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Low-Valent Organometallics—Synthesis, Reactivity, and Potential Applications

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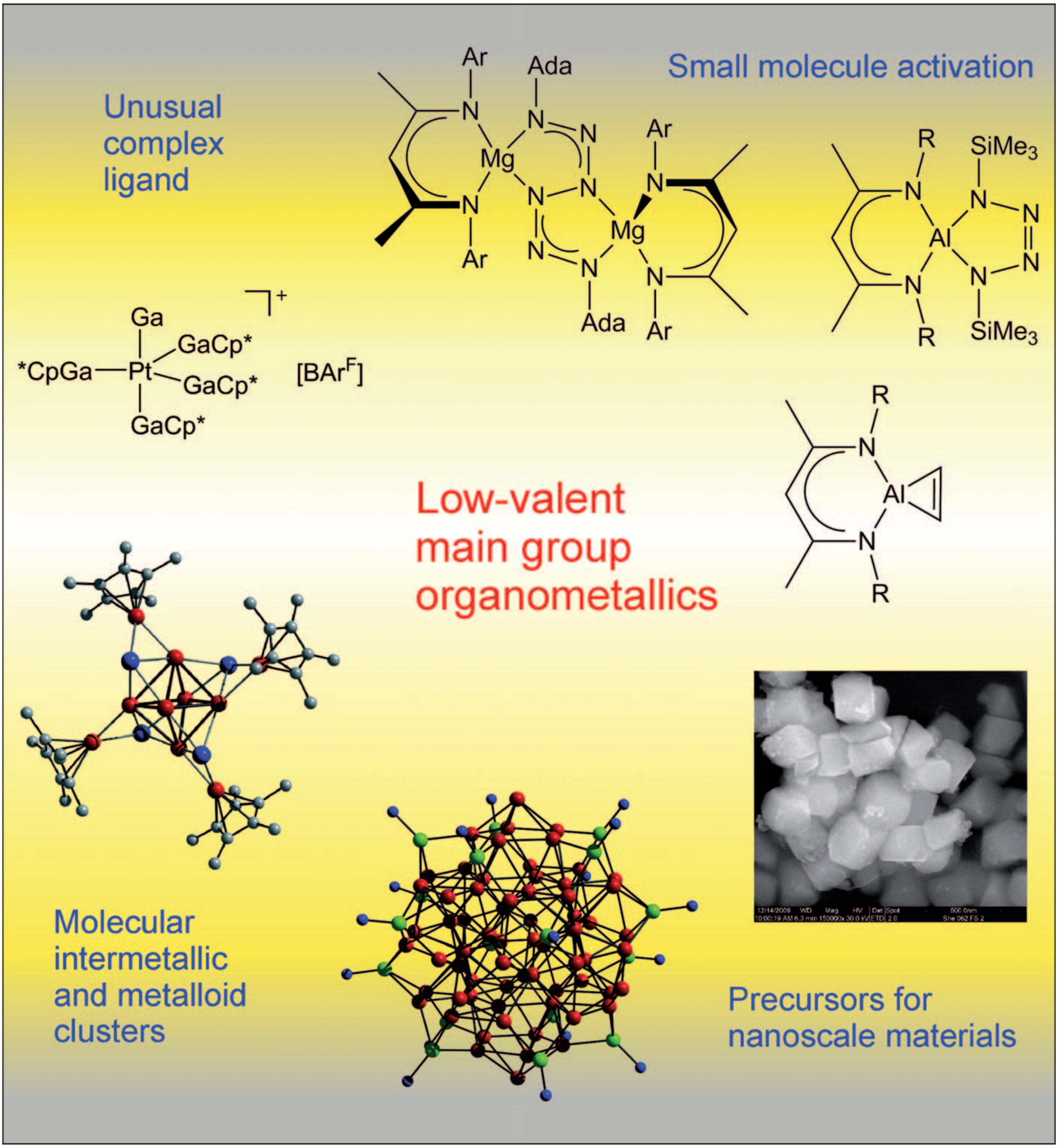


Abstract: General concepts for the synthesis and stabilization of low-valent organometallic complexes of Groups 2, 12, 13, and 15 metals and common structural motifs are described. While kinetically stabilized complexes are in the focus for more than two decades, the principle of base-stabilization only recently allowed the synthesis of unforeseen compounds. As-prepared complexes not only show fascinating structural diversities, but exhibit also very interesting chemical properties. Low-valent complexes are of particular interest in the synthesis of novel molecular complexes, but may also find applications as tailor-made precursors for the synthesis of nanosized materials.

Keywords: low-valent compounds • main group elements • materials science • metal–organic frameworks • transition metals

Introduction

The synthesis and characterization of low-valent organometallic complexes of main-group elements has received a steadily growing interest over the last decades owing to the general interest in fundamental molecular processes of the formation and breaking of metal–metal bonds. Moreover, the so-called "classical double-bond rule",[1] according to which the formation of stable element–element double bonds is restricted to elements of the second row of the periodic table, has also largely motivated these studies, which not only resulted in the synthesis of novel multiple-bonded main-group-element complexes,[2] but also unforeseen complexes in unusual oxidation states such as metal-rich "metalloid" cluster complexes[3] have been structurally characterized for the first time. In addition, low-valent complexes exhibit fascinating chemical and physical properties, which make them very promising precursors in materials sciences.

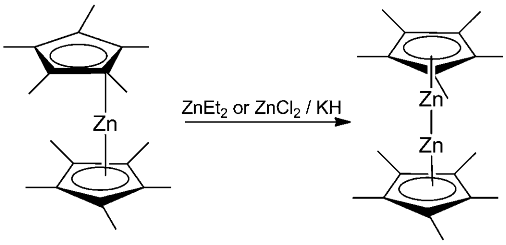
Herein, general synthetic approaches for low-valent Group 2 (Mg), 12 (Zn), 13 (Al, Ga, In) and 15 (Sb, Bi) metal complexes are briefly summarized and central reaction patterns, which are of significant interest for their potential application as suitable reagent in metal organic synthesis, are described. In addition, their potential capability to serve as novel, tailor-made precursors for the synthesis of nanostructured materials will be demonstrated.

Synthesis and Reactivity of Metal–Metal Bonded Complexes

Metal complexes containing metal–metal single and multiple bonds are typically synthesized by Wurtz-analogous coupling reaction of halide-substituted complexes or by salt elimination reaction starting with low-valent metal halides. The use of sterically demanding, very often chelating, organic substituents plays a crucial role (kinetic stabilization). In addition, strong Lewis bases (σ-donors) such as N-heterocyclic carbenes (NHCs) were found in recent years to be suitable for the synthesis of unforeseen complexes (base stabilization), such as $(NHC)_2Si_2$ containing a Si=Si double bond with Si atoms in the formal oxidation state 0.[4]

Kinetically Stabilized Complexes

Low-valent Mg, Ca, and Zn complexes: Even though $\{Hg_2\}^{2+}$ and $\{Cd_2\}^{2+}$ dications have been known for decades, it was not before 2004 when Carmona et al.[5] reported for the first time on the structural characterization of a complex containing a direct Zn−Zn bond.[6] Decamethyldizincocene $[Zn_2Cp^*_2]$ was unexpectedly obtained by reaction of $ZnEt_2$ and $[ZnCp^*_2]$ (Scheme 1). Since then, Zn−Zn bonds have been synthesized by reductive coupling reactions ($[Zn_2(DippNacnac_2)]$; DippNacnac = CH[MeC(2,6-$iPr_2C_6H_3$)N_2]),[7] by reaction of ZnX_2 with anionic ligands ($[Zn_2(dpp\text{-}Bian_2)]$ (dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene,[8] $[Zn_2\{[(2,6\text{-}iPr_2C_6H_3)NC(Me)]_2\}_2]$)[9] as well as by ligand exchange reactions ($[Zn_2(Mesnacnac_2)]$; MesNacnac = CH[MeC(2,6-$iPr_2C_6H_3$)N]$_2$).[10] Moreover, complexes of heavier Group 12 elements containing Cd−Cd[11] and Hg−Hg[11b] bonds have been synthesized and structurally characterized, including the complete series $[M_2Ar'_2]$ (M = Zn, Cd, Hg; Ar′ = 2,6-$Dipp_2$-C_6H_3).



Scheme 1. Synthesis of $[Zn_2Cp^*_2]$.

The central Zn−Zn bonds in as-formed Zn^I complexes range from 2.29 to 2.40 Å. They exhibit high s character (up to 95 %) except for $[Zn_2Ar'_2]$, in which the Zn−Zn bond is mainly build by an overlap of the zinc $4p_z$ orbitals.[7b] Calculated bond dissociation energies (BDE) of the Zn−Zn bond range from 55 to 70 kcal mol^{-1}, which is comparable to the

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energies computed for Zn_2H_2 (59 kcal mol^{-1}) and the dihalides Zn_2X_2 (57–67 kcal mol^{-1}).[12]

Motivated by the similarities between Zn and Group 2 metals, the synthesis of low-valent Group 2 complexes, the chemistry of which is also dominated by the oxidation state +II, was investigated in more detail. Mg^I compounds are known to exist under somewhat extreme conditions such as in deep space ($Mg^I(CN)$)[13] or matrixes at low temperatures (MgX, Mg_2X_2),[14] but organometallic complexes containing Mg–Mg have been prepared for the first time recently by reductive coupling reactions of RMgI (R = Priso = [$(DippN)_2CN$*i*Pr_2]), MesNacnac, DippNacnac, *t*BuNacnac).[15] In addition, [$K(thf)_3$]$_2$[LMg–MgL] (L = [(2,6-*i*$Pr_2C_6H_3$)NC(Me)]$_2^{2-}$) was obtained by reduction of a mixture of a diimine and $MgCl_2$ with excess K.[16] The Mg–Mg bond lengths in these complexes range from 2.808(1) to 2.9370(18) Å, which is longer than the sum of the covalent radii (2.72 Å), but significantly shorter than the distances in diatomic or elemental magnesium (3.890, 3.20 Å). The Mg–Mg σ bond in [$K(thf)_3$]$_2$[LMg–MgL] has considerable high p character (55 %), whereas those of the other Mg complexes show predominantly s character. An experimental charge density study of [$Mg_2(DippNacnac_2)$] (Figure 1) confirmed the covalent nature of the metal–metal interaction even though the electron density between the magnesium atoms is rather diffuse.[17]

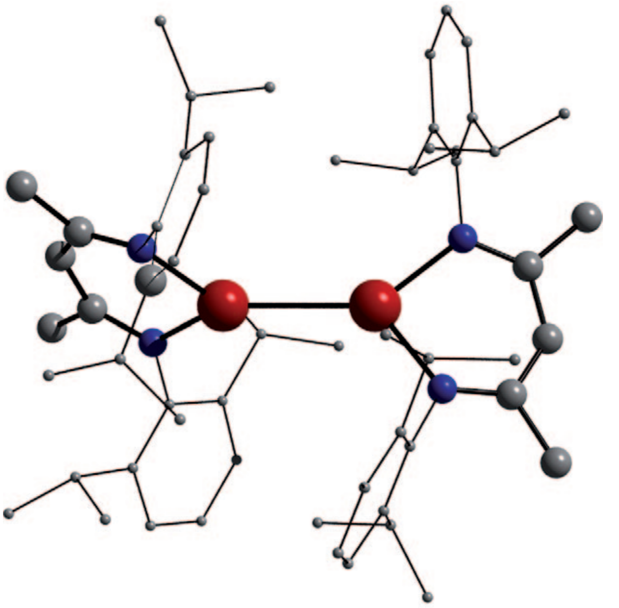


Figure 1. Structure of [$Mg_2(DippNacnac_2)$] (Dipp substituents reduced for clarity).

