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Structural motifs and reactivity of small molecules containing subvalent Group 13 elements: matrix isolation and quantum chemical studies

Hans-Jörg Himmel *
Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstrasse, Geb. 30.45, 76128 Karlsruhe, Germany

Received 19th June 2003, Accepted 23rd July 2003
First published as an Advance Article on the web 4th August 2003

This review analyses some aspects of the variety of different structures small molecular compounds of the subvalent Group 13 elements can adopt. The discussion of experimental work restricts itself to matrix isolation studies. The experimental results are compared with those obtained for related (more stable) molecules using experimental methods other than matrix isolation and with the results of quantum chemical studies. Special consideration is given to the structural changes between homologues. All the molecules dealt with represent highly unstable species or reaction intermediates which can nevertheless be retained and characterized at leisure with the aid of the matrix-isolation technique. The combination of experimental spectroscopic information and detailed quantum chemical calculations can be used as a framework to analyse in detail the molecular and electronic structures of these species, most of which were sighted only very recently in experiments. Trends and differences in reactivity will also be considered, where information (experimental or theoretical) is available.

Hans-Jörg Himmel studied chemistry in Heidelberg, Germany, where he received his diploma in 1994. In that year he started work for his Ph.D., first in Heidelberg then in Bochum under the supervision of Prof. Dr. Christof Wöll at the Institute of Physical Chemistry; this work, completed in 1998, was in the field of surface science. From 1998 to 2000 he joined the group of Prof. Tony Downs at the Inorganic Chemistry Laboratory in Oxford, UK, with funding from the Deutsche Forschungsgemeinschaft (DFG), and received a D.Phil. degree from the University of Oxford in 2000. Since October 2000 he has been working on his Habilitation at the Institute of Inorganic Chemistry in the University of Karlsruhe, receiving a Habilitanden-Stipendium from the DFG since 2001. His research interests center on reaction mechanisms in inorganic chemistry, with vibrational and UV/Vis spectroscopy as the major methods of experimental enquiry, the matrix isolation technique as a primary tool for forming and retaining reactive intermediates, and extensive use of quantum chemical modeling.

Hans-Jörg Himmel

DOI: 10.1039/b307051b

1 Introduction

The aim of this micro-review is to analyse some aspects of the variations of structure and reactivity displayed by simple molecules containing B, Al, Ga or In (E) atoms. All the species discussed herein have in common that they consist of only a few atoms and generally represent subvalent species (with E in a formal oxidation state less than +3).[1] Despite their comparative simplicity, their experimental generation and characterization require considerable effort and have in most cases been achieved only very recently. Hence, most of the species are highly reactive or represent reactive intermediates. The experimental characterization of these molecules has profited greatly from the development of the matrix-isolation technique, which provides a means of retaining intermediates. This technique is now well established and several review articles discuss the relevant details.[2] The basic principles of the method will not therefore be discussed here.

The discussion will focus on binary subvalent hydrides with the general formula E_2H_n; compounds of the Group 15 elements ENH_n and EPH_n (n = 2–4); the carbonyls ECO, $E(CO)_2$ and $E_2(CO)_2$; oxides and superoxides with the general formula EO_2; subvalent halides EX; and the organometallic derivatives ECH_3, $HECH_3$ (and for comparison also $HESiH_3$ and its precursor, the complex $E{\cdot}SiH_4$), and ECp* [Cp* = $C_5(CH_3)_5$]. It will be shown that the greatest change of structure occurs between homologues composed of B atoms on the one hand and of Al atoms on the other hand. This is in agreement with the trends established for other Groups in the periodic table. This change results from the subtle interplay of several effects. For the hydrides E_2H_n, for example, the reduced strength of the E–H bond, the decreasing possibilities for significant E–E multiple bond formation,[3] and the remarkable synergy of the bonding to the H atoms (which can be positively or negatively polarized, and be engaged in terminal as well as bridging bonds) are among the factors which have to be taken into account. The small number of atoms in the species under consideration in this account allows for a detailed quantum chemical analysis at high levels of theory which sheds some additional light on the bonding. Where possible, the results will be compared with those obtained for derivatives of the compounds which can be synthesized by more conventional means. In these derivatives, sterically demanding organic groups are attached to the atom or atoms to decrease the reactivity. However, these organic groups may have a significant influence on the geometry at the E atoms as well as on the bond properties in general. Accordingly, they are in several cases by no means "innocent".

Not much is known about the reactivity of the species addressed here, and most of what we know derives from predictions made on the basis of quantum chemical calculations. The only exceptions are provided by the subhalides EX (E = Al, Ga or In; X = F, Cl or Br) and AlCp*. These species can be produced in considerable amount and high purity in the gas phase, opening up the possibility of studying in depth their reactivity in matrix experiments. Concerning the theoretical contributions to the understanding of the reactivity, we concentrate on the heats of hydrogenation (for compounds of the type E_2H_2, E_2H_4, ENH_2 and ENH_4) and the heats of dimerization, which have been studied recently in our group. Finally, additional valuable information about bond strengths is derived from the fragmentation energies.

Some of the species discussed are not only of academic interest. They can be regarded as possible intermediates in CVD (chemical–vapour depostion) processes designed to generate metal or III/V semiconductor devices. Fig. 1 illustrates a possible pathway leading to a layer of GaN on a surface. It starts with a base-stabilized GaH_3 precursor [or with $Ga(CH_3)_3$] which is sprayed together with NH_3 in H_2 as carrier gas onto a surface at elevated temperatures. Under these conditions the precursor decomposes with the formation of Ga atoms at the surface as the first step. The atoms then react at the surface with NH_3 to yield subvalent species of the general formula $Ga_xN_xH_y$, which finally eliminate H_2 to give $(GaN)_x$. In the following discussion, ways of generating and characterizing experimentally species with the formula $GaNH_y$ in inert gas matrices will be discussed. The spectroscopic information about these subvalent species can be compared with spectra taken from surfaces during CVD processes, with the aim of seeking to identify some of the intermediates formed during the CVD processes. Of even greater interest for the fabrication of semiconductor devices are species of formula EPH_y which are also evaluated here. In the absence of NH_3 or PH_3, processes designed to generate metal coatings may give rise to E_xH_y species as possible intermediates, and the spectroscopic characterization of species of this kind is likely also to be relevant to the mechanisms leading to metal layers *via* CVD processes.

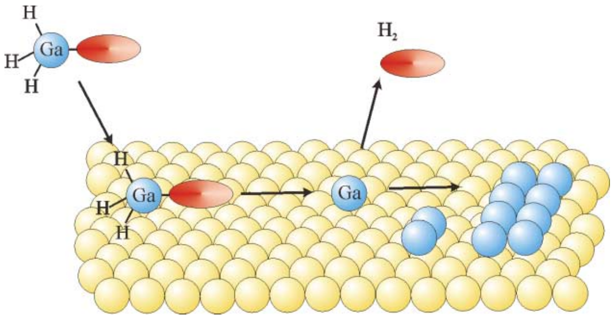


Fig. 1 Possible steps in the chemical vapour deposition of a base-stabilized GaH_3 precursor leading finally to a metal layer.

The reaction between metal atoms and O_2 is of fundamental interest for a better understanding of oxidation processes. The adsorption of O_2 at metal and III/V semiconductor surfaces has been studied extensively in the past to shed more light on the first steps of this process.[4] Tackling the problem from another perspective has led to studies of the response of metal atoms towards O_2 in the gas phase, as well as in inert gas matrices. It will be shown that the Group 13 element atoms Al, Ga or In react spontaneously to form cyclic molecules with O_2, which can be formally described as superoxo species. In the case of GaO_2, photolysis brings about conversion into the linear OGaO isomer. Surprisingly, linear OGaO has nearly the same energy as its cyclic isomer. This shows that cleavage of the O–O bond can be achieved by the metal atom and points the way to possible steps in an oxidation process.

Carbonyl complexes of the elements B, Al, Ga and In are also of considerable interest. While numerous transition metal carbonyls have been characterized experimentally, main group element carbonyls are still a rarity. It will be shown that the binding energies and also the measured wavenumbers of the *ν*(CO) stretching fundamentals of the Group 13 derivatives identified by matrix isolation signify M–CO bonds at least as strong as those formed by a late transition metal like Ni. This may come as a surprise in its implication that the difficulties in synthesizing main group element carbonyls are not for want of interaction energy. Indeed, it suggests that the preparation of CO derivatives of these elements may be possible, if one can manage to prevent them from undergoing further reactions. If so, it would not be the first time that matrix isolation experiments have spurred the development of strategies for synthesising new classes of compounds on a preparative scale.

