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Communications

Cage Fragmentation of P_4S_{10} by *t*-Bu_3Ga. Formation and Interconversions of a Novel Phosphorus−Sulfur−Gallium Ring System

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Phosphorus sulfides are known to react with a variety of transition metal derivatives to afford an interesting array of cage-intact and cage-fragmented products.[1] By contrast, little has been published concerning the reactions of the phosphorus sulfides with main-group organometallics. Since *t*-Bu_3Ga reacts with both S_8[2] and P_4,[3] we were prompted to investigate the reactivity of this Lewis acid toward phosphorus sulfides. A further point of interest is the prospect that the anticipated product(s) might serve as precursors to ternary P/Ga/S phases.

A 4:1 molar ratio of *t*-Bu_3Ga and P_4S_{10} in pentane solution was allowed to react for 12−14 h at ambient temperature.[4] Workup[5] of the reaction mixture afforded a 35% yield of a pale yellow crystalline product (**1**) with an elemental analysis consistent with the empirical formula $(t\text{-Bu})_2GaPS_3$. The presence of a low-intensity peak at *m/z* 932 (2.6%) in the CI-mass spectrum of **1**[6] implied a trimeric formulation for the product. Additionally, the observation of mass spectral peaks of significant intensity at *m/z* 622 (100%) and 310 (8%) suggested the facile production of dimeric and monomeric species in the vapor phase (*vide infra*). The ^1H, ^{13}C, and ^{31}P NMR spectra of **1**[6] each comprised a single peak thus indicating a symmetrical molecular architecture.

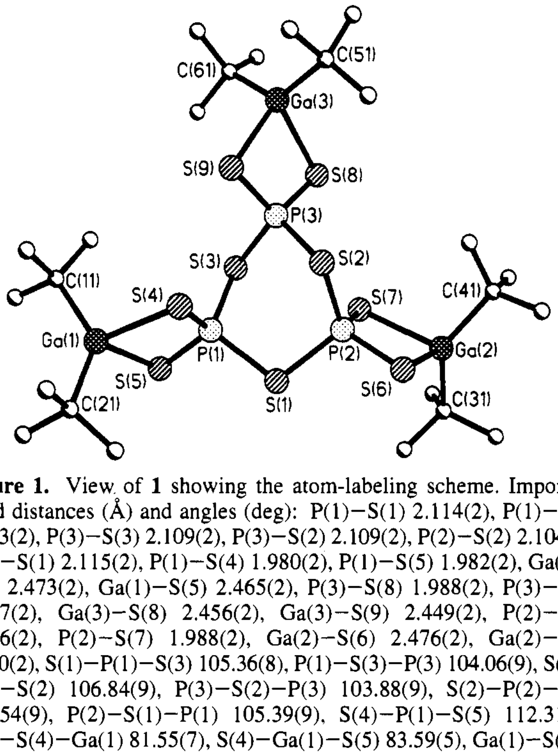

Figure 1. View of **1** showing the atom-labeling scheme. Important bond distances (Å) and angles (deg): P(1)−S(1) 2.114(2), P(1)−S(3) 2.113(2), P(3)−S(3) 2.109(2), P(3)−S(2) 2.109(2), P(2)−S(2) 2.104(2), P(2)−S(1) 2.115(2), P(1)−S(4) 1.980(2), P(1)−S(5) 1.982(2), Ga(1)−S(4) 2.473(2), Ga(1)−S(5) 2.465(2), P(3)−S(8) 1.988(2), P(3)−S(9) 1.987(2), Ga(3)−S(8) 2.456(2), Ga(3)−S(9) 2.449(2), P(2)−S(6) 1.986(2), P(2)−S(7) 1.988(2), Ga(2)−S(6) 2.476(2), Ga(2)−S(7) 2.450(2), S(1)−P(1)−S(3) 105.36(8), P(1)−S(3)−P(3) 104.06(9), S(3)−P(3)−S(2) 106.84(9), P(3)−S(2)−P(3) 103.88(9), S(2)−P(2)−S(1) 104.54(9), P(2)−S(1)−P(1) 105.39(9), S(4)−P(1)−S(5) 112.31(9), P(1)−S(4)−Ga(1) 81.55(7), S(4)−Ga(1)−S(5) 83.59(5), Ga(1)−S(5)−P(1) 81.70(7), S(9)−P(3)−S(8) 112.03(9), P(3)−S(8)−Ga(3) 81.62(7), S(8)−Ga(3)−S(9) 84.44(5), Ga(3)−S(9)−P(3) 81.84(7), S(6)−P(2)−S(7) 112.51(9), P(2)−S(6)−Ga(2) 81.24(7), S(6)−Ga(2)−S(7) 84.27(5), Ga(2)−S(7)−P(2) 81.88(7).

Detailed structural information was provided by an X-ray crystal structure analysis.[7] The crystalline state of **1** comprises individual $[(t\text{-Bu})_2GaPS_3]_3$ molecules (Figure 1), and there are no unduly short intermolecular contacts. The novel tetracyclic system features three four-membered GaS_2P rings, the phosphorus atoms of which are shared with a central six-membered

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(1) Goh, L. Y.; Chen, W.; Wong, R. C. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1728 and references therein.

