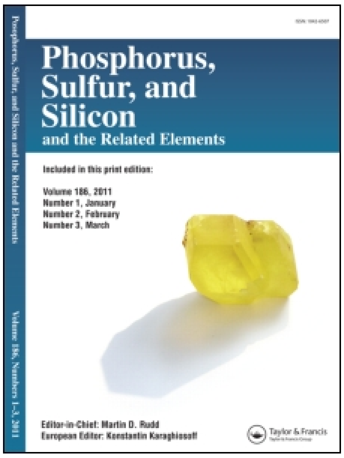
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Ring Systems of Aluminium-, Gallium-, and Indium Thiolates - A Comparison

Gerhard G. Hoffmann[a]; Roland Fischer[a]
[a] Institut für Anorganische Chemie der Universität Würzburg Am Hubland, Würzburg, Deutschland

To cite this Article Hoffmann, Gerhard G. and Fischer, Roland(1989) 'Ring Systems of Aluminium-, Gallium-, and Indium Thiolates - A Comparison', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 1, 97 — 104

To link to this Article: DOI: 10.1080/10426508908039697

URL: http://dx.doi.org/10.1080/10426508908039697

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silica, Vol. 41, pp. 97–104
Reprints available directly from the publisher
Photocopying permitted by license only

RING SYSTEMS OF ALUMINIUM-, GALLIUM-, AND INDIUM THIOLATES - A COMPARISON

GERHARD G. HOFFMANN, ROLAND FISCHER
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg, Deutschland

Abstract Main group III metal(III)halides react with trimethylsilyl organylsulfides to give dihalo(organylthio)metallanes. In the solid state diiodo(methylthio)gallane as well as diiodo(i-propylthio)gallane have shown to be present as dimers, whereas in solution these compounds are trimeric. Reactions between dihalo(organyl)metallanes and trimethylsilyl organylsulfides result via

$$RMHal_2 + (CH_3)_3SiSR' \longrightarrow R(R'S)MHal + (CH_3)_3SiHal$$

in case of gallium as metal atom in the formation of halo(organyl)(organylthio)metallanes, consequently compounds with three different ligands on the metal center. In case of aluminium and indium one has to take into account more complicated reaction pathways, which will be discussed in detail. Structural phenomena of the halo(organyl)(organylthio)metallanes in solution will be discussed by means of molecular weight determination- as well as NMR-spectroscopic studies.

On the Fourth Symposium in Paris we have shown that compounds of the type Hal_2GaSR are dimers in the solid state with the sulfur atoms of the thiolate groups in the bridging position, thus forming GaSGaS-fourmembered ring systems. Depending on the organic rest of the thiolate group it further could be elucidated that two isomers are possible and, as we could proof, are stable in the solid state. One species carries the organic rests R of the thiolate groups in the trans-position relative to the plane fourmembered ring [1], the other one carries the organic rests R of the thiolate groups in the cis-direction relative to the now folded, butterfly-shaped fourmembered ring.[2] In solution these compounds have shown to be trimeric by osmometric molecular weight determinations, except for derivatives, where the rest R equals phenyl or benzyl; these compounds are monomeric, perhaps of steric hindrance and electronic properties.

The most successful synthetic route leading to these compounds has found to be the reaction between gallium trihalides and trimethylsilyl organylsulfides (Equation 1). In benzene solution very good yields of the desired compounds are formed in addition to the corresponding trimethylsilyl halides.[3] This reaction could be extended to the aluminium- and indium trihalides as well.[4,5]

$$\mathrm{MHal_3 + (CH_3)_3SiSR \xrightarrow[\text{reaction-}\atop\text{conditiones}]{\text{different}} Hal_2MSR + (CH_3)_3SiHal} \quad (1)$$

$$\mathrm{Hal = Cl,\ Br,\ I;\ R = alkyl,\ aryl;\ M = Al,\ Ga,\ In}$$

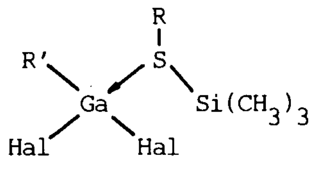
If one halogene atom in the gallium trihalides is substituted by an organic rest, such as methyl, isopropyl or phenyl, one should expect the reaction between these organyldihalogallanes and trimethylsilyl organylsulfides to yield the three times differently substituted organyl(organylthio)halogallanes, together with the corresponding trimethylsilyl halides (Eq. 2).

