$Bu + H, 63). IR (cm^{-1}): 1604 (m), 1588 (s), 1548 (m), 1448 (s), 1422 (s), 1361 (m), 1280 (w), 1267 (m), 1244 (w), 1156 (m), 1142 (s), 1088 (m), 1038 (w), 1013 (m), 812 (m), 752 (s), 649 (m). ^1H NMR (δ, d_6-DMSO): 8.08 [1H, d, J(H—H) = 5.3 Hz, 6-C*H*], 7.56 [1H, t, J(H—H) = 7.0 Hz, 4-C*H*], 7.24 [1H, d, J(H—H) = 8.1 Hz, 3-C*H*], 6.99 [1H, t, J(H—H) = 6.1 Hz, 5-C*H*], 1.00 [18H, s, $C(CH_3)_3$]. ^{13}C NMR (δ, d_6-DMSO): 170.2 (2-*C*), 146.3 (6-*C*H), 138.2 (4-*C*H), 125.5 (3-*C*H), 117.4 (5-*C*H), 30.3 [*C*$(CH_3)_3$], 24.4 [C(*C*$H_3)_3$].

$GaMe_2(Spy)$ (2)

A hexane suspension (30 cm^3) of HSpy (1.18 g, 10.60 mmol) was cooled to 0°C. To this was added via cannula $GaMe_3(OEt_2)$ (2.00 g, 10.60 mmol) in hexane (30 cm^3). Some gas evolution was observed, and the solution was stirred at room temperature overnight. During this time an off-white solid precipitated from the solution; NMR of this solid was consistent with $GaMe(Spy)_2$. The pale yellow supernatant was removed via cannula and concentrated to approximately one-third its original volume; upon standing in the dry box for several days, tiny white crystals precipitated. The product was extremely air sensitive and visibly degraded to a bright yellow oil upon exposure to air. Yield 0.25 g, 11%. M.p.: 126–127°C. MS (EI, *m/z*:, %) 209 (M^+, 20), 194 ($M^+ - Me$, 100), 179 ($M^+ - 2$ Me, 15). IR (cm^{-1}): 1600 (w), 1588 (m), 1548 (m), 1422 (s), 1272 (m), 1263 (m), 1197 (m), 1164 (m), 1139 (m), 1095 (br w), 1056 (w), 1013 (m), 751 (m), 636 (w). ^1H NMR (δ, d_6-DMSO): 7.99 [1H, d, J(H—H) = 5.0 Hz, 6-C*H*], 7.43 [1H, t, J(H—H) = 7.6 Hz, 4-C*H*], 7.17 [1H, d, J(H—H) = 8.1 Hz, 3-C*H*], 6.86 [1H, t, J(H—H) = 6.2 Hz, 5-C*H*], −2.37 (6H, s, CH_3). ^{13}C NMR (δ, d_6-DMSO): 171.0 (2-*C*), 145.8 (6-*C*H), 137.0 (4-*C*H), 126.8 (3-*C*H), 116.2 (5-*C*H), −1.8 (*C*H_3).

$Ga(^tBu)(Spy)_2$ (3)

Method 1. A 50 ml hexane (50 cm^3) solution of $Ga(^tBu)_3$ (1.40 g, 5.82 mmol) was added via cannula, with vigorous stirring, to a hexane (10 cm^3) suspension of HSpy (1.29 g, 11.63 mmol). The reaction mixture was then refluxed overnight, during which time a pale yellow solid precipitated. Cooling and removal of solvents *in vacuo* left a pale yellow solid; extraction and recrystallization from hot MeCN (*ca* 40 cm^3) at −10°C gave pale yellow needles. Yield *ca* 80%.

