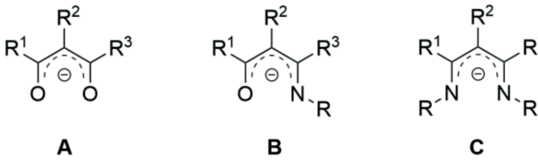
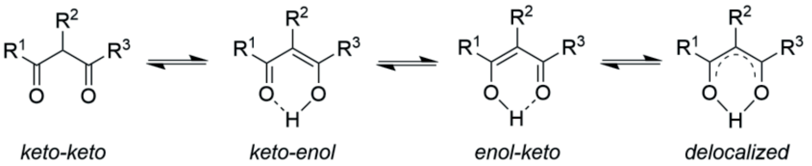
1 Introduction

1.1 History and Synthesis of the nacnac Ligand

Regarding the class of chelating ligand systems, the following three related monoanionic species **A** to **C** will be discussed in the context of this work (see Scheme 1-1), wherein all mentioned residues (R, R^1, R^2 and R^3) are mostly alkyl or aryl substituents. Starting with the *β*-diketonato or acetylacetonato ligand **A**,[1] also abbreviated as acac, it can be stated that this ligand system has widespread applications in coordination chemistry. Due to the keto-enol tautomerism in the parent diketone acacH depicted in Scheme 1-2, the remaining proton at the bridging methylene CHR^2 moiety is quite acidic and therefore prone to deprotonation reactions. The resulting negative charge can be easily stabilized by delocalization within the alternating double bonds of the C_3O_2 section, which is capable of chelating metal cations (*vide infra*).



Scheme 1-1: Different monoanionic chelating ligands: acetylacetonato (**A**), *β*-enaminoketonato (**B**) and *β*-diketiminato (**C**).



Scheme 1-2: Exemplary keto-enol tautomerism within the acacH ligand **A**.

The formal isoelectronic replacement of one oxygen atom of the diketone by an imine functionality NR leads to the formation of the *β*-enaminoketonato ligand system **B**.[2] By introducing this imine moiety, the delocalization of the negative charge is also taking place efficiently, but the additional substituent at the nitrogen atom can be varied to influence the electronic and steric properties of the ligand system **B**. Again, this class of ligands is well known in the literature because of its good coordination behaviour.

To complete the series, the *β*-diketiminato or *β*-dialdiminato ligand **C** – also called *N*-alkyl vinamidine or more concisely nacnac following from the nitrogen substitution of acac – has to be mentioned at this point. In contrast to ligand **B,** both keto or aldehyde functionalities are replaced by the same corresponding imine moiety, which improves the possibility of tuning the electronic and steric properties of the chelating ligand. In addition, more complex modifications of the nacnac ligand are known, where for example two different substituents at the imine nitrogen atom are present, or these residues work as a linking moiety between two imines to form a macrocyclic compound.[3] This class of monoanionic, bidentate ligands has received increasing attention in the last two decades due to their ability to form stable metal complexes, which is visualized in Figure 1-1. Obviously, since 1996 the number of publications containing the keyword "diketiminate" is increased continuously until 2005 to reach afterwards a steady level of average 80 publications per year up to the present date. In 2010, a maximum number of 115 publications related to this topic were recorded. This statistic reflects the high degree of interest in this ligand system in current research and shows that the nacnac ligands are today one of the most popular ligand systems in coordination chemistry.[4]