Organometallic E(I) derivatives like AlCp* are used in inorganic synthesis. At room temperature, this species is present as a tetramer $[AlCp^*]_4$. Only at elevated temperatures and in solution can monomeric AlCp* be detected, being then in equilibrium with the tetramer. The reactivity of the monomeric AlCp* can be analysed in detail through the medium of matrix-isolation experiments. Such an analysis certainly leads to a better understanding of the mechanisms of reactions involving AlCp*. Metastable solutions of the halides EX (E = Al or Ga; X = Cl, Br or I) have been used to synthesize a number of ligand-shielded Al and Ga clusters. As will be shown, these subvalent species are highly reactive under photo-activation. One of the aims of the matrix studies is to evaluate the potential and limits of a photochemistry which may ultimately lead to the preparation of new compounds on a preparative scale.

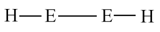
Finally, the reaction of Group 13 element atoms with SiH_4 gives evidence for the formation of a complex of the form $E{\cdot}SiH_4$, which can be converted reversibly into $HESiH_3$ upon selective photolysis. This reaction is of interest in relation to the mechanism of Si–H insertion processes at metal centres. This and related insertion reactions are key steps in many catalysis cycles.

2 Binary subvalent hydrides of the general formula E_2H_n (n = 2 or 4)

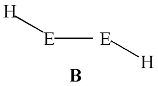
E_2H_2

For E = B, Al, Ga and In, subvalent hydrides of this formula have been characterized in matrix-isolation experiments. B_2H_2 can be generated as one of the products of the reaction between laser-ablated B atoms and H_2 in inert gas matrices. The molecule has been studied in solid Ar matrices using EPR[5] and IR[6] spectroscopy. The experiments show that the global energy minimum corresponds to a linear structure (**A**) with two unpaired electrons ($^3\Sigma_g^-$ ground electronic state) located in two mutually orthogonal π-orbitals. The energy required for fragmentation of the molecule into two singlet BH fragments amounts to about 450 kJ mol^{-1}. Fragmentation to give two triplet BH fragments requires *ca.* 700 kJ mol^{-1}. This is not far from the energy required to cleave the C–C bond in H_2CCH_2 (*ca.* 760 kJ mol^{-1}), also leading to two triplet (H_2C) fragments. Thus, it can be said that the B–B bond is strong and that significant π-bonding is present. Nevertheless, hydrogenation of HBBH to give the D_{2d} symmetric H_2BBH_2 is accompanied by a standard enthalpy change of as much as −237 kJ mol^{-1}. This value is *ca.* 100 kJ mol^{-1} more exothermic than the corresponding one for H_2CCH_2. Dimerization to give the T_d-symmetric B_4H_4 is also a highly exothermic reaction releasing *ca.* 500 kJ mol^{-1}. For comparison, dimerization of H_2CCH_2 (this time leading of course to the cyclic D_{4h}-symmetric cycloaddition product) is exothermic by less than 100 kJ mol^{-1}. Hence it appears that although the B–B bond in HBBH is strong, the molecule is highly reactive not because of any unusual instability, but because of its susceptibility to undergo further reactions.

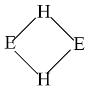
In the case of the heavier homologues, the linear form HEEH defines not a local energy minimum, but a saddle point on the energy hyper-surface. Instead, a *trans*-bent structure (**B**) with C_{2h} symmetry and singlet ground electronic state defines the corresponding local minimum with two terminal H atoms (structure **B**). The energy difference between this and the four other possible isomers (structures **C–E**) are, according to



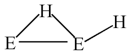
A



B



C



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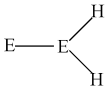
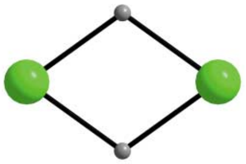


E

quantum chemical calculations, relatively small (< 50 kJ mol^{-1}), and the C_{2h} symmetric isomer does not define the global energy minimum. Instead, this minimum corresponds to the cyclic, D_{2h}-symmetric isomer (**C**). In matrix experiments, isomers of Al_2H_2 have been cited as the products of the reaction between Al atoms, produced by laser-ablation, and H_2.[7] Three isomers (**B**, **C** and **E**) of Ga_2H_2 and two isomers (**B** and **C**) of In_2H_2 have been generated by matrix reactions of the metal vapours with H_2.[8] In agreement with quantum chemical calculations, the spectroscopic data show that both these molecules prefer a cyclic structure with D_{2h} symmetry (**C**). Ga(μ-H)$_2$Ga is formed spontaneously from Ga_2 and H_2 at temperatures of 10 K (see discussion below).

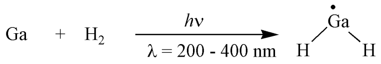
Selective photolysis of the matrix-isolated cyclic Ga(μ-H)$_2$Ga and In(μ-H)$_2$In molecules brings about isomerization. Hence, it was possible to characterize the molecules HGaGaH and HInInH in their *trans*-bent, C_{2h}-symmetric structures (**B**) as the products of photolysis with light at λ_{max} = 546 nm. With the synthesis and structural characterization of the first neutral RGaGaR compounds (R = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$),[9] interest in the bonding of such species has grown apace. The main question to be raised is: can Ga–Ga multiple bonding be achieved? At 262.7 pm, the Ga–Ga distances in the RGaGaR compounds studied by X-ray diffraction indicate that the interaction is relatively weak. Crystal structures have also been reported for compounds with the formula $(Na^+)_2(RGaGaR)^{2-}$ [*e.g.* R = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$],[10a] containing a species formally valence-isoelectronic with acetylene. This compound features a relatively short Ga–Ga distance of only 231.9 pm, causing a Ga–Ga "triple" bond to be invoked.[10b] However, recent theoretical studies indicate that the Na^+ ions are deeply engaged in the bonding, so that the compound is more adequately described as a "Ga_2Na_2 cluster".[11,12] Even in the case of Ga–Ga single bonds, the structural data accumulated over the years indicate that bond length alone is not a sufficient criterion of bonding. Hence it has been shown that this single bond can adopt a large range of distances [*e.g.* 238.7(5) pm for $Ga_2[Ga_2I_6]$[13a] and 254.1(1) pm for (Trip)$_2$GaGa(Trip)$_2$ (Trip = 2,4,6-iPr$_3$C$_6$H$_2$)].[13b] The spectroscopic analysis of HGaGaH clearly shows that the Ga–Ga bond is weak [as indicated indirectly by the relatively low wavenumber of the IR-active antisymmetric ν(Ga–H) mode]. A Ga–Ga bond distance of 258.5 pm, derived from calculations, is within the limits of the computational accuracy in agreement with the one found experimentally in RGaGaR compounds (R = Mes*$_2$C$_6$H$_3$ or 2,4,6-iPr$_3$C$_6$H$_2$), although the steric demands of the large organic groups may lead to a slight elongation. The interaction can be described as a relatively weak donor–acceptor bond between two GaH units. In agreement with this description, the H–Ga–Ga angle in HGaGaH is 121.3°.

HBBH

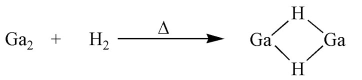


Ga(μ-H)$_2$Ga

One of the surprising results of the experiments leading to the formation of Ga_2H_2 is that the cyclic isomer is formed *spontaneously* in an Ar matrix at temperatures as low as 12 K as the product of the reaction between Ga_2 and H_2. By contrast, Ga atoms in their ^2P ground electronic state have been shown previously not to react with H_2; excitation of the Ga atom from its ^2P ground state into the ^2S or ^2D excited state is necessary to initiate insertion into H_2 leading then to the bent radical GaH_2.[14–16] A quantum chemical analysis of the differences in reactivity between a Ga atom and a Ga_2 dimer is noteworthy for the light it sheds on the unusual reactivity of clusters.[17] On the basis of the experimental results alone, the following conclusions can be drawn with respect to the reaction mechanism. (i) The reaction proceeds in a concerted fashion in one step. (ii) The reaction is subject to a marked isotopic effect which provides extra quantitative information about the mechanism. Ga_2 exhibits a $^3\Pi_u$ ground electronic state. However, the energy differences between this and the $^1\Sigma_g^-$, $^1\Sigma_g^+$, $^1\Pi_u$ and $^1\Delta_g$ excited states amount to not more than 6.8, 19.3, 46.3 and 56.0 kJ mol^{-1}, respectively.[17] The combined experimental and quantum chemical results show that for both the reaction of a Ga atom and of a Ga_2 dimer the total electronic state has to change in the course of the reaction, the approach of the two reactants proceeding along a high-symmetry pathway with C_{2v} symmetry. This change determines the barrier to reaction reached near the point at which the system changes its potential energy hypersurface from that appropriate to the electronic states of the reactants to that appropriate to the electronic state of the product. Because of the presence of several energetically accessible electronic states of Ga_2, the barrier is relatively small, provided that effective spin–orbit coupling provides a means of enabling an otherwise "forbidden" transition. By contrast, the energy levels of a Ga atom are much more widely spaced giving rise to a higher barrier to insertion. Similar arguments are applicable more generally to clusters, the reactivity of which can be explained, at least in some cases, by the possibility of facile change of the electronic state.



