

The reactivity of organoelement compounds with aluminium–aluminium, gallium–gallium and indium–indium bonds

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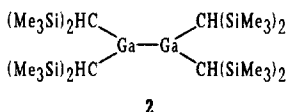
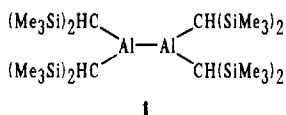
Abstract

Organoelement derivatives with aluminium–aluminium, gallium–gallium and indium–indium bonds were synthesized for the first time in our group eight years ago. They show a remarkable and unprecedented chemical reactivity and up to now six different types of reaction

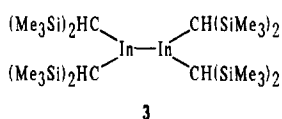
have been found, which are summarized in this review article: (i) The formation of adducts is observed with sterically less shielded Lewis-bases like H^- or Br^- . (ii) The treatment with strong reducing agents like the alkali metals or some alkyllithium derivatives yields radical anions with $1e\text{-M-M} \pi$ bonds. (iii) Sterically more shielded bases give a deprotonation of the substituent with the formation of heterocycles. (iv) Insertion reactions into the element–element bonds could be realized with atoms, whole molecules or molecular fragments. (v) A metathesis reaction with a ditellurium derivative gives a monomeric organo gallium telluride. (vi) An exchange of two alkyl substituents with the preservation of the element–element bond is observed by the reaction with carboxylic acids. © 1997 Elsevier Science S.A.

1. Introduction

Organoelement compounds with element–element single bonds between the elements of the third main-group (B, Al, Ga, In, Tl) are quite unusual, and it was not before 1980 that the groups of Berndt [1] and Nöth [2] synthesized the first tetraalkyldiboranes(4) containing a boron–boron bond. Some authors claimed the formation of alkyl derivatives with an Al–Al bond, but the products obtained were only poorly characterized, and the results could not be verified, whenever they were scrutinized by other groups. A dihydridotetraalkyldialanate(6) ($[\text{iBu}_2\text{HAl-AlHiBu}_2]^{2-}$) [3] proved to be a dimeric hydridotrialkylalanate [4], hexa(isobutyl)dialanate(6) [5] to be tetra(isobutyl)alanate ($\text{K}[\text{AliBu}_4]$) [6] and tetraisobutyldialane(4) [7] to be $\text{K}[\text{ClAliBu}_3]$ [8]. By clarifying the last product our group succeeded in the isolation of small amounts of $\text{K}_2[\text{Al}_{12}\text{iBu}_{12}]$ [9], which was the first organometallic polyborate analog of a heavier third main-group element to be characterized. In 1988 we described the first stable and fully characterized derivative (**1**) with an Al–Al single bond [10], which was stabilized by four bulky bis(trimethylsilyl)methyl groups [11] against a disproportionation reaction and was synthesized by the reduction of the corresponding chlorodialkylalane with potassium [10]. **1** shows a remarkable thermal stability and melts at 219°C with only minor decomposition. One year later we isolated the digallane(4) analog **2** [12] by the reaction of $\text{Ga}_2\text{Br}_4 \cdot 2\text{dioxane}$ [13] with bis(trimethylsilyl)methylolithium [11] and the diindane(4) analog **3** [14] by the similar reaction of $\text{In}_2\text{Br}_4 \cdot 2\text{TMEDA}$ [14, 15].



Due to the element–element bond and the formal oxidation state of +II for the elements Al, Ga and In these compounds should show a remarkable and unprecedented chemical reactivity, and numerous different types of reactions should be



possible: (i) addition of Lewis bases to the coordinatively unsaturated Al, Ga or In atoms; (ii) electron transfer into the empty p orbitals of the Al, Ga or In atoms and formation of compounds with element–element π bonding; (iii) the bis(trimethylsilyl)methyl groups exhibit C–H acidity, and carbanionic species should be obtainable by the reaction with strong bases, which might be stabilized by an interaction with the unsaturated central atoms; (iv) insertion of atoms and molecules into the element–element bonds as well as the element–carbon bonds; (v) ligand exchange; (vi) metathesis; (vii) irradiation. Most of these ideas are realized now in the course of systematic research activities in our group and will be described in this review article.

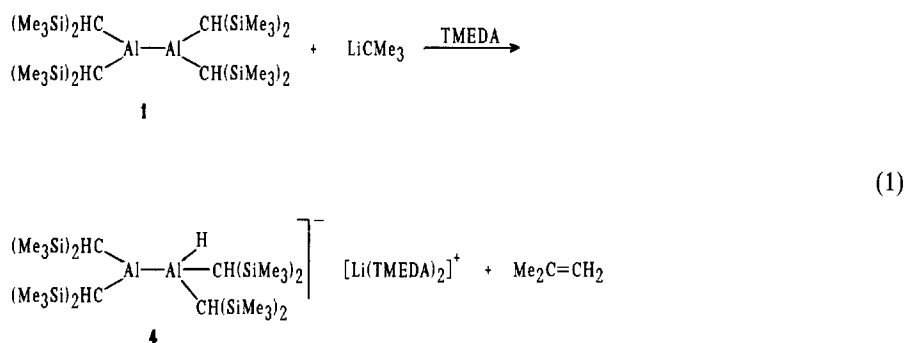
Following our syntheses of the first tetraalkyl dialane(4), digallane(4) and diindane(4) compounds numerous further tetrasilyl [16], tetraaryl [17–19] or tetraamino derivatives [20] were published in recent literature. While tetrahalogeno derivatives with Ga–Ga [13,21] or In–In bonds [15,22] and donor molecules or ions are known for at least three decades, an Al_2Br_4 adduct with an Al–Al bond was only recently reported [23]. Organoelement compounds containing a Tl–Tl bond are unstable with the bis(trimethylsilyl)methyl group, but can be isolated with more bulky substituents [16,24]. This paper is focused on the chemical reactivity of the tetraalkyl and tetraaryl dielement derivatives, and the bulk of the data concerning the reactivity of compounds 1 to 3.

2. Formation of adducts

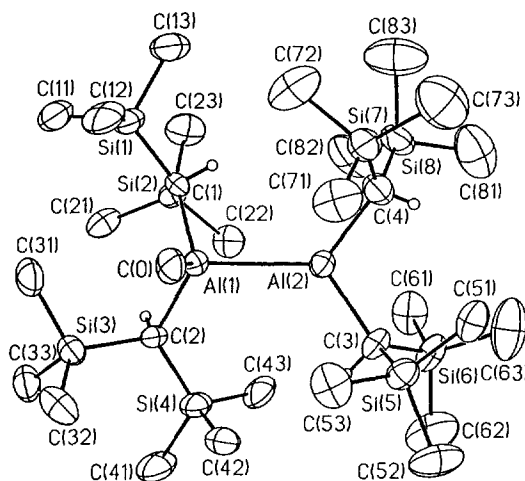
2.1. Reactions with ethyl, tert-butyl and methyl lithium

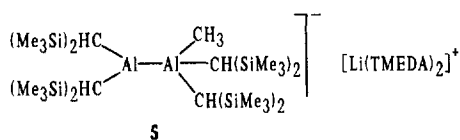
We expected three different types of reaction for the treatment of the dielement compounds 1, 2, and 3 with alkyl lithium derivatives: (i) formation of adducts with the carbanions as Lewis-bases, (ii) deprotonation of the bis(trimethylsilyl)methyl substituent, or (iii) cleavage of the element–element bond. Reactions similar to type (iii) are observed for instance with disilicon [25] or diphosphorus derivatives [26] and give the very important starting compounds lithium silanides and lithium phosphanides, respectively.

The dialane(4) derivative 1 reacts with *tert*-butyl or ethyl lithium in the presence of the chelating amine N,N,N',N'-tetramethylethylenediamine (TMEDA) to yield an identical product (4, Eq. (1)), which was identified by IR spectroscopy as a hydrido adduct of 1 by a broad absorption at 1620 cm^{-1} [27,28]. Although we did not detect the by-products isobutene or ethene in these reactions [29], the formation of 4 is clearly a consequence of a β elimination of alkenes from the lithium bases and the complexation of the remaining lithium hydride by 1.



Methyl lithium forms a similar methyl adduct (**5**) on treatment with **1** [27]. As shown by crystal structure determinations, the Lewis-bases do not bridge the Al_2 group by the formation of $3c-2e$ bonds, but are terminally bound to only one Al atom [27]. Thus, compounds are formed with a coordinatively saturated, tetracoordinated Al atom neighboring a coordinatively unsaturated, tricoordinated Al atom. There are indications from the molecular conformations in the solid state, that hyperconjugation is an important aspect in describing these molecules. While the substituents at the tetracoordinated metal centers occupy a staggered conformation to minimize steric repulsion, they are parallel at the tricoordinated Al atoms with the $\alpha\text{-C-Si}$ bonds in an optimal position for a hyperconjugative electron transfer into the empty p orbitals (Fig. 1). The Al–Al bond length is not affected by the addition of the hydrido ligand (266.0(1) pm in **1**; 266.7(3) pm in **4**), but is significantly lengthened in the methyl derivative **5** to 275.2(3) pm. While **4** is stable in solution at room temperature, **5** decomposes slowly with precipitation of elemental aluminium.





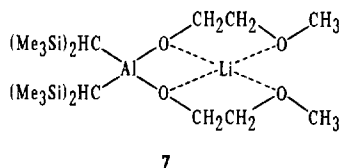
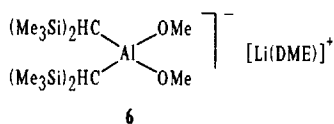
Compound **4** shows simple NMR spectra with only one singlet for the SiMe₃ and the AlCH protons, which remain unchanged on cooling solutions to $-50\text{ }^{\circ}\text{C}$ and indicate the fast exchange of the hydrido ligand or only very small differences in the chemical shifts. Compound **5**, however, exhibits split ¹H and ¹³C NMR resonances, thus, its asymmetric molecular shape is still preserved in solution [27].