Method 2. HSpy (3.04 g, 27.37 mmol) and $(^tBu)_2$GaCl (2.00 g, 9.12 mmol) were placed in a flask and toluene (50 cm^3) and NEt_3 (1.27 cm^3, 0.92 g, 9.12 mmol) were added via syringe. The mixture was stirred overnight, during which time a pale yellow solid had formed. The supernatant was removed via cannula, and the remaining solid was extracted with Et_2O. Removal of the Et_2O *in vacuo* gave a yellow solid which was recrystallized from MeCN to give needles. Yield *ca* 50%. M.p.: 199–201°C. MS (EI, *m/z*:, %) 637 ($2M^+ - {}^t$Bu, 15), 584 ($2M^+ -$ Spy, 8), 346 (M^+, 4), 289 ($M^+ - {}^t$Bu, 100), 236 ($M^+ -$ Spy, 10), 220 (pySSpy, 5), 179 ($M^+ - {}^t$Bu − Spy, 12), 111 (HSpy, 8). IR (cm^{-1}): 1608 (w), 1582 (m), 1550 (m), 1424 (s), 1281 (w), 1268 (m), 1242 (w), 1148 (w), 1139 (m), 1088 (w), 1038 (w), 1004 (m), 753 (m), 745 (m), 637 (m), 484 (w), 460 (w), 410 (w). ^1H NMR (δ, CD_3CN): 7.98 [2H, d, J(H—H) = 4.9 Hz, 6-C*H*], 7.61 [2H, t, J(H—H) = 8.1 Hz, 4-C*H*], 7.31 [2H, d, J(H—H) = 8.5 Hz, 3-C*H*], 7.02 [2H, t, J(H—H) = 6.5 Hz, 5-C*H*], 1.08 [9H, s, $C(CH_3)_3$]. ^{13}C NMR (δ, d_8-toluene): 167.2 (2-*C*), 145.4 (6-*C*H), 137.9 (4-*C*H), 124.6 (3-*C*H), 117.1 (5-*C*H), 30.1 [*C*$(CH_3)_3$], 24.8 [C(*C*$H_3)_3$].

$GaMe(Spy)_2$ (**4**)

Method 1. Pentane (20 cm^3) was added to HSpy (1.42 g, 12.81 mmol) and the resulting suspension cooled to 0°C. To this was added via cannula a pentane solution of $GaMe_3$ (5.0 cm^3, 0.85 M, 4.27 mmol) to which additional pentane (20 cm^3) had been added. Gas evolution was immediately observed. The pale yellow solution was allowed to warm to room temperature and was stirred overnight. Removal of pentane *in vacuo* left a pale yellow solid which was washed with toluene (30 cm^3); recrystallization from hot MeCN produced large pale yellow blocks. Yield 0.86 g, 66%.

Method 2. HSpy (1.85 g, 16.64 mmol) was suspended in toluene (40 cm^3) at 0°C and $GaMe_3$ (20.0 cm^3, 0.85 M, 17.08 mmol) was added via cannula. Vigorous gas evolution occurred. The bright yellow solution was stirred at room temperature for 2 h, during which time it lost colour and became a very pale yellow. Removal of the solvent *in vacuo* followed by recrystallization from pentane/toluene (3:1) produced off-white needles. Yield 1.88 g, 70%. M.p.: 119°C. MS (EI, *m/z*:, %) 289 ($M^+ - Me$, 100), 194 ($M^+ - Spy$, 24). IR (cm^{-1}): 1605 (w), 1581 (m), 1550 (m), 1447 (s), 1422 (m), 1283 (v w), 1263 (m), 1200 (m), 1151 (m), 1136 (s), 1088 (m), 1081 (m), 1038 (m), 1005 (m), 759 (s), 743 (m), 718 (s), 639 (s), 570 (m), 482 (m), 462 (m), 410 (m). ^1H NMR (δ, d_6-DMSO): 7.99 [2H, d, J(H—H) = 4.0 Hz, 6-C*H*], 7.58 [2H, t, J(H—H) = 7.8 Hz, 4-C*H*], 7.32 [2H, d, J(H—H) = 8.2 Hz], 6.98 [2H, t, J(H—H) = 6.2 Hz, 5-C*H*], 0.19 (3H, s, CH_3). ^{13}C NMR (δ, d_6-DMSO): 170.5 (2-*C*), 144.5 (6-*C*H), 138.8 (4-*C*H), 126.3 (3-*C*H) 117.0 (5-*C*H), −1.0 (CH_3).