(1)



(2)

So far, it has not been possible to study the chemistry of the E_2H_2 species in experiments. Theoretical calculations have therefore been carried out to assess the reactivity of these molecules. Hydrogenation to give E_2H_4 (with geometries to be discussed) is exothermic for all E_2H_2 species. The enthalpy change for the hydrogenation reaction decreases continuously in the order $B_2H_2 > Al_2H_2 > Ga_2H_2$ for the molecules in their global energy minimum structure. The value calculated for Al_2H_2 (−139.2 kJ mol^{-1}) is close to that calculated (−140.8 kJ mol^{-1}) and determined experimentally (−137 kJ mol^{-1}) for C_2H_4. However, the structure of Al_2H_2 leaves no hope of significant Al–H bonding. Hydrogenation of a *linear* HAlAlH molecule (with a triplet ground electronic state) to give a planar, D_{2h}-symmetric H_2AlAlH_2 molecule is, as expected, a much more exothermic process with an enthalpy change of *ca.* −200 kJ mol^{-1}.

Dimerization of the E_2H_2 species leads to E_4H_4, for which the global energy minimum form exhibits T_d symmetry. Dimerization of B_2H_2 is highly exothermic (ΔH^0 = −424.0 kJ mol^{-1}). For Al_2H_2 and Ga_2H_2 in their cyclic global energy minimum structures (D_{2h} symmetry), dimerization is considerably less exothermic (−211.0 / −185.5 kJ mol^{-1} for Al_2H_2 and −111.1 / −109.6 kJ mol^{-1} for Ga_2H_2).[18]

Fragmentation into two singlet GaH fragments requires 56.5 / 67.3 kJ mol^{-1} [MP2 / CCSD(T) estimates] in the case of the *trans*-bent isomer HGaGaH.[19] The corresponding fragmentation of HAlAlH, also in its C_{2h}-symmetric isomeric form, consumes about 65 kJ mol^{-1}. While these values are relatively small, the fragmentation of linear HBBH in its triplet ground electronic state to give singlet BH is, as already mentioned, accompanied by a much higher standard enthalpy change of 511.0 / 449.6 kJ mol^{-1} [MP2 / CCSD(T) estimates].

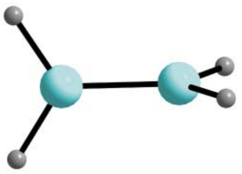
E_2H_4

So far, only one of the species E_2H_4 has been characterized experimentally.[20] The one exception is Al_2H_4, which has been cited very recently (see below). However, derivatives are known and these give preliminary ideas of possible structures. In the structurally analysed derivatives Ga_2Cl_4 and Ga_2Cl_3H, for example, salt-like structures of the form $Ga^+[GaCl_4]^-$[21a,b] and $Ga^+[GaCl_3H]^-$[21c] are adopted. In theoretical studies, planar, D_{2h}-symmetric structures, D_{2d}-symmetric structures with a dihedral angle of 90° between the two EH_2 units, and salt-like structures $E^+[EH_4]^-$ (for which at least three different isomers are possible depending on the position of the E^+ cation relative to the distorted $[EH_4]^-$ tetrahedron) have been analysed.

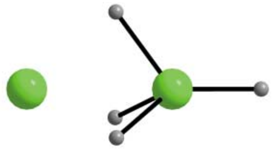
H_2BBH_2 is believed to exhibit a D_{2d}-symmetric global energy minimum structure.[22] For the heavier homologues Al_2H_4 and Ga_2H_4, salt-like structures $Al^+[AlH_4]^-$ and $Ga^+[GaH_4]^-$ seem to define the corresponding minima.[23] In these structures, the E^+ cation is located close to one of the faces of the slightly distorted EH_4^- tetrahedron, resulting in C_{3v} symmetry overall. However, other isomers have very similar energies. The energy difference between the global minimum and the D_{2d}-symmetric structure amounts to not more than 42.6 or 46.0 kJ mol^{-1} in the case of E = Al and 41.9 or 32.3 kJ mol^{-1} in the case of E = Ga (according to calculations with B3LYP or MP2, respectively).[12] The IR spectrum reported very recently for Al_2H_4 in an H_2 matrix indicates a D_{2d}-symmetric structure, although other bands have also been attributed to the salt-like molecule $Al^+[AlH_4]^-$ (with both C_{3v} and C_{2v} symmetries).[24]

Hydrogenation of H_2EEH_2 to give two planar EH_3 moieties is slightly exothermic for E = B (standard reaction enthalpies of −2.0/−4.1 kJ mol^{-1}, according to B3LYP/MP2), but endothermic for E = Al and Ga by +16.8/+27.1 and +50.4/+41.4 kJ mol^{-1}.

Fragmentation of H_2BBH_2 to give two BH_2 fragments requires a standard enthalpy change of +466.1/+461.8 kJ mol^{-1} [values quoted in the order B3LYP/CCSD(T)]. At 248.8/271.2 and 260.0/261.7 kJ mol^{-1}, the standard enthalpy change for fragmentation is, as anticipated, considerably smaller for H_2AlAlH_2 and H_2GaGaH_2 (also in their D_{2d} local energy minimum forms).



H_2BBH_2



$Ga^+[GaH_4^-]$

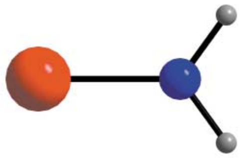
3 Group 13/15 compounds with the general formula ENH_n (n = 2–4)

ENH_2

HBNH is formed in experiments in which laser-ablated B atoms are co-deposited together with NH_3 in an Ar matrix.[25] From the presence in the IR spectrum of absorptions due to both a ν(B–H) and a ν(N–H) stretching fundamental it can immediately be concluded that the molecule carries one terminal B–H and one terminal N–H bond. Full valence complete active space (CASSCF) calculations with a cc-pVDZ basis set indicate that the molecule is linear and exhibits a $^1\Sigma^+$ ground electronic state. At 125.2 pm, the B–N distance is relatively short. The other possible isomer, the amide BNH_2 ($^1A_1$ ground electronic state) is *ca.* 170 kJ mol^{-1} higher in energy and has an elongated B–N distance (140.1 pm).

The heavier homologues can also be generated as products of the reaction between the Group 13 element atoms and NH_3 in Ar matrices.[26,27] If the metal atoms are thermally evaporated, photolysis is required and the reaction leads first to the insertion product $HENH_2$, a radical species detectable by its EPR spectrum,[28] and which decomposes in a second step upon further photolysis to give ENH_2. In the course of H atom migration through the matrix, H_2ENH_2 is formed as an additional product of the reaction with unchanged $HENH_2$. In the case of Al atoms, products from the reaction of one Al atom with two NH_3 moieties have also been traced.[29] In contrast to BNH_2, the presence of an absorption attributable to the deformation mode $\delta(NH_2)$ as well as the wavenumber measured for the ν(E–N) mode in the IR spectra leave no doubt that $AlNH_2$ and $GaNH_2$ are E(I) amides. The isomer HENH with terminal E–H and N–H bonds is estimated to occur 177.7, 188.4 and 257.5 kJ mol^{-1} (for E = Al, Ga and In, respectively) to higher energy of the amide ENH_2. In contrast to HBNH, these species are bent (C_s symmetry) with H–E–N angles of 167.2, 141.9 and 135.9° for E = Al, Ga and In, respectively.

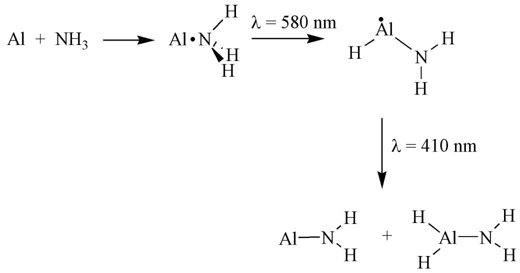
HBNH



$AlNH_2$

ENH_3

As already mentioned, the radicals $HAlNH_2$ and $HGaNH_2$ can be formed by reaction of Al or Ga atoms with NH_3. The insertion process of the metal atom into the N–H bond has been analysed in quantum chemical studies. The first stage of the reaction proceeds spontaneously to the complex $E{\cdot}NH_3$, which can be characterized experimentally by its IR, UV/Vis and EPR spectra.