Reactions of **1** with sterically more crowded lithium bases yielding radical anions (Section 3.1) or deprotonation products (Section 4) will be discussed below. Up to now, similar adducts could not be isolated with digallane(**4**) **2** and diindane(**4**) **3**. The reactions of **2** with methyl or *tert*-butyl lithium do not yield isolable products with ethyllithium and **2** a radical anion is formed, which is described below (Section 3.2). Most of the diindane(**4**) **3** is recovered, even when **3** is treated with an excess of methyl, ethyl or trimethylsilylmethyl lithium; a product could not be identified. A mixture of products is formed with neopentyllithium and **3**, from which only the pentane soluble neopentyl-bis[bis(trimethylsilyl)methyl]indane could be isolated and characterized.

2.2. Reactions with lithium alkoxides

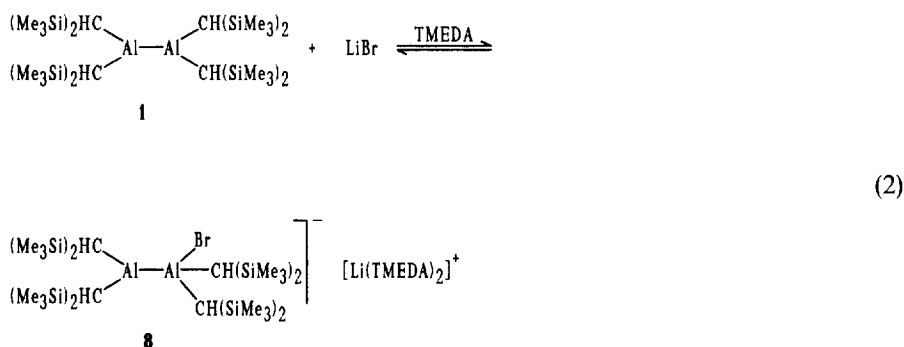
As described above, the two-electron donors H[−] and CH₃[−] add to the Al–Al bond by the terminal coordination of only one Al atom. In order to realize a bridging of the Al–Al bond by an interaction of a Lewis-base with both coordinatively unsaturated Al atoms, we treated the dialane(**4**) **1** with lithium alkoxides, from which we hoped, that they could act as four-electron donors. But in all reactions we observe a fragmentation of the starting compound. After optimization of the reaction conditions we found, that by the treatment of **1** with LiOMe or LiOCH₂CH₂OMe in a solution of 1,2-dimethoxyethane (DME) exactly one half of **1** is consumed by the formation of the dialkoxydialkylalanates **6** or **7**, which are both soluble in pentane or toluene. The potassium analog of **7** was characterized by a crystal structure determination [30] and exhibits a chelating aluminium alkoxide anion bound to the alkali metal cation as schematically shown below. The second half of the starting compound **1** gives a colorless, sparingly ether soluble and highly viscous product, which exhibits broad signals in the NMR spectra. Although no product could be isolated in a pure form, it seems, that a mixture of ether cleavage products is obtained. We suppose, that the Al–Al bond is cleaved by the Li alkoxides with the formation of the isolated dialkoxyalanates **6** or **7** and of a very reactive Al(I) intermediate, which spontaneously reacts with DME. While this assumption is rather speculative here, a reaction is discussed in Section 3.1.3, in which the intermediate formation of an Al(I) species is very plausible from the molecular structures of the isolated products. No reaction occurs at all in pentane or toluene solution. Treatment

of the digallane(4) derivative **2** with lithium alcoholates gives mixtures of many unknown products, and we did not succeed in the isolation of any pure compound.



2.3. Reaction with the soft Lewis-base LiBr

Because the hard bases LiOR gave fragmentation reactions with the dielement derivatives, we subsequently used the soft base Br^- as a four-electron donor and a potential bridging group. The addition of LiBr to **1** in pentane and TMEDA results in the quantitative precipitation of the adduct **8** (Eq. (2)), but the product dissociates into the starting compounds immediately after dissolution in diethylether, so that we were not able to detect any property of **8** in solution [31].



Single crystals of **8** were obtained by rapid recrystallization from very dilute solutions in pentane with a small amount of ether. The molecular structure is schematically shown in Eq. (2): The bromide ion does not occupy a bridging position, but coordinates terminally to only one Al atom as a two-electron donor. The Al–Al bond length (264.3(4) pm) [31] is slightly shorter than in the dialane(4) starting compound **1** (266.0(1) pm) [10], but the Al–Br bond is very long (247.6(3) pm) indicating only a weak Al–Br interaction in agreement with the facile dissociation in solution. The Al–Br bond is parallel to the empty p orbital of the

second Al atom, and possibly hyperconjugation leads to the weak coordinative bonding. Thus, up to now we did not succeed in bridging the Al–Al bond even with a potential four-electron donating atom, while in transition metal chemistry the bridging of metal–metal bonds by halide or hydride ions is quite common [32]. The reason is not well understood. The ring strain by the formation of three-membered heterocycles with two Al atoms may not be balanced by the sterically unfavoured interaction of the lone pairs with two parallel p orbitals. The low Lewis-acidity of the Al atoms due to the unusual oxidation state of +II and the hyperconjugation to the α -C–Si bonds may increase this effect.

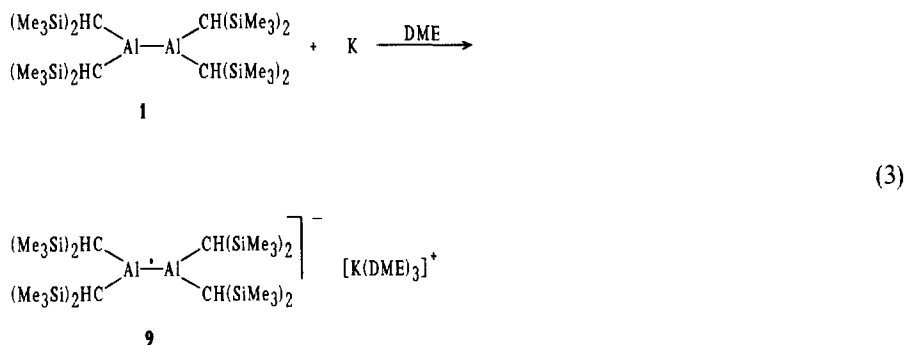
3. Electron transfer reactions

The Al, Ga and In atoms in compounds **1**, **2** and **3** have empty p orbitals, and we expected, that the transfer of electrons into these orbitals could lead to the formation of derivatives with Al–Al, Ga–Ga or In–In π bonds. Cyclic voltammetric investigations revealed, however, that only very strong reducing agents like the alkali metals were able to reduce these compounds.

3.1. Aluminium compounds

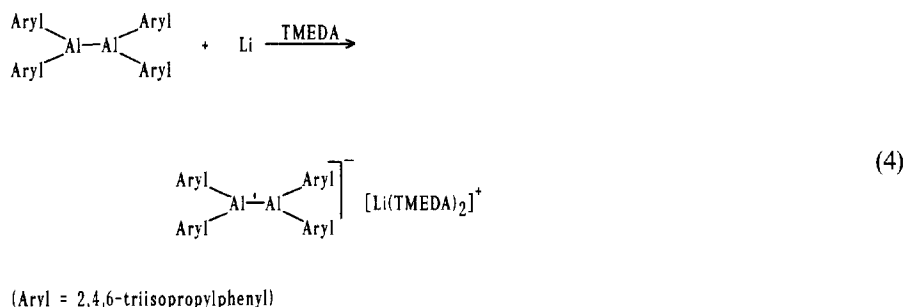
3.1.1. Dialuminium radical anions by the reaction with alkali metals

No reaction occurs when the dialane(4) **1** is treated with an excess of potassium in hexane at room temperature or in the boiling solvent over a period of several weeks. In DME, however, dark blue and extremely air-sensitive solutions are obtained with the complete consumption of **1** in less than 16 hours [33]. A dark-blue paramagnetic solid (**9**) is isolated by recrystallization, which exhibits an Al to K ratio of 2 to 1 and an undecet in the EPR spectrum caused by the coupling of an unpaired electron to two equivalent Al atoms. The g-value (2.0027) near that of the free electron, the low value of the coupling constant of 1.17 mT as well as its anisotropy [33] shows, that a radical anion of **1** has formed (Eq. (3)) with the unpaired electron localized in a π orbital of the Al–Al bond. A similar reaction is observed with sodium [33]. Solutions of **9** in DME can be stored at room temperature and daylight under argon for more than four weeks, before the blue color disappears. As shown by NMR spectroscopy a mixture of decomposition products is formed with dialane(4) **1** as the main-component.



While the derivatives of **9** synthesized in our group with $[\text{K}(\text{DME})_3]^+$ and $[\text{Na}(\text{DME})_3]^+$ as a counterion are X-ray amorphous, single crystals of $[\text{Li}(\text{TMEDA})_2]^+[\text{R}_2\text{Al}-\text{AlR}_2]^-$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) were obtained by Pörschke et al. on a similar route by the reaction of **1** with lithium in THF at -30°C and treatment of the product with TMEDA [34]. While dialane(4) **1** shows a slight deviation from planarity in the solid state (torsion angle $\text{C}-\text{Al}-\text{Al}-\text{C}$ 4°) [10], its radical anion exhibits an ideal plane Al_2C_4 molecular center. As expected for an one-electron $\text{Al}-\text{Al}$ π bond the $\text{Al}-\text{Al}$ bond is shortened to 253(1) pm (**1**: 266.0(1) pm).

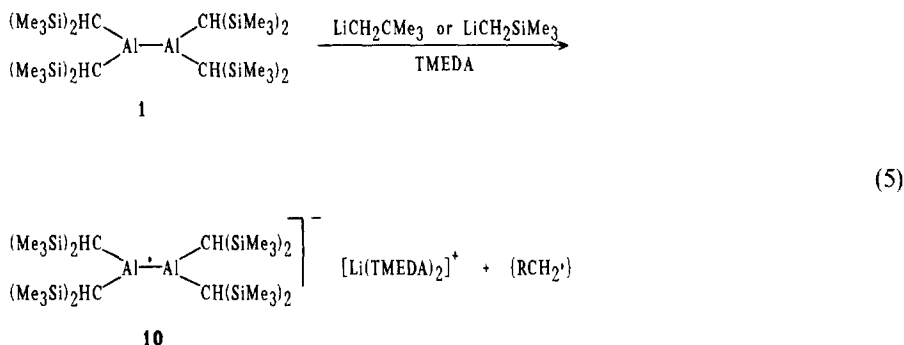
At the same time, a similar compound was obtained by Power et al. (Eq. (4)) by the treatment of a tetraaryldialane(4) (aryl = 2,4,6-triisopropylphenyl) with lithium in diethylether and TMEDA [17]. The torsion angle across the $\text{Al}-\text{Al}$ bond changes from 44.8° in the neutral starting compound to 1.4° in the radical anion, and the $\text{Al}-\text{Al}$ bond is shortened by 17.7 pm from 264.7(3) to 247.0(2) pm. The $\text{Al}-\text{C}$ bonds are lengthened in both radical anions by 5.8 and 2.5 pm in comparison with the corresponding dialane(4) derivatives. The EPR spectrum of the tetraaryldialuminium radical is very similar to that of **9** ($g = 2.0048$), and the small coupling constant to the Al atoms ($a_{\text{Al}} = 1.04$ mT) is consistent with the location of the electron in a π orbital.