The metal atoms in these complexes reach the oxidation state I upon formation of a metal–metal bond, which is kinetically stabilized by bulky organic substituents. In contrast, Westerhausen et al. recently demonstrated, that the Ca^I complex [$(thf)_3Ca\{\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3\}Ca(thf)_3$] (Figure 2) can be stabilized by an aromatic ligand (2,4,6-triphenylbenzene), the π* orbital of which is in between the ionization energies of the first (6.11 eV) and second ionization (11.87 eV) of calcium. The Ca atoms in this "inverse" Ca^I sandwich complex adopt opposite positions of the doubly negatively charged arene ligand with a Ca–Ca distance of 4.279(3) Å.[18]

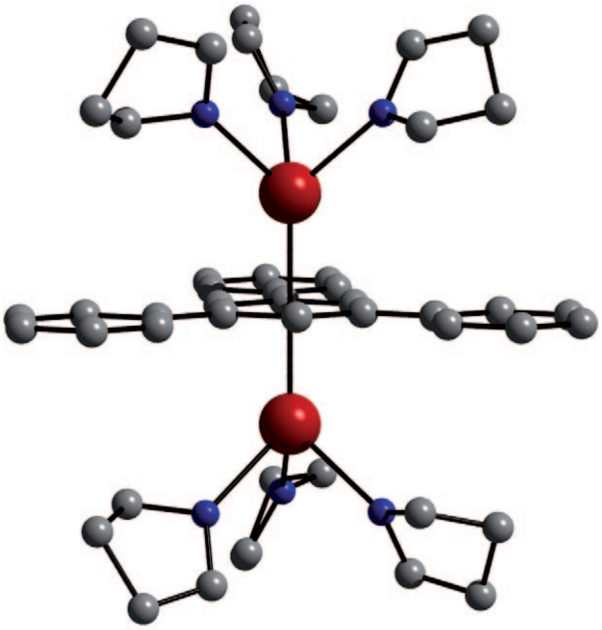


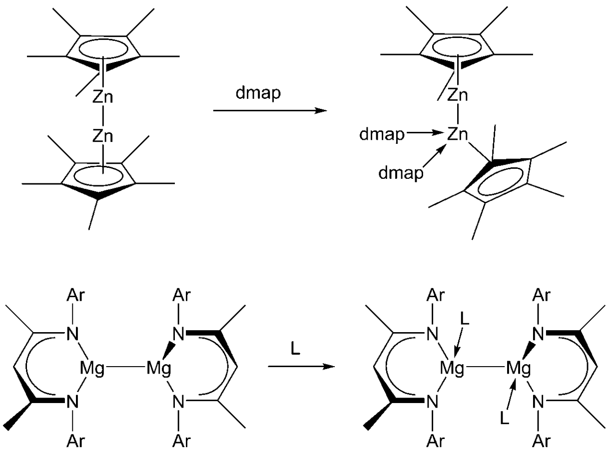
Figure 2. Structure of the inverse sandwich Ca^I complex.

As-described low-valent Group 2 and 12 metal complexes have been used in several reactions, demonstrating their high potential for the synthesis of unusual complexes as summarized in the following.

Adduct formation: Mg^I complexes, except for the bulky *t*BuNacnac–magnesium(I) and the diimine complex, were found to react with several Lewis bases with subsequent formation of the corresponding bisadducts [R(base)Mg–Mg(base)R], in which both Mg atoms are coordinated by a single Lewis base.[19] In contrast, [$Cp^*{}_2Zn_2$] was found to react with dmap with formation of [$Cp^*Zn\text{–}Zn(dmap)_2Cp^*$], in which both dmap molecules unexpectedly bind in a *geminal* binding mode to only one Zn atom (Scheme 2).[20]

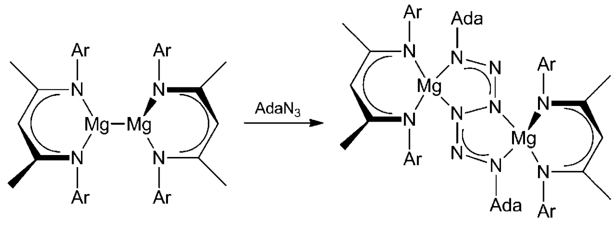
The metal–metal bond lengths in these base-stabilized complexes are significantly elongated, most likely due to the higher coordination number of the metal center and, in case of [$Mg_2(DippNacnac)_2$], due to the diffuseness of the electron density between the magnesium atoms.

Redox reactions: Magnesium(I) dimers serve as two-center/two-electron reducing agents toward a variety of unsaturated organic substrates, such as carbodiimides, isocyanates, azides, azobenzene and cyclooctatetraene. As was expected, their reactivity is inversely proportional to the steric bulk of their substituents.[15,21]



Scheme 2. Adduct formation reactions of Zn^I and Mg^I complexes.

Sterically less hindered Mg^I complexes react with $AdaN_3$ (Ada = 1-adamantyl) with N–N bond formation, yielding complexes with an unusual bridging $[AdaN_6Ada]^{2-}$ unit (Scheme 3), whereas reactions with *t*BuN=C=O proceeded with C–C bond formation. The resultant oxamide ligand was found to coordinate two Mg centers in a novel N,O,O-ligating fashion. In contrast, sterically more hindered Mg^I complexes, such as the *t*BuNacnac-substituted derivative, did not react with CyN=C=NCy (Cy = cyclohexyl) and PhN=NPh.

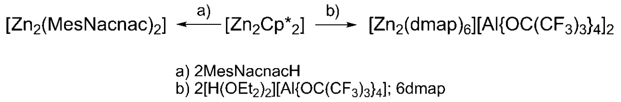


Scheme 3. Reaction of a Mg^I dimer with adamantylazide.

Very recently, Jones et al. reported on the reduction reaction of an N-heterocyclic carbene (NHC) adduct of $GeCl_2$ with various reducing agents. While reactions with sodium metal and KC_8 failed to give any low-valent Ge complex, the reaction with $[Mg_2(MesNacnac_2)]$ yielded the NHC-stabilized digermene $[Ge_2(NHC)_2]$ (NHC = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr_2-C_6H_3), in which the Ge atoms adopt the formal oxidation state zero.[22] The Ge–Ge bond length (2.3490(8) Å) is typical for digermenes (2.344 Å), but significantly longer than typical values observed for digermynes (2.206–2.285 Å). This reaction clearly demonstrates that Mg^I complexes may serve as very selective reducing agents in metal organic chemistry.

Of particular interest would be the reaction of the low-valent organozinc and -magnesium complexes with dihydrogen. Unfortunately, no signs of hydrogenation reaction were found for dizincocene and Mg^I complexes when treated with H_2, even at elevated temperatures. Only the reaction of $[Mg_2(MesNacnac_2)]$ with H_2 at higher hydrogen pressures of approximately 70 atm and 80 °C yielded numerous products, most likely due to cleavage and/or hydrogenation of the β-diketiminate substituent. The formation of Mg hydride species was not observed in any case.

Protonation reaction: Carmona et al. reported on reactions of $[Zn_2Cp^*_2]$ with several H-acidic reagents such as H_2O, *t*BuOH, and NCXyl (Xyl = 2,6-Me_2Ph),[5] but only disproportionation with subsequent formation of elemental zinc and the Zn^{II} complexes was observed. In contrast, the reaction of $[Zn_2Cp^*_2]$ with MesnacnacH at low temperature occurred with protonation of the Cp* substituent and formation of $[Zn_2(Mesnacnac_2)]$ (Scheme 4).[10a] The Zn–Zn bond is preserved in this reaction, which may open a general synthetic pathway to low-valent organozinc complexes, including complexes that cannot be obtained from Wurtz-analogous coupling reactions. The reaction of $[Zn_2Cp^*_2]$ with $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ yielded $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$, which exhibits a (base-stabilized) $\{Zn_2\}^{2+}$ dication (Figure 3).[10b]



$$[Zn_2(MesNacnac)_2] \xleftarrow{a)} [Zn_2Cp^*_2] \xrightarrow{b)} [Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$$

a) 2MesNacnacH
b) $2[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$; 6dmap

Scheme 4. Protonation reaction of $[Zn_2Cp^*_2]$.

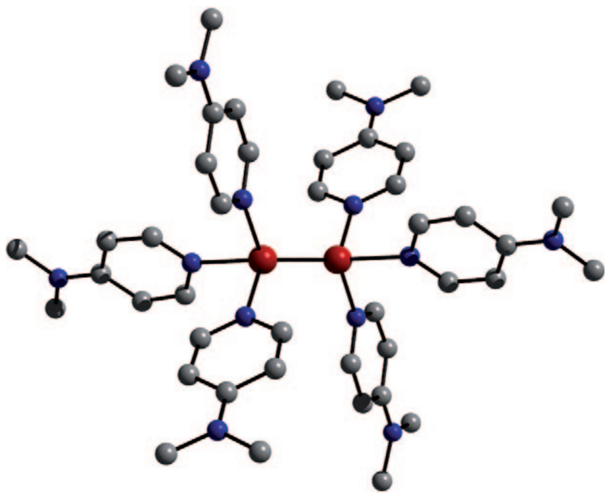


Figure 3. Structure of the dmap-stabilized $\{Zn_2\}^{2+}$ ion.