$Ga(Spy)_3$ (**5**)

HSpy (1.48 g, 13.32 mmol) was suspended in toluene (50 cm^3). After cooling the suspension to −78°C, a pentane solution of $GaMe_3$ (5.20 cm^3, 0.85 M, 4.44 mmol) was added via cannula. Slow gas evolution was observed during the addition. After warming to room temperature and refluxing overnight, the bright yellow solution was allowed to cool very slowly. Within 1 h, pale green needles had formed. The product was then isolated by removing the solvent via cannula. Yield 1.29 g, 73%. Compound **5** may also be formed by refluxing compounds **1**, **2**, **3** or **4** with the correct number of equivalents of HSpy in toluene. M.p.: 227–228°C. MS (EI, *m/z*:, %) 289 ($M^+ - Spy$, 100). IR (cm^{-1}): 1603 (w), 1581 (m), 1543 (m), 1418 (m), 1263 (m), 1241 (w), 1140 (m), 1083 (br w), 1038 (w), 1010 (w), 754 (m), 648 (w), 487 (w), 468 (w), 410 (w). ^1H NMR (δ, d_6-DMSO): 7.74 [2H, d, J(H—H) = 3.7 Hz, 6-C*H*, 4-C*H*], 7.43 [1H, d, J(H—H) = 7.7 Hz, 3-C*H*], 7.10 (1H, s, 5-C*H*). ^{13}C NMR (δ, d_6-DMSO): 169.8 (2-*C*), 143.5 (6-*C*H), 140.4 (4-*C*H), 124.4 (3-*C*H), 117.9 (5-*C*H).

$GaCl(Spy)_2(NEt_3)$ (**6**)

To a solution of $GaCl_3$ (1.00 g, 5.68 mmol) HSpy (1.89 g, 17.03 mmol) in toluene (50 cm^3) was added NEt_3 (2.36 cm^3, 1.720 g, 17.03 mmol) was added via syringe, and the solution immediately became clear. However, after stirring for 1 h a white precipitate had formed. The supernatant was removed via cannula and the solvent removed *in vacuo* to leave a pale yellow solid. Yield *ca* 50%. MS (EI, *m/z*:, %) 324 ($M^+ - NEt_3$, 15), 289 ($M^+ - Cl - NEt_3$, 18), 216 [GaCl(Spy), 100]. ^1H NMR (δ, d_6-DMSO): 7.64 [2H, d, J(H—H) = 4.0 Hz, 6-C*H*], 7.40 [2H, t, J(H—H) = 7.8 Hz, 4-C*H*], 7.26 [2H, d, J(H—H) = 8.2 Hz], 6.73 [2H, t, J(H—H) = 6.2 Hz, 5-C*H*], 2.97 [6H, q, J(H—H) = 7.1 Hz, NCH_2], 6.73 [9H, t, J(H—H) = 7.1 Hz, NCH_2CH_3].

$In(Spy)_3$ (**7**)

Method 1. Toluene (25 cm^3) was added to HSpy (1.09 g, 9.84 mmol) and the resulting suspension cooled to −78°C. A solution of $InMe_3$ (0.32 g, 3.28 mmol) in toluene (25 cm^3) was then added via cannula. Gas evolution was observed as the solution warmed to room temperature. After stirring overnight, an off-white powder had precipitated; removal of the solvent via cannula followed by extraction and recrystallization from hot MeCN produced pale green needles of $In(Spy)_3$. Yield 36%.

Method 2. $InCl_3$ (2.00 g, 9.04 mmol) was suspended in toluene (30 cm^3) and cooled to −78°C. To this was added via a large cannula a suspension of 2-mercaptopyridine (3.01 g, 27.10 mmol) in toluene (30 cm^3). After warming to room temperature, NEt_3 (3.65 cm^3, 2.74 g, 27.10 mmol) was added via syringe, and the solution immediately became clear. However, after stirring for 1 h a white precipitate had formed. The supernatant was removed via cannula and the solvent removed *in vacuo* to leave a pale yellow solid. Extraction with hot MeCN followed by recrystallization left pale green crystals, yield 0.31 g, 8%.