(2) Cowley, A. H.; Jones, R. A.; Harris, P. R.; Atwood, D. A.; Contreras, L.; Burek, C. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1143. Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315.

(3) Power, M. B.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1353.

(4) A solution of 1.00 g (4.14 mmol) of *t*-Bu_3Ga in 5.0 mL of pentane was added to a suspension of 0.462 g (1.04 mmol) of P_4S_{10} in 5.0 mL of pentane at room temperature. The resulting suspension was stirred for 14 h at ambient temperature, following which the unreacted P_4S_{10} was removed by filtration. The volume of the filtrate was reduced to approximately 5 mL. Cooling of this saturated solution to −20 °C for 3 weeks resulted in a 35% yield (0.340 g) of pale yellow crystalline **1** (mp 155°C (dec)). Anal. Calcd for **1**, $C_{24}H_{54}Ga_3P_3S_9$: C, 30.89; H, 5.83. Found: C, 30.13; H. 5.91. In the thermolysis experiment, 100 mg of **1** in 5 mL of toluene was heated at 75 °C for 2 h. The conversion of **1** to **2** was quantitative as indicated by ^{31}P NMR spectroscopy. Small crystals of **2** (mp 130 °C (dec)) were grown from toluene solution at −20 °C. Anal. Calcd for **2**, $C_{16}H_{36}Ga_2P_2S_6$: C, 30.88; H, 5.83. Found: C, 30.77; H, 5.89.

(5) Kovar, R. A.; Derr, H.; Brandan, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.

(6) ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS ext.): **1**, δ 1.22 (s, 54 H, *t*-Bu); **2**, δ 1.18 (s, 18 H, *t*-BuGa), 1.32 (d, 18 H, *t*-BuP, *J* 22.5 Hz). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 295 K, TMS ext.): **1**, $\delta = 29.2$ (s, $C(CH_3)_3$); **2**, $\delta = 23.7$ (d, $PC(CH_3)_3$, $J = 2.25$ Hz), 28.8 (s, $GaC(CH_3)_3$), 45.9 (d, $PC(CH_3)_3$, $J = 44.1$ Hz). The quaternary carbons attached to gallium were not detected. ^{31}P NMR (121.5 MHz, C_6D_6, 295 K, H_3PO_4 ext.): **1**, $\delta = 29.2$ (s); **2**, $\delta = 111.0$ (dectet, $J = 22.5$ Hz). MS (CI, CH_4): **1**, *m/z* 932 (M^-, 2.6%), 874 (M^- − *t*-Bu − H, 58%), 622 (dimer$^-$, 100%), 565 (dimer$^-$ − *t*-Bu, 88%), 310 (monomer$^-$, 8%); **2**, *m/z* 622 (M^-, 73%), 565 (M^- − *t*-Bu, 100%).

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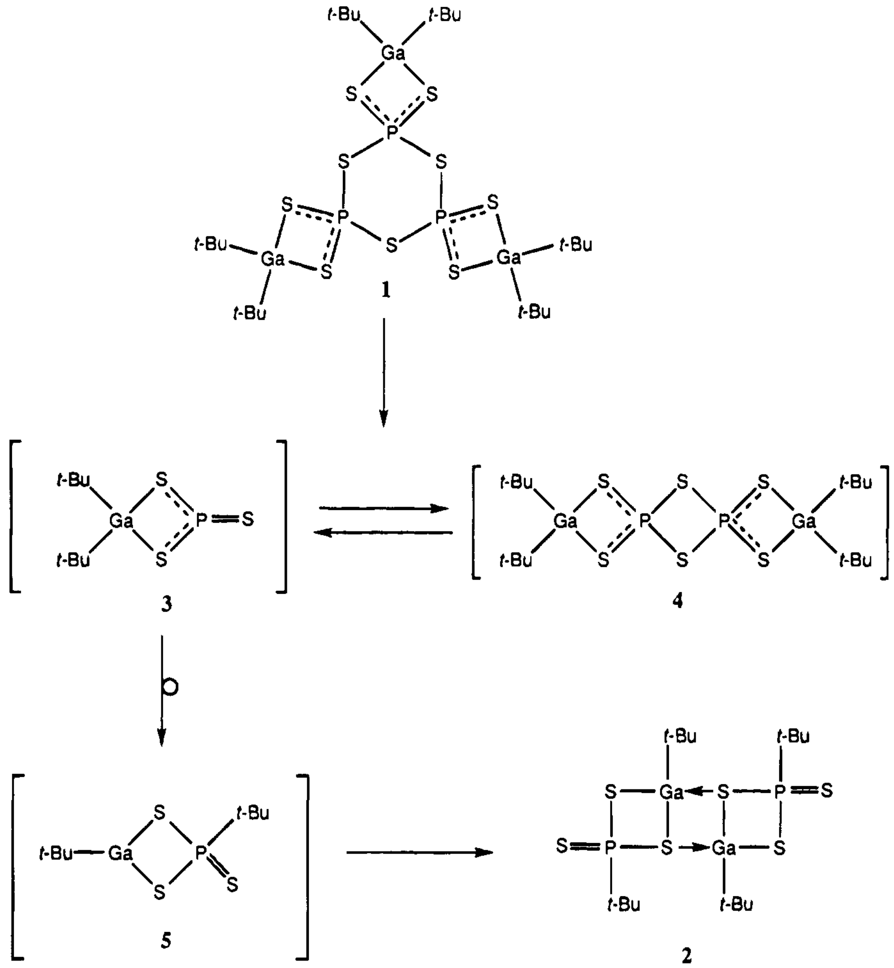
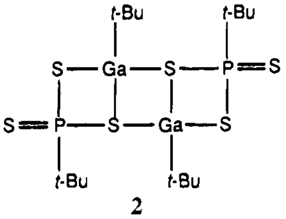
Scheme 1