The rather low stability of the $\{Zn_2\}^{2+}$ dication, which was previously observed in a melt of Zn in $ZnCl_2$ and characterized by Raman spectroscopy,[23] is in remarkable contrast to the known $\{Hg_2\}^{2+}$ and $\{Cd_2\}^{2+}$ dications and has been subject to several theoretical studies.[24] The Zn–Zn bond lengths of the dication $[Zn_2(dmap)_6]^{2+}$ of 2.419(1) Å atom is significantly elongated compared to $[Zn_2Cp^*_2]$ (2.305(3) Å) and the calculated force constant of the Zn−Zn bond of 1.09 mdyne Å^{-1} is in between that one reported for $\{Zn_2\}^{2+}$ in $Zn/ZnCl_2$ (0.6 mdyne Å^{-1})^{24} and $[Zn_2Cp^*_2]$ (1.42 mdyne Å^{-1}).[25] The Raman spectrum of $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$ shows a vibration at 174 cm^{-1}, that exhibits some Zn−Zn character. Moreover, an absorption band at 175 cm^{-1} was reported for the $\{Zn_2\}^{2+}$ dication in $Zn/ZnCl_2$ glasses, in which the dication most likely exists as Zn_2Cl_2 unit, for which theoretical calculations predict an a_{1g} vibration at 194 cm^{-1}.

Low-valent group Al, Ga, and In complexes: In 1988, Uhl et al. firstly succeeded in the synthesis and structural characterization of a compound containing an Al−Al bond and the Al atoms in the formal oxidation state II.[26] Since then, the number of structurally characterized metal–metal bonded species of the type $[R_2M{-}MR_2]$ containing Al–Al,[27] Ga–Ga,[28] and In–In[29] bonds has systematically increased.[30] Complexes of the desired type were obtained by reductive coupling reactions and by salt elimination reactions starting with $[M_2X_4(dioxane)_2]$ (M = Ga, In; X = Cl, Br), which contain a central metal–metal single bond. In addition, Group 13 metal complexes, with the metal centers in the formal oxidation state +I, were synthesized by reductive coupling reactions of RMX_2 and by salt elimination reactions using (metastable) solutions of MCl (M = Al, Ga In; X = Cl, Br, I).[31] These complexes typically form oligomeric structures such as tetrahedral $[(MR)_4]$ and octahedral $[(MR)_6]$ cluster-type complexes, but structures have also been observed, such as monomeric [MR]; dimeric [RM=MR]; chain-like structures, such as a linear In_6 chain in $[In_6R_6I_2]$;[32] and a "double tetrahedron" $[\{(Me_3Si)_3C\}_3Ga_3]Ga{-}Ga[Ga_3\{C(SiMe_3)_3\}]$,[33] in which two Ga_4 tetrahedra are bridged by a single gallium–gallium bond. In addition, the synthesis and bonding situation of multiply bonded complexes has been thoroughly investigated.[34] By far the most controversially discussed complex of this class is $Na_2[\{Ga(2,6\text{-}Dipp_2\text{-}C_6H_3)\}_2]$,[35] which was described as a digallyne containing a Ga≡Ga triple bond. The Ga−Ga bond length is extremely short 2.319(3) Å and the central C-Ga-Ga-C unit adopts a "*trans*-bent" orientation as was also observed in triple-bonded complexes of heavier Group 14 elements of the type [RE≡ER] (R = (2,6-Dipp$_2$-C$_6$H$_3$); E = Ge, Sn, Pb).[36] The analogues Al complex $Na_2[\{Al(2,6\text{-}Dipp_2\text{-}C_6H_3)\}_2]$ shows comparable structural features.[37]

Metal-rich (metalloid) clusters $[M_nR_m]$ ($m < n$) with formal oxidation numbers between 0 and I have been largely explored by the Schnöckel group. The number of metal atoms that are only bound to other metal atoms range from one as observed in $[Al_7R_6]^-$ (R = N(SiMe$_3$)$_2$)[38] up to 38 in $[Al_{50}Cp^*_{12}]$[39] or even 57 in $[Al_{77}R_{12}]^{2-}$.[40] The metal atom topology in metalloid clusters often reflects the topology of the metal itself, as was shown for N(SiMe$_3$)$_2$-stabilized Al_7, Al_{12}, Al_{14}, Al_{69}, and Al_{77} clusters, in which the arrangement of the Al atoms mimics the close-packed structure of Al metal. The structural diversity observed in metalloid Ga complexes is even more extreme and reflects the more extensive variety of the different Ga phases. For instance, $[Ga_{18}R_8]$ and $[Ga_{22}R_8]$ (R = tBu$_3$Si) each contain a "cube-box" of eight GaR units, in which the remaining Ga atoms are either arranged as observed in the normal pressure modification of β-Ga or in the high-pressure modification Ga^{III}. The largest metalloid Group 13 element clusters $[Ga_{84}R_{20}]^{x-}$ (R = N(SiMe$_3$)$_2$, $x = 3, 4$; Figure 4) contain 60 naked Ga atoms.[41] Their central Ga_2 unit is surrounded by 32 Ga atoms, which consists of two icosahedral Ga_{11} moieties connected through a puckered Ga_{10} ring and which exhibits, to some extent, the icosahedra substructure of δ-gallium. These novel Ga_{84} clusters not only have fascinating structural features, but they are also very interesting due to their electronic properties, since they show metallic conductivity[42] and even superconductivity.[43]

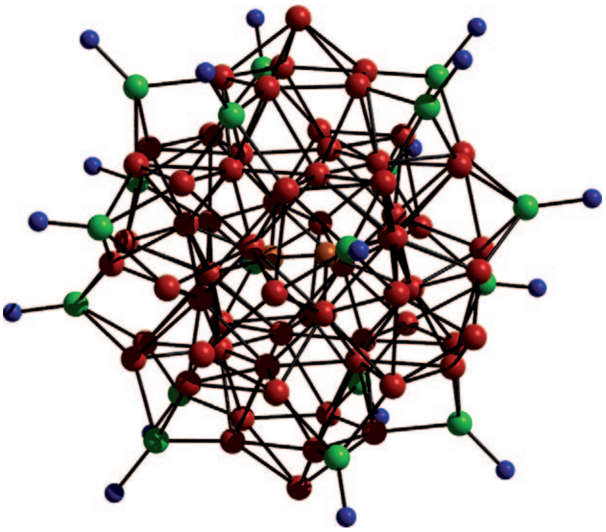
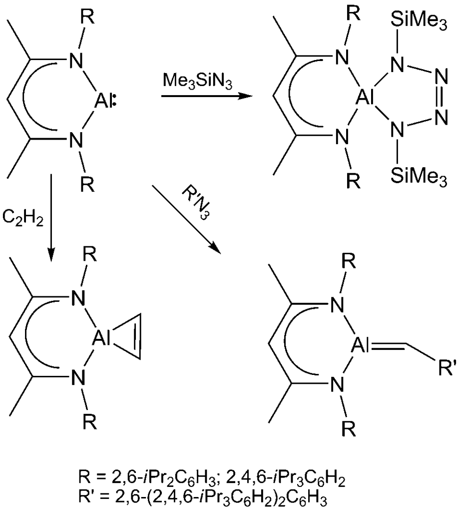


Figure 4. Reduced representation of the giant Ga_{84} cluster; substituents bearing a Ga atom are in green; central Ga_2 unit is in orange.

Since the synthesis of low-valent Group 13 complexes has been reviewed several times,[44] this article rather concentrates on their reactivity. The best investigated complexes are Uhl's $[M_2R_4]$ complexes (R = CH(SiMe$_3$)$_2$),[45] for which several general reaction types have been explored. Of particular interest are electron-transfer reactions, Lewis base addition reactions, and ligand exchange reactions, which proceed under preservation of the central M−M bond. In addition, insertion reactions into the M−M bond have been investigated, in detail.[46] Comparable reactivity patterns have been observed for monomeric, carbene-like diyls [MR], dimetallenes [RM=MR], and cluster-type complexes $[(MR)_x]$ ($x = 4$, 6). Moreover, these complexes were found to serve as novel main-group element ligands in complex chemistry due to the presence of an electron lone pair.

Redox reactions: Reactions with electron-rich azides RN_3, diazenes RN=NR, and diazoalkenes R_2CN_2 yielded novel complexes including the first complexes containing M=N double bonds (Scheme 5).[47] $[(2,6\text{-Dipp-}C_6H_3)M{=}N\{2,6\text{-}(4\text{-}t\text{BuXyl})\text{-}C_6H_3\}]$ (M = Al,[48] Ga, In[49]) were obtained from reactions of $[M(2,6\text{-Dipp-}C_6H_3)]$ with the sterically encumbered azide $2,6\text{-}(4\text{-}t\text{BuXyl})\text{-}C_6H_3N_3$. These complexes adopt *trans*-bent CM=NC cores and the M–N bonding in these compounds can be interpreted as an interaction between the triplet form of the nitrene Ar′N and the monovalent M^I species, even though its triplet form is higher in energy than the singlet form. According to theoretical calculations, the double-bonding character within these compounds is relatively weak. In contrast, reactions with sterically less demanding azides typically yielded oligomeric species, as was shown in several reactions with [AlCp*][50] and [GaCp*],[51] respectively. Moreover, $[Al^I(\text{DippNacnac})]$ showed some very surprising reactions with Me_3SiN_3, yielding the first aluminatetrazole containing an AlN_4 ring, whereas the reaction with acetylene yielded the first stable aluminacyclopropene.[52]

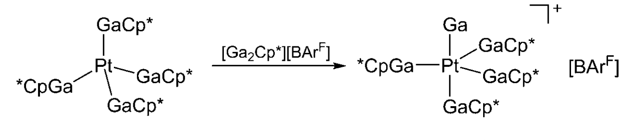


Scheme 5. Reactions of low-valent Group 13 complexes with electron-rich azides, diazenes, and acetylene.