(3)

The reaction energy for formation of this complex amounts to not less than about −50 kJ mol^{-1}. At 50 kJ mol^{-1}, according to an SCF (self-consistent field) MO estimate, the activation barrier to $HAlNH_2$ formation is relatively small. In fact, experiments have shown that IR radiation is sufficient to bring about tautomerization from $Al{\cdot}NH_3$ to $HAlNH_2$ in a solid Ar matrix. An alternative way is to photolyse the complex with λ = 440 nm light, which corresponds to the absorption maximum of the complex in the UV/Vis spectrum, and can be assigned to a perturbed metal-localized $^2S \longleftarrow {}^2P$ electronic excitation. The analysis of the EPR spectrum measured for $HAlNH_2$ shows, as anticipated, that the unpaired electron is mainly centred at the Al atom, making it an authentic Al(II) compound. The $HENH_2$ species all exhibit planar structures, implying some interaction between the p orbitals at the N and the E atoms. However, the energy difference between pyramidal and planar forms of NH_3 and its derivatives is very small,[30] and the planar structure could easily be stabilized by other influences, *e.g.* hyperconjugative effects as shown by Cl_3SiNH_2[30b] and numerous other molecules.

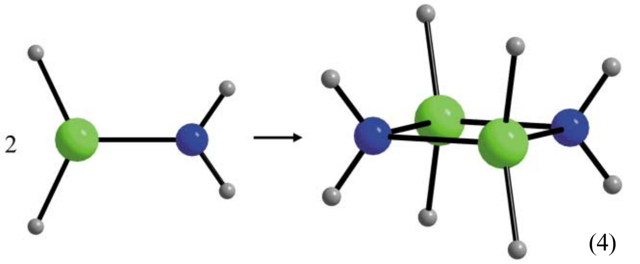
As to its reactivity, $HAlNH_2$ has been shown to form with NH_3 a complex $HAlNH_2{\cdot}NH_3$ with a binding energy of *ca.* 80 kJ mol^{-1}. In the course of the complexation, the geometry at the N atom of the amide group becomes pyramidal, a change caused by the reduced π interaction within the $HAlNH_2$ unit. The p-orbital at the Al atom interacts now with the NH_3 molecule and cannot establish a π-interaction with the p-orbital at the N atom of the NH_2 group. The $HAlNH_2{\cdot}NH_3$ complex can also be traced by its EPR spectrum.

ENH_4

H_2BNH_2 ("inorganic ethylene") can be formed *via* pyrolysis of a B_2H_6/NH_3 mixture or of $H_3B{\cdot}NH_3$.[31] The molecule exhibits a planar, C_{2v}-symmetric structure. On a preparative scale, the molecule is isolable only in its BH_3-stabilized form, $H_2B(\mu\text{-}H)(\mu\text{-}NH_2)BH_2$, in the form of derivatives like $Cl_2BN(CH_3)_2$, or as oligomers or polymers.

It has been shown that H_2AlNH_2, H_2GaNH_2 and H_2InNH_2 can be formed in the course of the photolytically induced reactions between E atoms and NH_3, with the radical species $HENH_2$ being the identifiable precursors.[27,32] All three molecules exhibit a planar geometry with C_{2v} symmetry. The IR data obtained for several isotopomers ($H_2E^{14}NH_2$, $D_2E^{14}ND_2$ and $H_2E^{15}NH_2$) allowed the force constant f(E–N) to be determined *via* normal coordinate analysis. Values of 408.1, 397.0 and 315.3 N m^{-1} are thus found for H_2AlNH_2, H_2GaNH_2 and H_2InNH_2, respectively.[30] According to quantum chemical calculations, the barriers to rotation about the E–N bond amount to 161.9, 50.6, 65.7 and 51.5 kJ mol^{-1} for E = B, Al, Ga and In, respectively. For H_2CCH_2, the barrier is found experimentally to be 272 kJ mol^{-1}.[33] The results point to a reduced π-interaction in the H_2ENH_2 species, in agreement with the polar character of the E–N bond. At 177.9 pm for E = Al, 182.1 pm for E = Ga and 197.0 pm for E = In, nevertheless, the E–N bonds in H_2ENH_2 are calculated to be relatively short.

While the hydrides H_2ENH_2 can be stabilized in the form of their monomers only in solid inert-gas matrices, derivatives of all the species have been synthesized on a preparative scale.[34] However, these monomeric derivatives are stable only if highly encumbered ligands like 2,4,6-tBu$_3$C$_6$H$_2$ and 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ are used.[35] Otherwise, oligomerisation occurs. Dimerisation of the H_2ENH_2 species leads to cyclic, D_{2h}-symmetric products.



(4)

The enthalpy changes for dimerisation amount to −67 (B), −237 (Al) and −245 (Ga) kJ mol^{-1} according to coupled-cluster single double triple (CCSD(T)) calculations.[18]

4 Group 13/15 compounds with the general formula EPH_n (n = 2–4)

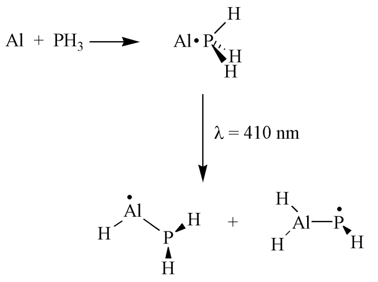
EPH_2

In the case of the reaction of a Group 13 metal atom with NH_3, the amide ENH_2 is found to be a major product. The analogous reaction with PH_3 gives, however, no evidence for the corresponding phosphide EPH_2, a species for which information has to date come exclusively from quantum chemical calculations. According to such calculations, EPH_2 exhibits C_s symmetry. In contrast to ENH_2 (C_{2v} symmetry), it is non-planar with a pyramidal configuration at the P atom.

Another possible isomer is HEPH featuring terminal E–H and P–H bonds. This is 43.5 (Al), 69.6 (Ga) and 183.1 (In) kJ mol^{-1} higher in energy than EPH_2. As with the N homologue, HEPH species are bent, but this time with E–P–H angles of 84.3, 85.9 and 94.8° for E = Al, Ga and In, respectively, although the calculations indicate that the potential well is extremely shallow with respect to the bending coordinates.

EPH_3

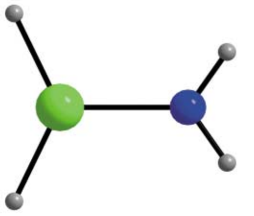
Matrix reactions of the metal atoms with PH_3 afford species of the general formula EPH_n. The complex $Al{\cdot}PH_3$, which is formed spontaneously, is recognisable by its IR spectrum. Photolysis brings about insertion of the metal atom into the P–H bond leading to the radical species $HAlPH_2$, with the unpaired electron residing at the Al atom. However, in contrast to its homologue $HAlNH_2$, another isomer, namely H_2AlPH, is formed, in which the unpaired electron is located at the P atom. Experiments with Ga and In follow the same pattern. According to quantum chemical calculations, the energy difference between the $HEPH_2$ and the H_2EPH isomers amounts to 1.4, 19.9 and 52.6 kJ mol^{-1} in favor of $HEPH_2$ for E = Al, Ga and In, respectively.



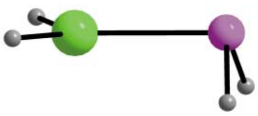
(5)

EPH_4

So far, no species with the formula EPH_4 has been detected in experiments. Quantum chemical calculations predict a C_s-symmetric global energy minimum structure; in contrast to the homologue H_2ENH_2, this features a pyramidal configuration at the P atom. The difference between H_2ENH_2 and H_2EPH_2 reflects the larger barrier to inversion of phosphines compared with amines. The E–P distances are calculated to be 233.8, 233.1 and 253.6 pm for H_2AlPH_2, H_2GaPH_2 and H_2InPH_2, respectively.[30]



H_2GaNH_2

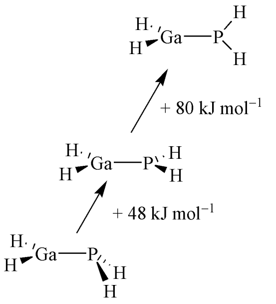


H_2GaPH_2

To assess the capability for π-interaction, calculations have also been carried out for the H_2EPH_2 molecules in their planar

C_{2v}-symmetric structures, which no longer define minima on the potential energy hyper-surface. The energy difference between this planar structure and the global energy minimum, 17.6, 41.0, 47.4 and 52.5 kJ mol^{-1} for E = B, Al, Ga and In, respectively,[30] can be used as an estimate of the barrier to inversion. In the case of PH_3, the difference is *ca.* 150 kJ mol^{-1}. Thus, the planar structures are stabilized through significant π-interaction. It has been argued that the non-planarity of the structures indicates a weaker capability for π-interaction. However, the calculations show that a detailed analysis has to include the differences in the inversion barrier between amines and phosphines. For NH_3, the inversion barrier is *ca.* 24 kJ mol^{-1}, as compared with *ca.* 150 kJ mol^{-1} for PH_3. Thus, in the case of amides, a weak π-interaction, which can be fully established only in the planar form, is sufficient to bring about the change to a planar ENH_2 skeleton.