Method 3. Indium(I) chloride, InCl (0.500 g, 3.33 mmol) and 2-mercaptopyridine (1.11 g, 9.98 mmol) were placed as solids in a flask, to which toluene (50 cm^3) was added. NEt_3 (0.46 cm^3, 0.34 g, 3.33 mmol) was then added via syringe. After

stirring overnight, an off-white solid had precipitated and a small amount of a dark solid, presumably indium metal, had formed. The supernatant was removed via cannula, and the solvent removed *in vacuo* to leave a pale yellow solid. Extraction with hot MeCN followed by recrystallization produced pale green crystals, yield 0.11 g, 8%. M.p.: 225–226°C. MS (EI, *m/z*:, %): 445 (M^+, 95), 335 ($M^+ - Spy$, 100), 225 ($M^+ - 2Spy$, 20). IR (cm^{-1}): 1592 (w), 1577 (m), 1543 (m), 1415 (m), 1265 (m), 1245 (w), 1233 (m), 1134 (s), 1081 (m), 1036 (m), 1002 (m), 756 (s), 642 (m), 484 (m), 460 (m), 405 (m). ^1H NMR (δ, d_6-DMSO): 7.78 [3H, d, J(H—H) = 4.5 Hz, 6-C*H*], 7.67 [3H, t, J(H—H) = 6.8 Hz, 4-C*H*], 7.40 [3H, d, J(H—H) = 6.7 Hz, 3-C*H*], 7.08 [3H, t, J(H—H) = 5.4 Hz, 5-C*H*]. ^{13}C NMR (δ, d_6-DMSO): 168.5 (2-*C*), 145.4 (6-*C*H), 139.4 (4-*C*H), 124.2 (3-*C*H), 118.2 (5-*C*H).

Reaction of $Ga(^tBu)_3$ *with* HS_2PPh_2

Addition of Ph_2PS_2H (0.70 g, 2.8 mmol) to a pentane solution (60 cm^3) of $Ga(^tBu)_3$ (0.67 g, 2.8 mmol) resulted in the immediate formation of a white precipitate. After stirring for 1 h, the volatiles were removed under vacuum. The crude product showed a mixture of $[(^tBu)_2Ga\{\mu\text{-}S_2PPh_2\}]_2$ and $Ph_2P(S)SSP(S)Ph_2$ (1 : 9), which could be separated by recrystallization from CH_2Cl_2.

$[(^tBu)_2Ga(\mu\text{-}S_2PPh_2)]_2$ (**8**). MS (EI, *m/z*:, %): 807 ($2M^+ - {}^tBu$, 10), 375 ($M^+ - {}^tBu$, 50). ^1H NMR (δ, $CDCl_3$): 7.91 [8H, m, *o*-C*H*], 7.56 [4H, m, *p*-C*H*], 7.32 [8H, m, *m*-C*H*], 1.11 [36H, s, Ga-C(CH_3)$_3$].

$Ph_2P(S)SSP(S)Ph_2$. MS (EI, *m/z*:, %): 498 (M^+, 50). ^1H NMR (δ, $CDCl_3$): 7.80 [8H, d, d, J(P—H) = 14.2 Hz, J(H—H) = 9.3 Hz, *o*-C*H*], 7.43 [4H, m, *p*-C*H*], 7.40 [8H, m, *m*-C*H*].

$[(^tBu)_2Ga\{\mu\text{-}O(S)PPh_2\}]_2$ (**9**)

A solution of $Ga(^tBu)_3$ (0.88 g, 3.66 mmol) in pentane (30 cm^3) was added to a pentane suspension (20 cm^3) of $HO(S)PPh_2$ (0.85 g, 3.66 mmol) at −78°C. After stirring for 30 min a white precipitate formed which was collected by filtration. Yield *ca* 80%.