Activation of small molecules such as H_2 and P_4 as well as reactions with elemental chalcogens is of particular interest and has been investigated in detail. While H_2 activation so far has not been observed with low-valent Group 13 metal complexes,[53] both phosphorus and chalcogen atoms were found to insert into the M–M bond of low-valent Group 13 complexes. For instance, the reaction of P_4 and $[(AlCp^*)_4]$ yielded $[Al_6Cp^*_6P_4]$,[54] whereas $[(GaCTms_3)_3P_4]$ (Tms = $SiMe_3$) was obtained from the reaction with $[(GaCTms_3)_4]$.[55] Reactions with elemental chalcogens proceeded with complete oxidation of the M_4 cluster and subsequent formation of heterocubanes $[(RME)_4]$ (M = Al, Ga, In; E = S, Se, Te),[56] whereas the reaction of $[(InCTms_3)_4]$ with propylene sulfide occurred with partial oxidation and formation of the mixed-valent cluster $[In_4(CTms_3)_4S]$.[57] Moreover, less aggregated complexes, such as dimeric $[(GaE\{HC(MeCDippN)_2\})_2]$ (E = O, S)[58] and monomeric $[ME(t\text{Bu}_2\text{Tp})]$ (M = Ga, In; E = S, Se, Te; Tp = tris(3,5-*tert*-butylpyrazolyl)hydroborato) were synthesized.[59] The monomeric compounds show the shortest M–E bond lengths due to their multiple bonding character,[60] which is very rare for heavier p-block elements. Surprisingly, the reaction of $[In(t\text{Bu}_2\text{Tp})]$ with sulfur did not yield $[InS(t\text{Bu}_2\text{Tp})]$, but the novel tetrasulfido complex $[In(t\text{Bu}_2\text{Tp})(\eta^2\text{-}S_4)]$.[61]

Coordination chemistry: Univalent Group 13 diyl complexes $[(MR)_x]$ have been applied in coordination chemistry, since the M^IR fragment, which is isolobal with CO and PR_3, exhibits σ-donor and π-acceptor properties. In particular [MCp*] (M = Al, Ga) were found to be suitable donor ligands for a wide range of main group and transition metals.[62] The Lewis basicity of Group 13 diyls was found to steadily decreases with increasing atomic number of the Group 13 element and β-diketiminato substituted diyls were found to express a higher Lewis basicity than Cp*-substituted diyls, most likely due to the increased negative charge at the gallium atom.[63]

Fischer et al. recently demonstrated in a series of very interesting publications, that even MeGa, which is unstable under ambient conditions, as well as “naked” Ga^+ and In^+ may serve as ligands in transition metal chemistry. The MeGa ligand was synthesized in situ by reaction of the Rh complex $[Rh(Cp^*Ga)_4\{Ga(Me)Cp^*\}]$ with $[H(OEt_2)_2][BAr^F]_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$),[64] whereas the complexes $[GaPt(GaCp^*)_4][BAr^F]_4$ and $[InPt(PPh_3)_3][BAr^F]_4$, in which “naked” Ga^+ and In^+ ligands exclusively act as σ and π acceptors,[65] were prepared by reaction of $[PtL_4]$ (L = GaCp*, PPh_3) with $[Ga_2Cp^*][BAr^F]_4$, which was obtained from the protonation reaction of [GaCp*] with $[H(OEt_2)_2][BAr^F]_4$,[66] and $In[BAr^F]_4$, respectively, Scheme 6.

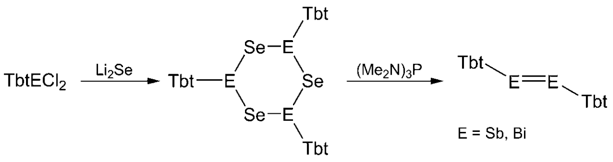


Scheme 6. Synthesis of a Pt complex with a naked Ga^+ acceptor ligand.

Low-valent Sb and Bi complexes: Low-valent Group 15 complexes of the type E_2R_4 with the Group 15 element in the formal oxidations state II have been intensely studied in the last century. In fact, As_2Me_4, which was discovered by Cadet in 1757, belongs to the first metal organic complexes ever synthesized.[67] Due to the steadily decreasing E–E bond strength with increasing atomic number, the stability of distibines and dibismuthines is rather low. However, they were found to act as monodentate and bidentate ligands in complexation reactions with transition and main group metal complexes.[68]

These reactions either proceeded with preservation or under cleavage of the central E–E bond. For instance, distibines react with Group 13 metal–organics with formation of heterocycles of the general type $[(R_2MSbR'_2)_x]$ (M = Ga, In; $x = 2, 3$; Figure 5).[69] The Sb–Sb bond cleavage was also observed in the reaction of [AlCp*] with Sb_4tBu_4, which yielded the new complex $[(AlCp^*)_3Sb_2]$.[70] Reactions with elemental chalcogens were also found to proceed with insertion of the chalcogen into the E–E bond.

In addition, complexes containing an E=E double bond have received increasing interest in recent years. Doubly bonded species were either stabilized in the coordination sphere of a transition-metal complex[71] or by sterically demanding substituents such as Tbt (2,4,6-$[(CH(SiMe_3)_2]_3$-C_6H_2) and Bbt (2,6-$[(CH(SiMe_3)_2]_2$-4-$[C(SiMe_3)_3]$-C_6H_2) as was shown by Tokitoh et al. (Scheme 7).[72] Very recently, a novel type of Bi=Bi doubly bonded compound was obtained by reaction of $[Bi(OR)_3]$ with the Ga–NHC analogue $[Ga^I(DippNacnac)]$.[73]



Scheme 7. Synthesis of [RE=ER] containing E=E double bonds.

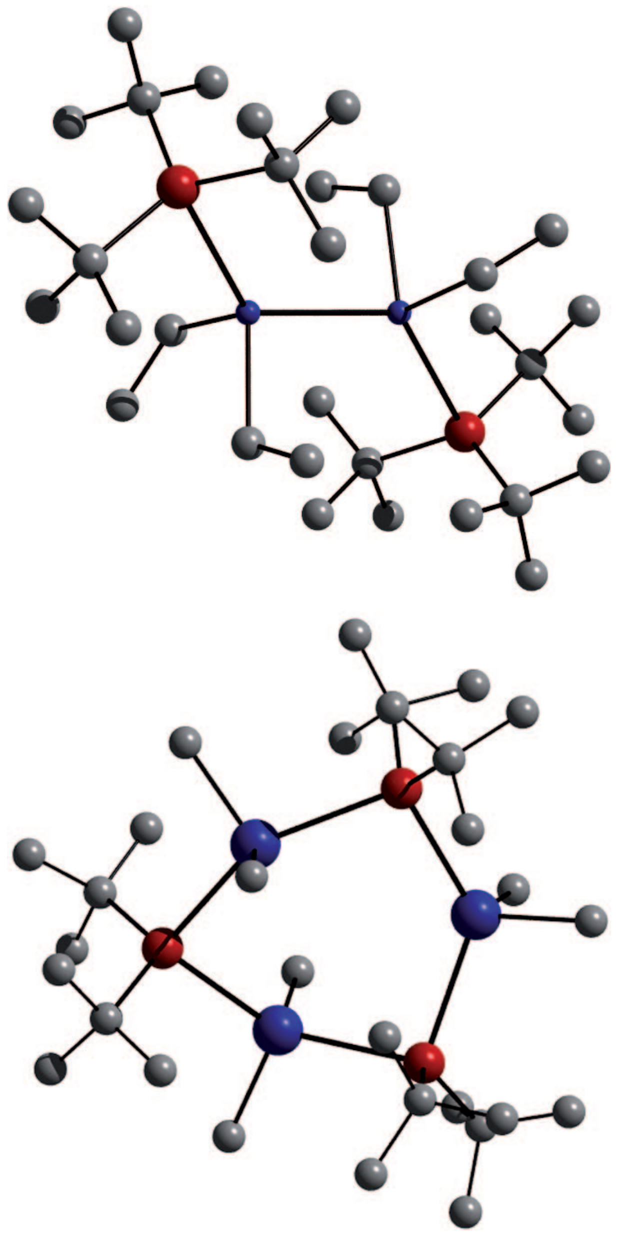


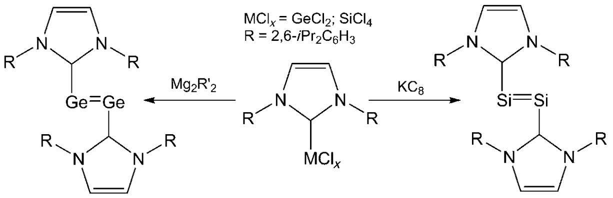
Figure 5. Structure of $[\{Bi_2Et_4\}\{Ga(tBu)_3\}_2]$ (top) and $[\{Me_2GaSbMe_2\}_3]$ (bottom).

The reactivity of as described distibenes and dibismuthenes has also been investigated. Reduction of $[Sb_2Bbt_2]$ with Li metal yielded the stibene radical anion, in which the Sb–Sb bond is elongated due to the population of the antibonding π* orbital.[74] In addition, reactions with elemental chalcogens and chalcogen transfer reagents $R_3P{=}E$ (E = Se, Te) were found to proceed either with formation of four-membered $(REO)_2$ and three-membered heterocycles of the type R_2E_2Se and R_2E_2Te, whereas sulfurization reactions of $[E_2Bbt_2]$ (E = Sb, Bi) with S_8 resulted in the formation four-, five-, and six-membered heterocycles.[75]

Base-Stabilized Complexes

The synthesis of metal–metal bonds was typically achieved by use of sterically demanding (chelating) organic substituents, which exhibit a kinetically stabilizing effect. However, recent pioneering studies of Robinson et al. demonstrated that the concept of base-stabilization is also very useful for the synthesis of novel main-group element complexes.[2a] In a series of papers, the capability of DippNHC, which is known to be an excellent σ-donor ligand,[76] for the stabilization of unforeseen molecules including diborene B_2H_2,[77] P_2,[78] As_2,[79] Si_2Cl_2 and even Si_2[4] has been demonstrated. Moreover, DippNHC was also found to be able to stabilize dichloro- and dibromosilylene SiX_2,[80] a Ga_6 octahedron $[Ga_6Mes_4(DippNHC)_2]$[81] and diatomic Ge_2, which was obtained from the reduction with a Mg^I complex.[22]

The diatomic Si_2 and Ge_2molecules can be regarded as novel, soluble silicon and germanium allotropes[82] that are stabilized by two Lewis bases (Scheme 8), whereas P_2L_2



Scheme 8. Synthesis of singlet Si^0 and Ge^0 dimers.

