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Azides of the heavier Group 13 elements

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Dedicated to Professor Peter Paetzold

Contents

Abstract

The current knowledge about azides of the heavier Group 13 elements is reviewed. Only *neutral* compounds of the general formula $R_{3-x}M(N_3)_x(D)_y$ and MN_3 (M = Al, Ga, In, Tl; R = organic or inorganic substituent; D = neutral donor; $y = 0$–3) are taken into account. The syntheses of Group 13 azides of the formal oxidation number +III can either be achieved by salt metathesis, σ bond metathesis, or substitution reactions. The synthesis, structures, properties, and applications of mono-, di-, and triazides including inter- and intramolecular donor-stabilized compounds are discussed.

Keywords: Azides; Group 13 elements; Chemical vapor deposition; Nitrides

1. Introduction

The chemistry of covalent azides can be traced back to the synthesis of HN_3 by Curtius in 1890 [1]. Since then, chemists of several generations have been attracted to the field of covalent azides. Still today, the preparation of a new azide is a challenge for a synthetic chemist, because one never knows exactly how dangerous the target compound is. Furthermore, unwanted azide byproducts might be more hazardous than the wanted product itself and can initiate violent explosions.

The first organometallic azides Ph_2BiN_3, $PhBi(N_3)_2$, and $PhTl(N_3)_2$ were reported by Challenger and Richards in 1934 [2], with the thallium compound being the oldest example of the kind of compounds reviewed here. This article compiles the knowledge about azides of the heavier Group 13 elements. Only *neutral* compounds of the general formula $R_{3-x}M(N_3)_x(D)_y$ and MN_3 (M = Al, Ga, In, Tl; R = organic or inorganic substituent; D = neutral donor; $y = 0$–3) are taken into account. Salt-like compounds with anions containing the Group 13 element and azido groups, e.g. $[M(N_3)_4]^-$, are not included.

The importance of the nitrides AlN, GaN, InN and $Al_xGa_yIn_{1-x-y}N$ for micro- and opto-electronic de-

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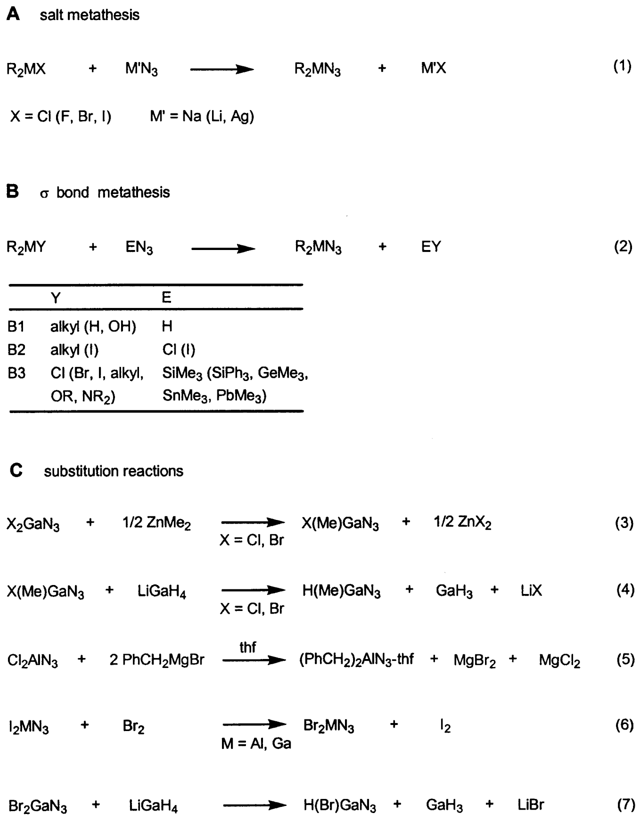
vices [3–9] have pushed the Group 13 azide chemistry a large step forward within the last few years. New azides were synthesized to be used as single-source precursors for the chemical vapor deposition of nitrides (CVD process). A single-source precursor already contains the elements of interest in a single molecule, often directly bound together. The azide group seems to be the optimal build-in nitrogen source and nitrides were successfully deposited without additional nitrogen sources (see Section 6).

2. Monoazides

2.1. Syntheses of monoazides of the types R_2MN_3 and $R(R')MN_3$

The syntheses of Group 13 azides of the formal oxidation number +III can either be achieved by salt metathesis (A), σ bond metathesis (B), or substitution reactions (C) (Scheme 1). Even though the methods are exemplified for the synthesis of monoazido compounds, they can be used for the synthesis of di- and triazides as well. The majority of known azides are accessible through methods A and B; substitution reactions (method C) are only applicable in special cases. Scheme 1 gives an overview of reactants; the less often applied compounds are given in parentheses.



Scheme 1. General synthetic methods for Group 13 azides (less often applied starting compounds are given in parentheses).

Table 1 compiles data of known symmetrical substituted monoazides of the empirical formula R_2MN_3 ($M = Al–Tl$; R = H, alkyl, aryl, amino, and halogen).

Azidodiethylalane, Et_2AlN_3, the first published dialkylelementazide, was synthesized by Prince and Weiss from Et_2AlCl and NaN_3 in benzene (method A) [18]. Independent of their work, Müller and Dehnicke reacted ClN_3 with Et_3Al in a 1:1 ratio (method B2) to obtain Et_2AlN_3 [19]. Several synthetic methods can be used for the simple azidodialkyl compounds. This might be illustrated for azidodimethylalane, which was prepared for the first time from Me_2AlI and Me_3SiN_3 or Ph_3SiN_3 (method B3) [10]. In the case of the commonly used Me_3SiN_3, the vapor pressures of the reaction products Me_2AlN_3 and Me_3SiI are very similar, which prevents the isolation of pure Me_2AlN_3. This difficulty is eliminated by the use of Ph_3SiN_3 resulting in Ph_3SiI as a product with a substantially lower vapor pressure than the targeted aluminum azide. Shortly after, the synthesis of Me_2AlN_3 by the chloroazide method B2 was published [12]. Furthermore, trimethylalane can be reacted either with Me_3SiN_3 (method B3) [11] or with hydrazoic acid, HN_3 (method B1) [13] to give pure azidodimethylalane.

An interesting variation of the silylazide method B3 was recently used for the synthesis of azidoindanes R_2InN_3 ($R = {}^{i}Pr, {}^{t}Bu$) [24]. Stirring of R_3In for 10 min with one equivalent of MeOH yields R_2InOMe, which reacts with one equivalent of Me_3SiN_3 to give the respective azide R_2InN_3 and the siloxane Me_3SiOMe.

The first totally inorganic monoazide Cl_2AlN_3 was synthesized from Cl_3Al and Me_3SiN_3 in 1972 (method B3) [35]. A few years later, Dehnicke and Krüger used IN_3, prepared from NaN_3 and I_2, for the reaction with MI_3 (M = Al, Ga) to obtain the azidodiiodo compounds I_2MN_3 [39]. These azides can be converted to the bromides Br_2MN_3 by the action of Br_2 [39]. Recently, Kouvetakis et al. [36–38] synthesized the dichloro and dibromo gallanes and indanes X_2MN_3 using the azidosilyl method B3 applied for Cl_2AlN_3 by Wiberg et al. [35] before. In the case of the gallanes X_2GaN_3 the intermediate Lewis acid–base adducts $Me_3SiN_3–GaX_3$ (X = Cl, Br) could be isolated and analyzed by single-crystal X-ray analyses [37,40,42]. As expected, the α-nitrogen atom of the azido group coordinates to the gallium atom. Gentle heating of these intermediates afforded X_2GaN_3 and $XSiMe_3$. Respective intermediates were observed by NMR spectroscopy for the synthesis of Me_2AlN_3 from Me_3SiN_3 and Me_3Al and for the synthesis of Me_2GaN_3 from Me_3GeN_3 and Me_3Ga [11].

The preparation of the parent azidogallane H_2GaN_3, which was explored by the Kouvetakis group recently, can be envisioned as a highlight of Group 13 azide

Table 1
Symmetrical substituted azides of the type R_2MN_3 [a]

R	Al	Ga	In	Tl
Me	B3 ($Me_2AlI+Me_3SiN_3$ or Ph_3SiN_3) [10], ($AlMe_3+Me_3SiN_3$) [11]; B2 [12]; B1 [13]	B3 ($Me_3Ga+Me_3GeN_3$) [11]; B1 and B2 [13]; A [14] [b]	B3 ($Me_3In+Me_3SnN_3$) [11]; B1 [15] [b]	B2 and B1 ($Me_2TlOH+HN_3$) [16]; A ($Me_2TlI+AgN_3$) [17] [b]
Et	A [18]; B2 [19]; B2 [20]; A and B1 [c] [21]	B2 [12,22]; A [23]	B2 [12]	B2 [12]
^{i}Pr			B3 ($^iPr_2InOMe+Me_3SiN_3$) [d] [24] [b]	
Bu		A [25,26] [e]	A [f] [26]	A [f] [26]
^{s}Bu		A [25]		
^{t}Bu			B3 ($Me_3SiN_3+{}^tBu_2I$-$InOMe$) [d] [24] [b]	
$(Me_3Si)_2CH$	B3 [g] [27] [b]			
Ar		A (Ar = Mes) [25] [b]		A (Ar: Ph; $Ph_2TlF+NaN_3$) [28]; A (Ar = Ph, *o*-, *m*-, *p*-tolyl) [29]
Cp				A ($Cp_2TlCl+KN_3$) [30]
Ind [h]				A ($Ind_2TlCl+KN_3$) [30]
Me_2N	A [31]	A [32] [b] [31]		
pip [i]	A [33] [a]			
tmp [j]		A [32]		
F	B2 [k] ($Et_2AlF+ClN_3$) [34]			
Cl	B3 [35]	B3 [36,37]	B3 [38]	
Br	C ($I_2AlN_3+Br_2$) [39]	C ($I_2GaN_3+Br_2$) [39]; B3 ($Br_3Ga+Me_3SiN_3$) [40]	B3 ($Br_3In+Me_3SiN_3$) [38]	
I	B2 (AlI_3+IN_3) [39]	B2 (GaI_3+IN_3) [39]		
H		A ($H_2GaCl+LiN_3$) [41]; C ($Br_2GaN_3+LiGaH_4$) [l] [40]		