3.1.2. Dialuminium radical anions by the reaction with alkylolithium derivatives

As shown above (Section 2.1), the dialuminium(4) derivative **1** reacts with methyl-lithium to yield the adduct methyltetraalkyldialanate(5) **5** and with *tert*-butyl or ethyl lithium after a β elimination to yield hydridotetraalkyldialanate(5) **4** [27]. Quite different products are isolated with neopentyl or trimethylsilylmethyl lithium, where both are sterically more shielded than methyllithium and cannot give a β elimination. They react with **1** in the presence of TMEDA in pentane at low temperatures as strong reducing agents to yield by an electron transfer the dark blue dialane(4) radical anion **10** (Eq. (5)), which could be separated by filtration and characterized by elemental analyses and EPR spectra [33]. The alkyl radicals formulated in Eq. (5) were not detected. The synthesis of the radical anion according to Eq. (5) is the most preferable preparative method, because the product is formed at low temperature and with a short reaction time in a very pure form, which could be used for further experiments without purification. With neopentyllithium a by-product could be extracted from the precipitate in some cases in trace amounts,

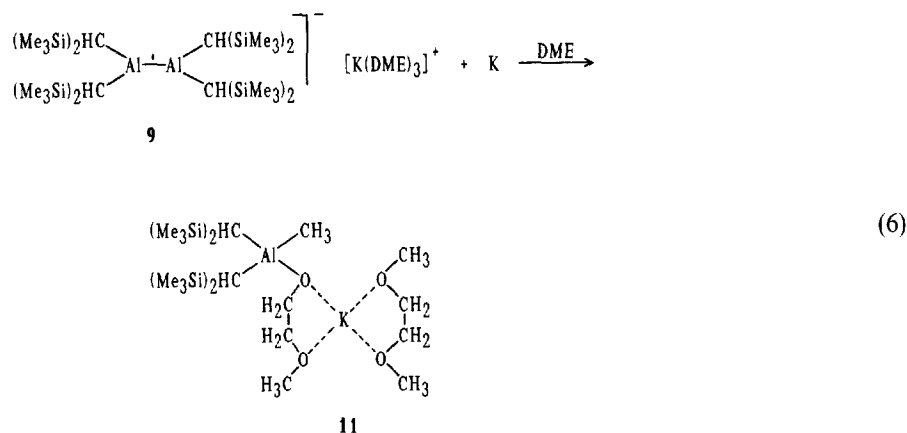
which was identified by a crystal structure determination as the deprotonation product (17) of dialane(4) **1**. This was the first evidence, that deprotonation reactions could be realized with **1**; we will discuss this compound in Section 4.

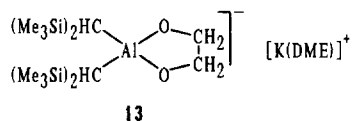
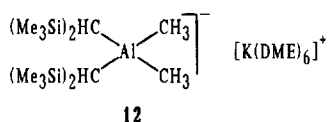


3.1.3. Reaction of the dialane(4) radical anion **9** with potassium

All electron transfer reactions with dialane(4) derivatives gave a radical anion by the transfer of only one electron, which is localized in a π orbital of the Al–Al bond. Similar reactions have been observed with tetraalkyldiborane(4) compounds with ESR spectroscopic evidence for diborane(4) radical anions [35]. The transfer of two electrons with formation of B=B double bonds was reported in recent literature with diaminodiaryldiborane(4) or tetraaryldiborane(4) derivatives [36]. In order to realize the transfer of a second electron with the dialuminium compound also, we treated the dialane radical anion **9** with an excess of potassium.

The blue color of **9** disappears when the mixture is stirred in DME for three days. Three colorless compounds are formed without further spectroscopically detectable impurities, which cannot be separated by recrystallization or distillation [30,37]. The NMR spectra give indications of ether cleavage products, and we synthesized some possible derivatives with alkoxy substituents, which are partially published in [30] and [37]. By a comparison of the NMR data we finally could identify all three decomposition products (**11** to **13**), which are summarized in Eq. (6).





Potassium[(2-methoxy-1-ethanolato)(methyl)alanate] **11** was characterized by a crystal structure determination [30]. The anion acts with its both oxygen atoms as a chelating Lewis-base and coordinates the potassium cation, which in addition is bound to a DME molecule. A one-dimensional coordination polymer is formed in the solid state by an interaction of the potassium ion with the methyl group of a neighboring molecule, which results in a short intermolecular $\text{K} \cdots \text{C}$ contact of 327 pm and a flattened coordination geometry of the four oxygen atoms bound to potassium [30]. A similar lithium derivative is quantitatively formed when dialane(4) **1** is treated with an excess of elemental lithium in DME at room temperature [30]. The second product of the reaction of **9** with potassium is dimethylalanate **12**, which was characterized by spectroscopic methods and elemental analysis; remarkably, it crystallizes with six DME molecules in each formula unit. A glycolato unit is bonded in a chelating manner to the AlR_2 fragment of the third product (**13**), which also is a one-dimensional coordination polymer in the solid state and polymerizes via potassium bridges between glycolato oxygen atoms (Fig. 2) [37].

The mechanism of the reaction of elemental potassium with the radical anion **9** seems to be clear from the constitution of these three products. The first compound formed is the alkoxymethylalanate **11**, which is the product of an insertion of a dialkylaluminum(I) fragment into a C–O bond of a DME molecule or in other words of an oxidative addition of a C–O bond to Al(I) yielding the normal oxidation state of +3. The compounds dimethylalanate **12** and glycolatoalanate **13** are always detected in equimolar amounts, they are formed by a second insertion of Al(I) into the remaining O–Me bond of the DME fragment of **11** yielding an intermediate with two Al–Me moieties bridged by a glycolato dianion. A following dismutation reaction leads to the more symmetrical products **12** and **13**. Thus, as originally intended, a dialkylaluminate(I) (with aluminium in a formal oxidation state of +1) is formed by the treatment of **9** with an excess of potassium, but only as a reactive intermediate, which is unstable under the conditions needed to facilitate the electron transfer and decomposes under insertion into DME molecules.

3.2. Gallium compounds

The first known digallane(4) radical anion (**15**) with an $1e\text{-Ga-Ga}$ π bond was published in 1993 by the group of Power [18]. It was obtained by the reaction of

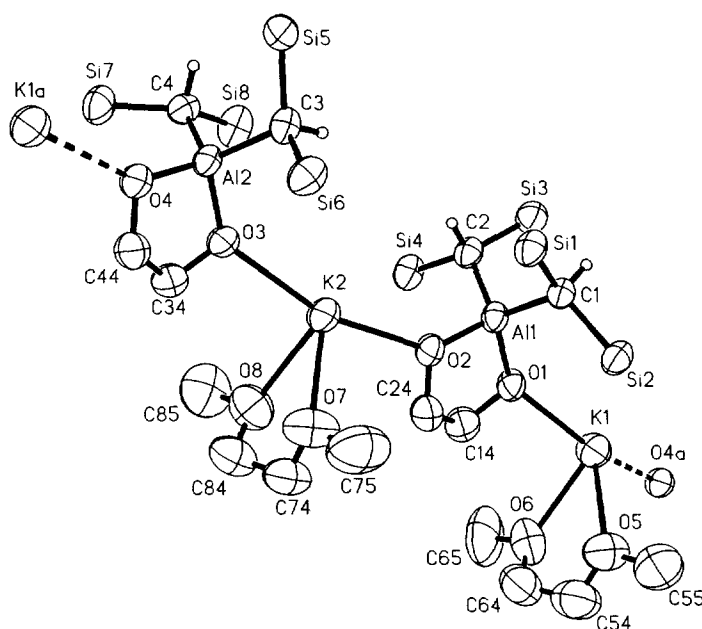
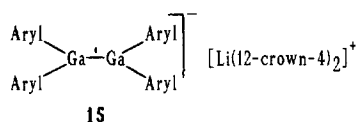
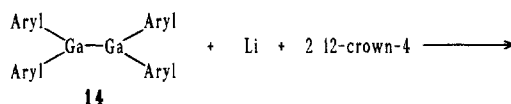


Fig. 2. Chain segment out of the crystal structure of **13** [37]. Methyl groups of SiMe_3 substituents are omitted for clarity.

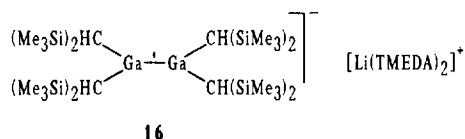
tetrakis[tri(isopropyl)phenyl]digallane(4) **14** with lithium in diethylether (Eq. (7)); black crystals of the digallane(4) radical anion **15** were isolated in 80% yield after the addition of the crown ether 12-crown-4. The crystal structure of **15** [18] reveals a significantly shortened Ga–Ga distance (234.3(2) pm) compared to the corresponding neutral digallane(4) derivative **14** (251.5(3) pm) and a flattened molecular center C_2GaGaC_2 with a torsion angle of 15.5° (43.8° in **14**) as expected from the occupation of the π orbital of the Ga–Ga bond by one electron. This model is verified by small coupling constants observed in the EPR spectrum (3.54 mT ^{69}Ga ; 4.39 mT ^{71}Ga) [18].