$$\mathrm{R'GaHal_2 + (CH_3)_3SiSR \longrightarrow R'(Hal)GaSR + (CH_3)_3SiHal} \quad (2)$$

$$\mathrm{R' = CH_3,\ i\text{-}C_3H_7,\ Ph;\ R = alkyl,\ aryl;\ Hal = Cl,\ Br,\ I}$$

This reaction of course is a Lewis-acid-base-reaction in which the first step must be the interaction of the Lewis-acid with the Lewis-base under the formation of the Lewis-acid-base-adduct (Eq.3)

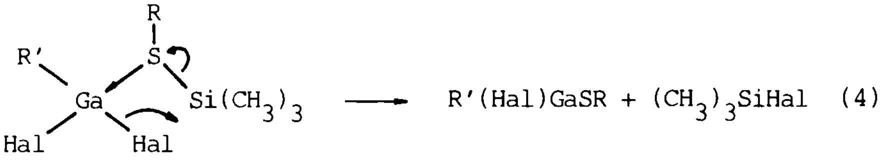
$$\mathrm{R'GaHal_2 + (CH_3)_3SiSR \rightleftharpoons}$$



(3)

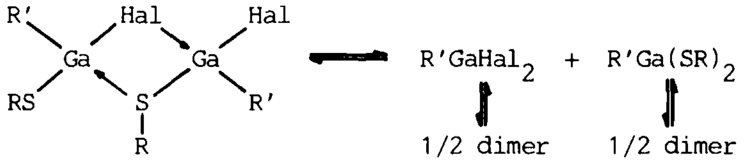
This adduct should be able to split off trimethylsilyl halide in a following step (Eq. 4) and thus the overall reaction should lead to the desired organyl(organylthio)halogallanes.

And indeed, we were able to synthesize the alkyl(organylthio)halogallanes [6,7] and the phenyl(organylthio)chlorogallanes [8] via



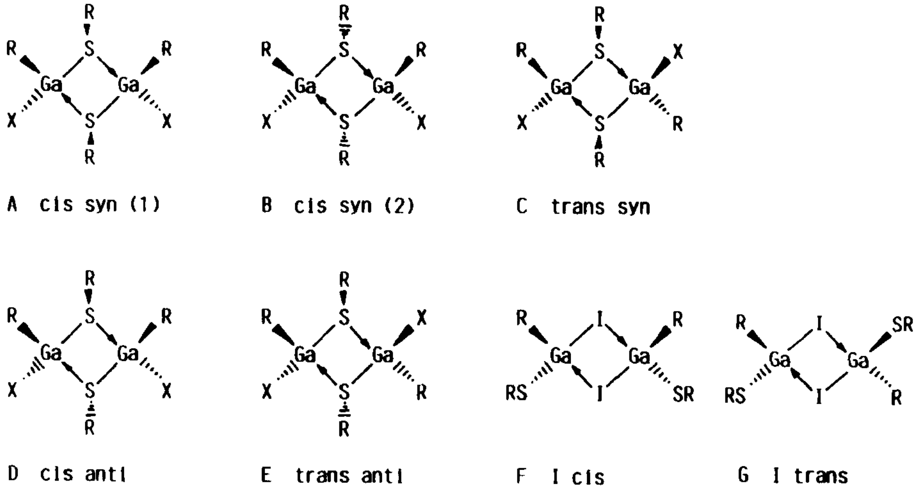
(4)

this method. The reactions of the chloro- as well as bromogallanes with the silylsulfides are spontaneous, exothermic, and the products are formed in high yields. Diiodomethylgallane on the other hand reacts very slowly with the silylsulfides, and even at elevated temperatures the equillibra between educts, adduct, and products are not totally shifted to the side of the products. This fact easily can be proofed by NMR-spectroscopic measurements. At roomtemperature the NMR-spectra of these compounds indicate that there must exist a mixture of different isomers in solution, because the proton resonance signals of the organic rests of the thiolate groups are broadened to such an extent that one cannot distinguish the splitting scheme. Furthermore, the methyl(organylthio)halogallanes show several signals for the methyl group attached to the gallium atom. For a mere dimeric arrangement of these compounds one has to expect a lot of isomers (Figure 1). If the halogene atom is chlorine or bromine , respectively, the possibility of five thiolate bridged forms is given: two cis-syn-species, one, where the rests R of the bridging thiolate groups are pointing to the exocyclic alkyl- or aryl groups (A), the other one, with the rests R of the bridging thiolate groups pointing to the exocyclic halogene atoms (B); one trans-syn-species (C), one cis-anti- (D) and one trans-anti-species (E). If the halide is iodide, one has to discuss two iodine-bridged species as well, namely the cis (F) and the trans (G) isomere. Besides these highly symmetric forms one has to take into account a lot of asymmetric bridged species as well. These species should be able to equillibrate with the organyldihalogallanes and the organylbis(organylthio)gallanes which themselves may be dimers in solution (Eq. 5).