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses.
[b] Characterized by single-crystal X-ray analysis.
[c] In situ preparation of Et_2AlN_3 for organic synthesis.
[d] In situ preparation of R_2InOMe from R_3In and HOMe.
[e] The authors claim the successful synthesis of Bu_2GaN_3 from a H_2O–pyridine (1:1) solvent mixture. The data of the product do not agree with the ones described in Ref. [25].
[f] See also comment e.
[g] $[(Me_3Si)_2CH]_2AlN_3$ can be synthesized from $[(Me_3Si)_2CH]_4Al_2$ and Me_3SiN_3 with photochemical activation.
[h] Ind = indenyl (C_9H_7).
[i] pipH = piperidine.
[j] tmpH = 2,2,6,6-tetramethylpiperidine.
[k] F_2AlN_3 is only mentioned, but not characterized.
[l] D_2GaN_3 is accessible using $LiGaD_4$.

chemistry [40,41]. This parent compound was synthesized for the first time by a salt metathesis from H_2GaCl and LiN_3 (method A) [41]. However, this method requires high-quality H_2GaCl, a compound which is difficult to synthesize and maintain as a pure substance at ambient temperatures [43]. H_2GaN_3 can be easier

Table 2
Asymmetrical substituted azides of the type $R(R')MN_3$ [a]

Al	Ga
$Me(I)AlN_3$: B3 ($Me_2AlI+Me_3SiN_3$) [10]; $Et(Cl)AlN_3$: B2 [34]; $Me(Cl)AlN_3$ [b]: B3 [44]; $Me(Br)AlN_3$ [b]: C ($Br_2AlN_3+ZnMe_2$) [44]	$H(Cl)GaN_3$ [b]: A ($Cl_2GaH+LiN_3$) [41]; $H(Br)GaN_3$: C ($Br_2GaN_3+LiGaH_4$) [40]; $H(Me)GaN_3$: C ($Me(X)GaN_3+LiGaH_4$; X = Cl, Br) [45]; $Me(Cl)GaN_3$ [b]: C ($Cl_2GaN_3+ZnMe_2$) [45]; $Me(Br)GaN_3$ [b]: C ($Br_2GaN_3+ZnMe_2$) [45]; $Cp^*Ga[(Me_3Si)_2N]GaN_3$ [b]: ($Cp^*Ga+Me_3SiN_3$) [c] [46]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses. Indium and thallium azides of this type are unknown.
[b] Characterized by single-crystal X-ray analysis.
[c] $Cp^* = Me_5C_5$.

prepared via a reduction of Br_2GaN_3 with an excess of $LiGaH_4$ [40]. Attempts to synthesize the parent azidoalane by similar methods were unsuccessful. At best, they resulted in unstable, explosive polymers of the empirical formula H_xAlN_3 [44].

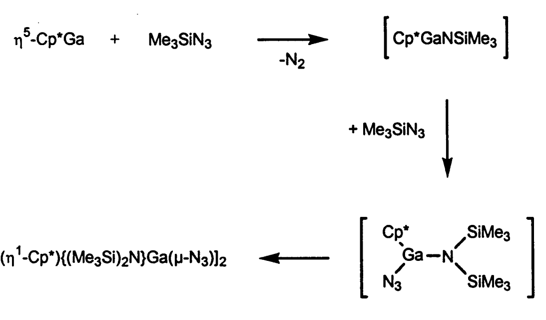
As it can be seen from Table 2, the only asymmetrical substituted monoazides known so far are either alanes or gallanes. The first azide of the type $R(R')MN_3$ have been synthesized by σ bond metathesis B3, i.e. Me_2AlI and Me_3SiN_3 react to give $Me(I)AlN_3$ [10]. A series of new azido gallanes, $H(X)GaN_3$ (X = Cl, Br, Me) and $Me(X)GaN_3$ (X = Cl, Br), have been synthesized either by salt metathesis (Eq. (8)), by substitution reaction with $LiGaH_4$ (Scheme 1, eqs. (4), (7) or with dimethylzinc (Scheme 1, Eq. (3)) [40,41,45]. Similar methods have been used to prepare the aluminum azides $Me(X)AlN_3$ (X = Cl, Br) [44].

$$HGaCl_2 + LiN_3 \longrightarrow H(Cl)GaN_3 + LiCl \qquad (8)$$

The reaction of pentamethylpentadienylgallium, Cp*Ga, with the azides $XylN_3$ (Xyl = 2,6-dimethylphenyl) and Me_3SiN_3 results in two different types of product [46]. The reaction with the organic azide in a 1:1 ratio gives the dimer $(Cp{*}GaNXyl)_2$, the first dimeric iminogallane with the unusually low coordination number three at the gallium atoms. However, trimetylsilylazide reacts in a 2:1 ratio with Cp*Ga resulting in an asymmetrical substituted azidogallane $[(Me_3Si)_2N]Cp{*}GaN_3$ which crystallizes as a dimer. Jutzi et al. interpreted the reaction as depicted in Scheme 2 [46]. The iminogallane $Cp{*}GaNSiMe_3$ is purposely formed during the first step of the reaction sequence, accompanied by the loss of N_2. This intermediate reacts further with one equivalent of Me_3SiN_3 to give the characterized amino(azido)gallane in a yield of 86%.

2.2. *Structures of monoazides of the types R_2MN_3 and $R(R')MN_3$*

All known molecular azides (Tables 1 and 2) are oligomers. The first investigation on the degree of oligomerization was performed on Et_2AlN_3 [19,20]. This azide is shown by cryoscopy to be trimeric in benzene. Vibrational analysis by IR and Raman spectroscopy indicates that azidodiethylalane trimerizes via the α-N atom of the N_3 group to give a planar six-membered ring (Fig. 1B; D_{3h} symmetry). Similar investigations on the azides Me_2MN_3 (M = Al, Ga, Tl) and Et_2MN_3 (M = Ga, In, Tl) [10,12,13,16,22] led to the conclusion that the aluminum and gallium species are trimers, the indium azide is probably a dimer, and the thallium compound is an ionic solid composed of R_2Tl^+ cations and N_3^- anions. The first azidoalane to be characterized by crystallography was $[(Me_3Si)_2HC]_2AlN_3$ [27]. Surprisingly, the compound trimerizes via the γ-N atoms to form non-planar 12-membered rings in the solid-state (Fig. 1C and Fig. 2). This unusual structure might be a consequence of the bulky $(Me_3Si)_2HC$ ligands which prevent oligomerization via the more basic α-N atoms.



Scheme 2. Formation of $\{Cp{*}Ga[(Me_3Si)_2N]GaN_3\}_2$.

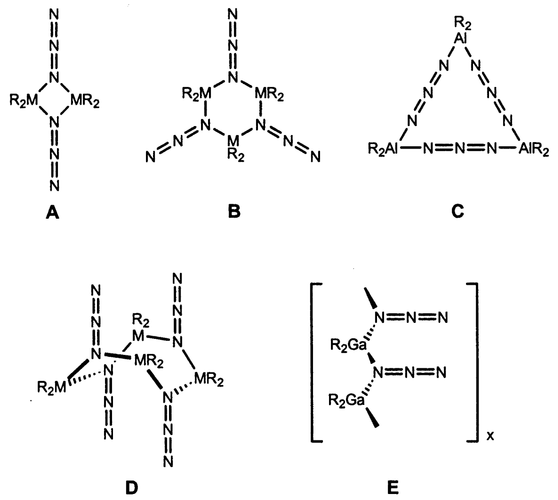


Fig. 1. Structures of monoazides R_2MN_3.

Azidodimethylgallane was the first structurally characterized monoazide R_2MN_3. Single-crystal X-ray determination shows repeating Me_2GaN_3 units linked via

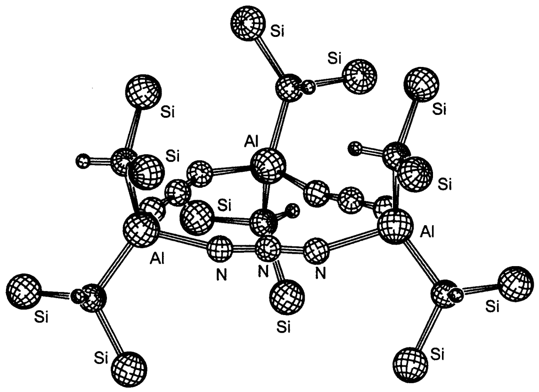


Fig. 2. Molecular structure of $[(Me_3Si)_2HC]_2AlN_3$. SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [27]; methyl groups are omitted for clarity.

α-N atoms to form spirals along the *a*-axis of an orthorhombic unit cell (Fig. 1E) [14]. Mes_2GaN_3 (Mes = 2,4,6-trimethylphenyl) oligomerizes via the α-N atoms to form dimers [25]. In accordance with the solid-state structure, molecular mass determination by cryoscopy has shown that Mes_2GaN_3 dissolves as dimers in benzene [25]. The amino(azido)gallane $(Me_2N)_2GaN_3$ crystallizes as dimers, but in contrast to the mesityl compound Me_2N groups are in bridging positions. These dimeric units are further associated by dative interactions between γ-N atoms of the terminal azido groups and Ga atoms of adjacent four-membered rings (Fig. 1A). Even though the intermolecular Ga–N distances are rather long (343 pm), the gallium geometry is significantly distorted from tetrahedral to trigonal bipyramidal. A comparable linkage of dimers was found for the indium azides $^iPr_2InN_3$ and $^tBu_2InN_3$ [24]. The relatively short $In{-}N_\gamma$ contacts of 266 pm indicate stronger intermolecular bonds in comparison with the gallane $[Me_2N(N_3)Ga(\mu\text{-}NMe_2)]_2$. An even more complex structure was found for Me_2InN_3 in the solid-state. Based on mass spectrometry, it was proposed that Me_2InN_3 consists of trimers [11]. However, single-crystal X-ray analysis has shown that Me_2InN_3 forms a three dimensional network of dimeric units (Fig. 1A) [15]. Each In atom of a dimer $(Me_2InN_3)_2$ exhibits *two* intermolecular contacts to γ-N atoms of azido groups of adjacent dimers (average In–N distance of 292 pm). This gives a distorted octahedral coordination at indium with two Me groups, two α-N atoms (intramolecular), and two γ-N atoms (intermolecular).

The heaviest Group 13 element forms ionic salts. The structure of dimethylthallium azide can be described as distorted NaCl type structure exhibiting linear Me_2Tl^+ and linear N_3^- units [17]. This result is in agreement with the earlier conclusions drawn from vibrational spectroscopy of Me_2TlN_3 [16].