(7)

(Aryl = 2,4,6-triisopropylphenyl)

We obtained a digallium radical anion (**16**) by the treatment of **2** with ethyllithium in the presence of TMEDA, DME or trimethyltriazinane [38]. **16** is much more reactive than the aluminium derivative **10**, and decomposes in ethereal solutions even at $-50\text{ }^{\circ}\text{C}$ in few days and is extremely air-sensitive. The Ga–Ga distance is shortened to 240.1(1) pm (254.0 pm in **2**) and the molecular center (Ga_2C_4) is exactly planar. The Ga–C bond lengths are significantly lengthened to 206.5(4) pm compared to **2** (199.6 pm), which might be due to (i) an enlarged steric interaction between the substituents by the shortened Ga–Ga distance and (ii) a decreased hyperconjugative interaction between the α -Si–C bonds and the Ga p orbitals caused by the occupation of the Ga–Ga π orbital by one electron. A similar, but half as large effect was observed by Power et al. in the radical anion **15** [18]. **16** shows large coupling constants of 5.75 mT (^{69}Ga) and 7.28 mT (^{71}Ga) in the EPR spectrum at room temperature, which exhibit a strong temperature dependence with much smaller values at low temperatures (200 K: 4.28 and 5.45 mT, respectively) closer to that found for compound **15**. The larger coupling constants at room temperature may be explained by an enhancement of the s character of the single occupied molecular orbital and indicate, that the molecular center deviates from planarity. **16** would thus resemble Lappert's distannene R_2SnSnR_2 ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) with a “non-classical” Sn–Sn double bond [39]. If **2** is treated with ethyllithium in the absence of a chelating Lewis-base, elemental gallium is precipitated, and the ligand exchange products $\text{Li}[\text{GaEt}_4]$ and bis(trimethylsilyl)methylolithium can be isolated.

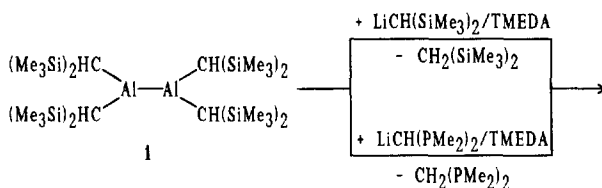


Up to now we did not succeed in the synthesis of a diindium(4) radical anion, neither by the treatment of the diindane(4) **3** with alkali metals nor by reactions with several alkyllithium derivatives. Also, there are no reports in the literature about diindium(4) radical anions.

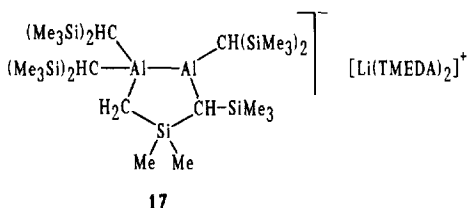
4. Deprotonation of dialane(4) **1**

All reactions of **1** with the strong bases LiR ($\text{R} = -\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CMe}_3$, $-\text{CH}_2\text{SiMe}_3$) described so far did not yield a deprotonation product, but adducts or radical anions. Only with $\text{LiCH}_2\text{CMe}_3$ we found a further derivative in trace amounts, which was identified by a crystal structure determination as the product of a deprotonation reaction (**17**) [28]. We succeeded in synthesizing this compound in a high yield by the treatment of **1** with the sterically more crowded lithium bases $\text{LiCH}(\text{SiMe}_3)_2$ or $\text{LiCH}(\text{PMe}_2)_2$ in the presence of TMEDA [28]. The deprotonation occurs, as schematically shown in Eq. (8), at a methyl group of a SiMe_3 substituent; the carbanion formed is stabilized by the interaction with an unsaturated Al atom yielding an up to now unknown five-membered $\text{Al}_2\text{C}_2\text{Si}$ hetero-

cycle with an Al–Al bond.



(8)



17 crystallizes with and without ether molecules, and both crystal forms were characterized by crystal structure determinations showing, however, only small differences in conformation, bond lengths and bond angles [28]. The Al–Al bond lengths (264.1(2) and 266.5(3) pm) remain almost unchanged compared to **1**. The methine protons at the tricoordinated Al atom have a strongly differing environment. The α -C–H bond of the heterocycle is parallel to the empty p orbital at the Al atom, while that of the terminal $\text{CH}(\text{SiMe}_3)_2$ group lies within its nodal plane. This situation leads to an extreme difference in the chemical shifts of these protons of 1.75 ppm ($\delta = -1.27$ and 0.48 ppm, respectively) [28].

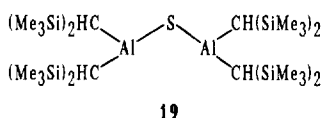
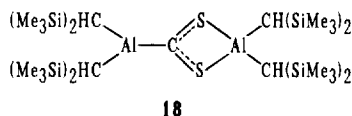
5. Insertion reactions

By far the most extensive results concerning the reactivity of the dielement compounds **1** to **3** were obtained with insertion reactions, and we succeeded in the insertion of single atoms as well as whole molecules or molecular fragments into the element–element bonds, while the insertion into the element–carbon bonds has not yet been observed.

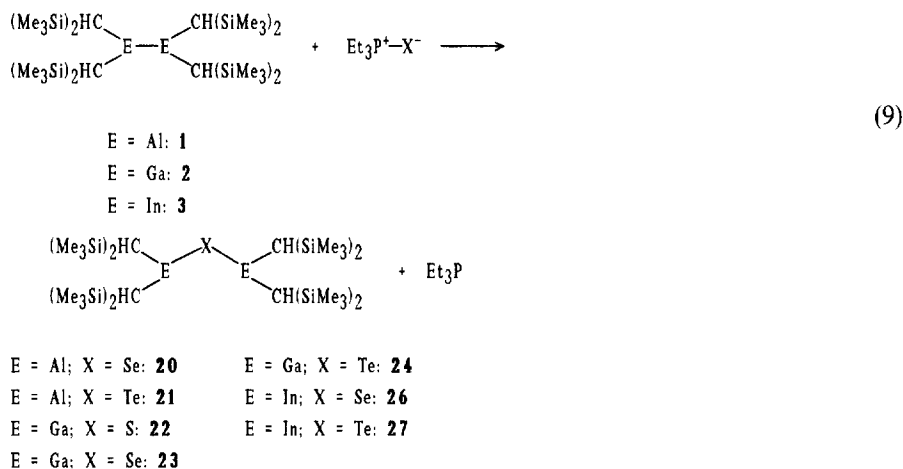
5.1. Insertion of chalcogen atoms

The first insertion of a chalcogen atom into the Al–Al bond of **1** was observed by the reaction with carbon disulfide, which was not realized with stoichiometric amounts of the starting compounds, but only in CS_2 as the solvent over a period of 24 hours at room temperature. Two products were isolated [40]: (i) The yellow dithiocarbonyl derivative **18** is formed by the insertion of a complete molecule CS_2 ; both Al atoms and the five inner carbon atoms in **18** lie almost ideally within a plane, while the CS_2 moiety is arranged perpendicular to this plane, so that a π interaction of the delocalized CS_2 π bond to the unsaturated tricoordinated Al atom, which is reverse to that found in dithiocarbamates, can be excluded. (ii) The insertion

of a sulfur atom is observed by the cleavage of a C=S double bond (colorless **19**), the molecular structure is discussed below. Further bis(trimethylsilyl)methyl products could not be detected by NMR spectroscopy, the missing C=S fragment may give oligomers or polymers, which possibly account for the dark red color of the reaction mixtures.

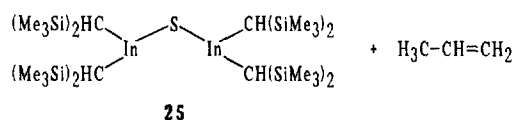
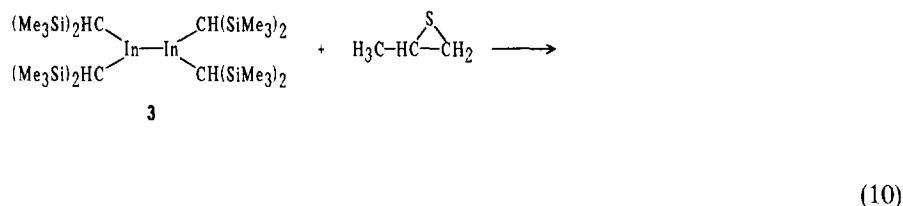


Triethylphosphoniumchalcogenides Et_3PX ($\text{X} = \text{S}, \text{Se}, \text{Te}$) were successfully employed as chalcogen atom donors in the syntheses of the further chalcogen bridged dialuminium, digallium and diindium derivatives with the exception of the In–S–In compound (Eq. (9)). Et_3PSe and Et_3PTe react completely with **1**, **2** and **3** in 0.5 to 24 hours at room temperature, and the chalcogenides are isolated in over 80% yield [41–44]. No reaction occurs, however, under similar conditions with **2** and Et_3PS , and much more drastic reaction conditions must be used with boiling toluene over a period of 30 hours and a threefold excess of triethylphosphoniumsulfide [41].



The diindium(4) derivative **3** is thermally less stable than **2** [14], and decomposition is observed in boiling toluene with the precipitation of elemental indium and without the formation of the In–S–In product **25**. We succeeded in synthesizing **25**

by the reaction of **3** with propylene sulfide, which yields **25** after three hours at room temperature in over 90% yield (Eq. (10)) [44].



Some spectroscopic characteristics of all compounds are listed in Table 1. The carbon and hydrogen atoms in α position to aluminium, gallium or indium show a significant shift to lower field with increasing mass of the bridging atom. The only exception is observed with the α carbon atoms of the Al–S–Al and Al–Se–Al derivatives **19** and **20**. The IR spectra are very similar and allow the assignment of the element–chalcogen stretching vibrations (Table 1), as far as they are observable with conventional IR techniques; they exhibit the expected dependence on the mass of the chalcogen atoms.