The barriers to rotation about the E–P axis can be used to estimate the strength of the π-bond in the planar H_2PEH_2 molecule. Unlike the bond length, the barrier is not strongly affected by the polarity of the bond. For H_2BPH_2, a value of 170 kJ mol^{-1} is obtained. It may come as a surprise that the estimate is not smaller than that calculated for H_2BNH_2 (162 kJ mol^{-1}). In fact, the high value signals that π-bonding in H_2BPH_2 cannot be weaker than in H_2BNH_2. However, it has been pointed out that the σ-bond strength changes during the rotation. In the transition state, the σ-bond is stronger because the bond distance can relax to its optimal value. Therefore the barrier to rotation is a *lower* limit to the actual π-bond strength. Nevertheless, it can be said that the non-planarity of the H_2EPH_2 molecules is caused not by a reduced capacity for π-bonding but by the increased height of the inversion barrier. In the case of planar H_2AlPH_2, H_2GaPH_2 and H_2InPH_2, the barrier to rotation is calculated to be 66, 80 and 65 kJ mol^{-1}, respectively,



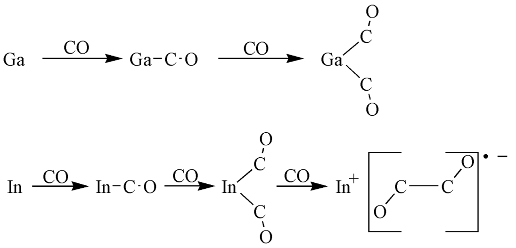
(6)

i.e. not very different from the values estimated for H_2AlNH_2, H_2GaNH_2 and H_2InNH_2. Of course, all these values are much smaller than that derived for H_2CCH_2 (272 kJ mol^{-1}).[36] They are close to the barrier estimated for H_2SnSnH_2 (82 kJ mol^{-1}).[37]

5 Carbonyls

ECO and $E(CO)_2$

BCO has been characterized by EPR [38] and IR [39] spectroscopy. The molecule favours a $^4\Sigma^+$ ground electronic state. The spin density on the B atom is *ca.* 0.83 au. BCO is *ca.* 295 kJ mol^{-1} more stable than its isomer BOC. For E = Al, Ga or In, the carbonyls ECO and $E(CO)_2$ can be formed spontaneously when the E atoms are brought together with CO in an Ar matrix.[40,41] The proportion of CO in the matrix determines the relative proportions of the mono- and di-carbonyl. In contrast to BCO, the ground electronic state of AlCO, GaCO and InCO has only one unpaired electron. The $^2\Pi$ state adopted by the molecule in its linear form is unstable towards bending in the case of AlCO. According to quantum chemical calculations, the Al–C–O angle in AlCO is *ca.* 173°. In the case of GaCO and InCO, a linear geometry is adopted; in consequence, no ESR signal can be detected.



(7)

The wavenumber (in cm^{-1}) measured for the *ν*(CO) stretching fundamental decreases in the series BCO[39] 2002.3 > InCO[40] 1920.8 > GaCO[40] 1875.6 > AlCO[41] 1867.7. It has been argued that the Group 13 monocarbonyls do not afford an obvious correlation between *ν*(C–O) and the extent of π-backbonding. A trend can be established from the calculated distances E–C (213.2 pm for AlCO, 222.6 pm for GaCO, and 244.0 pm for InCO) and C–O (117.6 pm for AlCO, 116.6 pm for GaCO, and 116.4 pm for InCO). These values indicate that the E–C bond strengths decrease in the order AlCO > GaCO > InCO.

The dicarbonyl $B(CO)_2$ has been characterized by its IR spectrum.[39] For the heavier homologues, IR and, in the cases of $Al(CO)_2$[42] and $Ga(CO)_2$,[43] EPR spectra have been reported. According to the EPR studies, the bonding in $Al(CO)_2$ and $Ga(CO)_2$ is fairly similar. It can be explained if sp^2 hybridisation of the metal atom is assumed. The two vacant hybrid orbitals are then engaged in a σ-type dative interaction with the two CO molecules. A significant degree of back-donation is achieved through overlap of the p Al or Ga orbital perpendicular to the molecular plane with antibonding π* orbitals of the CO molecules.

The most striking feature of some of the structures is the significant deviation of the E–C–O angle from 180°. The angle is calculated to be 173, 165.4, 163.1 and 174.0° for AlCO, $Al(CO)_2$, $Ga(CO)_2$ and $In(CO)_2$, respectively. Several reasons for the deviation are discussed in the literature.[44] Among them are the repulsive interaction between the s orbital of the metal atom and the σ orbital of the CO group, and, in the case of the dicarbonyls, an attractive interaction between the C atoms of the two CO groups.

The binding energy is higher than in other known complexes of the elements (*e.g.* $Al{\cdot}NH_3$ or $Al{\cdot}SiH_4$[45]). AlCO, GaCO and InCO have energies of −81, −61 and −43 kJ mol^{-1} with respect to the metal atom in its ^2P ground state and CO. In the case of the dicarbonyls $Al(CO)_2$, $Ga(CO)_2$ and $In(CO)_2$, the corresponding energies amount to −176, −125 and −85 kJ mol^{-1}, respectively. The binding energies are thus comparable with those of late transition metal carbonyls.

Interestingly, $In(CO)_2$ is not photostable, but can be converted by the action of broad-band photolysis into $In^+(C_2O_2)^-$ (*e.g.* with CO reduction). An inspection of the molecular orbitals shows that excitation of an electron into the singly occupied orbital (exhibiting b_1 symmetry) should increase the bonding between the two C atoms, thus accounting possibly for the observed photoreaction.

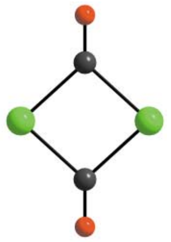
Dimerisation of BCO leads to linear OCBBCO (*quantum vis*). This reaction is exothermic by as much as *ca.* −580 kJ mol^{-1}. The dimerisation of AlCO and GaCO, giving this time cyclic $Al(\mu\text{-}CO)_2Al$ and $Ga(\mu\text{-}CO)_2Ga$ (*quantum vis*) is exothermic by *ca.* −180 and −143 kJ mol^{-1}, respectively. Reactions of BCO appear to be more exothermic than comparable reactions of the heavier homologues, in line with the general trends established for the subvalent species discussed here.

$E_2(CO)_2$

Very recently, $B_2(CO)_2$ has been described as one of the products generated in the reactions between laser-ablated B atoms and CO.[46] The experiments indicate that it results from dimerisation of two BCO molecules. The molecule is linear ($^1\Sigma_g^+$ ground electronic state) with two terminal CO groups and features a strong B–B bond. With a distance estimated at 147.0 pm by CCSD(T) calculations, the B–B bond shows some evidence of "triple-bond" character.

For $Ga_2(CO)_2$, a cyclic structure with D_{2h} symmetry is adopted with two bridging CO groups, $Ga(\mu\text{-}CO)_2Ga$,[40] and a Ga ··· Ga distance of 318.8 pm. This again illustrates the tendency of the heavier homologues to avoid direct E–E bonding. The molecule has a singlet ground electronic state, but interestingly a triplet state seems to be very close in energy. The wavenumber of 1774 cm^{-1} measured for the antisymmetric ν(CO) fundamental indicates a significant binding energy. Indeed, according to DFT calculations, the energy with respect to Ga atoms in their ^2P ground electronic state and CO amounts to -265 kJ mol^{-1}.