Recently, Kouvetakis et al. characterized the molecular structures of a series of asymmetrically substituted aluminum and gallium azides, $Me(X)MN_3$ (X = Cl, Br) [44,45] and $H(Cl)GaN_3$ [41] (see Table 2). The first published example of this type was $H(Cl)GaN_3$ which forms a cyclooctane-like Ga_4N_4 heterocycle via N_3 bridges (Fig. 1D and Fig. 3). The eight-membered rings exhibit chlorine in an alternating up and down position with the idealized molecular point group symmetry S_4. These heterocycles are associated via Ga–Cl contacts ranging from 353 to 373 pm to form chains in the crystal lattice [41]. The methyl derivatives $Me(Cl)GaN_3$ [45] and $Me(X)AlN_3$ (X = Cl, Br) [44] show a comparable cyclooctane-like structure, but in contrast to $[H(Cl)GaN_3]_4$ significant intermolecular contacts could not be detected. A six-membered ring structure was found for $Me(Br)GaN_3$ in the solid-state (Fig. 1B) [45]. The crystallographic analysis revealed two kinds of disorder which were successfully modeled in the structure. This model indicates that the mayor fraction of these molecules form trimers with three μ-N_3 groups and the minor fraction exhibits two μ-N_3 groups and one μ-Br ligand.

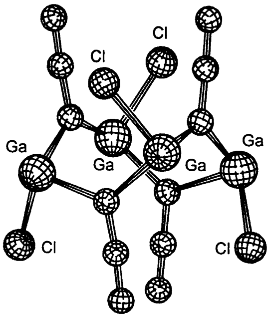


Fig. 3. Molecular structure of $H(Cl)GaN_3$. SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [41]; H atoms are omitted.

Table 3 shows single-crystal X-ray data for N_3 groups from selected molecular azides. Typically, $N_\alpha{-}N_\beta$ bonds are longer than $N_\beta{-}N_\gamma$ bonds. This can be interpreted as a higher bond order for the terminal N–N bond, showing a pre-formation of the N_2 molecule. Distinction between $N_\alpha{-}N_\beta$ and $N_\beta{-}N_\gamma$ bonds is not possible for $[\{(Me_3Si)_2CH\}_2Al(\mu\text{-}N_3)]_3$ with the unique azide bridged structure (Fig. 1C and Fig. 2).

Azide groups are nearly linear with $N_\alpha{-}N_\beta{-}N_\gamma$ angles in the range of 175–180°. Based on a simple molecular picture linearity is expected, but more detailed quantum mechanical analysis has shown that slightly bent azido groups should be formed [48].

2.3. Syntheses and structures of donor-stabilized monoazides

The use of appropriate bases results in Lewis acid–base adducts which are not further associated. Nitrogen or oxygen donors have been used either *inter*- or *intramolecularly* (Tables 4 and 5). The simple adducts compiled in Table 4 are commonly synthesized by adding the respective base to the azide. The pure azides R_2MN_3 are not known for $(C_6H_5CH_2)_2MN_3$–thf (M = Al, Ga) and $H_2AlN_3{-}NMe_3$. The benzyl derivatives were prepared from the thf adducts of the chlorides $(C_6H_5CH_2)_2MCl$–thf by salt metathesis with NaN_3 (Scheme 1; method A) [50]. $H_2AlN_3{-}NMe_3$ was synthesized by a 1:1 reaction of $H_3Al{-}NMe_3$ and hydrazoic acid (Scheme 1; method B1) [44]. The adduct $H_2AlN_3{-}NMe_3$ is quite reactive and looses the amine and hydrogen on standing at ambient temperature to yield a polymeric solid which is extremely shock sensitive [44].

So far, only $Me_2AlN_3{-}NH_2^tBu$ [49] and $Cl_2InN_3(thf)_2$ [38] have been characterized in the solid-state. The molecular units of the aluminum compound are linked

Table 3
Selected bond lengths (pm) and angles (°) for molecular monoazides

	$N_\alpha{-}N_\beta$	$N_\beta{-}N_\gamma$	$M{-}N_\alpha$	$N_\alpha{-}N_\beta{-}N_\gamma$
$[\{(Me_3Si)_2CH\}_2Al(\mu\text{-}N_3)]_3$ [27]	114 [a] [112.7(6)–115.4(5)]	114 [a] [112.7(6)–115.4(5)]	193 [a] [190.4(5)–194.4(4)]	176 [a] [175.3(5)–177.3(6)]
$[Me(Cl)Al(\mu\text{-}N_3)]_4$ [44]	126.0(7)	111.2(8)	190.5(5)	178.0(6)
$[Me(Br)Al(\mu\text{-}N_3)]_4$ [44]	126.4(8)	113.8(8)	194.2(7)	178.2(8)
$[(C_5H_{10}N)(N_3)Al(\mu\text{-}NC_5H_{10})]_2$ [b] [33]	116.9(6)	112.2(6)	180.5(4)	176.5(7)
$[Me_2Ga(\mu\text{-}N_3)]_x$ [14]	120.1(9)	112.1(9)	205 [a] [203.9(6), 205.1(6)]	179.3(9)
$[Mes_2Ga(\mu\text{-}N_3)]_2$ [25]	122 [a] [121.9(3), 122.6(3)]	113 [a] [113.3(3), 113.6(3)]	205 [a] [204.2(2)–204.8(1)]	180 [a] [179.6(2), 179.6(2)]
$[(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2$ [32]	117.7(5)	113.8(5)	191.9(4)	175.6(5)
$[H(Cl)Ga(\mu\text{-}N_3)]_4$ [41]	125 [a] [123(2)–126(2)]	113 [a] [112(2)–115(2)]	201 [a] [197(2)–206(2)]	177 [a] [176(2)–179(2)]
$[Me(Cl)Ga(\mu\text{-}N_3)]_4$ [45]	126(2)	109(2)	196(2)	177(2)
$[(\eta^1\text{-}Cp^*)\{(Me_3Si)_2N\}Ga(\mu\text{-}N_3)]_2$ [46]	123.5(3)	113.5(3)	207 [a] [206.1(2), 207.6(2)]	177.8(3)
$[Me_2In(\mu\text{-}N_3)]_2$ [15]	118 [a] [117.9(6)–118.7(6)]	116 [a] [115.1(6)–115.9(6)]	239 [a] [239.0(4)–239.5(4)]	180 [a] [179.5(5)–179.6(5)]
$[^{i}Pr_2In(\mu\text{-}N_3)]_2$ [24]	119.4(2)	113.8(3)	236 [a] [229.6(2), 243.3(1)]	178.9(2)

[a] Average value.
[b] $C_5H_{10}NH$ = piperidine.

via hydrogen bridges, which are formed between the nitrogen atoms of the amine donor and N_3 groups from adjacent molecules (Fig. 4). One H atom of the $^{t}BuNH_2$ ligand is associated to an α-N atom and the second H atom is associated to a γ-N atom.The indium compound $Cl_2InN_3(thf)_2$ exhibits a unique molecular structure in the solid-state (Fig. 5). It crystallizes as dimers with a planar $Cl_2InN_2InCl_2$ core. Two thf ligands for each In atom complete the octahedral coordination of the metals [38].

Except for the complex (salen)AlN_3, all known intramolecularly coordinated azides have been synthesized by the salt metathesis method A (Table 5). Fig. 6 depicts the different types of intramolecularly coordinated azides. By using ligands capable of intramolecular coordination, monomeric azides have been synthesized with either four- or fivefold coordination at the metal center. The structurally characterized complexes carry either a 3-dimethylaminopropyl, $Me_2N(CH_2)_3$, a 2-[(dimethylamino)methyl]phenyl, 2-$(Me_2NCH_2)C_6H_4$, or a rigid porphyrin ligand.

The azide $Me_2N(CH_2)_3Al(N_3)^{t}Bu$, a liquid at ambient temperature, was crystallized in a capillary using a miniature zone melting procedure [53]. It crystallizes as monomeric units without intermolecular contacts (Fig. 7). Table 6 compiles selected bond lengths and angles of donor-stabilized monoazides. As expected, the geometries of the N_3 groups are similar to those discussed earlier for the oligomeric monoazides (Table 3). All three azides of the type $[Me_2N(CH_2)_3]_2MN_3$ (M = Al, Ga, In) have been structurally characterized by single-crystal X-ray analysis. The aluminum and gallium compounds show trigonal bipyramidal coordination of the metal centers with two nitrogen donor atoms at apical positions. The molecules are not further associated in the crystal lattice. In contrast, the indium monoazide $[Me_2N(CH_2)_3]_2InN_3$ forms a chain structure with symmetrical In–NNN–In bridges in the backbone of the polymer resulting in octahedral coordination of the In atoms. The first structurally analyzed Group 13 porphyrin azide is (oep)GaN_3 [58]. The coordination polyhedron around gallium is an almost perfect square pyramid (Fig. 8 and Table 6).

Table 4
Adducts of monoazides [a]

Al	Ga	In
$Me_2AlN_3{-}NH^{t}_{2}Bu$ [b] [49]; $Et_2AlN_3{-}thf$ [18]; $(C_6H_5CH_2)_2AlN_3{-}thf$: C ($Cl_2AlN_3 + C_6H_5CH_2MgBr$ + thf) [c] [50]; $Me(Cl)AlN_3{-}NMe_3$ [44]; $H_2AlN_3{-}NMe_3$: B1 ($H_3Al{-}NMe_3 + HN_3$) [44]	$Et_2GaN_3{-}NMeHNH_2$: A ($Et_2GaCl{-}NMeHNH_2 + NaN_3$) [M.M. Sung, C. Kim, S.H. Yoo, C.G. Kim, Y. Kim, Chem. Vap. Deposition 8 (2002) 50]; $(C_6H_5CH_2)_2GaN_3{-}thf$: B3 [$(C_6H_5CH_2)_2GaCl{-}thf + Me_3SiN_3$] [c] [50]; $Cl_2GaN_3{-}NMe_3$ [37,42]; $Cl_2GaN_3{-}NMe_2Et$ [37]; $H_2GaN_3{-}py$ [40]; $H_2GaN_3{-}NMe_3$ [40]; $H_2GaN_3{-}NC_7H_{13}$ [d]: A ($H_2GaCl{-}NC_7H_{13} + NaN_3$) [51]	$Cl_2InN_3(D)_2$: D = thf [b], *py* [38]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses; azides of this type are unknown for Tl.
[b] Characterized by single-crystal X-ray analysis.
[c] The free azide is unknown.
[d] NC_7H_{13} = quinuclidine.