All derivatives **19** to **27** are monomeric both in solution and in the solid state. Table 2 summarizes some important crystal structure data of these compounds, a corresponding methylene bridged dialuminium derivative [46] is included as well as the product of the insertion of an oxygen atom (**28**) [45], which will be discussed below. Most of the insertion products of the heavier chalcogens and the Al–CH₂–Al compound crystallize isotypically in the orthorhombic space group Pcca

Table 1

Selected NMR (ppm) and IR spectroscopic data (cm^{−1}) of chalcogen bridged dialuminium, digallium and diindium derivatives (R₂E–X–ER₂; R = CH(SiMe₃)₂, E = Al, Ga or In, X = chalcogen)

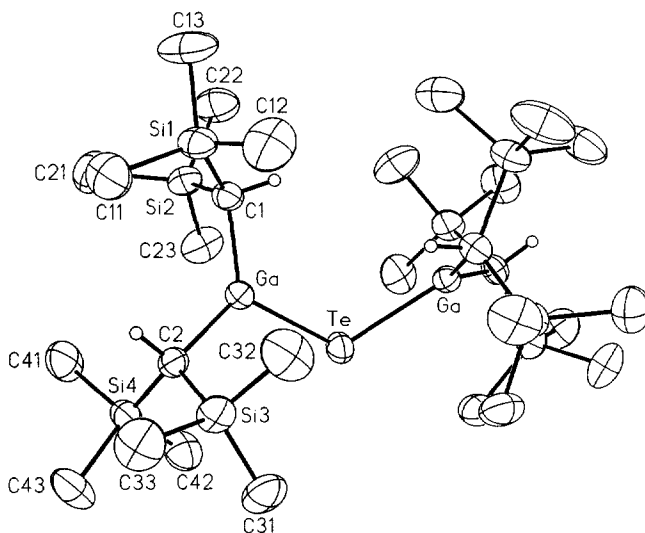
E–X–E	$\delta(^1\text{H})$ E–C–H	$\delta(^{13}\text{C})$ E–C	$\nu\text{E–C}$	$\nu\text{E–X}$	Lit.
Al–O–Al 28	−0.54	9.0	534,500	—	[45]
Al–S–Al 19	−0.16	16.6	532,510	470	[40]
Al–Se–Al 20	−0.01	14.6	530,500	394	[41]
Al–Te–Al 21	0.22	17.3	529,492	374	[42]
Ga–S–Ga 22	0.60	22.1	519,498	413	[41]
Ga–Se–Ga 23	0.77	23.7	517,496	280	[41]
Ga–Te–Ga 24	1.05	26.4	513,490	—	[43]
In–S–In 25	0.63	25.2	496,480	370	[44]
In–Se–In 26	0.75	26.2	494,478	—	[44]
In–Te–In 27	0.95	27.5	492,476	—	[44]

Table 2

Comparison of important structural parameters of bridged dialuminium, digallium and diindium compounds ($R_2E-X-ER_2$; $R = CH(SiMe_3)_2$, $E = Al, Ga$ and In , $X = \text{chalcogen or methylene}$)

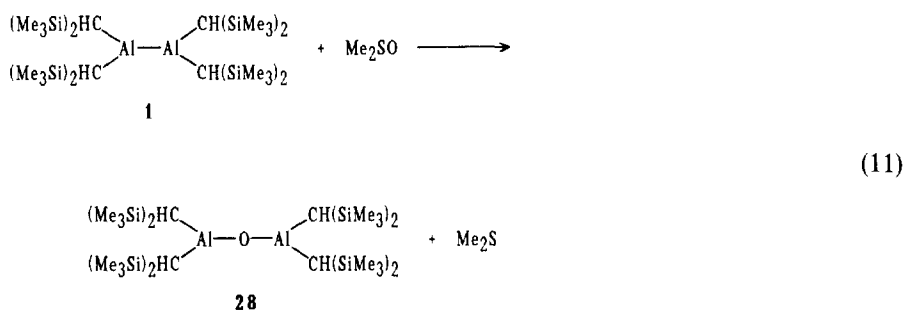
	E–X (pm)	E–X–E (deg)	Lit.
Al–CH ₂ –Al	193.8(1)	129.6(2)	[46]
Al–O–Al 28	168.77(4)	180.0	[45]
Al–S–Al 19	218.7(4)	117.5(3)	[40]
Al–Se–Al 20	231.9(1)	114.71(6)	[41]
Al–Te–Al 21	254.9(1)	110.40(6)	[42]
Ga–S–Ga 22	221.97(7)	117.04(5)	[41]
Ga–Se–Ga 23	234.39(5)	113.45(3)	[41]
Ga–Te–Ga 24	255.21(4)	109.82(2)	[43]
In–S–In 26	239.6(3)	114.6(2)	[44]
In–Se–In 27	251.87(5)	109.96(3)	[44]
In–Te–In 28	271.7(1)	105.42(2)	[44]

with the bridging atom located on a twofold crystallographic rotation axis (Fig. 3). The In–Te–In derivative exhibits another space group ($C2/c$), but the molecular structure is almost indistinguishable from that of the other chalcogenides, while **25** (In–S–In) has a deviating molecular conformation (see below). All compounds show a bent E–X–E group with the most acute angles at the tellurium atoms. This is caused by the different strength of the steric repulsion between the bulky substituents, which is stronger in the Al–CH₂–Al derivative with very short Al–C distances and weaker in the tellurium bridged derivatives with long element–tellurium bonds. The E–X bond lengths are among the shortest found in literature. While the Ga–X bonds



differ only slightly from the values calculated from the covalent radii, the In–X and Al–X bonds are shortened on average by 6 and 15 pm, respectively. This clearly resembles the electronegativity trend with gallium as the most electronegative and aluminium the most electropositive element. Thus, the shortening is probably not caused by π interaction between the chalcogen lone pairs and empty p orbitals at Al, Ga or In, but by charge separation and electrostatic E–X attraction. All molecules show a staggered conformation of the ER_2 units to minimize steric repulsion between the bulky substituents, only the In–S–In derivative is flattened with an angle of 41.7° between the normals of the InC_2 planes.

The insertion of an oxygen atom into the Al–Al bond does not occur in the reaction of **1** with R_3PO derivatives. We successfully used trimethylamine *N*-oxide and *N*-sulfinylaniline as oxygen donors or preferentially dimethyl sulfoxide (DMSO) due to its easy handling (Eq. (11)) [45]. The crystals of the dialuminoxane **28** obtained include 10 to 20% of the μ -hydroxo compound $[\text{R}_2\text{Al}(\text{OH})]_{2,3}$ **31**, which could not be removed by repeated recrystallization. After many unsuccessful attempts to fractionate the mixture or to synthesize **28** on another route [45] pure **28** was obtained by the treatment of the raw product with isobutyllithium to trap the hydroxide; we will discuss this reaction below.



The crystal structure of **28** (Fig. 4) reveals a very short Al–O bond length of 168.77(4) pm, a linear Al–O–Al bridge and a plane molecular center (Al_2OC_4) [45]. The methine protons in the ^1H NMR spectra resonate far upfield ($\delta = -0.54$ ppm) from the corresponding protons of **1** ($\delta = 0.36$ ppm) and lie between the values of threefold ($\delta = -0.20$ to -0.45 ppm) and fourfold ($\delta < -0.55$ ppm) coordinated bis(trimethylsilyl)methylaluminium(III) compounds. Also, the resonance of the carbon atom ($\delta = 9.0$ ppm) is at higher field than usually observed in compounds with tricoordinated Al atoms (Table 1). These data correspond to an increase of charge density on the Al atoms similar to amino or alkoxy boranes and possibly verify a π interaction between oxygen lone pairs and the empty p orbitals at the metal atoms [45].

Dialuminoxane **28** forms two adducts with one or two molecules of trimethylamine *N*-oxide (**29** and **30**) [47], which in contrast to the linear Al–O–Al moiety in **28** and despite an increased steric stress show bent Al–O–Al groups with angles of 162.3 and 161.4° , respectively. The Al–O bond lengths amount to 174 pm on average to

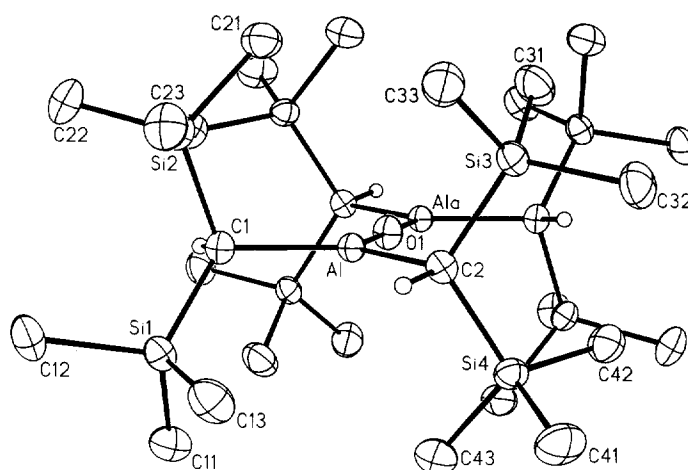
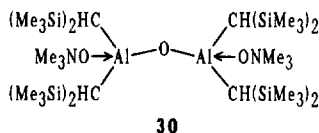
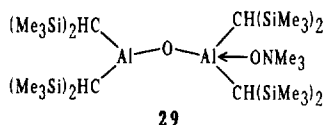


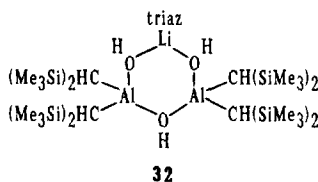
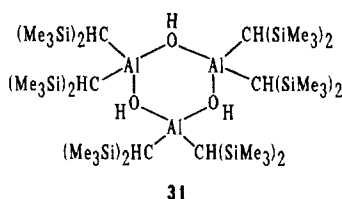
Fig. 4. Molecular structure of **28** ($R_2Al-O-AlR_2$) [45].

the tetracoordinated Al atoms, while to the coordinatively unsaturated Al atom in **29** a significantly shorter bond (168.7(4) pm) is observed [47].



The μ -hydroxo aluminium derivative **31** could be synthesized in an almost quantitative yield by the reaction of **1** with DMSO after the addition of a stoichiometric amount of water [48]. Although we did not succeed in growing single crystals to determine its crystal structure, pure **31** seems to be a trimer in the solid state on the basis of mass spectrometric results; a similar trimeric structure has been detected for $[(Me_3C)_2AlOH]_3$ [49].