OCBBCO



Ga(-μCO)₂Ga

6 Oxides

EO_2

BO_2 can be generated by reaction of laser-ablated B atoms with O_2. It has been identified not only in inert gas matrices,[47] but also in the gas phase.[48] However, the main product of the gas-phase reaction between B atoms and O_2 is BO.[48c] This has been explained by the large surplus of energy released in the course of the formation of BO_2 (about 200 kcal mol^{-1}) which brings about immediate decomposition into BO and O in the gas phase, where the energy cannot be dissipated fast enough by the environment. If the same reaction is carried out in a matrix environment, however, the matrix is able to take up the energy, as well as inhibiting the escape of potential decomposition products, and BO_2 is found to be the dominant product. BO_2 exhibits a linear global energy minimum in a $^2\Pi$ ground electronic state. Interest in this molecule arises partially from the Renner–Teller-effect,[49] which can be studied in detail.[49] The effect leads to a splitting of the bending vibrational states. In the case of BO_2, the $\upsilon = 1 \longleftarrow 0$ band (due to the bending mode ν_2) consists of eight transitions (see Fig. 2), of which the following six are electric dipole-allowed [with energy difference (in cm^{-1}) given in parenthesis]: from $^2\Pi_{3/2}$ to $^2\Sigma_u^+$ (406.27), $^2\Delta_{5/2}$ (443.39) and $^2\Sigma_u^-$ (634.46), and from $^2\Pi_{1/2}$ to $^2\Sigma_u^+$ (257.03), $^2\Delta_{3/2}$ (440.29) and $^2\Sigma_u^-$(485.22). The $^2P_{1/2}$ level lies 149.24 cm^{-1} above the $^2P_{3/2}$ level.[48] Transitions from the $^2P_{1/2}$ level are visible in the gas-phase spectra, but not in the spectra of an inert gas matrix at 4–15 K.

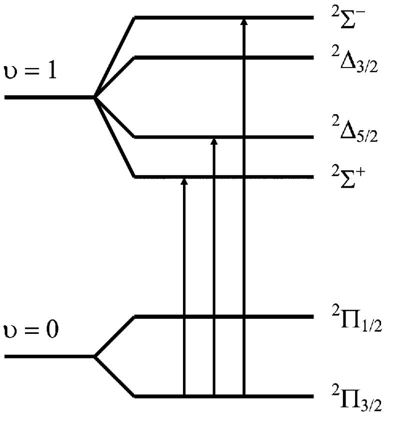
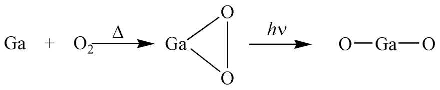


Fig. 2 Vibrational level splitting for the bending mode ν_2 of BO_2 due to the Renner–Teller effect.

On the other hand, thermally generated Al, Ga and In atoms react with O_2 to give cyclic, C_{2v} symmetric EO_2.[50] If the atoms are generated by laser-ablation, however, both the linear ($D_{\infty h}$ symmetry, $^2\Pi_g$ electronic ground state) and the cyclic (C_{2v} symmetry, $^2A_2$ electronic ground state) EO_2 forms are traceable in the spectra.[51] The cyclic forms can be approximately described as superoxo derivatives $E^+[O_2^-]$. According to CASSCF calculations,[52] the superoxo form is only 46 kJ mol^{-1} more stable than the linear OGaO isomer. Indeed, linear OEO is formed when the matrix-isolated cyclic EO_2 is subjected to photolysis.



(8)

Very recently, it has been shown that cyclic GaO_2 can be converted extremely efficiently into its linear isomer by irradiation with the 488 or 514 nm lines of an Ar^+ ion laser[53] In the case of InO_2, however, these lines do not cause isomerization. Accordingly, the Raman spectrum excited at $\lambda = 488$ or 514 nm for InO_2 shows the signals characteristic of the cyclic form, while the corresponding spectrum for GaO_2 shows only the signals characteristic of linear OGaO.

E_2O_2

B_2O_2 exhibits a linear global energy minimum geometry with a direct B–B bond and two terminal B–O bonds ($D_{\infty h}$ symmetry).[47] It can be formed either by dimerisation of BO or by reaction between B_2 and O_2. According to quantum chemical calculations, the dimerisation of BO to give B_2O_2 is exothermic to the extent of *ca.* 475 kJ mol^{-1}. Al_2O_2, Ga_2O_2 and In_2O_2 are also stable as linear molecules but feature no direct E–E bond, consisting only of E–O bonds (AlOAlO, GaOGaO and InOInO) to give a molecule with $C_{\infty v}$ symmetry.[51,54]

In addition to the linear forms, salt-like structures are also found.[53] Thus, the bands due to the species $Ga^+[GaO_2]^-$ were previously assigned to free GaO_2^-, with no reference to the associated cation. In experiments with thermally generated metal vapor, however, it is not possible to form free anions in the absence of a corresponding cation, and a combination of experimental and theoretical results indicates that the corresponding cation is Ga^+. $Ga^+[GaO_2]^-$ is formed upon photolysis of a matrix containing Ga_2 and O_2.

7 Subvalent halides EX (X = F, Cl or Br)

Metastable solutions of AlX and GaX have been prepared and used in the past to synthesize new metalloid cluster compounds. It is beyond the scope of this article to discuss this field, especially as it has already attracted a number of review articles.[55] Here we concentrate instead on the reactivity of EX monomers in a solid inert-gas matrix at low temperature. The monomers AlX and GaX can be generated by passing HX gas (or, in the case of X = F, better CHF_3) through a Knudsen-type cell containing the liquid metal at temperatures between 900 and 1000 °C. InCl can be evaporated directly from the solid material at temperatures of *ca.* 550 °C. The stretching fundamentals of the halides can be detected in IR experiments. For example, InCl trapped in an Ar matrix gives rise to a doublet feature at 293.9/287.8 cm^{-1} caused by $^{35}Cl/^{37}Cl$ isotope splitting. The wavenumbers are shifted with respect to those of the gaseous molecule (315.6 cm^{-1} for $In^{35}Cl$) as a result of the solvating effect of the matrix environment.

In contrast to the other species discussed here, some experimental information about the reactivity of these species is to hand. Thus, the reactions of AlX with H_2,[56] HX,[57] O,[58a] O_2,[59] CH_4,[60] and C_2H_2[61] (see Fig. 3), of GaX with O,[58b] H_2[62] and HCl,[63] and of InCl with H_2 and HCl[64] have been studied experimentally. All these reactions require photolysis, the most likely effect of which is excitation of the EX monomer from its $^1\Sigma$ ground electronic state to its $^3\Pi$ excited state (the singlet–triplet conversion being achieved either through spin–orbit coupling or with the help of the surrounding matrix).[65]

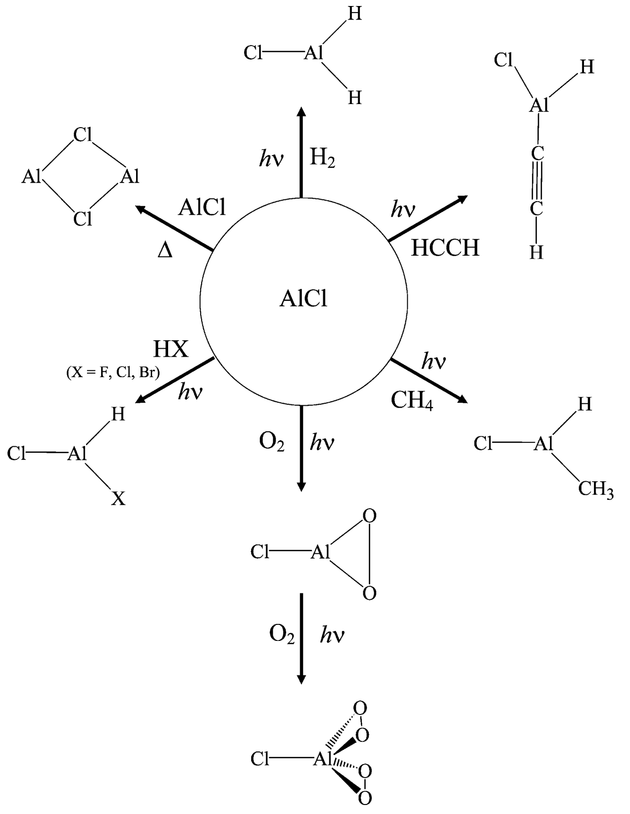
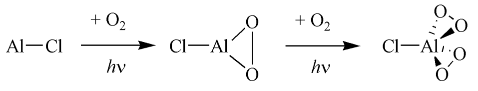


Fig. 3 Summary of the experimentally studied reactions of matrix-isolated AlCl monomers.

The reaction of photoactivated AlX with O_2 leads to the peroxo species $XAlO_2$ with C_{2v} symmetry and, with increased O_2 concentrations in the matrix, to the bis(superoxo) species $XAl(O_2)_2$ exhibiting a triplet ground electronic state.