(L = DippNHC) is the base-stabilized form of the high-temperature phosphorus allotrop P_2. The formation of these novel types of low-valent main-group-element complexes not only is very interesting in regard to their unforeseen structural features, but may also open a new synthetic approach to novel main-group complexes in the near future. Moreover, the principle of base-stabilization is expected also to allow the synthesis of novel transition-metal complexes.

Potential Applications of Low-Valent Metal Complexes in Material Sciences

The search for new nanoscale materials, such as binary and multinary III–V, III–VI, II–VI and V–VI materials, which exhibit potential applications in opto- and microelectronic devices due to their semiconducting and thermoelectric properties, significantly increased the demand for novel, tailor-made precursors. One-dimensional nanowires and two-dimensional material films are typically obtained from top-down processes. However, the increasing demand for smaller and smaller device architectures has led to new synthetic procedures, which are typically referred to as bottom-up approaches. Nanosized materials are formed by wet chemical processes in solution (soft chemistry methods) or through gas-phase-based techniques, such as MOCVD (metal organic chemical vapor deposition) processes. Since the design of the specific molecular precursors used in these processes plays a key role, the interest in novel precursor systems has systematically increased over the last decade. Single-source precursors,[83] which contain the specific element combination of the desired material preformed at the molecular level within a single molecule, are promising candidates for the synthesis of nanoscale materials, since their most important chemical and physical properties, such as volatility, stability, and decomposition temperatures, can be controlled to some extent. In the following, some selected examples are shown, which demonstrate the high potential of novel low-valent precursors in the synthesis of nanoscale materials.

Materials synthesis through gas-phase MOCVD processes

Deposition of GaSb and GaS films: As-mentioned before, distibines $Sb_2R'_4$ react with $[GaR_3]$ with formation of completely alkyl-substituted heterocycles $[(R_2GaSbR'_2)_x]$[69] that are not accessible by any other standard synthetic procedure. These heterocycles are suitable single-source precursors for the deposition of high-quality, crystalline GaSb films (Figure 6) in HV-MOCVD (high vacuum metal organic chemical vapor deposition) processes at deposition temperatures as low as 400 °C,[84] which is about 100 °C below typical deposition temperatures achieved with standard precursors (SbR_3 and GaR_3).

The polycrystalline film consists of agglomerated GaSb particles as was shown by TEM (transmission electron mi-

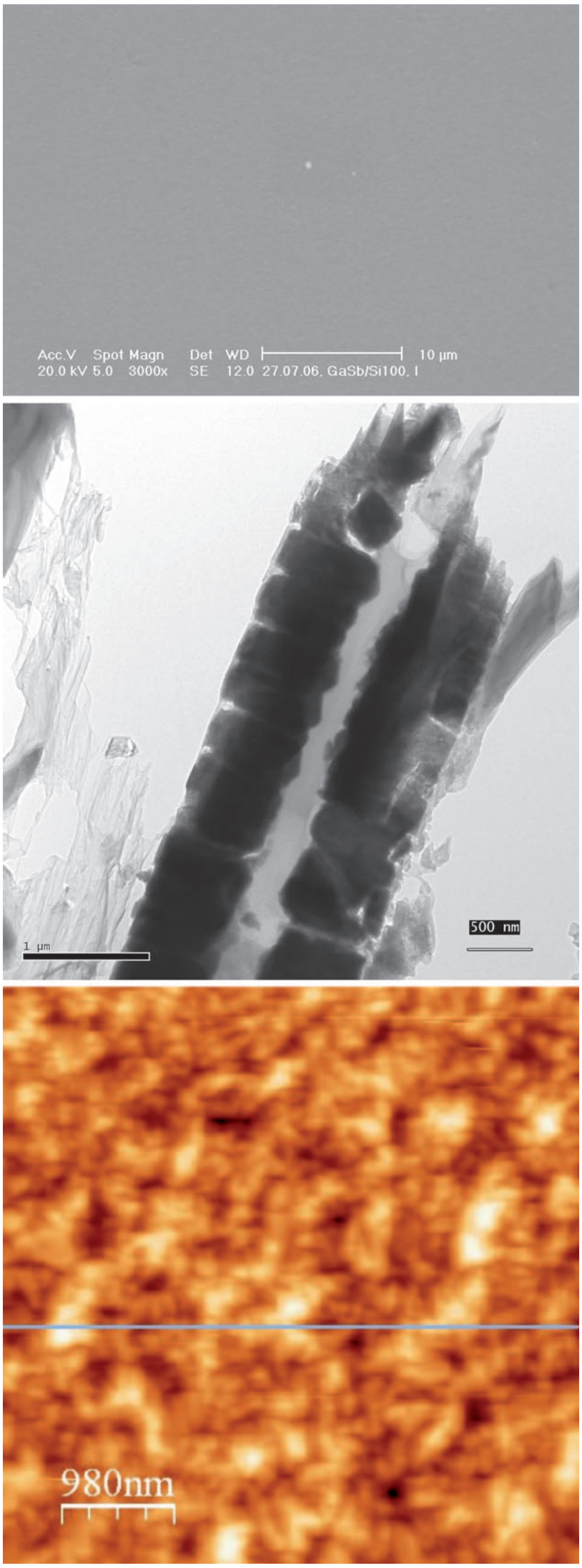


Figure 6. REM (top), TEM (middle), and AFM (bottom) pictures of a GaSb film deposited at 410 °C.

croscopy) and carbon contaminations were only found on the surface of the films. The roughness of these GaSb films was as low as 10 nm as shown by AFM (atomic force microscopy).

Lowering deposition temperatures may become an important issue when it comes to the synthesis of metastable materials. A prominent example was given by Barron et al., demonstrating the potential of cubane-type [{GaS(*t*Bu)}$_4$] precursors for the synthesis of a new metastable cubic GaS.[85] Heterocubanes [(MER)$_4$] (M = Al, Ga, In; E = S, Se, Te) are generally accessible by reaction of low-valent Group 13 diyls MR as well as MR$_3$ with elemental chalcogens. The deposition of cubic GaS was achieved under low-temperature conditions at 380 °C, which turned out to be essential, since the metastable cubic phase readily undergoes phase transition into the thermodynamically stable hexagonal phase at higher temperatures. Traditional precursors for the MOCVD deposition of GaS films are GaMe$_3$ and H$_2$S, which typically require decomposition temperatures above 500 °C according to their rather strong Ga−C bonds, consequently yielding the hexagonal phase of GaS.

Deposition of GaSb and Bi nanowires: Semiconducting nanowires nowadays steadily receive an increasing interest due to their advantageous physical properties,[86] which render them very promising for potential applications in nanoelectronics and optoelectronics.[87] They were grown by MOVPE (metal–organic vapor-phase epitaxy)[88] according to the so-called VLS mechanism (vapor–liquid–solid),[89] in which a low-melting metal, such as a Au nanoparticle, serves as preferential site for adsorption of the reactant(s) and nucleation site for the nanowire growth. The diameter of the growing nanowire is controlled by the size of the droplets, even though the role of the size of the catalytic particle is still discussed.[90]

We began only recently to investigate the use of distibines in MOCVD processes. Distibines exhibit significantly lower decomposition temperatures compared to trialkylstibines. For instance, Sb$_2$Et$_4$ decomposes between 100 to 250 °C, whereas SbEt$_3$ starts to decompose at temperatures above 400 °C.[91] Consequently, distibines can be used in the Ga-assisted growth of GaSb nanowires at very low temperature of 250 °C (Figure 7).[92] In addition, the single-source precursor [*t*Bu$_3$Ga-Sb*i*Pr$_3$]was found suitable for the growth of GaSb nanowires at 350 °C in closed glass ampoules.

Solution-based synthesis of nanoscale E$_2$Te$_3$ (E = Sb, Bi) and Bi particles: The wet-chemical approach to nanoscale materials is also intensely investigated.[93] The synthesis of E$_2$Te$_3$ (E = Sb, Bi), which belong to the most important thermoelectric materials, and Bi nanoparticles is of particular interest, since Bi nanowires show strong diameter-dependent properties, such as superconductivity and increased magneto resistance, and even stronger increases in the figure of merit (*ZT*) are predicted in quantum wires.[94] Suitable single-source precursors of the type [R$_2$E-Te-ER$_2$] were synthesized by reaction of elemental Te with the distibine Sb$_2$Et$_4$ and dibismuthine Bi$_2$Et$_4$. Wet-chemical synthesis typically uses capping agents, which stabilize the nanoparticle. The effect of TOPO (TOPO = trioctylphosphine oxide) on the synthesis of Sb$_2$Te$_3$ nanoparticles, which were obtained at 160 °C from the single-source precursor [(SbEt$_2$)$_2$Te], is clearly visible. Isolated, crystalline Sb$_2$Te$_3$ nanoplates were obtained in the presence of TOPO, whereas in its absence, larger agglomerates were obtained (Figure 8).[95]

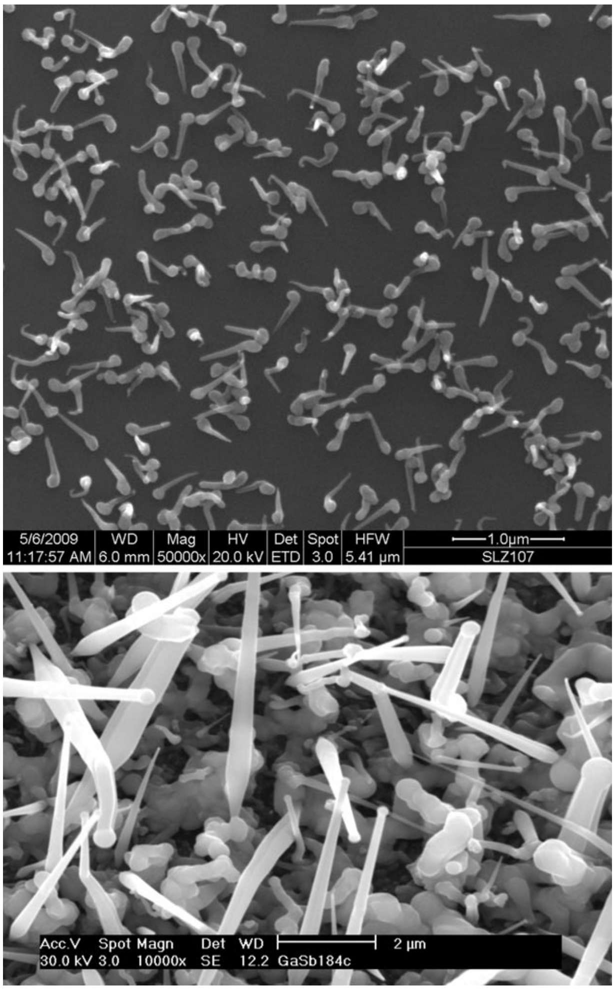


Figure 7. REM pictures of GaSb nanowires obtained from Sb$_2$Et$_4$ at 250 °C (top) and [*t*Bu$_3$Ga−Sb(*i*Pr)$_3$] at 350 °C (bottom).