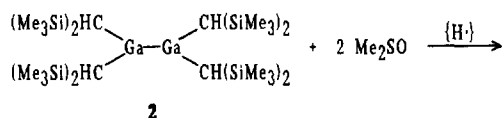
The impurity of **31** in the dialuminoxane **28** could be removed by treatment of the reaction mixture (Eq. (11)) with isobutyllithium. As shown by IR spectroscopy, the expected deprotonation did, however, not occur. In order to clarify the reaction mechanism we treated **31** with the lithium base and isolated the crystalline compound **32** in 84% yield, in which one dialkyl aluminium fragment of the six-membered heterocycle of **31** is replaced by a Li(triazinane) group [48]. Further products could not be identified, so that the reaction could not completely be elucidated. Thus, not



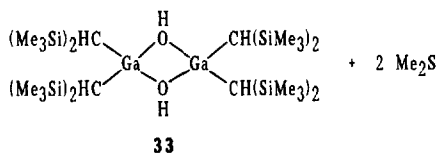
(triaz = N,N',N''-trimethyl triazinan)

a deprotonation, but a exchange reaction is initiated by the addition of the lithium base. Presumably, the acidity of the OH groups is strongly reduced by the coordination to the electropositive Al atoms.

The complete reaction of digallane(4) **2** with DMSO requires at least a twofold excess of DMSO and a long reaction time of six days in boiling toluene (Eq. (12)) [48]. We observe the quantitative formation of tetraalkyldi(μ -hydroxo)digallium **33** without further NMR spectroscopically detectable impurities. In contrast to the corresponding Al derivative **31** we found a dimeric formula unit by FD mass spectrometry, the cryoscopic determination of the molar mass in benzene and a crystal structure determination. The differing behavior of **1** and **2** on treatment with DMSO shows that the hydroxo derivatives are probably not formed by water impurities in DMSO, but by the reaction of radical intermediates with solvent molecules.



(12)

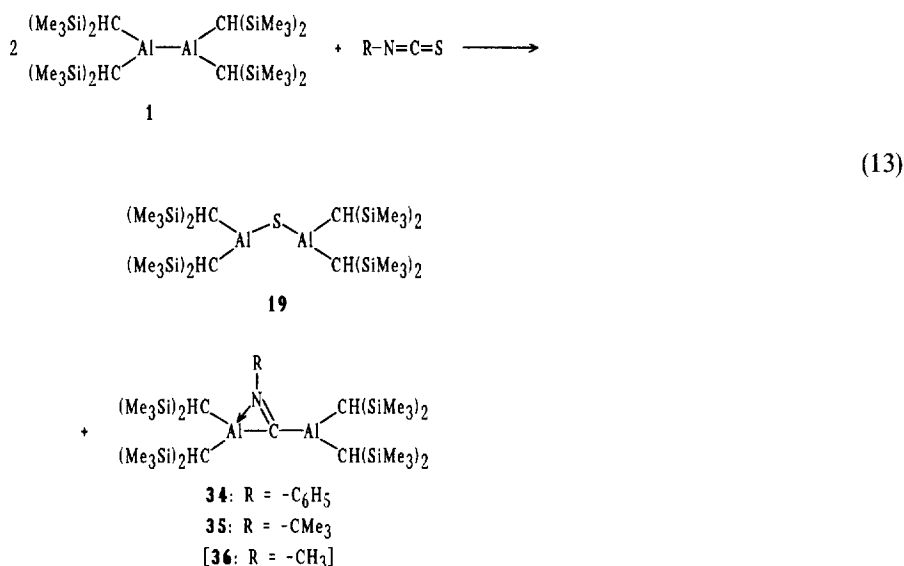


Up to now we have not succeeded in synthesizing an In–O–In derivative by the

reaction of diindane(4) **3** and DMSO. Due to its low thermal stability **3** decomposes before the insertion of an oxygen atom occurs.

5.2. Insertion reactions with isothiocyanates and isonitriles

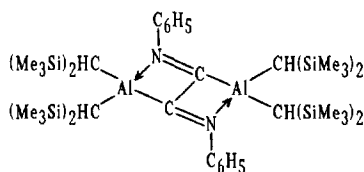
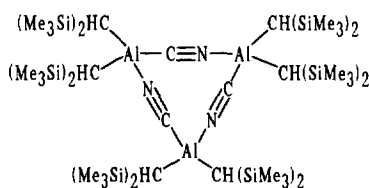
Dialane(4) **1** and phenyl or *tert*-butyl isothiocyanate react completely in less than one hour to yield two compounds, which were separated by recrystallization. The most readily soluble product of both reactions is the Al–S–Al derivative (**19**), while the second product is formed by the insertion of the remaining isocyanide (Eq. (13)) [50]. Thus, independent of the excess of isothiocyanate, a complete molecule R–NCS is not inserted into the element–element bond. Methyl isothiocyanate yields quantitatively the methylisonitrile insertion product under similar conditions without traces of the Al–S–Al compound [51]; elemental sulfur is probably formed as a by-product, which we were, however, not able to detect.



Compounds **34** and **36** show significant differences in some structural parameters [50,51]. The isocyanide carbon atom is inserted into the Al–Al bond in each compound, and three-membered AlCN heterocycles result from the interaction of the nitrogen lone pair with one Al atom. While in **34** (R = phenyl) the C–N bond length (130.6(5) pm) is only slightly lengthened compared to the standard value of a C–N double bond (128 pm), a very short C–N distance (123.9(8) pm) is found in **36** (R = methyl), which is intermediate in length between a double and a triple bond (116 pm). The Al–N bond (186.4(5) pm) in **34** is short compared to **36** (194.8(8) pm) or to Al–N “dative” bonds as defined by Haaland [52], which indicates a stronger Al–N interaction in the phenyl derivative. The different strength of the Al–N bonds in **34** and **36** is also evident from the NMR spectroscopic results: In **34** as well as in **35** we

observe the methine protons with strongly differing chemical shifts of -0.1 and -1.0 ppm, characteristic for tri- and tetracoordinated Al atoms. These signals are very close together in the methyl derivative **36** (-0.41 and -0.49 ppm). The methine resonances are only slightly changed on heating samples up to 100°C in D_8 -toluene, so a fast exchange of the nitrogen atom between both Al atoms can be excluded. One bis(trimethylsilyl)methyl resonance shows a splitting at low temperature, which must be interpreted in terms of a steric hindrance of the free rotation around the Al–C bond to the tricoordinated Al atom and is caused by the arrangement of the *N*-alkyl or *N*-aryl groups between the $\text{CH}(\text{SiMe}_3)_2$ substituents of that Al atom. Accordingly, the rotation barrier strongly depends on the size of the group at nitrogen, and the smallest barrier is observed with $\text{R}=\text{Me}$ (**36**), the largest with $\text{R}=\text{CMe}_3$ (**35**).

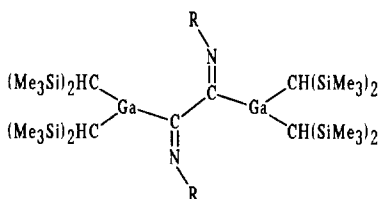
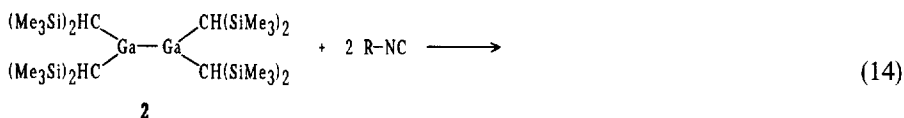
The bright yellow products **34** and **35** are also formed by the reaction of **1** with phenyl or *tert*-butyl isonitrile. While the *tert*-butyl product **35** is obtained in more than 80% yield, a dark red compound (**37**) crystallizes from the reaction mixtures with $\text{R}=\text{phenyl}$ as the less soluble component, before **34** is isolated in about 50% yield [50]. The red compound **37** can be synthesized by the reaction of **1** with phenyl isocyanide in a molar ratio of 1 to 2 [50]. It exhibits two isonitrile molecules inserted into the Al–Al bond with the formation of a carbon–carbon bond and two anellated four-membered AlC_2N heterocycles. The C–C (149.2(3) pm) and C=N (131.0(2) pm) bond lengths correspond to standard values, and the Al–N (204.0(2) pm) and Al–C (207.5(2) pm) bonds are substantially lengthened in comparison to the three-membered heterocycle in **34**.

**37****38**

A similar by-product has not been observed with *tert*-butyl isonitrile, due to the higher steric shielding by the *tert*-butyl group. When dialane(4) **1** is treated with *tert*-butyl isonitrile in the molar ratio of 1 to 2, three days at room temperature is required for the complete consumption of the monoinsertion product **35**. A mixture of several unknown products results, from which we isolated a colorless, crystalline compound (**38**) in a yield of only 26% [53]. A dialkylaluminium cyanide formed, which is a

trimer in the solid state with a nine-membered $\text{Al}_3\text{C}_3\text{N}_3$ heterocycle. **38** is the first of the long known dialkylaluminium cyanides to be structurally characterized, and similar compounds with smaller substituents show tetrameric or octameric molar masses in solution or mass spectra [54]. **38** is a dimer in benzene solution probably with both C atoms bound to one and both nitrogen atoms bound to the second Al atom as shown by NMR spectroscopy. Further products could not be isolated.

The insertion of only one isocyanide molecule into the Ga–Ga bond of **2** similar to dialane(4) **1** has not yet been realized, but two isonitriles are inserted in all reactions with the formation of a C–C single bond (Eq. (14)) [55]. We hoped to realize a monoinsertion by the treatment with sterically more shielded isocyanides like 2,6-dimethylphenyl isonitrile, but they do not react with **2** at all over a period of several weeks or in boiling solvents. The *tert*-butyl product **39** is yellow, the other products **40** to **43** exhibit an orange-red to deep red color. The SiMe_3 protons of the aryl products show only one sharp singlet in the NMR spectra in contrast to the Al compound **37**, and a splitting is observed only at low temperature; the *tert*-butyl derivative **39** exhibits two resonances at room temperature. The signals of the methine protons are shifted to higher field (0.1 to 0.3 ppm) compared to digallane(4) **2** (1.1 ppm), but not as far as is usually observed in compounds with tetracoordinated Ga atoms (< -0.1 ppm). The weak coordinative interaction between gallium and nitrogen with an easy unrestricted rotation around the inner Ga–C bonds, is also verified by the X-ray structure analyses of **39**, **40** and **43** [55]. The structures are similar to the aluminium derivative **37** with the very important exception, that we observe long Ga–N distances of 248.0(2) (**39**), 233.6(3) (**40**) and 226.7(3) (**43**) pm, which are all longer than usually observed in amino adducts with alkylgallium derivatives.