Table 5
Intramolecularly coordinated monoazides [a]

Al	Ga	In	Tl
$[Me_2N(CH_2)_3]_2AlN_3$ [b]: A ($Me_2N(CH_2)_3AlCl_2+NaN_3$) [49], A ($[Me_2N(CH_2)_3]_2AlX+NaN_3$; X = Cl, Br) [52]; *$[Me_2N(CH_2)_3]Al(N_3)^tBu$* [b]: A [52,53]; [2-*$(Me_2NCH_2)H_4C_6]_2AlN_3$* [b]: A [52]; [2-*$(Me_2NCH_2)H_4C_6]Al(N_3)^tBu$*: A [52]; *$MeN[(CH_2)_2(NSiMe_3)]_2AlN_3$* [b]: A [54]; *(salen)$AlN_3$* [c]: B1 [(salen)AlMe + HN_3] and C (salen$H_2+Et_2AlN_3$) [55]	*$[Me_2N(CH_2)_3]_2GaN_3$* [b]: A [56]; *$[Me_2N(CH_2)_3]Ga(N_3)^tBu$*: A [57]; *$[Me_2N(CH_2)_3]Ga(N_3)Me$*: A [57]; *$[Me_2N(CH_2)_2NEt]_2GaN_3$*: A [32]; *(por)$GaN_3$* [d]: A (por = omp, oep [a], tpp, tmtp, tptp; (por)GaX + NaN_3; X = Cl, O_2CMe) [58]	*$[Me_2N(CH_2)_3]_2InN_3$* [b,e]: A ($[Me_2N(CH_2)_3]_2InBr+Tl[PF_6]+NaN_3$) [59], A ($[Me_2N(CH_2)_3]_2InBr+Ag(O_3SCF_3)+NaN_3$) [d] [60]; *(por)$InN_3$* [f]: A (por = tpp and oep) [d] [61]	*(por)TlN_3* [d]: A (por = oep and tpp) [62], A (por = tpp [b], tmpp [b]; (por)$Tl(O_2CCF_3)+KN_3$) [63]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses.

[b] Characterized by single-crystal X-ray analysis.

[c] Used as a catalyst for asymmetric synthesis; salen = (*R*,*R*)-(−)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino or the (*S*,*S*)-(+) enantiomer.

[d] omp = 2,3,7,8,12,13,17,18-octamethylporphyrinato, oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato, tpp = 5,10,15,20-tetraphenylporphyrinato, tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinato, tptp = 5,10,15,20-tetra-*p*-tolylporphyrinato, tmpp = 5,10,15,20-tetra(4-methoxyphenyl)porphyrinato.

[e] A related compound of the formula $[Me_2N(CH_2)_3]_2InN_3–[Me_2N(CH_2)_3]_2In(O_3SCF_3)$ have been investigated by single-crystal analysis too.

[f] Used as 1,3-dipoles in cycloadditions.

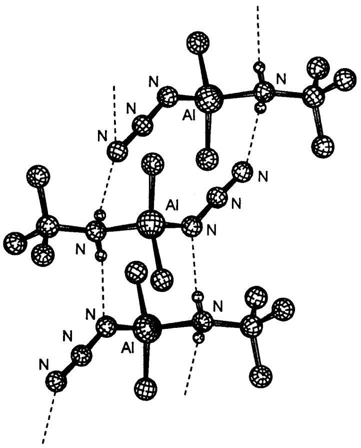


Fig. 4. Molecular structure of $Me_2AlN_3{-}NH_2^tBu$. SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [49]; H atoms are omitted for clarity.

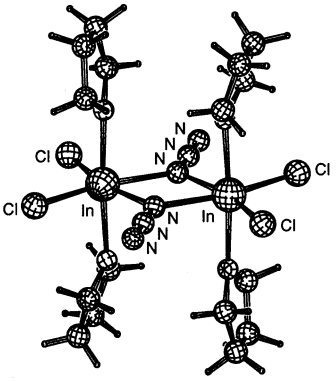


Fig. 5. Molecular structure of $[Cl_2InN_3(thf)_2]_2$. SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [38].

3. Diazides

In comparison with monoazides, the number of diazides are quite limited. Table 7 gives an overview of the known diazides and related adducts. The first compound of this type was synthesized by Challenger and Richards in 1934 by salt metathesis [2]. Starting from $PhTlCl_2$ and NaN_3, phenylthallium diazide was prepared in aqueous solution. So far, the known diazides have not been structurally characterized (Table 7). The alkyl derivatives $MeAl(N_3)_2$, $EtAl(N_3)_2$, and $EtGa(N_3)_2$ are soluble in thf, presumably as 1:1 adducts. Three adducts of $EtGa(N_3)_2$ with nitrogen bases have been synthesized and characterized by standard methods [57].

An interesting reaction has given transition metal substituted gallium diazides. Substitution reaction of $K[Cp(CO)_2Fe]$ with $Ga(N_3)_3$ in thf gives $[Cp(CO)_2Fe]Ga(N_3)_2$ which can be isolated as a pyridine adduct, and $[(OC)_4Co]Ga(N_3)_2{-}NMe_3$ can be obtained in a similar fashion.

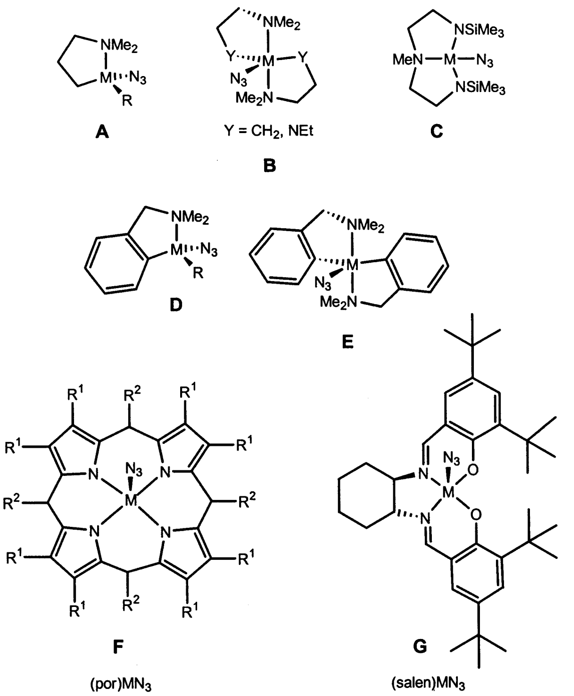


Fig. 6. Structures of intramolecularly coordinated monoazides.

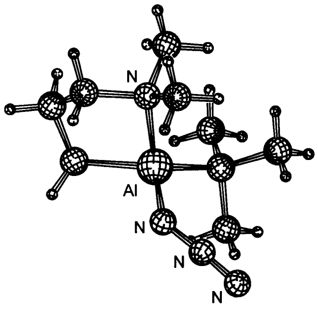


Fig. 7. Molecular structure of $Me_2N(CH_2)_3Al(N_3)^tBu$. SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [53].

Five intramolecularly coordinated diazido complexes are known (Table 8), which all exhibit one or two amine donors. They are synthesized by salt metatheses from the respective chlorides with NaN_3 (Fig. 9). Cowley et al. characterized $[2,6\text{-}(Me_2NCH_2)_2H_3C_6]Ga(N_3)_2$ by single-crystal X-ray analysis [67]. The geometry can be described as a trigonal bipyramidal coordination of the Ga atom with two donor nitrogen atoms at the apical positions (Fig. 10), but the molecules are not further associated in the solid-state. The azide groups show the expected alternating bond lengths with comparable values to monoazides [$N_\alpha{-}N_\beta$: 121.2(5), 118.1(5) pm; $N_\beta{-}N_\gamma$: 113.9(6), 113.0(6) pm; $Ga{-}N_\alpha$: 191.4(4), 192.8(4) pm; $N_\alpha{-}N_\beta{-}N_\gamma$: 173.5(6), 176.1(5)°] [67]. A similar structure, with monomers in the crystal lattice, was found for the diazidogallane $[Et_2N(CH_2)_2]_2N\text{-}Ga(N_3)_2$ [$N_\alpha{-}N_\beta$: 119.1(5), 119.2(5) pm; $N_\beta{-}N_\gamma$:

Table 6
Selected bond lengths (pm) and angles (°) for donor stabilized monoazides

	CN [a]	$N_\alpha{-}N_\beta$	$N_\beta{-}N_\gamma$	$M{-}N_\alpha$	$N_\alpha{-}N_\beta{-}N_\gamma$
$Me_2AlN_3{-}NH_2{}^tBu$ [49]	4	120.2(2)	113.9(2)	190.1(1)	176.3(1)
$[Me_2N(CH_2)_3]Al(N_3){}^tBu$ [53]	4	120.0(4)	114.4(4)	185.8(3)	176.4(3)
$(Me_2NCH_2)H_4C_6]_2AlN_3$ [52]	5	116.1(6)	115.3(7)	186.4(6)	175.5(7)
$[Me_2N(CH_2)_3]_2AlN_3$ [52]	5	119.1(2)	114.5(2)	189.7(2)	176.9(2)
$[Me_2N(CH_2)_3]_2GaN_3$ [56]	5	120.7(8)	113.2(9)	200.5(5)	178.0(8)
(oep)GaN_3 [b] [58]	5	117.2(2)	114.6(3)	195.5(2)	176.4(2)
$[Cl_2(thf)_2In(\mu\text{-}N_3)]_2$ [38]	6	121(2)	113(2)	224.2(8)	180.0(4)
$[\{Me_2N(CH_2)_3\}_2In(\mu\text{-}N_3)]_x$ [60]	6	116.5(2) [c]	116.5(2) [c]	252.6(2)	180
(tpp)TlN_3 [b] [63]	5	121.0	117(1)	220.2(9)	177(1)
(tmpp)TlN_3 [b] [63]	5	121.0	113.9(7)	220.5(6)	176.4(9)

[a] Coordination number.

[b] oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato, tpp = 5,10,15,20-tetraphenylporphyrinato, tmpp = 5,10,15,20-tetra(4-methoxyphenyl)porphyrinato.

[c] N_β coincides with a center of inversion.