P_3S_3 ring. The four-membered phosphinodithioate rings adopt a propeller-type arrangement around the six-membered ring. The P_3S_3 moiety exists in a twist-boat conformation with average bond angles at phosphorus and sulfur of 105.58(9) and 104.44(9)°, respectively. The P–S bond distances, which range from 2.104(2) to 2.114(2) Å, fall within the single bond range but are slightly shorter than those reported[8] for the phosphorus(III) ring system $[SP(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ (2.115(3) and 2.142(3) Å). The P–S bond distances in the phosphinodithioate rings are considerably shorter than those in the P_3S_3 ring (average 1.985(2) Å) and indicative of a bond order in excess of one. The bond angles at phosphorus (average 112.28(9)°) exceed those at sulfur (average 81.64(7)°) and gallium (average 84.10(5)°), and the rings deviate from planarity by a slight folding (~10°) along the sulfur–sulfur vector. To our knowledge, **1** represents the first example of a gallium phosphinodithioate. However, phosphinodithioate complexes of indium are known and the metrical parameters for **1** are similar to those for $In(S_2PR_2)_3$ (R = Me,[9] Et,[10] Ph[9]).

The behavior of **1** on thermolysis is interesting. Flash vacuum sublimation of **1** with a temperature ramp of 25 to 200 °C in 5 min afforded **2**. A similar result was obtained when the



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thermolysis was conducted under milder conditions (toluene, 75 °C); however, in this case a transient ^{31}P NMR singlet was observed at δ 33.8 during the conversion of **1** to **2**. Although it has not been possible to obtain crystals of **2** suitable for X-ray analysis, the proposed formulation is consistent with analytical and spectroscopic data.[4,6] Thus the CI mass spectrum of **2** exhibits a sharp cutoff at *m/z* 622 which corresponds to the molecular ion. This assignment was confirmed by HRMS (calculated for $C_{16}H_{36}{}^{69}Ga_2P_2S_6$, *m/z* 619.9128; found, *m/z* 619.9120). The presence of equal abundances of *t*-Bu groups on gallium and phosphorus was evident from integration of the respective ^1H NMR peaks. The identity of the P-*t*-Bu moieties was established by the presence of a dectet resonance in the

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(7) Crystal structure data for **1**, $C_{24}H_{54}Ga_3P_3S_9$: M = 933.25, triclinic, space group $P\bar{1}$, Z = 2, a = 12.986(1) Å, b = 13.330(2) Å, c = 13.706(1) Å, α = 78.05(1)°, β = 84.07(1)°, γ = 66.97(1)°, V = 2135.5 Å^3, ϱ_{calcd} = 1.451 g/cm^3, Mo Kα, λ = 0.710 73 Å, μ = 2.45 nm^{-1}. A total of 7502 independent reflections were collected on a Siemens P4 diffractometer at 193 K with 2θ between 4.5 and 50.0° using the $\theta-2\theta$ scan mode and a graphite monochromator. The structure was solved by direct methods and refined (full-matrix, least squares) on F^2 to a final conventional R value of 0.0449. The *t*-Bu groups are disordered.

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^{31}P NMR spectrum; ^{31}P coupling was also evident in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Moreover, the ^{31}P chemical shift of **2** ($\delta = 111.0$) is comparable to that of $\overline{\mathrm{SCH_2CH_2S}}\mathrm{P(S)}$-*t*-Bu ($\delta = 129.0$),[11] a compound with a very similar coordination environment at phosphorus. Regarding the mechanism of conversion of **1** to **2** (Scheme 1), it is proposed that the trimer (**1**) is converted initially into an equilibrating mixture of the monomer (**3**) and dimer (**4**). As noted earlier, there is mass spectroscopic evidence for the formation of these species in the vapor phase. Moreover, the transient ^{31}P NMR peak at $\delta = 33.8$, which was observed during the mild thermolysis of **1**, can be attributed tentatively to the dimer (**4**). In turn, the monomer (**3**) can undergo isomerization to **5** via a 1,3 shift of the *t*-Bu moiety from gallium to phosphorus. The final step in the conversion is the dimerization of **5** to **2**.

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Supplementary Material Available: Tables of X-ray crystallographic data, bond lengths and angles, atomic coordinates, and thermal parameters and a figure showing complete atom labeling for **1** (8 pages). Ordering information is given on any current masthead page.

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