R = $-\text{CMe}_3$: **39**

R = $-\text{C}_6\text{H}_4(\text{p-O-Me})$: **42**

R = $-\text{C}_6\text{H}_5$: **40**

R = $-\text{C}_6\text{H}_4(\text{o-O-Me})$: **43**

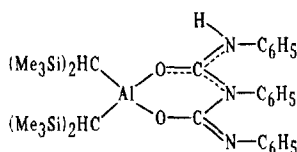
R = $-\text{C}_6\text{H}_4(\text{o-Me})$: **41**

Digallane(4) **2** does not react with phenyl or *tert*-butyl isothiocyanates, even in the presence of a large excess or in boiling solvents [55]. The diindium(4) derivative

3 has not yet been investigated with regard to its reactivity against thiocyanates or isonitriles.

5.3. Phenyl isocyanate

We used phenyl isocyanate to avoid the cleavage of the carbon–chalcogen double bond as observed in the reactions of isothiocyanates with **1** and to insert a complete molecule into the element–element bond. But no reaction occurs with stoichiometric amounts of the isocyanate, and **1** must be dissolved in a large excess of pure phenyl isocyanate with a long reaction time of more than four days. A mixture of many unknown products was obtained from which a bis(trimethylsilyl)methylaluminium compound was isolated by recrystallization in very low yield and characterized by a crystal structure determination (**44**) [51]. It seems, that hard oxygen bases like alcoholates (Section 2.2) or cyanates preferentially give a fragmentation of the dialane(4) **1**, while a great variety of dialuminium derivatives is obtained with soft Lewis-bases.



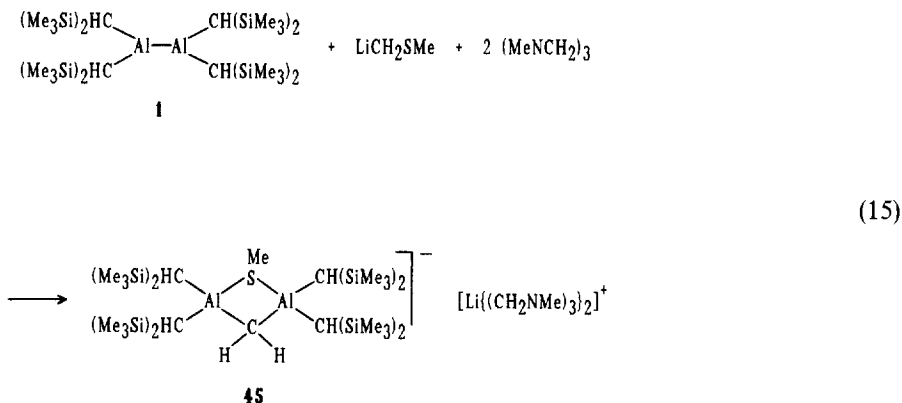
44

The aluminium atom in **44** is bound to two alkyl substituents and coordinated by a chelating ligand, which is formed by the trimerization of phenyl isocyanate with the loss of one CO group and addition of one hydrogen atom from the isocyanate solvent or from traces of water. A very interesting bonding situation results with a delocalized π bond involving four atoms (CN_2O) at one carbon atom of the heterocycle. The bond between the nitrogen atom of the ring and the second carbon atom is a normal C–N single bond (145.1(4) pm), while the exocyclic C–N bond at this carbon atom corresponds to a localized double bond (126.2 pm). Compound **44** could be synthesized in a yield of 66% by reaction of dialkylaluminiumchloride with the Li-salt of the ligand [51]. Digallane(4) **2** does not react with isocyanates.

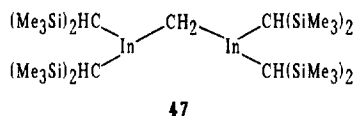
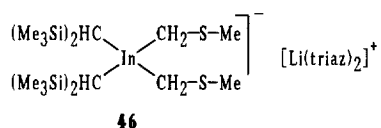
5.4. Insertion of carbene

The insertion of carbenes CR_2 into the element–element bonds of compounds **1** to **3** is of particular interest, because such reactions would open up an easy route for the synthesis of 1,1-dialuminium, digallium and diindium carbon compounds, which potentially could react as chelating Lewis-acids. As a precursor for the formation of the carben CH_2 we used the deprotonated dimethyl sulfide LiCH_2SMe [56]. The dialuminium(4) derivative **1** reacts with LiCH_2SMe in the presence of the chelating triazinane ligand to give a colorless compound (**45**) in about 50% yield, in which a CH_2 group is inserted between both Al atoms (Eq. (15)) [57]. The methylene bridged dialuminium group coordinates the remaining thiometh-

anolate fragment to form a four-membered Al_2CS heterocycle, which is strongly folded across the $\text{C}\cdots\text{S}$ axis by 30.2° . Recently, we synthesized the free dialuminium derivative by the reaction of $\text{Cl}_2\text{Al}-\text{CH}_2-\text{AlCl}_2$ with $\text{LiCH}(\text{SiMe}_3)_2$ [46], which shows short bonds between Al and the bridging carbon atom (193.8(1) pm); the terminal Al–C bond lengths amount to 195.7(2) pm. All Al–C bonds in **45** are considerably lengthened to 204.1 pm on average.



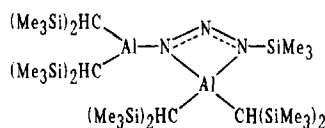
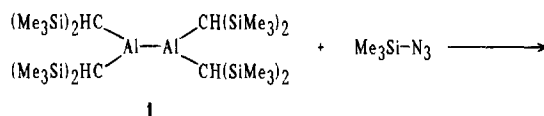
The reactions of digallane(4) **2** and diindane(4) **3** with LiCH_2SMe are much more complicated and have not yet been elucidated completely. At least two compounds are formed in the reaction of **3**, which were spectroscopically identified as the tetraalkyl indate **46** and the neutral methylene bridged diindium derivative **47** [57].



5.5. Insertion of trimethylsilyl azide

Trimethylsilyl azide and dialane(4) **1** react completely within 30 minutes at room temperature to give **48** in over 80% yield (Eq. (16)) [58], in which the azido group is inserted into the Al–Al bond with its terminal nitrogen atom. The nitrogen atom bound to the trimethylsilyl group is coordinated to one Al atom, while the second Al atom remains coordinatively unsaturated. Thus, compound **48** can be described

as a dialkylaluminum cation R_2Al^+ coordinated by a chelating triazenide anion $[R_2Al-N-N-N-SiMe_3]^-$ with a delocalized π bond. The N–N bond lengths (132.0 pm on average) correspond to a N–N bond order of 1.5. Compound **48** decomposes on heating to 60 °C with the liberation of N_2 ; we have not yet been able to isolate a product of this reaction, which possibly would open up a route to alkyl dialuminum imides.



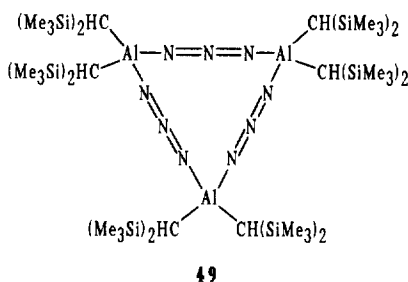
(16)

An excess of trimethylsilyl azide does not further react with the monoinsertion product **48** at room temperature and in the dark. But on irradiation with the laboratory lights or a weak UV source through the glass wall of the reaction vessel over a period of 10 minutes a further product is formed (**49**), which was identified as a dialkylaluminum azide by IR spectroscopy (the stretching vibrations of a N₃ group) and a crystal structure determination [58]. Hexamethyldisilane could be detected by gas chromatography as a by-product. **49** is a trimer in the solid state with a twelve-membered Al₃N₉ heterocycle. The head-to-tail bridging by the azido group in **49** might be due to steric reasons and seems to be quite unusual, because a 1,1-bridging by only one nitrogen atom was deviated from the IR spectra of dimethyl or diethyl aluminium azide [59] and has been detected by crystal structure determinations in [(Me₃Al)₂N₃]⁻ [60] and Me₂GaN₃ [61]. Compound **49** decomposes slowly in solution with precipitation of an insoluble product, which still shows N₃ stretching vibrations in the IR spectrum, but could not be further characterized. Complete decomposition is observed when the mixture of **48** and trimethylsilyl azide is irradiated by a mercury lamp in a quartz apparatus within only a few seconds. Besides the synthesis given in Eq. 24, compound **49** is easily obtained in a high yield by the reaction of the corresponding dialkylaluminium chloride with trimethylsilyl azide [58].

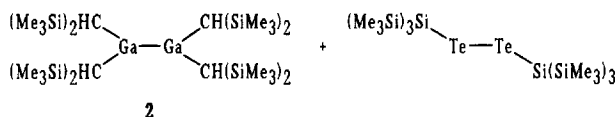
According to its reduced reactivity compared to the dialuminium(4) compound **1** digallane(4) **2** does not react with trimethylsilyl azide even under drastic reaction conditions.

6. Metathesis reaction

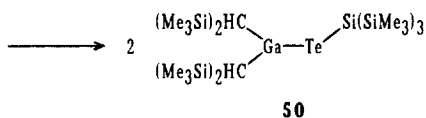
Only one reaction of this very important type has been completely clarified. When digallane(4) **2** is treated in toluene at 100 °C with the sterically highly shielded



ditelluride $\text{RTe}-\text{TeR}$ ($\text{R} = \text{Si}(\text{SiMe}_3)_3$) [62], a gallium telluride (**50**) is formed in four days, which is a monomer in solution and in the solid state (Eq. (17)) [63]. A hindered rotation is observed at low temperature in the ^1H , ^{13}C and ^{29}Si NMR spectra for the $\text{CH}(\text{SiMe}_3)_2$ groups, while the resonances of the $\text{Si}(\text{SiMe}_3)_3$ group remain unchanged. The short Ga–Te bond length (253.5(1) pm) and particularly the planar molecular conformation of the inner atoms C_2GaTeSi might be interpreted in terms of some π interaction between the electronically unsaturated Ga atom and a tellurium lone pair.