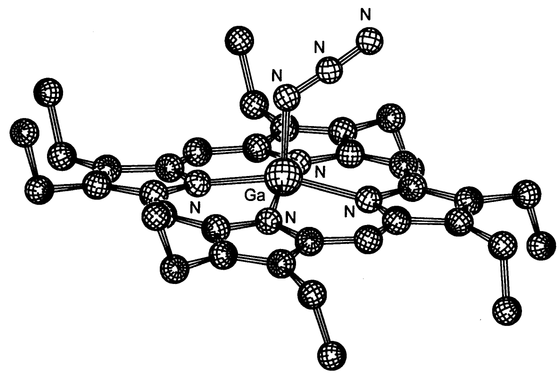


Fig. 8. Molecular structure of (oep)GaN_3 (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato) SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [58]; H atoms are omitted for clarity.

Table 8
Intramolecularly coordinated diazides [a]

Ga	In
$Me_2N(CH_2)_3Ga(N_3)_2$ [b]: C ($Ga(N_3)_3 + Li(CH_2)_3NMe_2$) [65], A [56,57] [c]; $[Me_2N(CH_2)_2]EtN]Ga(N_3)_2$: A [d] [66]; $[Et_2N(CH_2)_2]_2NGa(N_3)_2$ [b]: A [66]; [2,6-$(Me_2NCH_2)_2H_3C_6]Ga(N_3)_2$ [b]: A [67]	$Me_2N(CH_2)_3In(N_3)_2$: A ($Me_2N(CH_2)_3InBr_2 + NaN_3$) [68]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses; aluminum and thallium compounds of this type are unknown.

[b] Characterized by single-crystal X-ray analysis.

[c] Different molecular structure of $[Me_2N(CH_2)_3]Ga(N_3)_2$ as in Ref. [65], see text for details.

[d] Alternatively this diazide can be synthesized from $Me_2N(CH_2)_2NHEt$ and $Me_3N{-}Ga(N_3)_3$.

115.5(6), 115.2(5) pm; $Ga{-}N_\alpha$: 192.3(4), 194.5(4) pm; $N_\alpha{-}N_\beta{-}N_\gamma$: 175.5(5), 175.3(5)°] [66]. In contrast to these coordinatively saturated gallanes, the diazide $Me_2N(CH_2)_3Ga(N_3)_2$ with only one amine donor is associated in the solid-state. The molecular structure of this species was determined by two different single-crystal analyses [56,65]. The first crystals were grown in a sealed capillary from the melt directly on the diffractometer [65]. The poor quality of the crystal grown resulted in a limited quality data set, however, the principal structural features were determined showing dimers with a central Ga_2N_2 ring, which had been formed through association via the α-nitrogen atoms of the azido groups (Fig. 11A). Crystals grown from a purer batch of the azide $Me_2N(CH_2)_3Ga(N_3)_2$ under

Table 7
Diazides of the type $RM(N_3)_2$ and related adducts [a]

Al	Ga	Tl
$MeAl(N_3)_2$: B1 [64], B3 ($Me(I)AlN_3 + Me_3SiN_3$) [10]; $EtAl(N_3)_2$ (dismutation of $EtClAlN_3$) [b] [34]; $ClAl(N_3)_2$: B3 [35]	$EtGa(N_3)_2$: A [57]; $EtGa(N_3)_2{-}D$ (D = NC_7H_{13} [c], py, $NH_2{}^tBu$) [57]; $[Cp(CO)_2Fe]Ga(N_3)_2{-}py$ [d]: C ($K[Cp(CO)_2Fe] + Ga(N_3)_3 + py$) [65]; $[(OC)_4Co]Ga(N_3)_2{-}NMe_3$ [d]: C ($K[(CO)_4Co] + Ga(N_3)_3 + py$) [65]	$PhTl(N_3)_2$: A [2]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses; indium compounds of this type are unknown.

[b] $EtAl(N_3)_2$ is mentioned, but not characterized.

[c] NC_7H_{13} = quinuclidine.

[d] The free azide is unknown.

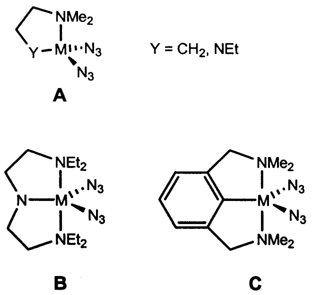


Fig. 9. Structures of intramolecularly coordinated diazides.

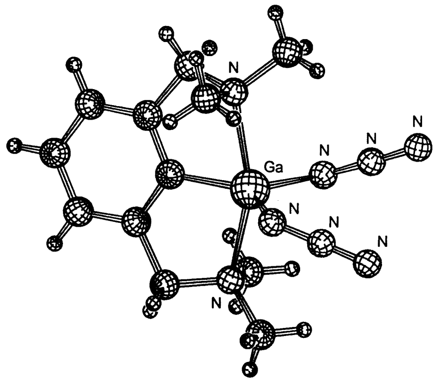


Fig. 10. Molecular structure of $[2,6\text{-}(Me_2NCH_2)_2H_3C_6]Ga(N_3)_2$ SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [67].

different conditions gave a better crystallography data set [56]. Moreover, the molecules showed a new type of association in the crystal lattice (Fig. 11B). Tetramers were formed by head-to-tail azide bridges between Ga atoms, which can be described as a dimer of dimers [56]. The stronger dimeric unit is shown in Fig. 11B, where two gallium diazides are linked via one $Ga{-}N_\gamma$ contact of 281.4(5) pm. These dimers are associated through N–Ga contact of 306.9(6) pm between Ga1 and N3 (a γ-N atom of a neighboring molecule) to form a centrosymmetric dimer of dimers (Fig. 11B). The structural parameters of the azide groups are $N_\alpha{-}N_\beta = 116{-}118$ pm, $N_\beta{-}N_\gamma = 114{-}115$ pm, $Ga{-}N_\alpha = 187{-}190$ pm, and $N_\alpha{-}N_\beta{-}N_\gamma$: 174–176°.

4. Triazides

The triazides of aluminum and gallium were synthesized for the first time in Wiberg's group from diethylether solutions of the respective hydrides EH_3 and three equivalents of hydrazoic acid (method B1; Table 9) [69,70]. These azides have been obtained as colorless solids, which were soluble in thf. The first report of a structurally characterized triazido alane, $py_3Al(N_3)_3$, appeared in 1996 [49]. In the same year, there were two reports of the analogous gallane [65,71] and a year later the respective indium compound was described [60]. All three compounds $py_3E(N_3)_3$ exhibit octahedrally coordinated metal centers with a *mer* configuration of the two ligand sets. The aluminum compound is depicted in Fig. 12 as a representative example. Besides the tripyridine compounds, only the simple 1:1 adducts of $Ga(N_3)_3$ with amine donors were synthesized by Fischer et al. The adducts with Me_3N and Et_3N have been characterized by single-crystal X-ray structural determinations (Fig. 13). Table 10 shows selected bond lengths and angles of donor-stabilized triazido compounds. Most of the azido groups exhibit the expected bond length alternation: the $N_\alpha{-}N_\beta$ bond is longer than the $N_\beta{-}N_\gamma$ bond. This alternation is only weakly pronounced for the indium species, which agrees with a more ionic description of the indium azide bonds [60].

Table 9
Triazides $M(N_3)_3$ and related adducts [a]

Al	Ga	In
$Al(N_3)_3$: B1 (AlH_3+HN_3) [c] [69], B1 [d] [72]; $py_3Al(N_3)_3$ [b] (A + py) [49]	$Ga(N_3)_3$: B1 (GaH_3+HN_3) [70], A [65], (from $Et_3N{-}Ga(N_3)_3$) [73]; $py_3Ga(N_3)_3$ [b,e] (A + py) [65], B3 [$Ga(NMe_2)_3+Me_3SiN_3$ + py] [f] [71]; $(N_3)_3Ga{-}thf$ [g] [65]; $(N_3)_3Ga{-}NMe_3$ [b] [56,65]; $(N_3)_3Ga{-}NEt_3$ [b] [65], ($Na[Ga(N_3)_4]+NEt_3$) [56,73], $(N_3)_3Ga{-}NMe_2R$ ($R = n\text{-}C_8H_{17}$, $n\text{-}C_{10}H_{21}$) [56]; $(N_3)_3Ga{-}NC_7H_{13}$ [h] [65]	$py_3In(N_3)_3$ [b] [60]; $(terpy)In(N_3)_3$ [i] [68]; $[(terpy)In(N_3)_2(O_2C(CH_2)_3OH]$ [b] [68] [j]

[a] Variations with respect to the general synthetic methods A, B1–B3, and C (Scheme 1) are mentioned in parentheses; thallium compounds of this type are unknown.

[b] Characterized by single-crystal X-ray analysis.

[c] $Al(N_3)_3$ was obtained trough method A with thf as the solvent, but the solvent could not be removed completely [74].

[d] Matrix isolation IR spectroscopy of the monomer.

[e] Single-crystal X-ray structural data for $py_3Ga(N_3)_3$ available in Ref. [65,71].

[f] $py_3Ga(N_3)_3$ can be obtained by a dismutation reaction of $(Me_2N)_2GaN_3$ in pyridine.

[g] $Ga(N_3)_3$ dissolves probably as a mono thf adduct; not isolated.

[h] NC_7H_{13} = quinuclidine

[i] terpy = 2,2′,2″-terpyridine.

[j] Crystals were accidentally obtained from a decomposition reaction of $(terpy)In(N_3)_3$ in thf.

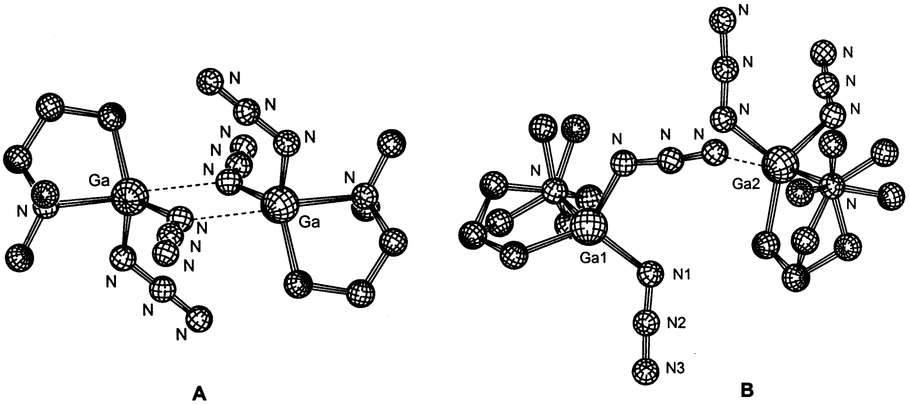


Fig. 11. Molecular structures of $Me_2N(CH_2)_3Ga(N_3)_2$ SCHAKAL [47] drawing based on the data of single-crystal X-ray determinations of Refs. [65,56].