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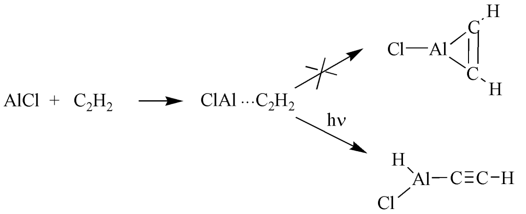
The reaction with one O_2 molecule to give the peroxo species is calculated to be exothermic by -140.3, -149.8 and -153.4 kJ mol^{-1} for AlF, AlCl and AlBr, respectively. The corresponding reactions of monovalent gallium or indium halides, GaX or InX, are calculated to be *endothermic*, and experiments have indeed failed to find evidence of any reaction product. Interestingly, the calculations indicate that the first triplet excited state of $XAlO_2$ has an energy only 38 (F), 39 (Cl) and 40 (Br) kJ mol^{-1} higher than that of the singlet ground electronic state. In the triplet electronic states, the O–O distances are markedly elongated (229.9, 229.1 and 228.9 pm *vs.* 166.0, 165.3 and 165.1 pm in the singlet ground electronic state). The reactions of these peroxo species with an additional O_2 molecule leading to the bis(superoxo) species are exoergic by -152, -143 and -138 kJ mol^{-1} for $FAlO_2$, $ClAlO_2$ and $BrAlO_2$, respectively.

AlCl, GaCl and even InCl react readily under photoactivation with H_2 to give H_2ECl (E = Al, Ga or In). The experiments show that the reaction proceeds in a concerted fashion. The mechanism has been studied in some depth by quantum chemical calculations.[65] The overall reaction proceeds with a reaction energy of -75.6, -11.3 and $+59.0$ kJ mol^{-1} for AlCl, GaCl and InCl, respectively. The calculations indicate that the barrier is substantial (*ca.* 250 kJ mol^{-1}) for the reaction of AlCl in its ground electronic state ($^1\Sigma$). However, once the halide has been excited into its $^3\Pi$ state, the barrier to reaction is very small. The change from the triplet (^3B in C_{2v} symmetry) to the singlet (^1A in C_{2v}) energy curve is presumably achieved through spin–orbit coupling. Although the reaction is endothermic in the case of InCl, H_2InCl is produced in high yield. This is a consequence of the high barrier for decomposition back to InCl and H_2.

The photoactivated reactions of AlCl with CH_4 and C_2H_2 have also been studied.



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In both cases, the Al atom inserts into the C–H bond leading to $HAl(Cl)CH_3$ and $HAl(Cl)C_2H$, respectively.[60,61] According to quantum chemical calculations, both reactions are exothermic (reaction energies of -43.2 kJ mol^{-1} and -113.0 kJ mol^{-1}, respectively). By contrast, the alumina–cyclopropene derivative is not formed in matrix experiments. In agreement with the experimental findings, calculations indicate that this has an energy *ca.* 51 kJ mol^{-1} higher than that of the acetylide $HAl(Cl)C_2H$.

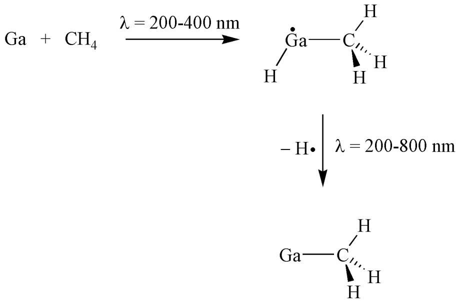
In additional experiments, the dimers of AlX and GaX have been cited in inert gas matrices with higher concentrations of the halide and characterized by their IR spectra.[66] These dimers exhibit a planar cyclic structure with D_{2h} symmetry, as attested by the IR spectrum of $(AlCl)_2$ which shows a band near 270 cm^{-1} with a complex $^{35}Cl/^{37}Cl$ isotope splitting pattern.

In our laboratory we are currently trying to use the experiences gained from the subvalent halide and cyclopentadienyl derivatives (see below) of Group 13 elements isolated in inert gas matrices to establish new photochemical methods on a preparative scale. The matrix experiments clearly show that the reactivity of the electronically excited species is much higher than that in their ground electronic states.

8 Organometallic derivatives

ECH_3 and $HECH_3$ (E = B, Al, Ga or In)

Thermally evaporated Al, Ga or In atoms have been shown to insert into the C–H bonds of CH_4 upon selective photoactivation ($^2S \longleftarrow {}^2P$ or $^2D \longleftarrow {}^2P$ atomic transitions) giving as product the bent radical $HECH_3$ with C_s symmetry.[67,68]



(11)

The consumption of the metal atoms in the course of the reaction can be followed by UV/Vis spectroscopy. No complex E·CH_4 can be traced, but this is expected to have a very small binding energy. $HAlCH_3$ has been characterized by its IR spectrum,[68] $HGaCH_3$ by its IR,[69] UV/Vis [69b] and EPR [16] spectra, and $HInCH_3$ by its IR spectrum.[67] $HGaCH_3$ exhibits a broad electronic transition with a maximum at *ca.* 600 nm. Laser-ablated B atoms react with CH_4 to yield not only the insertion product $HBCH_3$, but also the species H_2CBH_2, H_2CBH, and HBCBH.[70] Further photolysis with broad-band UV/Vis radiation ($200 \le \lambda \le 800$ nm) brings about decomposition, at least in the case of E = Ga or In, with ECH_3 being the detectable and photostable end-product.

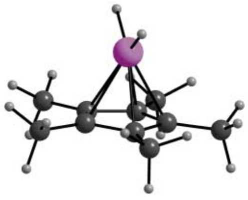
The methyl compounds ECH_3 (the simplest low valent organometallic derivatives of the Group 13 elements) all exhibit C_{3v} symmetry.[67,71] BCH_3 is found in inert-gas matrices when laser-ablated B atoms are co-deposited with CH_4.[70] $AlCH_3$ has been characterized in the gas phase using neutralization-reionization mass spectroscopy (NRMS), resonance-enhanced multiphoton spectroscopy (REMPI),[71] and pure rotational spectroscopy.[72] On the basis of the rotational spectrum, an Al–C distance of 199.4 pm has been derived. On the basis of the experimentally observed IR spectra, the force constants *f*(E–C) are found to be 354.3, 184.8, 165.3 and 158.4 N m^{-1} for BCH_3, $AlCH_3$, $GaCH_3$ and $InCH_3$, respectively, while the corresponding E–C distances are 155.4, 199.4, 204.9 and 222.6 pm.

AlCp* [Cp* = $C_5(CH_3)_5$]

This compound can be synthesized on a preparative scale and kept in its tetrameric form, $[AlCp^*]_4$, in the solid and in solution at room temperature.[73] Temperature-dependent NMR studies of solutions show that at elevated temperatures the tetramer is in equilibrium with the monomer. Even at temperatures as high as 100 °C, however, the tetramer is favored over the monomer. The compound can be evaporated (vapour pressure at 140 °C about 0.05 Torr). Electron diffraction measurements of the vapour at low pressure show only the monomer;[74] the Al–C, C–C (C atoms within the C_5 ring), C–CH_3, and C–H bond distances are thus found to be 238.8, 141.4, 152.9, and 111.0 pm, respectively. The most intense IR absorption of the matrix-isolated molecule occurring at 417.6 cm^{-1} can be assigned to the symmetric *ν*(Al–Cp*) fundamental,[73] the relatively high wavenumber possibly indicating a significant degree of Cp* ⟶ Al back-donation.

H_2AlCp^* [Cp* = $C_5(CH_3)_5$]

The reaction of photoactivated AlCp* in an Ar matrix with H_2 affords the Al(III) species Cp^*AlH_2. Presumably the effect of photolysis is comparable with that suggested for AlX (X being a halide) and involving a more or less metal-centred electronic transition. In Cp^*AlH_2, the C_5 ring is still bound in an η^5-fashion to the Al atom. Very recently, it has been shown that the energy differences between η^5-, η^3-, η^2- and η^1-coordination modes are very small (less than 10 kJ mol^{-1}), allowing the AlH_2 unit to move almost freely over all of the ring area.[75] In sharp contrast to this situation, the homologue $CpBH_2$ strongly avoids η^5-coordination, exhibiting instead η^2-coordination in its global energy minimum form.

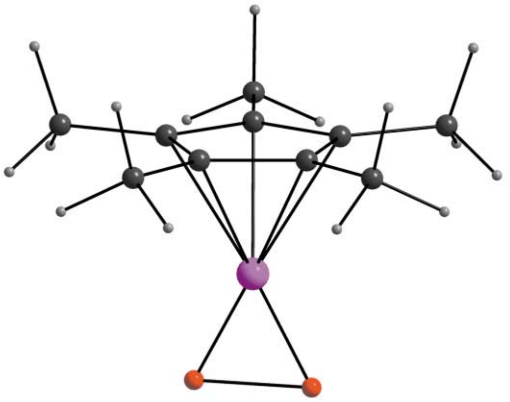


H_2AlCp^*

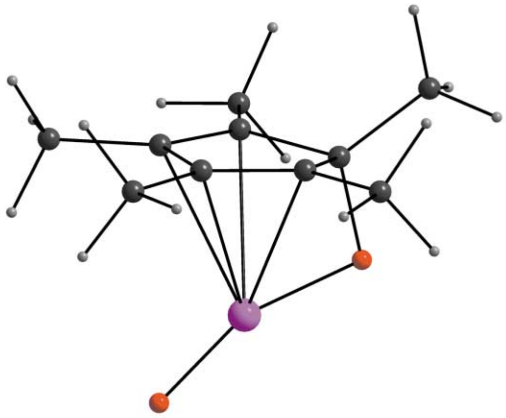
Experiments are under way to study the photoactivated reaction between AlCl and CpH. This is expected to give the Al(III) species HAl(Cl)Cp. The coordination mode of the C_5 ring in this product will be of considerable interest.