(5)

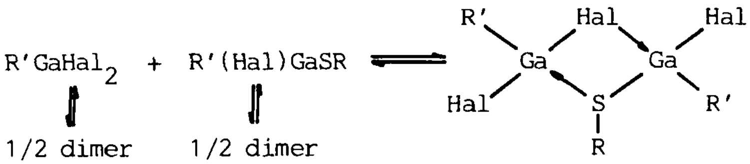
Furthermore, one has to discuss a lot of asymmetric dimers which are built up from two different sorts of compounds, such as the organyldihalogallanes and the organyl(organylthio)halogallanes (Eq. 6).



A cis syn (1) B cis syn (2) C trans syn

D cis anti E trans anti F I cis G I trans

FIGURE 1 Isomers of a dimeric arrangement.



(6)

And of course trimers and higher oligomers cannot be excluded. These species themselves have to be discussed as different geometrical isomers as shown for example for the two possible plane arrangements of the trimer (Fig. 2).

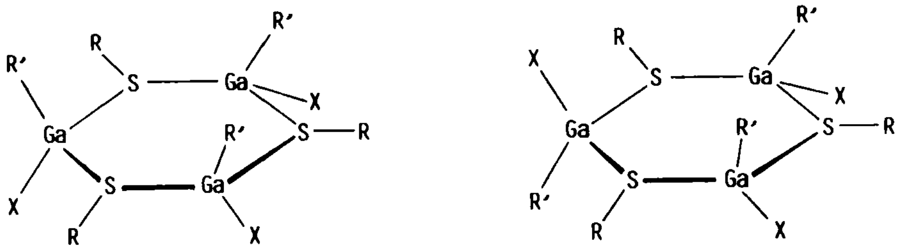


FIGURE 2 Isomers of a plane trimeric arrangement.

Osmometric molecular weight determinations in benzene solution have revealed the methyl(alkylthio)chlorogallanes to be tetrameric. The methyl(alkylthio)bromo- and -iodogallanes with small alkyl-groups on the thiolate rest, such as methyl or ethyl, tend to be trimeric in benzene solution, whereas those compounds where the alkyl-groups attached to the sulfur atoms are longchained (e.g. n-propyl) or bulky (e.g. i-propyl) exhibit a tetrameric oligomerisation in solution. The corresponding phenyl(alkylthio)chlorogallanes are higher associated in benzene solution. Oligomers with up to ten units have been found. Besides these findings, all organyl(phenylthio)- as well as organyl(benzylthio)halogallanes are monomers in benzene solution; this fact may be due to steric hindrance and electronic properties.

On the other hand, mass spectra of some of the methyl(organylthio)halogallanes have shown the alkylthio-derivatives to be dimeric, whereas the phenylthio-derivative again occupies a monomeric arrangement.[9]

The very complex behaviour of these compounds in solution may be the reason, why up till now no suitable crystals could be prepared to elucidate the structur of these interesting compounds in the solid state.

To proof the fact that these three times differently substituted compounds are stable in solution and are not subject to an immediate symmetrisation reaction under the formation of compounds with higher symmetry, we have investigated the Lewis-acid-base-behaviour against trimethylamin.[6,8] These investigations could show very clearly (Eq. 7) that the organyl(organylthio)halogallanes are formed and are stable in solution for at least some time. By the way, the thus formed Lewis-acid-base-adducts are chiral compounds.

$$R'(RS)GaHal + N(CH_3)_3 \longrightarrow R'(RS)HalGa \leftarrow N(CH_3)_3 \qquad (7)$$

$R' = CH_3$, Ph; R = alkyl, Hal = Cl, Br, I

The reaction between organyldihaloindanes and the trimethylsilyl organylsulfides do not follow the expected route under the formation of the desired organyl(organylthio)haloindanes (Eq. 8). The only product which can be isolated is the corresponding dihalo-

$$R'InHal_2 + (CH_3)_3SiSR \longrightarrow Hal_2InSR + (CH_3)_3SiR' \qquad (8)$$

R' = phenyl; Hal = Cl, I; R = alkyl, aryl

(organylthio)indane.[10] This reaction path may be due to the very weak indium-carbon-bond, which only lies in the range of 160 kJ/mol compared with about 250 kJ/mol for the corresponding gallium-carbon-bond-energy.[11] But because of this very weak indium-carbon-bond the desired compounds can be prepared by the reaction of dimethylhaloindanes with mercaptanes. The thus formed compounds are completely insoluble in organic solvents except DMSO. This fact, however, may be a hint that the organyl(organylthio)haloindanes are polymers rather than lower oligomers or even monomers. Investigations in this field are still in hand.