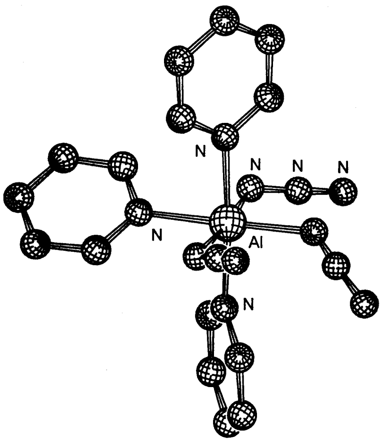


Fig. 12. Molecular structure of $py_3Al(N_3)_3$ SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [49]; H atoms are omitted for clarity.

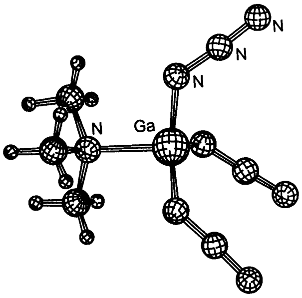


Fig. 13. Molecular structure of $Me_3N{-}Ga(N_3)_3$ SCHAKAL [47] drawing based on the data of the single-crystal X-ray determination of Ref. [56].

There are two exceptions from the expected bond length alternation. The azido group *trans* to the pyridine ligand in $py_3Al(N_3)_3$ and $py_3In(N_3)_3$ show a *shorter* $N_\alpha{-}N_\beta$ bond (105.2(5) and 106.0(4) pm) than the $N_\beta{-}N_\gamma$ bond (121.4(6) and 121.3(4) pm). This surprising result was attributed to solid-state effects [60].

Table 10
Selected bond lengths (pm) and angles (°) for structurally characterized triazides

	CN [a]	$N_\alpha{-}N_\beta$	$N_\beta{-}N_\gamma$	$M{-}N_\alpha$	$N_\alpha{-}N_\beta{-}N_\gamma$
$py_3Al(N_3)_3$ [49]	6	105.2	121.4	200.6	176.6
		119.6	114.9	195.2	176.7
		118.6	114.7	195.3	176.2
$py_3Ga(N_3)_3$ [65,71] [b]	6	119.4	114.2	200.5	176.4
		119.9	114.5	200.7	177.1
		120.8	115.8	200.7	178.8
$py_3In(N_3)_3$ [60]	6	106.0	121.3	219.3	175.4
		116.6	117.1	223.5	176.0
		115.6	117.3	223.3	176.7
$Me_3N{-}Ga(N_3)_3$ [56]	4	121.5	114.0	188.8	175.5
		121.3	114.5	188.7	175.6
		121.7	113.7	189.2	175.3

[a] Coordination number.
[b] Data taken from Ref. [71].

5. Element(I) azides

The simplest azido species of the Group 13 elements are compounds of the type MN_3. All of these element(I) azides are known as molecular compounds from recent matrix-isolation investigations (Table 11); the bulk material is only known for thallium. Thallium monoazide, which can be crystallized from aqueous solutions, is an ionic solid with a tetragonal distorted CsCl type structure [80,81]. The linear N_3^- groups are symmetrically surrounded with N–N distances of 118 pm (corrected for thermal motions) [81]. Similar structures have been found for alkaline salts KN_3, RbN_3, and CsN_3 [80].

Recently, Andrews et al. investigated the co-deposition of laser-ablated metals Al [75,76], Ga, In, and Tl [78] with N_2 at 10 K. A set of element nitrogen species M_xN_y were isolated in N_2 matrices by these experiments and characterized by IR spectroscopy. Among these species the monoazides MN_3 have been characterized

Table 11
Molecular element(I) azides MN_3

AlN_3	GaN_3	InN_3	TlN_3
Laser-ablated $Al+N_2$ [a] [75,76]	$Ga(N_3)_3+h\nu$; UV–vis spectroscopy in solution [77]; laser-ablated $Ga+N_2/N$ [a] [78]; thermolysis of $[Me_2N(CH_2)_3]Ga(N_3)_2$ [b] [79]	Laser-ablated $In+N_2$ [a] [78]	Laser-ablated $Tl+N_2$ [a] [78]

[a] Matrix-isolation IR spectroscopy of MN_3 in solid N_2.
[b] Matrix-isolation IR spectroscopy of GaN_3 in solid Ar.

Table 12
IR vibrational frequencies (cm^{-1}) of matrix-isolated element(I) azides MN_3 [a]

	AlN_3 [75,76]	GaN_3 [78,79]	InN_3 [78]	TlN_3 [78]
$\nu_{as}(N_3)$	2144.0 (2150.9) [b]	2096.8 (2103.6) [b] 2106.0 [c]	2074.5 (2076.6, 2073.4)[b]	2048.8[b]
$\nu_s(N_3)$	1386.0 (1391.9) [b]	1328.3 (1331.3) [b] 1340.3 [c]	1323.9 (broad)[b]	– [d]
$\nu(MN)$	509.7 [b]	– [d] 395.7 (397.4) [c]	– [d]	– [d]

[a] Data are given for the most abundant isotopomer; values in parentheses are due to matrix site effects.
[b] Matrix-isolation IR spectroscopy of MN_3 in solid N_2.
[c] Matrix-isolation IR spectroscopy of GaN_3 in solid Ar.

for the first time (Table 12). The assignments were supported by density functional calculations and measured isotopic shifts. Three normal modes were assigned for the aluminum species, two normal modes for the gallium and indium compounds, and only one normal mode for the thallium azide in the experimental IR spectra (Table 12). The frequencies of the asymmetric stretching mode of the N_3 groups decrease from 2144.0 for aluminum to 2048.8 cm^{-1} for thallium, with the latter value approaching the frequency of 2002.9 cm^{-1} for N_3^- isolated in N_2 matrices [82]. This trend clearly reflects an increasing ionic bonding between the Group 13 element and the azide group. Furthermore, the intensity ratio between the asymmetric and the symmetric N_3 stretching mode is expected to increase with increasing ionic character of the azide ligand, and for N_3^- only the asymmetric mode is IR active. This expectation matches the observed intensity ratios: 8:1 for GaN_3, 18:1 for InN_3; for TlN_3 a symmetric N_3 stretching mode was not detected [78].

Gallium(I) azide was trapped in an excess of solid argon from the pyrolysis of the intramolecularly coordinated gallium diazide $Me_2N(CH_2)_3Ga(N_3)_2$ [79]. This reactive intermediate has been identified among other thermolysis products because it was selectively bleached by an irradiation of the matrix-isolated thermolysis products with an Xe arc lamp (Fig. 14) [79]. In this work GaN_3 was characterized by three IR bands at 2106.0, 1340.3, and 395.7 cm^{-1} assigned to $\nu_{as}(N_3)$, $\nu_s(N_3)$, and $\nu(GaN)$, respectively (Table 12).

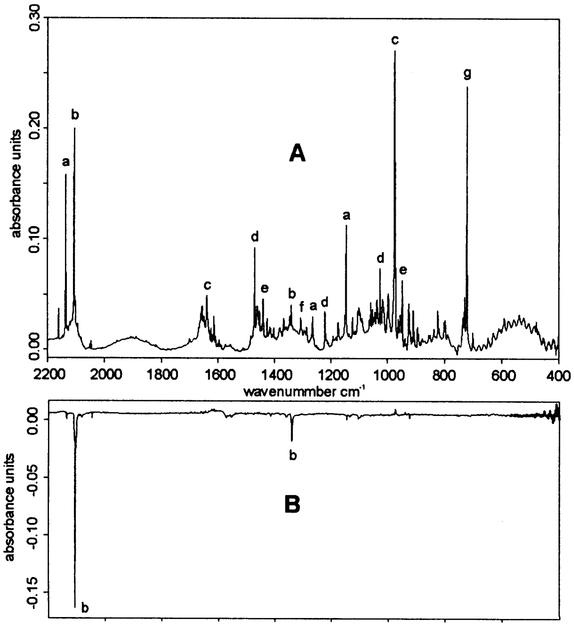


Fig. 14. (A) Products of thermolysis of $Me_2N(CH_2)_3Ga(N_3)_2$ at 520 °C trapped in excess of argon at 15 K: (a) HN_3; (b) GaN_3; (c) NH_3; (d) $H_2C{=}NCH_3$; (e) $H_2C{=}CH_2$; (f) CH_4; (g) HCN. (B) Difference IR spectrum obtained by irradiation of the product matrix A; negative IR bands indicate disappearing species (Ref. [79] Repro-

Gallium monoazide was detected for the first time by photolysis reaction of $Ga(N_3)_3$ dissolved in acetonitrile [77]. The authors assumed that the irradiation of triazidogallane resulted in a reductive elimination according to Eq. (9).

$$Ga(N_3)_3 \xrightarrow[MeCN]{h\nu} GaN_3 + 3\,N_2 \tag{9}$$

The irradiation experiment was monitored by UV–vis absorption and emission spectroscopy. The evolution of N_2 gas was accompanied by a new absorption at $\lambda_{max} =$ 298 nm and the product showed luminescence at $\lambda_{max} =$ 475 nm ($\lambda_{exc} = 300$ nm). The assignment of the product to GaN_3 was mainly based on a similar absorption/emission behavior of Ga^+ in alkali halides [77].

6. Properties and applications of azides

All azides are potentially explosive, but for the majority of compounds reviewed in this article, no spontaneous explosions have been reported. In general, an increase of the nitrogen content is usually accompanied by an increase in the degree of hazard involved; e.g. triazides are usually more dangerous than diazides or monoazides. But in comparison with azido boranes, the azides of the heavier Group 13 elements are relatively harmless. This might be illustrated by a comparison of the properties of Me_2BN_3 [83,84] and Me_2AlN_3 [10]. While the borane is explosive the alane is just pyrophoric. Among the monoazido compounds (Tables 1, 2, 4 and 5) only Cl_2AlN_3 was described to be explosive [10]. The parent gallane, H_2GaN_3, should be handled with care. The neat compound is stable at room temperature, but can explode by contacts with sharp objects [40,41]. An example of a thermally robust monoazide is the intramolecularly coordinated alane $[2\text{-}(Me_2NCH_2)H_4C_6]_2AlN_3$ with fivefold coordinated aluminum (Table 5 and Fig. 6E). This organometallic species can be purified by sublimation (140 °C/10^{-3} Torr) and it melts without decomposition at 147–149 °C [52].