(17)

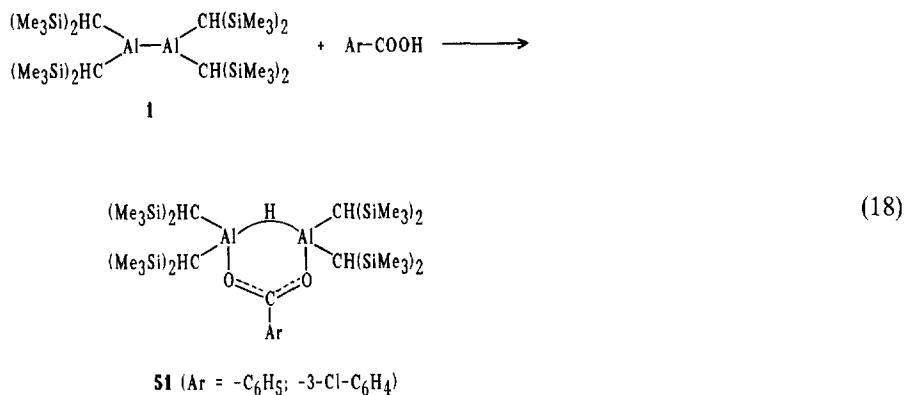


7. Ligand exchange reactions – reactions with carboxylic acids

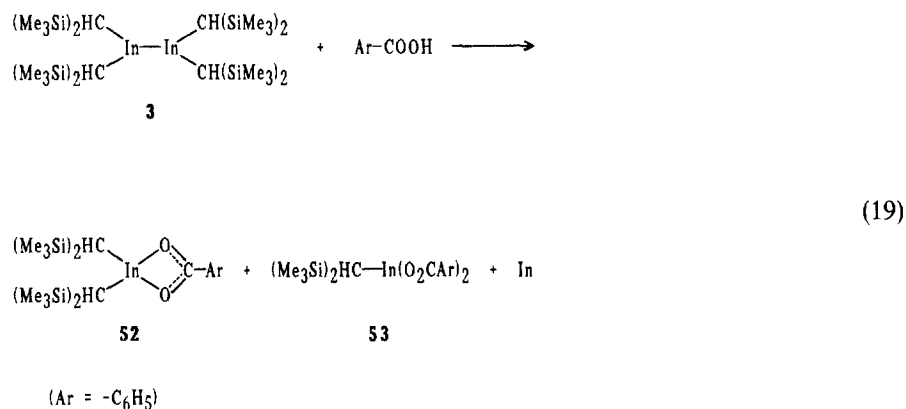
The replacement of the alkyl substituents of the dielement compounds **1** to **3** by the treatment with acidic reagents and release of alkane without breaking the element–element bond would open up an easy route to fascinating new compounds. As acidic components we first of all used carboxylic acids, which we hoped would prevent a disproportionation reaction by a chelating coordination of the aluminium, gallium or indium atoms.

Dialane(4) **1** does, however, not react with benzoic acid by the formation of bis(trimethylsilyl)methane, but by an insertion into the O–H bond (Eq. (18)). An organoaluminium hydride (**51**) is formed as the main product, in which both Al atoms are bridged by a hydrido and a carboxylato anion [64]. Bis(trimethylsilyl)methyl-di(carboxylato)aluminium was be isolated as a by-product

from further acidolysis. **51** is an important compound, which gives insight into the first step of the hydrolysis of derivatives with aluminium in an unusual low oxidation state including elemental aluminium. It seems, that the aluminium atom first inserts into the O–H bond by the formation of an Al–H group, which subsequently is further hydrolyzed by release of elemental hydrogen.

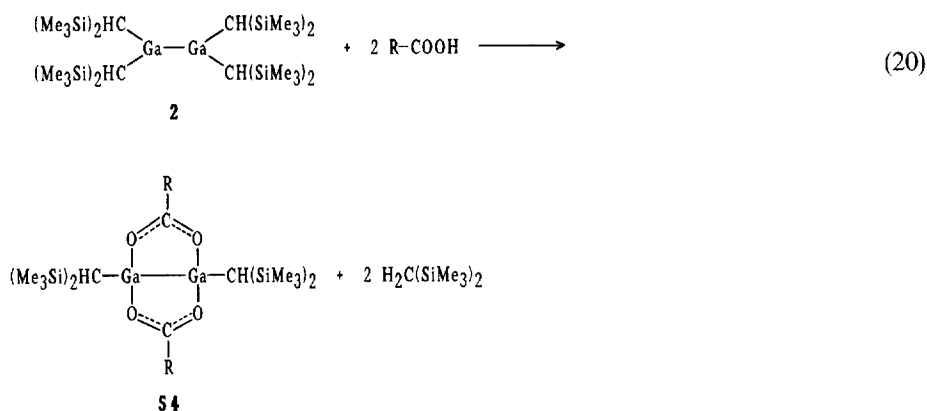


When the diindium(4) compound **3** is treated with carboxylic acids, precipitation of elemental indium is observed, and a product similar to the Al–H derivatives **51** could not be detected. The divergent behavior of the dialuminium and diindium derivatives might be due to the instability of the In–H bond, which usually leads to the spontaneous release of hydrogen and disproportionation. Two products are isolated (Eq. (19)) [64] with one (**52**) or two (**53**) carboxylato groups bound to indium, which can both be described as products of the acidolysis of the corresponding trialkylindium derivative with benzoic acid, and, indeed, can both be synthesized best by such a route [64].



While only minor amounts of bis(trimethylsilyl)methane are formed on treatment of dialane(4) **1** and diindane(4) **3** with carboxylic acids, the alkane is quantitatively

formed with digallane(4) **2**. But the gallium derivative is only completely consumed when the starting compounds are applied in a stoichiometric ratio of 1 (**2**) to 2 (acid), and two alkane molecules are released each formula unit of **2** (Eq. (20)). As shown by a crystal structure determination of the 4-bromo-phenyl derivative **54**, the Ga–Ga bond remains uncleaved and a single product forms with terminal bis(trimethylsilyl)methyl substituents and two carboxylato groups bridging the Ga–Ga bond (Fig. 5). The Ga–Ga bond length is shortened to 238.5(2) pm compared to 254.1(1) pm in **2** [65]. Remarkably, the angle between both Ga₂O₂C heterocycles amounts to almost 90° and the Ga–Ga–C angle approaches linearity (158.2° on average). In contrast to the intensively yellow tetraalkyldigallium(4) derivative **2** the carboxylato digallium compounds are colorless and the UV/vis absorption at 370 nm, characteristic of the element–element bonds, is not observed. This difference results from the enhancement of the coordination number at the gallium atoms and verifies that the color of the tetraalkyl dielement compounds **1** to **3** could be explained by a transition involving the π orbital of the Al–Al, Ga–Ga or In–In bond.



(R = -CMe₃, -C₆H₅, -4-Br-C₆H₄, -3,5-Me₂C₆H₃)

8. Conclusion

The first stable and fully characterized organoelement derivatives with an Al–Al, a Ga–Ga or an In–In bond were published by our group about nine years ago. In that time these new type of compounds have proved to open up a quite new and fascinating field of third main group chemistry. A lot of further derivatives are synthesized now by other groups, and a great number of different and unprecedented reactions have been observed as described in this article. But we are far from being at an end, and many further reactions have to be done and problems to be solved to gain a complete insight into the chemical properties of these compounds. Some important and up to now unrealized ideas are, for instance, the formation of adducts

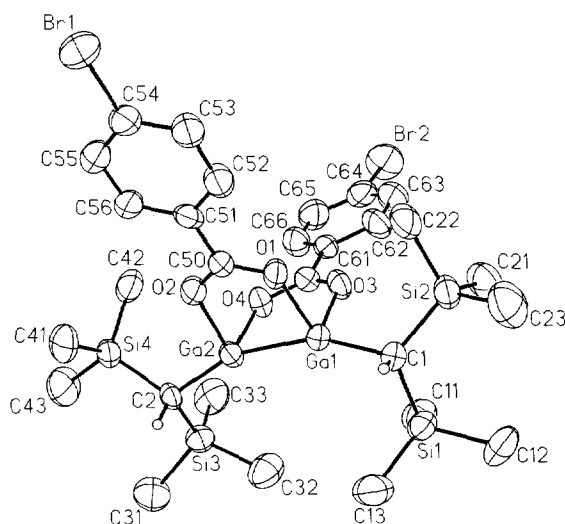


Fig. 5. Molecular structure of **54** $\{\text{Ga}_2\text{R}_2(\mu\text{-O}_2\text{CR}')_2\}$; $\text{R}' = \text{-4-bromo-phenyl}\}$ [65].

with two Lewis-basic centers, which would be isoelectronic to disilicon derivatives, the transfer of two electrons with the isolation of stable products, the insertion of transition metal fragments etc. Furthermore, some reactions mark only the beginning of interesting and extensive research activities like metathesis or ligand exchange, which are intensively investigated now in our group.

The reactions described allow some preliminary conclusions on the reactivity trends: Dialane(4) **1** is the most reactive of the dielement derivatives giving much better results with soft than with hard Lewis bases. The formation of adducts or the deprotonation have only been observed with **1**. Similarly, many insertion reactions are restricted to the Al derivative like the reactions with trimethylsilyl azide or isocyanates, while others like those with isonitriles give different products with the heavier homologues, which could however, be explained by their lower reactivity. Only one electron can be transferred into the π orbital of the element–element bonds, and the radical anions become less stable with the heavier elements but were not isolated with indium at all [66]. This is paralleled by the lower stability of compounds with double bonds between the heavier elements of the fourth and fifth main group. The Ga–Ga bond is the most stable of the element–element bonds discussed here, and is, in contrast to the Al or In analog, retained by the treatment with acidic reagents, which lead to very interesting substituent exchange reactions. In some respects, the chemistry of the dialuminium(4), digallium(4) and diindium(4) derivatives resembles that of unsaturated compounds of the fourth main-group elements like disilenes [67] and many comparable insertion reactions of e.g. carbenes or chalcogen atoms into the π bond are described. However, the element–element bond is completely opened with the Al, Ga and In derivatives, while the bond order is reduced in the case of the disilenes, and heterocycles still containing a Si–Si bond are formed.

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