On the other side we have made some investigations on the reaction between methyldihaloalanes and trimethylsilyl organylsulfides. Surprisingly these reactions do not follow one reaction path only. Methyldichloroalane and trimethylsilyl methylsulfide do not form the three times differently substituted methyl(methylthio)chloroalane. Surprisingly the only reaction product which can be detected is dichloro(organylthio)alane (Eq. 9). But the NMR-spectra of the initially formed crude reaction product shows two

$$CH_3AlCl_2 + (CH_3)_3SiSCH_3 \longrightarrow Cl_2AlSCH_3 + (CH_3)_4Si + ? \quad (9)$$

singuletts which can be assigned to the methyl protons of the thiolate group and the methyl protons of the methyl group attached to the aluminium atom. The intensity ratio of these two signals is 2:1. After sublimation of the crude product in vacuum line, the only product which can be collected and identified by analytical methods and spectroscopic measurements is the above mentioned dichloro(methylthio)alane in about 50 % yield. The insoluble residue could not be identified till now.[10]

The homologous trimethylsilyl organylsulfides investigated in this connection react with methyldichloroalane in the expected way under the formation of the methyl(organylthio)chloroalanes as main products (Eq. 10). A multitude of proton resonance signals

$$CH_3AlCl_2 + (CH_3)_3SiSR \longrightarrow CH_3(Cl)AlSR + (CH_3)_3SiCl \quad (10)$$

$$R = \text{alkyl, but not } CH_3$$

for the different alkyl groups indicates that these compounds again must occupy several different isomeric forms as well as different association grades in solution.

A sufficient explanation of these differences in the behaviour of trimethylsilyl methylsulfide on the one hand and its higher homologous on the other against methyldichloroalane cannot be given at the moment. However, it is wellknown that methyldihaloalanes react with trimethylhalosilanes under the formation of aluminium trihalides and tetramethylsilan [12-17] and this fact may be transferred to some of these reactions as well.

Finally, the reactions between methyldiiodoalane and the trimethylsilyl organylsulfides lead to the 1:1-adducts, respectively. These adducts are rather stable in solution and one cannot find a further reaction under the formation of methyl(organylthio)iodoalanes. But if the adducts are heated solvent-free in vacuum line for several hours, the products formed contain the desired compounds in high yields as indicated by NMR-spectroscopic measurements.

ACKNOWLEDGMENT

I thank Prof.Dr.Dr.h.c. M. SCHMIDT for making these investigations possible, the Fonds der Chemischen Industrie for financial support, the SIEMENS AG and the CONDEA AG for chemical gifts.

REFERENCES

1. G.G. Hoffmann, Phosphorus Sulfur, 28, 167 (1986).
2. G.G. Hoffmann and Ch. Burschka, Angew.Chem.Int.Ed.Engl., 24, 970 (1985).
3. G.G. Hoffmann, Chem.Ber., 116, 3858 (1983).
4. G.G. Hoffmann, J.Organomet. Chem., 335, 143 (1987).
5. G.G. Hoffmann, J.Organomet. Chem., 338, 305 (1988).
6. G.G. Hoffmann, J.Organomet. Chem., 273, 187 (1984).
7. G.G. Hoffmann, Z.Naturforsch., 40b, 335 (1985).
8. G.G. Hoffmann and H. Meixner, Z.Anorg.Allg.Chem., 523,121(1985).
9. G.G. Hoffmann, Habilitationsschrift, (Würzburg, 1985).
10. G.G. Hoffmann, unpublished results.
11. D.G. Tuck, in Comprehensive Organometallic Chemistry, edited by G. Wilkinson (Pergamon Press, Oxford 1982), Vol. 1, Chap.7.
12. G.A. Russell, J.Am.Chem.Soc., 81, 4815 (1959).
13. G.A. Russell, J.Am.Chem.Soc., 81, 4825 (1959).
14. G.A. Russell, J.Am.Chem.Soc., 81, 4831 (1959).
15. L.M. Antipin, V.V. Ponomarev and V.F. Mironov, Bull.Acad.Sci. USSR, Engl.Transl., 1968, 2495.
16. A.L. Leffler, Inorg.Chem., 7, 2651 (1968).
17. V.V. Ponomarev, S.A. Golubtsov and K.A. Andrianov, Bull.Acad. Sci. USSR, Engl.Transl., 1968, 2583.