As mentioned before, the diazides are potentially more hazardous than comparable monoazido species. All diazides that are not inter- or intramolecularly coordinated by a Lewis base must be handled with great care (Tables 7 and 8). For example, $ClAl(N_3)_2$ has been described to explode when heated above 100 °C [35]. However, because this diazide contained small amounts of $Al(N_3)_3$, it is not clear if pure $ClAl(N_3)_2$ would behave similarly. $MeAl(N_3)_2$, the first published aluminum diazide [64] have been reported to be shock insensitive, but $EtAl(N_3)_2$ have been described as a highly explosive material [34]. Again, it is not clear if indeed pure $EtAl(N_3)_2$ is highly explosive, because the authors only suspected that a explosive residue of a distillation was $EtAl(N_3)_2$. Diazidoethylgallane, $EtGa(N_3)_2$, explodes when heated rapidly above 281 °C [57]. The coordination of Lewis bases to azides can tremendously enhance their thermal stability. That might be illustrated with the intramolecularly coordinated gallium diazide $[2,6\text{-}(Me_2NCH_2)_2H_3C_6]Ga(N_3)_2$ (Fig. 10 and Table 8), which sustains vapor phase heating at 400 °C [67].

The triazido compounds $Al(N_3)_3$ and $Ga(N_3)_3$ are colorless, moisture and shock sensitive solids, which are soluble in thf (Table 9). The solvent-free gallane melts reversibly at 232 °C, but attempts to sublime the compound in high vacuum (25–180 °C; 10^{-3}–10^{-8} Torr) resulted in detonation [65].

Table 13
Azide precursors applied for thin films depositions of Group 13 nitrides

AlN	GaN	InN
Me_2AlN_3 [85,86]	Me_2GaN_3 [14,87]	Me_2InN_3 [15]
Et_2AlN_3 [85,86,88,89]	Et_2GaN_3 [23,89]	
$[Me_2N(CH_2)_3]_2AlN_3$ [49,90]	$[Me_2N(CH_2)_3]_2GaN_3$ [56]	$[Me_2N(CH_2)_3]_2InN_3$ [59,60,90,91]
$(Me_2N)_2AlN_3$ [31]	$(Me_2N)_2GaN_3$ [32]	
$Me_2AlN_3{-}NH_2^tBu$ [49,90]		
	$Me_2N(CH_2)_3Ga(N_3)_2$ [90,92,93]	
	$[Et_2N(CH_2)_2]_2NGa(N_3)_2$ [66]	
	H_2GaN_3 [40,41,94]	
	Cl_2GaN_3 [36,37,42,95]	
	$Cl_2GaN_3{-}NMe_3$ [37]	
	$Et_2GaN_3{-}NMeHNH_2$ [MM. Sung, C. Kim, S.H. Yoo, C.G. Kim, Y. Kim, Chem. Vap. Deposition 8 (2002) 50]	

The azides of the heavier Group 13 elements have been mainly applied for materials chemistry and organic synthesis. In the areas of materials chemistry, azides were used for the deposition of Group 13 nitrides either as thin films or as nano-scaled materials. The nitrides AlN, GaN, and InN as well as the alloys $Al_xGa_yIn_{1-x-y}N$ can be used for micro- and optoelectronic devices; of particular interest are blue and ultraviolet laser diodes for high-density optical storage and other applications [3–9]. Usually, thin films of Group 13 nitrides are deposited on suitable substrates by metal organic chemical vapor deposition techniques (MOCVD) using trimethyl compounds Me_3M ($M = Al$, Ga, In) and a large excess of ammonia. An alternative to this classical method can be found in the use of single-source precursors, compounds which already contains the elements of the desired solid film in a *single* molecule. The main advantage of single-source over classical precursors is the possibility to deposit nitrides at much lower temperatures. From a chemical point of view, Group 13 azides are promising single-source precursors, because they already contain the two elements of interest *directly* bound together with the N_3 group perfectly suited for the production of N atoms. Gallium nitride is the most interesting material among the Group 13 nitrides, because it exhibits a direct band gap of 3.4 eV and can be used as the basic material for blue LEDs and lasers. Beyond this background it is understandable that most of the work aiming at the deposition of materials from Group 13 azides were focused on GaN. Table 13 shows the azides which have been used for the thin film depositions. The first reports where the well-known azides Me_2AlN_3 [85,86], Et_2AlN_3 [85,86,88,89], and Et_2GaN_3 [23,89] were applied as single-source precursors appeared in 1988–1989. For most of the investigations (Table 13) standard CVD techniques with different substrates have been tested; e.g. sapphire (α-Al_2O_3), Si, SiC, and GaAs in different crystallographic orientations. The most common substrate for epitaxially grown GaN (wurtzite-type) is sapphire(0001). Under some special CVD conditions, the growth of porous columnar GaN layers [96] and InN whiskers [91] was observed.

Some of the single-source azide precursors have also been used for the preparation of nano-sized materials and different techniques were employed; e.g. pyrolyses of bulk precursors, pyrolyses of precursors inside porous templates (like MCM 41), thermolyses of precursors in high-boiling solvents, and CVD under special conditions. Et_2AlN_3 has been used for AlN nanoparticles [97], H_2GaN_3 [41], Et_2GaN_3 [98], D–Ga$(N_3)_3$ (D = donor ligand) [65,73,99–102], and $Me_2N(CH_2)_3Ga(N_3)_2$ [101,102] for GaN nanoparticles, R_2InN_3 (R = ^{i}Pr, ^{t}Bu) [24] and $[Me_2N(CH_2)_3]_2InN_3$ [91] for InN nanoparticles and TlN_3 [103] for Tl nanoparticles. Among the Group 13 nitrides, the growth of InN is most challenging because this material begins to lose nitrogen around 500 °C [24]. Recently, Buhro and co-workers reported a successful low-temperature synthesis of crystalline InN fibers. The fibers are formed by thermolyses of azidoindanes R_2InN_3 (R = ^{i}Pr, ^{t}Bu) in refluxing diisopropylbenzene at 203 °C in the presence of the reducing agent H_2NNMe_2 [24]. The authors proposed a solution–liquid–solid (SLS) growth mechanism to explain the results.

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References

[1] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 1st ed., Pergamon Press, Amsterdam, 1984, p. 12.
[2] F. Challenger, O.V. Richards, J. Chem. Soc. (1934) 405.
[3] A.C. Jones, C.R. Whitehouse, J.S. Roberts, Chem. Vap. Deposition 1 (1995) 65.
[4] I. Akasaki, H. Amano, J. Cryst. Growth 146 (1995) 455.
[5] D.A. Neumayer, J.G. Ekerdt, Chem. Mater. 8 (1996) 9.
[6] T. Matsuoka, Adv. Mater. 8 (1996) 496.
[7] F.A. Ponce, D.P. Bour, Nature 386 (1997) 351.
[8] S. Nakamura, G. Fasol, The Blue Laser Diode, GaN Based Light Emitters and Lasers, Springer, Berlin, Heidelberg, 1997.
[9] S. Nakamura, Science 281 (1998) 951.
[10] N. Wiberg, W.-C. Joo, H. Henke, Inorg. Nucl. Chem. Lett. 3 (1967) 267.
[11] N. Röder, K. Dehnicke, Chimia 28 (1974) 349.
[12] J. Müller, K. Dehnicke, J. Organomet. Chem. 12 (1968) 37.
[13] J. Müller, Z. Naturforsch. Teil. b 34 (1979) 531.
[14] D.A. Atwood, R.A. Jones, A.H. Cowley, J.L. Atwood, S.G. Bott, J. Organomet. Chem. 394 (1990) C6.
[15] B.-J. Bae, J.E. Park, B. Kim, J.T. Park, J. Organomet. Chem. 616 (2000) 128.
[16] J. Müller, Z. Anorg. Allg. Chem. 381 (1971) 103.
[17] Y.M. Chow, D. Britton, Acta Crystallogr. Sect. B 31 (1975) 1922.
[18] M.I. Prince, K. Weiss, J. Organomet. Chem. 5 (1966) 584.
[19] K. Dehnicke, J. Strähle, D. Seybold, J. Müller, J. Organomet. Chem. 6 (1966) 298.
[20] J. Müller, K. Dehnicke, Z. Anorg. Allg. Chem. 348 (1966) 261.
[21] B.Y. Chung, Y.S. Park, I.S. Cho, B.C. Hyun, Bull. Korean Chem. Soc. 9 (1988) 269.
[22] J. Müller, K. Dehnicke, J. Organomet. Chem. 7 (1967) P1.
[23] J. Kouvetakis, D.B. Beach, Chem. Mater. 1 (1989) 476.
[24] S.D. Dingman, N.P. Rath, P.D. Markowitz, P.C. Gibbons, W.E. Buhro, Angew. Chem. Int. Ed. Engl. 39 (2000) 1470.
[25] S. Schulz, M. Nieger, J. Chem. Soc. Dalton Trans. (1998) 4127.
[26] T.N. Srivastava, K. Kapoor, Chem. Soc. Rev. A 17 (1979) 611.
[27] W. Uhl, R. Gerding, S. Pohl, W. Saak, Chem. Ber. 128 (1995) 81.
[28] W. Beck, E. Schuierer, K. Feldl, Angew. Chem. Int. Ed. Engl. 5 (1966) 249.
[29] T.N. Srivastava, K.K. Bajpai, J. Inorg. Nucl. Chem. 34 (1972) 1458.
[30] N. Kumar, B.L. Kalsotra, R.K. Multani, J. Inorg. Nucl. Chem. 36 (1974) 1157.
[31] D.A. Neumayer, C.J. Carmalt, M.F. Arendt, J.M. White, A.H. Cowley, R.A. Jones, J.G. Ekerdt, Mater. Res. Soc. Symp. Proc. 395 (1996) 85.
[32] D.A. Neumayer, A.H. Cowley, A. Decken, R.A. Jones, V. Lakhotia, J.G. Ekerdt, J. Am. Chem. Soc. 117 (1995) 5893.
[33] J.S. Silverman, C.J. Carmalt, D.A. Neumayer, A.H. Cowley, B.G. McBurnett, A. Decken, Polyhedron 17 (1998) 977.
[34] V. Krieg, J. Weidlein, Z. Anorg. Allg. Chem. 368 (1969) 44.
[35] N. Wiberg, W.-C. Joo, K.H. Schmid, Z. Anorg. Allg. Chem. 394 (1972) 197.
[36] J. Kouvetakis, J. McMurran, D.B. Beach, D.J. Smith, Mater. Res. Soc. Symp. Proc. 395 (1996) 79.
[37] J. Kouvetakis, J. McMurran, P. Matsunaga, M. O'Keeffe, J.L. Hubbard, Inorg. Chem. 36 (1997) 1792.
[38] C. Steffek, J. McMurran, B. Pleune, J. Kouvetakis, T.E. Concolino, A.L. Rheingold, Inorg. Chem. 39 (2000) 1615.
[39] K. Dehnicke, N. Krüger, Z. Anorg. Allg. Chem. 444 (1978) 71.
[40] J. McMurran, D. Dai, K. Balasubramanian, C. Steffek, J. Kouvetakis, Inorg. Chem. 37 (1998) 6638.
[41] J. McMurran, J. Kouvetakis, D.C. Nesting, D.J. Smith, J.L. Hubbard, J. Am. Chem. Soc. 120 (1998) 5233.
[42] J. Kouvetakis, M. O'Keeffe, L. Brouseau, J. McMurran, D. Williams, D.J. Smith, Mater. Res. Soc. Symp. Proc. 449 (1997) 313.
[43] M.J. Goode, A.J. Downs, C.R. Pulham, D.W.H. Rankin, H.E. Robertson, J. Chem. Soc. Chem. Commun. (1988) 786.
[44] J. Kouvetakis, J. McMurran, G. Steffek, T.L. Groy, J.L. Hubbard, L. Torrison, Main Group Met. Chem. 24 (2001) 77.
[45] J. Kouvetakis, J. McMurran, C. Steffek, T.L. Groy, H.J. Hubbard, Inorg. Chem. 39 (2000) 3805.
[46] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, Organometallics 18 (1999) 2037.
[47] E. Keller, SCHAKAL-97, A Computer Program for the Graphical Representation of Molecular and Crystallographic Models, University of Freiburg, Germany, 1997.
[48] I.C. Tornieporth-Oetting, T.M. Klapötke, Angew. Chem. Int. Ed. Engl. 34 (1995) 511.