Thermal decomposition of Bi$_2$Et$_4$ between 50 and 100 °C in the presence of suitable capping agents yielded homogeneous, crystalline Bi cubes with an average size of up to 200 nm, depending on the reaction time (Figure 9). These are the lowest deposition temperatures ever achieved and these promising results clearly show that precursor chemistry plays a crucial role in the synthesis of nanostructured materials.[95]

Intermetallic nanomaterials through solution-based synthesis: The capability of Group 13 diyls to coordinate as two-electron donor ligand to various transition-metal complexes was already mentioned. Moreover, Ga diyls such as [GaCp*]

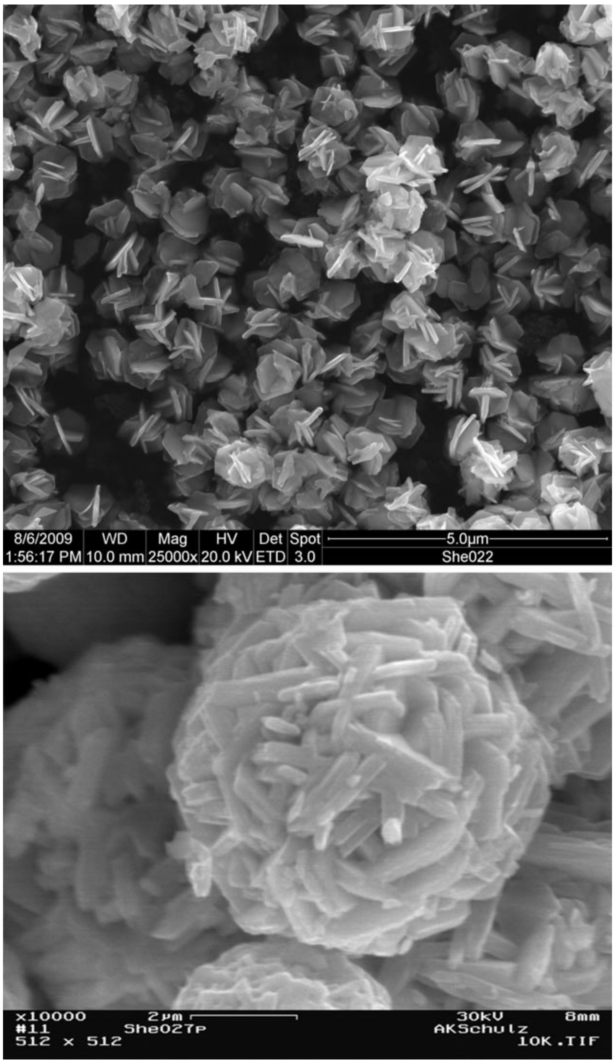


Figure 8. REM pictures of Sb_2Te_3 nanoparticles obtained from $[(SbEt_2)_2Te]$ with (top) and without TOPO (bottom) at 150 °C.

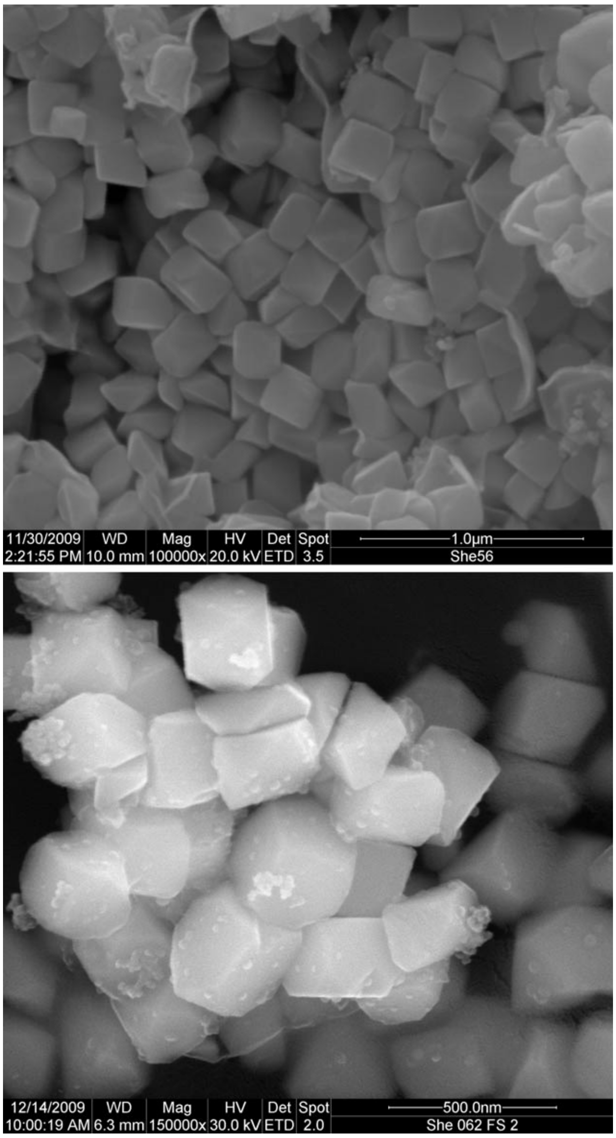


Figure 9. REM pictures of Bi nanocubes obtained from Bi_2Et_4 at 100 °C.

and [Ga(DippNacnac)] were also very recently used in the Fischer group for the synthesis of unforeseen molecular, metal-rich intermetallic complexes. The reaction of $[Mo(CO)_4(GaCp^*)_2]$ with four equivalents of $ZnMe_2$ yielded $[\{Mo(CO)_4\}_4(Zn)_6(\mu\text{-}ZnCp^*)_4]$ (Figure 10),[96] which may be viewed as a cut-out of Hume–Rothery-type intermetallic compounds. In addition, the reaction of $[Mo(GaCp^*)_6]$ with fourteen equivalents of $ZnMe_2$ resulted in the formation of $[\{MoZn_{12}Me_9Cp^*_3]$.[97] This reaction was shown to proceed through the intermediate formation of $[\{MoZn_4Ga_4Me_4Cp^*_4]$ and $[\{MoZn_8Ga_2Me_6Cp^*_4]$, respectively, which were also structurally characterized.

Moreover, the reaction of [Ga(DippNacnac)] with $SnCl_2$ yielded two novel metalloid tin clusters, $[Sn_7\text{-}\{GaCl(DippNacnac)\}_2]$ and $[Sn_{17}\{GaCl(DippNacnac)\}_4]$ (Figure 10).[98] The Sn_{17} core is composed of two identical Sn_9 clusters that share a common vertex. If the Ga atom in the {GaCl(DippNacnac)} moiety is described as Ga^{III} species $\{GaCl(DippNacnac)\}^+$, the Sn_{17} cluster has to be viewed as Sn_{17}^{4-} unit, which according to its 40 electrons fulfils the Jellium model. The two Sn_9^{2-} clusters both adopt distorted trigonal prismatic structures.

These complexes not only highlight the distinct structural variety that can be seen in metal cluster complexes, but also offer a bridge between (metalloid) cluster complexes and classical Werner coordination complexes. These novel types of complexes are only accessible by tuning the reducing and trapping properties of the reducing agents. Low-valent Group 13 diyls MR may be somehow the most ideal candidates for further studies, since the variation of the substituents R allows the tuning, to some extent, of their steric demand, their Lewis basicity, and their redox potential. Using these new synthetic strategies, new intermetallic complexes, far beyond the means of what classical solid-state chemistry can offer, might be accessible in the future.

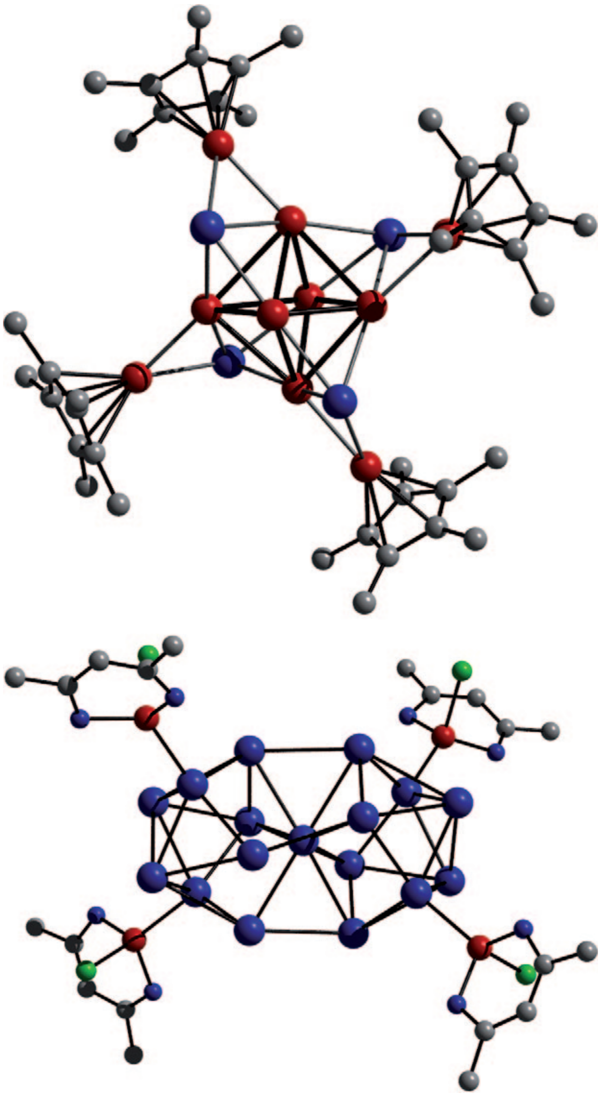


Figure 10. Reduced representations of $[\{Mo(CO)_4\}_4(Zn)_6(\mu\text{-}ZnCp^*)_4]$ (top) and $[Sn_{17}\{DippNacnacGaCl\}_4]$ (bottom).