$[(^tBu)_2Ga\{\mu\text{-}O(S)PPh_2\}]_2$ (**9a**). MS (EI, *m/z*:, %): 834 ($2M^+$, 8), 777 ($2M^+ - {}^tBu$, 45), 651 {$(^tBu)_2Ga[O(S)PPh_2]_2$, 75}. IR (cm^{-1}): 1962 (w), 1856 (w), 1824 (w), 1769 (w), 1196 (m), 1164 (m), 1133 (s), 1046 (m), 1046 (m), 1018 (m), 991 (m), 725 (s), 693 (m), 654 (w), 555 (m). ^1H NMR (δ, $CDCl_3$): 7.81 [12H, br m, *o*- and *p*-C*H*], 7.33 [8H, m, *m*-C*H*], 0.95 [18H, s, C(CH_3)$_3$], 0.89 [18H, s, Ga-C(CH_3)$_3$].

$[(^tBu)_2Ga\{\mu\text{-}O(S)PPh_2\}]_2$ (**9b**). MS (EI, *m/z*:, %): 834 ($2M^+$, 5), 777 ($2M^+ - {}^tBu$, 50), 417 (M^+, 40), 360 ($M^+ - {}^tBu$, 100). IR (cm^{-1}): 1960 (w), 1856 (w), 1822 (w), 1771 (w), 1095 (s), 744 (m), 722 (s), 687 (m), 650 (m), 504 (m). ^1H NMR (δ, $CDCl_3$): 7.85 [12H, m, *o*- and *p*-C*H*], 7.40 [8H, m, *m*-C*H*], 0.97 [36H, s, Ga-C(CH_3)$_3$].

$[(^tBu)_2Ga(\mu\text{-}O_2PPh_2)]_2$ (**10**)

To a solution of HO_2PPh_2 (0.30 g, 1.38 mmol) in pentane (25 cm^3) was added a solution of $Ga(^tBu)_3$ (0.33 g, 1.38 mmol) in pentane (25 cm^3) at −78°C. The reaction was allowed to warm to room temperature, and stirred for 1 h, after which time a white precipitate formed which was collected by filtration. Yield *ca* 60%. MS (EI, *m/z*:, %): 800 ($2M^+$, 5), 743 ($2M^+ - {}^tBu$, 10), 400 (M^+, 10), 343 ($M^+ - {}^tBu$, 100). IR (cm^{-1}): 1981 (w), 1913 (w), 1820 (w), 1773 (w), 1197 (s), 1167 (s), 1133 (s), 1069 (w), 1051 (s), 1025 (m), 998 (m), 816 (m), 751 (m), 727 (s), 695 (s), 564 (s), 537 (m). ^1H NMR (δ, $CDCl_3$): 7.74 [8H, m, *o*- and *p*-C*H*], 7.38 [12H, m, *m*-C*H*], 0.81 [36H, s, Ga-C(CH_3)$_3$].

$Ga(S_2PMe_2)_3$ (**11**)

To a solution of $GaCl_3$ (0.24 g, 1.25 mmol) in $CHCl_3$ (25 cm^3) was added a $Na(S_2PMe_2)_3 \cdot 2(H_2O)$ (0.74 g, 3.75 mmol). The reaction mixture was stirred at room temperature for 4 h, then filtered to remove the resulting NaCl. The solution was concentrated until precipitation initiated. The addition of hexane (20 cm^3) produced a voluminous white precipitate, which was filtered. Colourless crystals were obtained by recrystallization from acetone. Yield *ca* 95%. M.p. = 158–160°C (dec.), MS (EI, *m/z*:, %): 351 [$M^+ - SPMe_2$, 3], 319 [$M^+ - S_2PMe_2$, 100], 227 [$Ga(S_2PMe_2)SH^+$, 5], 93 ($SPMe_2^+$, 5). IR (cm^{-1}): 600 (s, ν_{asym} PS_2), 475 (vs, ν_{sym} PS_2). ^1H NMR (δ, $CDCl_3$): 2.19 [d, J(P—H) = 11.4 Hz, P-CH_3]. ^{13}C NMR (δ, $CDCl_3$): 29.4 [d, J(P—C) = 52.2 Hz, P-*C*H_3]. ^{31}P NMR (δ, $CDCl_3$): 57.1 (s).