[49] R.A. Fischer, A. Miehr, H. Sussek, H. Pritzkow, E. Herdtweck, J. Müller, O. Ambacher, T. Metzger, J. Chem. Soc. Chem. Commun. (1996) 2685.

[50] M.A. Munoz-Hernandez, D. Rutherford, H. Tiainen, D.A. Atwood, J. Organomet. Chem. 582 (1999) 103.

[51] B. Luo, J. Victor, G. Young, W.L. Gladfelter, Inorg. Chem. 39 (2000) 1705.

[52] J. Müller, R.A. Fischer, H. Sussek, P. Pilgram, R. Wang, H. Pritzkow, E. Herdtweck, Organometallics 17 (1998) 161.

[53] J. Müller, R. Boese, J. Mol. Struct. 520 (2000) 215.

[54] N. Emig, F.P. Gabbaï, H. Krautscheid, R. Réau, G. Bertrand, Angew. Chem. Int. Ed. Engl. 37 (1998) 989.

[55] J.K. Myers, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 8959.

[56] A. Devi, H. Sussek, H. Pritzkow, M. Winter, R.A. Fischer, Eur. J. Inorg. Chem. (1999) 2127.

[57] A. Miehr, M.R. Mattner, R.A. Fischer, Organometallics 15 (1996) 2053.

[58] A. Coutsolelos, R. Guilard, A. Boukhris, C. Lecomte, J. Chem. Soc. Dalton Trans. (1986) 1779.

[59] R.A. Fischer, A. Miehr, T. Metzger, E. Born, O. Ambacher, H. Angerer, R. Dimitrov, Chem. Mater. 8 (1996) 1356.

[60] R.A. Fischer, H. Sussek, A. Miehr, H. Pritzkow, E. Herdtweck, J. Organomet. Chem. 548 (1997) 73.

[61] R. Guilard, S.S. Gerges, A. Tabard, P. Richard, M.A. El Borai, C. Lecomte, J. Am. Chem. Soc. 109 (1987) 7228.

[62] A.G. Coutsolelos, A. Tsapara, D. Daphnomili, D.L. Ward, J. Chem. Soc. Dalton Trans. (1991) 3413.

[63] M.O. Senge, K. Ruhlandt-Senge, K.J. Regli, K.M. Smith, J. Chem. Soc. Dalton Trans. (1993) 3519.

[64] E. Wiberg, H. Michaud, Z. Naturforsch. Teil. b 9 (1954) 497.

[65] R.A. Fischer, A. Miehr, E. Herdtweck, M.R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauf, C.R. Pulham, S. Parsons, Chem. Eur. J. 2 (1996) 1353.

[66] H. Sussek, O. Stark, A. Devi, H. Pritzkow, R.A. Fischer, J. Organomet. Chem. 602 (2000) 29.

[67] A.H. Cowley, F.P. Gabbai, F. Olbrich, S. Corbelin, R.J. Lagow, J. Organomet. Chem. 487 (1995) C5.

[68] R.A. Fischer, H. Sussek, H. Parala, H. Pritzkow, J. Organomet. Chem. 592 (1999) 205.

[69] E. Wiberg, H. Michaud, Z. Naturforsch. Teil. b 9 (1954) 495.

[70] E. Wiberg, H. Michaud, Z. Naturforsch. Teil. b 9 (1954) 502.

[71] C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, J. Chem. Soc. Chem. Commun. (1996) 1453.

[72] C.J. Linnen, D.E. Macks, R.D. Coombe, J. Phys. Chem. Sect. B 101 (1997) 1602.

[73] A.C. Frank, F. Stowasser, H. Sussek, H. Pritzkow, C.R. Miskys, O. Ambacher, M. Giersig, R.A. Fischer, J. Am. Chem. Soc. 120 (1998) 3512.

[74] E. Wiberg, H. Michaud, Z. Naturforsch. Teil. b 9 (1954) 496.

[75] L. Andrews, M. Zhou, G.V. Chertihin, W.D. Bare, Y. Hannachi, J. Low Temp. Phys. 26 (2000) 736.

[76] L. Andrews, M. Zhou, G.V. Chertihin, W.D. Bare, Y. Hannachi, J. Phys. Chem. Sect. A 104 (2000) 1656.

[77] H. Kunkely, A. Vogler, Z. Naturforsch. Teil. b 53 (1998) 1180.

[78] M. Zhou, L. Andrews, J. Phys. Chem. Sect. A 104 (2000) 1648.

[79] J. Müller, S. Bendix, J. Chem. Soc. Chem. Commun. (2001) 911.

[80] U. Müller, Z. Anorg. Allg. Chem. 392 (1972) 159.

[81] C.S. Choi, E. Prince, J. Chem. Phys. 64 (1976) 4510.

[82] R. Tian, J.C. Facelli, J. Michl, J. Phys. Chem. 92 (1988) 4073.

[83] P.I. Paetzold, H.-J. Hansen, Z. Anorg. Allg. Chem. 345 (1966) 79.

[84] P. Paetzold, E. Eleftheriadis, R. Minkwitz, V. Wölfel, R. Gleiter, P. Bischof, G. Friedrich, Chem. Ber. 121 (1988) 61.

[85] R.K. Schulze, D.R. Mantell, W.L. Gladfelter, J.F. Evans, J. Vac. Sci. Technol. A 6 (1988) 2162.

[86] D.C. Boyd, R.T. Haasch, D.R. Mantell, R.K. Schulze, J.F. Evans, W.L. Gladfelter, Chem. Mater. 1 (1989) 119.

[87] V. Lakhotia, D.A. Neumayer, A.H. Cowley, R.A. Jones, J.G. Ekerdt, Chem. Mater. 7 (1995) 546.

[88] W.L. Gladfelter, D.C. Boyd, J.W. Hwang, R.T. Haasch, J.F. Evans, K.L. Ho, K.F. Jensen, Mater. Res. Soc. Symp. Proc. 131 (1989) 447.

[89] K.-L. Ho, K.F. Jensen, J.-W. Hwang, W.L. Gladfelter, J.F. Evans, J. Cryst. Growth 107 (1991) 376.

[90] R.A. Fischer, A. Miehr, O. Ambacher, T. Metzger, E. Born, J. Cryst. Growth 170 (1997) 139.

[91] A. Devi, H. Parala, W. Rogge, A. Wohlfart, A. Birkner, R.A. Fischer, J. Phys. IV 11 (2001) 577.

[92] A. Miehr, O. Ambacher, W. Rieger, T. Metzger, E. Born, R.A. Fischer, Chem. Vap. Deposition 2 (1996) 51.

[93] A. Devi, W. Rogge, A. Wohlfart, F. Hipler, H.W. Becker, R.A. Fischer, Chem. Vap. Deposition 6 (2000) 245.

[94] J. McMurran, J. Kouvetakis, D.J. Smith, Appl. Phys. Lett. 74 (1999) 883.

[95] J. McMurran, M. Todd, J. Kouvetakis, D.J. Smith, Appl. Phys. Lett. 69 (1996) 203.

[96] A. Wohlfart, A. Devi, F. Hipler, H.W. Becker, R.A. Fischer, J. Phys. IV 11 (2001) 683.

[97] Y. Yaping, Z. Keyan, G. Zhanxian, S. Yu, L. Bingling, J. Univ. Sci. Technol. Beijing 4 (1997) 43.

[98] Y.M. Zhao, K.Y. Zhou, Y.C. Yuan, Chin. Chem. Lett. 8 (1997) 185.

[99] A.C. Frank, R.A. Fischer, Adv. Mater. 10 (1998) 961.

[100] H. Winkler, A. Birkner, V. Hagen, R.S.I. Wolf, H.v. Seggern, R.A. Fischer, Adv. Mater. 11 (1999) 1444.

[101] A. Manz, A. Birkner, M. Kolbe, R.A. Fischer, Adv. Mater. 12 (2000) 569.

[102] H. Winkler, A. Devi, A. Manz, A. Wohlfahrt, W. Rogge, R.A. Fischer, Phys. Status Solidi A 177 (2000) 27.

[103] P.J. Herley, W. Jones, Z. Phys. D: At. Mol. Clusters 26 (1993) 159.