Summary and Outlook

Low-valent main-group metal complexes are no longer laboratory curiosities, since in the last two decades general pathways for their synthesis were established by use of kinetically stabilizing (bulky) and electronically stabilizing substituents (Lewis bases). Moreover, the development of metastable solutions of Group 13 monohalides MX has opened new synthetic pathways in Group 13 metal complexes. Hopefully, the most recent synthesis of Mg_2Cl_2 has comparable effects.[14] The novel (metalloid) complexes not only fascinate due to the large structural variety, but also due to their sometimes unexpected reactivity, which allowed the synthesis of unforeseen complexes. Moreover, their potential to serve as novel precursors for the synthesis of nanoscale materials, which often has to be performed under kinetically-controlled reaction conditions, render them very interesting for various applications in material sciences. In addition, they might be valuable models for mimicking reactions of bulk phases as was shown recently by Schnöckel et al., who investigated the reaction of an Al_{13} cluster with singlet oxygen, hence modeling the corrosion of bulk aluminum.[99]

Acknowledgements

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[1] K. Pitzer, *J. Am. Chem. Soc.* **1948**, *70*, 2140.

[2] a) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201; b) E. Rivard, P. P. Power, *Inorg. Chem.* **2007**, *46*, 10047.

[3] The term “metalloid” has been established for the description of metal complexes in which the number of direct metal–metal bonds exceeds the number of metal–ligand bonds.

[4] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. SchaeferononIII, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069.

[5] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136.

[6] Prior to these studies, the formation of $[Zn]^+$ cations in microporous materials was reported: a) K. Seff, *Microporous Mesoporous Mater.* **2005**, *85*, 351; b) Y. Tian, G.-D. Li, J.-S. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 6622; c) S. Zhen, D. Bae, K. Seff, *J. Phys. Chem. B* **2000**, *104*, 515; d) F. Rittner, A. Seidel, B. Boddenberg, *Microporous Mesoporous Mater.* **1998**, *24*, 127; in addition, Zn_2H_2 was trapped in an Ar matrix at 12 K and characterized by vibrational spectroscopy and computational calculations: e) X. Wang, L. J. Andrews, *J. Phys. Chem. A* **2004**, *108*, 11006; f) T. M. Greene, W. Brown, L. Andrews, A. J. Downs, G. V. Chertihin, N. Runeberg, P. Pyykkö, *J. Phys. Chem.* **1995**, *99*, 7925.

[7] a) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* **2007**, *129*, 693; b) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 5939; *Angew. Chem. Int. Ed.* **2006**, *45*, 5807; c) Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. von R. Schleyer, H. F. Schaefer III, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, *127*, 11944; d) X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang, B. Wu, *Chem. Commun.* **2007**, 2363; e) Y.-C. Tsai, D.-Y. Lu, Y.-M. Lin, j.-K. Hwang, J.-S. K. Yu, *Chem. Commun.* **2007**, 4125.

[8] I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem.* **2007**, *119*, 4380; *Angew. Chem. Int. Ed.* **2007**, *46*, 4302.

[9] Y. Liu, S. Li, X.-J. Yang, P. Yang, J. Gao, Y. Xia, B. Wu, *Organometallics* **2009**, *28*, 5270.

[10] a) S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics* **2009**, *28*, 1590; b) S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser, R. Boese, *Angew. Chem.* **2009**, *121*, 5859; *Angew. Chem. Int. Ed.* **2009**, *48*, 5748.

[11] a) Z. Zhu, R. C. Fischer, J. C. Fettinger, E. Rivard, M. Brynda, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 15068; b) Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2007**, *129*, 10847.

[12] E. Carmona, A. Galindo, *Angew. Chem.* **2008**, *120*, 6626; *Angew. Chem. Int. Ed.* **2008**, *47*, 6526.

[13] S. Petrie, *Aust. J. Chem.* **2003**, *56*, 259.

[14] a) R. Köppe, P. Henke, H. Schnöckel, *Angew. Chem.* **2008**, *120*, 8868; *Angew. Chem. Int. Ed.* **2008**, *47*, 8740; b) X. Wang, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 11511.

[15] a) S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754; b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938.

[16] Y. Liu, S. Li, X.-J Yang, P. Yang, B. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 4210.

[17] J. Overgaard, C. Jones, A. Stasch, B. B. Iversen, *J. Am. Chem. Soc.* **2009**, *131*, 4208.

[18] S. Krieck, H. Görls, L. Yu, M. Reiher, M. Westerhausen, *J. Am. Chem. Soc.* **2009**, *131*, 2977.

[19] S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, *120*, 9219; *Angew. Chem. Int. Ed.* **2008**, *47*, 9079.

[20] D. Schuchmann, U. Westphal, S. Schulz, U. Flörke, D. Bläser, R. Boese, *Angew. Chem.* **2009**, *121*, 821; *Angew. Chem. Int. Ed.* **2009**, *48*, 807.

[21] S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem.* **2009**, *121*, 3017; *Angew. Chem. Int. Ed.* **2009**, *48*, 2973.

[22] A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701.

[23] D. H. Kerridge, S. A. Tariq, *J. Chem. Soc. A* **1967**, 1122.

[24] a) M. Kaupp, H. G. von Schnering, *Inorg. Chem.* **1994**, *33*, 4179; b) M.-S. Liao, Q.-E. Zhang, W. H. E. Schwarz, *Inorg. Chem.* **1995**, *34*, 5597; c) K. K. Pandey, *J. Mol. Struct.* **2007**, *825–846*, 59; d) M. Hargittai, *Chem. Rev.* **2000**, *100*, 2233.

[25] D. del Rio, I. Resa, A. Rodriguez, L. Sánchez, R. Köppe, A. J. Downs, C. Y. Tang, E. Carmona, *J. Phys. Chem. A* **2008**, *112*, 10516.

[26] W. Uhl, *Z. Naturforsch. B* **1988**, *43*, 1113.

[27] a) R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983; b) N. Wiberg, K. Amelunxen, T. Blank, H. Nöth, J. Knizek, *Organometallics* **1998**, *17*, 5431.

[28] a) W. Uhl, M. Layh, T. Hildenbrand, *J. Organomet. Chem.* **1989**, *364*, 289; b) X. He, R. A. Barlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem.* **1993**, *105*, 761; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717.

[29] a) W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139; b) M. S. Hill, P. B. Hitchcock, R. Pongtavornpinyo, *Angew. Chem.* **2005**, *117*, 4303; *Angew. Chem. Int. Ed.* **2005**, *44*, 4231; c) R. J. Wright, A. D. Phillips, N. J. Hardman, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 8538; d) P. J. Brothers, K. Hübler, U. Hübler, B. C. Noll, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1996**, *108*, 2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2355.

[30] J. A. J. Pardoe, A. J. Downs, *Chem. Rev.* **2007**, *107*, 2.

[31] AlCl is a high-temperature species that can be prepared by reaction of Al and HCl at 1200°C: K. M. Tacke, H. Schnöckel, *Inorg. Chem.* **1989**, *28*, 2895.

[32] M. S. Hill, P. B. Hitchcock, R. Pongtavornpinyo, *Science* **2006**, *311*, 1904.

[33] A. Schnepf, R. Köppe, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 1287; *Angew. Chem. Int. Ed.* **2001**, *40*, 1241.

[34] Y. Wang, G. H. Robinson, *Organometallics* **2007**, *26*, 2.

[35] J. Su, X.-W. Li, C. Crittendorn, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471; the X-ray crystal structure of $Na_2[\{Ga(2,6\text{-}Dipp_2\text{-}C_6H_3)\}_2]$ was also determined by Power et al.: B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 3643; *Angew. Chem. Int. Ed.* **2000**, *39*, 3500.

[36] a) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785; b) A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930; c) L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524.

[37] R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 6099; *Angew. Chem. Int. Ed.* **2006**, *45*, 5953.

[38] A. Purath, R. Köppe, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3114; *Angew. Chem. Int. Ed.* **1999**, *38*, 2926.

[39] J. Vollet, J. R. Hartig, H. Schnöckel, *Angew. Chem.* **2004**, *116*, 3248; *Angew. Chem. Int. Ed.* **2004**, *43*, 3186.

[40] A. Ecker, E. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379.

[41] a) A. Schnepf, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 733; *Angew. Chem. Int. Ed.* **2001**, *40*, 711; b) A. Schnepf, B. Jee, H. Schnöckel, E. Weckert, A. Meents, D. Lubbert, E. Herrling, B. Pilawa, *Inorg. Chem.* **2003**, *42*, 7731.

[42] O. N. Bakharev, N. Zelders, H. B. Brom, A. Schnepf, H. Schnöckel, L. J. de Jongh, *Eur. Phys. J. D* **2003**, *24*, 101.

[43] J. Hagel, M. T. Kelemen, G. Fischer, B. Pilawa, J. Wosnitza, E. Dormann, H. v. Löhneysen, A. Schnepf, H. Schnöckel, U. Neisel, J. Beck, *J. Low Temp. Phys.* **2002**, *129*, 133.

[44] a) H. Schnöckel, H. Köhnlein, *Polyhedron* **2002**, *21*, 489; b) H. Schnöckel, *Dalton Trans.* **2005**, 3131; c) G. Linti, H. Schnöckel, *Coord. Chem. Rev.* **2000**, *285*, 206; d) A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532.

[45] a) W. Uhl, *Coord. Chem. Rev.* **1997**, *163*, 1; b) W. Uhl, *Chem. Soc. Rev.* **2000**, *29*, 259; c) W. Uhl, *Adv. Organomet. Chem.* **2004**, *51*, 53.

[46] S. Schulz in *Comprehensive Organometallic Chemistry III, Vol. 3* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Amsterdam, **2007**, pp. 287–342.

[47] R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 12498.

[48] N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink, P. P. Power, *Angew. Chem.* **2001**, *113*, 2230; *Angew. Chem. Int. Ed.* **2001**, *40*, 2172.

[49] R. J. Wright, A. D. Phillips, T. L. Allen, W. H. Fink, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 1694.