$Cp^*Al(O_2)$ [Cp* = $C_5(CH_3)_5$]

The reaction of AlCp* with O_2 should lead to a molecule with the formula Cp^*AlO_2. One possible structure for this product features the O_2 unit coordinated in a side-on fashion to the Al centre. Such a structure resembles that found in the peroxo species $XAlO_2$ (X = F, Cl or Br). Quantum chemical calculations predict O–O, Al–O and Al–C bond distances of 163.9, 173.1 and 218.9–219.9 pm, and an O–Al–O bond angle of 56.5° for such a species. According to the calculations, however, this represents only a local minimum, but not the global minimum structure on the potential energy hyper-surface. It is estimated to be 133.2 kJ mol^{-1} (130.3 kJ mol^{-1} including ZPE corrections) less stable than a structure in which the O–O bond is completely cleaved and one of the O atoms bridges the Al atom and one of the C atoms of the C_5 ring. The two Al–O distances now differ significantly (162.8 pm for the terminal Al–O bond *vs.* 177.0 pm for the bridging Al–O bond). The O–Al–O bond angle is 158.0°. As a consequence of the direct bond between the ring and one of the O atoms, the Al–C distances vary significantly, measuring 244.2, 252.0, 252.1, 256.1 and 256.1 pm.



Cp^*AlO_2



Cp*OAlO

Hetero-cubane species of the general formula $(RAlO)_4$ (R being H, Cp, Cp* or other organic groups) are a rarity. One of the few examples is provided by the compound $[tBu_3SiAl(\mu_3\text{-}O)]_4$.[76] Crystals contain a mixture of this compound together with $[tBu_3SiAl]_4$ (molar ratio 1 : 2). The rarity is surprising since numerous heterocubanes with the formulae $(RAlS)_4$ {*e.g.* $[tBuAl(\mu_3\text{-}S)]_4$},[77a] $(RAlSe)_4$ {*e.g.* $[(Me_3Si)_3CAl(\mu_3\text{-}Se)]_4$,[77b]}, or $(RAlTe)_4$ {*e.g.* $[(Me_3Si)_3CAl(\mu_3\text{-}Te)]_4$} [77b] are known. Quantum chemical calculations [78] suggest that the synthesis should be carried out at lower temperatures (below 245 K), because the formation of $(RAlO)_4$ from RAlO monomers is entropically disfavoured. However, this explanation is not fully satisfying. We believe that the problems are caused at least partially by the readiness of the oxygen to attack the organic group attached to the Al atoms, a conclusion supported impressively by the geometry calculated for the lowest energy product of the reaction between AlCp* and O_2.

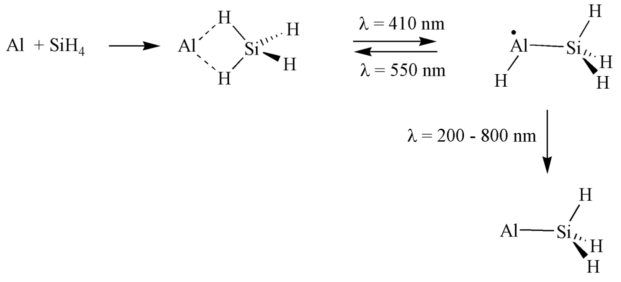
9 Silane derivatives

A complex between Al atoms and SiH_4 has been detected recently by its IR spectrum.[45] In such a complex the metal atom can be located close to an edge (η^2-coordination), a face (η^3-coordination) or a corner (η^1-coordination) of a slightly distorted SiH_4 tetrahedron. The experimental results, together with quantum chemical calculations, indicate that the metal atom is η^2-coordinated. The IR spectra also give detailed information about the dimensions of the complex. Coordination leads to the elongation of the two Si–H bonds directed towards the Al atom and shortening of those directed away from it. McKean *et al.*[79] have established a correlation between the wavenumber measured for an "isolated" ν(Si–H) stretching fundamental (measured for an $SiHD_n$ moiety) and r_0(Si–H).

$$r_0(\text{Si–H})\ (\text{pm}) = 187.29 - 0.01798\ \nu_{\text{is}}\ (\text{Si–H})\ (\text{cm}^{-1})$$

This correlation is reported to have a predictive capability in relation to r_0 values of better than ±0.3 pm (at least for silane derivatives with fully saturated bonding). If this formula is applied, a value of Δr_0(Si–H) = 0.77 pm results for the difference between the distances of the Si–H bonds pointing towards and those pointing away from the metal atom. According to an MP2 estimate, the complex is only very weakly bound (*ca.* 5.4 kJ mol^{-1}), with Si–H distances (r_e values) measuring 150.5 and 149.5 pm.

Photolysis with light having λ_{max} = 410 nm brings about tautomerization to the insertion product $HAlESiH_3$. This reaction is exoergic by *ca.* 57 kJ mol^{-1} according to MP2 calculations. Interestingly, this insertion product can be converted reversibly back to the complex by selective photolysis at λ_{max} = 550 nm. The reaction with Ga atoms proceeds in a similar fashion.



10 Conclusions

It has been shown that a variety of new subvalent compounds of the Group 13 elements has been generated and characterized in the last years using the matrix-isolation technique. These species shed light on the bond properties and the structures Group 13 metals can be engaged in. In most cases the structures of the energetically favored isomeric forms change dramatically between the B containing species and its heavier homologues. In several cases the spin multiplicity also undergoes changes. *E.g.* BCO assumes a $^4\Sigma^+$ ground electronic state, but AlCO, GaCO and InCO exhibit spin multiplicities of 2 ($^2\Pi$ ground electronic state for the linear molecule, which is, however, in the case of AlCO unstable toward bending). In the global energy minimum form, B_2H_2 is linear with a spin multiplicity of 3 (two unpaired electrons), while Al_2H_2, Ga_2H_2 and In_2H_2 all have a cyclic, D_{2h} symmetric geometry with a singlet electronic ground state. It was possible to generate a number of model compounds which are ideally suited to analyse in detail interesting bond properties. *E.g.* our experiments succeeded in the generation of the new monomeric compounds H_2ENH_2 (E = Al, Ga and In). Several subvalent hydride molecules with E–N and E–P bonds were also characterized. The experimental data allowed for a detailed characterization which included also normal coordinate analysis yielding accurate *f*(E–N) force constants. In other experiments it was possible to find access to the simplest organometallic compounds of Ga and In in their oxidation state +1, namely $GaCH_3$ and $InCH_3$. Finally, it was possible for the first time to characterize experimentally the species HGaGaH and HInInH featuring direct E–E bonds.

In addition to their help to answer longstanding fundamental questions, the experiments described in this micro-review are of interest to improve our understanding of fundamental reaction mechanisms. *E.g.* the products of the reactions between the metal atoms and NH_3 or PH_3 might play an important role in chemical vapour deposition processes designed to fabricate new III/V semiconductor coatings. The characterization of elementary steps occurring in the course of the "oxo-addition" of SiH_4 to metal atoms can contribute to our knowledge of catalytic cycles. The reactivity of monovalent halides and cyclopendatienyl-complexes, which are, in their oligomeric (and often solvent-stabilized) form, widely used in inorganic synthesis, has also been studied. These studies show that the matrix-isolated species are relatively inert in their ground electronic state. When photoactivated, however, they are highly reactive and insert readily *e.g.* into H_2 and into the C–H bond of CH_4. The experiences acquired with the matrix-isolated species can be used in future work to develop a new photochemistry which allows the preparation of new species on a preparative scale.

Acknowledgements

The author gratefully acknowledges financial support from the *Deutsche Forschungsgemeinschaft*.

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3 A shortening of the E–E bond due to multiple bonding brings about destabilization of the σ-bond. This destabilization often overcompensates the energy gain by formation of a second bond. Thus, it is not only the capability for establishing a second (π) bond, but also the effect this has on the first (σ) bond, which has to be taken into account.

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