$Ga(S_2PEt_2)_3$ (**12**)

The reaction was carried out as above with $GaCl_3$ (0.22 g, 1.22 mmol) and $Na(S_2PEt_2)_3 \cdot 2(H_2O)$ (0.80 g, 3.66 mmol). Yield *ca* 85%. M.p. = 95–96°C (dec.), MS (EI, *m/z*:, %): 407 [$M^+ - SPEt_2$, 2], 375 [$M^+ - S_2PEt_2$, 100], 255 [$Ga(S_2PEt_2)SH^+$, 6], 121 ($SPEt_2^+$, 7). IR (cm^{-1}): 591 (vs, ν_{asym} PS_2), 465 (s, ν_{sym} PS_2). ^1H NMR (δ, $CDCl_3$): 2.15 [18H,

Table 3. Summary of X-ray diffraction data

Compound	$GaMe(Spy)_2$ (**4**)	$[('Bu)_2Ga(\mu\text{-}O_2PPh_2)]_2$ (**10**)
Empir. formula	$C_{11}H_{11}GaN_2S_2$	$C_{40}H_{56}Ga_2O_4P_2$
Cryst. size, mm	$0.32 \times 0.35 \times 0.44$	$0.3 \times 0.3 \times 0.6$
Cryst. system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	8.400(2)	9.626(5)
b (Å)	12.400(6)	10.899(7)
c (Å)	12.987(6)	11.716(7)
α (°)		108.77(5)
β (°)	104.23(3)	106.66(4)
γ (°)		99.74(4)
V (Å^3)	1311.2(9)	71067(1)
Z	4	1
D(calcd)(g cm^{-3})	1.545	1.248
μ (mm^{-1})	2.391	1.372
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)	graphite monochromator
Temp. (K)	298	298
2θ range (°)	4.0–40.0	4.0–40.0
No. collected	1423	2187
No. ind.	1214	2001
No. obsd	1131 ($\|F_o\| > 2.0\sigma\|F_o\|$)	1763 ($\|F_o\| > 4.0\sigma\|F_o\|$)
Weighting scheme	$w^{-1} = \sigma^2(\|F_0\|)$	$w^{-1} = \sigma^2(\|F_o\|)$
R	0.038	0.069
R_w	0.040	0.085
Largest diff. peak (eÅ^{-3})	0.56	1.31

dq, J(P—H) = 10.8 Hz, J(H—H) = 7.5 Hz, P-CH_2CH$_3$], 1.30 [12H, dt, J(P—H) = 21.9 Hz, J(H—H) = 7.5 Hz, P-CH$_2$CH_3]. ^{13}C NMR (δ, $CDCl_3$): 31.3 [d, J(P—C) = 48.1 Hz, P-CH$_2$CH$_3$], 7.07 [d, J(P—C) = 4.7 Hz, P-CH$_2$$HH_3$]. ^{31}P NMR ($\delta$, $CDCl_3$): 77.6 (s).

X-Ray crystallographic studies

A crystal data summary is given in Table 3. Crystals of compounds **4** and **10** were mounted under argon in a glass capillary glued into the goniometer head. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[27] using a Nicolet R3m/v diffractometer operating in the omega scan mode. Data collection was controlled by using the Nicolet P3 program.[28] Crystal symmetry and space groups were determined by the program XPREP. Further experimental data are given in Table 3. The structure was solved using the direct methods program XS, which revealed the position of most of the heavy atoms. Most but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed atom contributors in the final cycles, d(C – H) = 0.96 Å and U(iso) = 0.08 Å^2. Details of the refinement are given in Table 3. Atomic scattering factors and anomalous scattering parameters were as given in ref. 29.

Acknowledgments—Financial support for this work was provided by the National Science Foundation and with a NASA Graduate Student Researchers Award (C. C. L.). A. R. B. expresses thanks to Dr Jim Davis for bringing Alan Hynes to the research group.

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