[50] a) S. Schulz, L. Häming, R. Herbst-Irmer, H. W. Roesky, G. M. Sheldrick *Angew. Chem.* **1994**, *106, 1052; Angew. Chem. Int. Ed. Engl.* **1994**, 33, 969; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 969; b) S. Schulz, A. Voigt, H. W. Roesky, L. Häming, R. Herbst-Irmer, *Organometallics* **1996**, *15*, 5252; c) S. Schulz, F. Thomas, W. Priesmann, M. Nieger, *Organometallics* **2006**, *25*, 1392.

[51] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1999**, *18*, 2037.

[52] S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27*, 457.

[53] In contrast, Stephan et al. showed that frustrated Lewis acid-base pairs allow reversible H_2 binding at 25°C; see for instance: a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124; b) S. J. Geier, T. M. Gilbert, D. W. Stephan, *J. Am. Chem. Soc.* **2008**, *130*, 12632; c) M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52.

[54] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem.* **1994**, *106*, 225; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 199.

[55] W. Uhl, M. Benter, *Chem. Commun.* **1999**, 771.

[56] a) W. Uhl, M. Benter, W. Saak, P. G. Jones, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1622; b) W. Uhl, M. Pohlmann, *Chem. Commun.* **1998**, 451; c) W. Uhl, R. Graupner, M. Pohlmann, S. Pohl, W. Saak, *Chem. Ber.* **1996**, *129*, 143; d) S. Schulz, H. W. Roesky, H.-J. Koch, G. M. Sheldrick, D. Stalke, A. Kuhn, *Angew. Chem.* **1993**, *105*, 1828; *Angew. Chem. Int. Ed.***1993**, *32*, 1729.

[57] W. Uhl, R. Graupner, W. Hiller, M. Neumayer, *Angew. Chem.* **1997**, *109*, 62; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 62.

[58] N. J. Hardman, P. P. Power, *Inorg. Chem.* **2001**, *40*, 2474.

[59] For a review on terminal chalcogenido complexes, see: M. C. Kuchta, G. Parkin, *Coord. Chem. Rev.* **1998**, *176*, 323.

[60] A detailed description of the electronic structure of these complexes is given by: C. J. Green, J. L. Suter, *Dalton Trans.* **1999**, 4087.

[61] M. C. Kuchta, G. Parkin, *Main Group Chem.* **1996**, *1*, 291.

[62] a) C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R. A. Fischer, *Eur. J. Inorg. Chem.* **2004**, 4161; b) R. J. Baker, C. Jones, *Coord. Chem. Rev.* **2005**, *249*, 1857; c) G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V. M. Rayón, *Coord. Chem. Rev.* **2003**, *238*, 55; d) P. W. Roesky, *Dalton Trans.* **2009**, 1887.

[63] N. J. Hardman, P. P. Power, J. D. Gorden, C. L. B. Macdonald, A. H. Cowley, *Chem. Commun.* **2001**, 1866.

[64] T. Cadenbach, C. Demel, D. Zacher, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 3487; *Angew. Chem. Int. Ed.* **2008**, *47*, 3438.

[65] B. Buchin, C. Demel, T. Cadenbach, I. Fernández, G. Frenking, R. A. Fischer, *Angew. Chem.* **2006**, *118*, 5331; *Angew. Chem. Int. Ed.* **2006**, *45*, 5207.

[66] B. Buchin, C. Demel, T. Cadenbach, R. Schmid, R. A. Fischer, *Angew. Chem.* **2006**, *118*, 1091; *Angew. Chem. Int. Ed.* **2006**, *45*, 1074.
[67] For a historical review, see: D. Seyferth, *Organometallics* **2001**, *20*, 1488.
[68] a) H. J. Breunig, R. Rösler, *Coord. Chem. Rev.* **1997**, *163*, 33; b) L. Balasz, H. J. Breunig, *Coord. Chem. Rev.* **2004**, *248*, 603.
[69] S. Schulz, *Adv. Organomet. Chem.* **2003**, *49*, 225.
[70] S. Schulz, T. Schoop, H. W. Roesky, L. Häming, A. Steiner, R. Herbst-Irmer, *Angew. Chem.* **1995**, *107*, 1015; *Angew. Chem. Int. Ed.* **1995**, *34*, 919.
[71] C. Jones, *Coord. Chem. Rev.* **2001**, *215*, 151.
[72] a) N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, *277*, 78; b) T. Sasamori, N. Tokitoh, *Dalton Trans.* **2008**, 1395.
[73] G. Prabusankar, C. Gemel, P. Parameswaran, C. Flener, G. Frenking, R. A. Fischer, *Angew. Chem.* **2009**, *121*, 5634; *Angew. Chem.* Int. Ed. **2009**, *48*, 5526.
[74] T. Sasamori, E. Mieda, N. Nagahora, K. Sato, D. Shiomi, T. Takui, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 12582.
[75] T. Sasamori, E. Mieda, N. Takeda, N. Tokitoh, *Chem. Lett.* **2004**, *33*, 104.
[76] a) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829; b) D. Bourissou, O. Guerret, F. P. Gabbaie, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; c) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913.
[77] Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412.
[78] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970.
[79] M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2010**, *16*, 432.
[80] a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683; b) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687.
[81] B. Quillian, P. Wei, C. S. Wannere, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2009**, *131*, 3168.
[82] C. A. Dyker, G. Bertrand, *Science* **2008**, *321*, 1050.
[83] a) A. H. Cowley, R. A. Jones, *Angew. Chem.* **1989**, *101*, 1235; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1208; b) J. A. Jegier, W. L. Gladfelter, *Coord. Chem. Rev.* **2000**, *206–207*, 631; c) A. C. Jones, *Chem. Soc. Rev.* **1997**, *26*, 101; d) A. N. Gleizes, *Chem. Vap. Deposition* **2000**, *6*, 155; e) M. Lazell, P. O'Brien, D. J. Otway, J.-H. Park, *Dalton Trans.* **2000**, 4479.
[84] a) S. Schulz in *Topics in Organometallic Chemistry, Vol. 9* (Ed.: R. A. Fischer), Springer, Berlin, **2005**, pp. 101–124; b) S. Schulz, S. Fahrenholz, A. Kuczkowski, W. Assenmacher, A. Seemayer, K. Wandelt, *Chem. Mater.* **2005**, *17*, 1982; c) D. Schuchmann, M. Schwartz, S. Schulz, A. Seemayer, K. Wandelt, *J. Cryst. Growth* **2008**, *310*, 4715.
[85] A. N. MacInnes, M. B. Power, A. R. Barron, *Chem. Mater.* **1992**, *4*, 11.
[86] a) T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, W. E. Buhro, *Science* **1995**, *270*, 1791; b) A. M. Morales, C. M. Lieber, *Science* **1998**, *279*, 208; c) M. K. Sunkara, S. Sharma, R. Miranda, G. Lian, E. C. Dickey, *Appl. Phys. Lett.* **2001**, *79*, 1546; d) J. H. Lee, Z. M. Wang, Z. Y. AbuWaar, G. J. Salamo, *Cryst. Growth Des.* **2009**, *9*, 715.
[87] a) P. D. Yang, *MRS Bull.* **2005**, *30*, 85; b) Y. Huang, X. F. Duan, C. M. Lieber, *Small* **2005**, *1*, 142.
[88] W. Seifert, M. T. Borgström, K. Deppert, K. A. Dick, J. Johansson, M. W. Larsson, T. Martensson, N. Sköld, C. P. T. Svensson, B. A. Wacaser, L. R. Wallenberg, L. Samuelson, *J. Cryst. Growth* **2004**, *272*, 211.
[89] R. S. Wagner, W. C. Ellis, *Appl. Phys. Lett.* **1964**, *4*, 89.
[90] a) B. A. Wacaser, K. A. Dick, J. Johansson, M. T. Borgström, K. Deppert, L. Samuelson, *Adv. Mater.* **2009**, *21*, 153; b) M. T. Borgström, G. Immink, B. Ketelaars, R. Algra, E. P. A. M. Bakkers, *Nat. Nanotechnol.* **2007**, *2*, 541.
[91] N. Bahlawane, F. Reilmann, S. Schulz, D. Schuchmann, K. Kohse-Höinghaus, *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 1336.
[92] S. Schulz, M. Schwartz, A. Kuczkowski, W. Assenmacher, *J. Cryst. Growth* **2010**, *312*, 1475.
[93] a) N. L. Pickett, P. O‘Brien, *Chem. Rec.* **2001**, *1*, 467; b) Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2009**, *121*, 62; *Angew. Chem. Int. Ed.* **2009**, *48*, 60.
[94] a) B. Weitzel, H. Micklitz, *Phys. Rev. Lett.* **1991**, *66*, 385; b) S. Cho, Y. Kim, A. J. Freeman, G. K. L. Wong, J. B. Ketterson, L. J. Olafsen, I. Vurgaftman, J. R. Meyer, C. A. Hoffman, *Appl. Phys. Lett.* **2001**, *79*, 3651; c) L. D.; Hicks, M. S. Dresselhaus, *Phys. Rev. B* **1993**, *47*, 16631 Hicks, M. S. Dresselhaus, *Phys. Rev. B* **1993**, *47*, 12727; d) L. D.; Hicks, M. S. Dresselhaus, *Phys. Rev. B* **1993**, *47*, 16631; e) A. Boukai, K. Xu, J. R. Heath, *Adv. Mater.* **2006**, *18*, 864.
[95] S. Schulz, S. Heimann, W. Assenmacher, unpublished results.
[96] T. Cadenbach, C. Gemel, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 9286; *Angew. Chem. Int. Ed.* **2008**, *47*, 9146.
[97] T. Cadenbach, T. Bollermann, C. Gemel, I. Fernandez, M. von Hopffgarten, G. Frenking, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 9290; *Angew. Chem. Int. Ed.* **2008**, *47*, 9150.
[98] G. Prabusankar, A. Kempter, C. Gemel, M. K. Schröter, R. A. Fischer, *Angew. Chem.* **2008**, *120*, 7344; *Angew. Chem. Int. Ed.* **2008**, *47*, 7234.
[99] R. Burgert, H. Schnöckel, A. Grubisic, X. Li, S. T. Stokes, K. H. Bowen, G. F. Ganteför, B. Kiran, P. Jena, *Science* **2008**, *319*, 438.