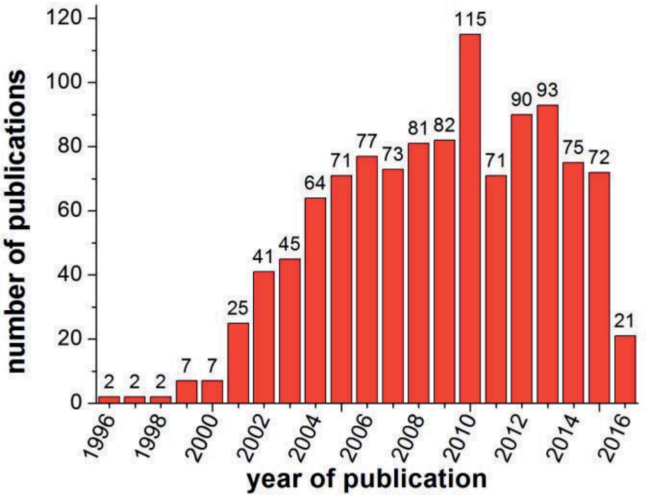
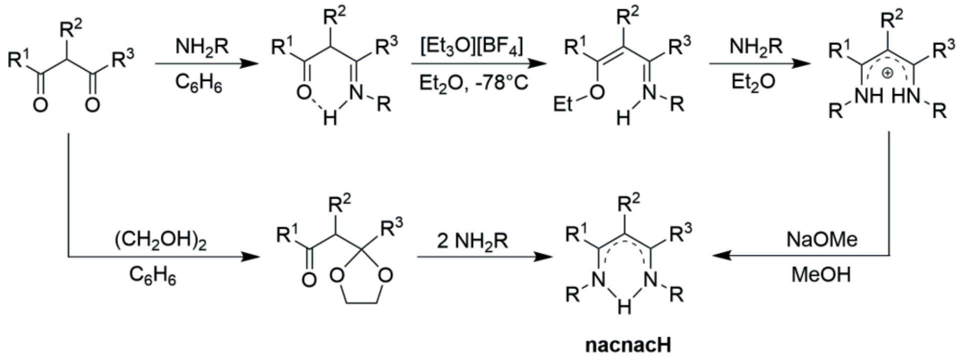


Figure 1-1: SciFinder search for the keyword "diketiminate" (executed at 13th may 2016).

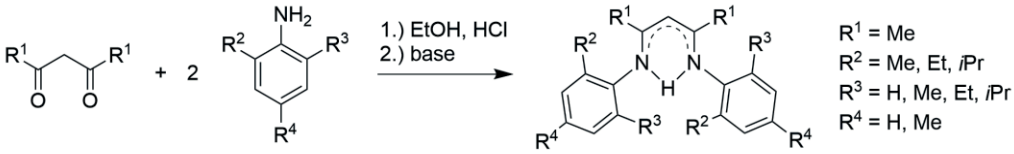
The synthesis of the parent *β*-diketimine ligands can be accomplished mainly by using two different pathways shown in Scheme 1-3, which were developed over three decades ago. The upper pathway shows the condensation reaction starting from the corresponding *β*-diketone and the desired primary amine NH_2R. In order to avoid that the reaction stops at the stage of the single-condensation product (the *β*-enaminoketonato ligand **B**), the reaction procedure contains some additional steps like methylation of the remaining keto functionality by usage of a Meerwein salt,[5] before the second condensation of the imine can take place.[6] Another route for the formation of mainly aryl substituted imines is shown in the bottom pathway: in this route, one ketone reacts selectively with ethylene glycol to give the corresponding ketal, which can than undergo the condensation reaction with the primary amine.[7]



Scheme 1-3: Synthetic pathways to the formation of nacnacH starting from the corresponding β-diketone.

For the generation of nacnac ligands which do not contain any additional substituents in the backbone of the ligand, 1,1,3,3-tetraalkoxy propanes can also be used as a precursor. For this reaction, the hydrochlorides of the corresponding aromatic amines were added at 50 °C to the acetal propane derivative in an aqueous ethanol solution to obtain the β-diketimine hydrochloride, which is further treated with aqueous sodium hydroxide solution.[8]

Since the first described synthesis of the Dipp substituted ligand $[\{N(Dipp)C(Me)\}_2CH]^-$ in 1997,[9] this derivate probably developed to one of the most studied nacnac ligand systems in current research topics. Due to this fact, a more facile synthetic approach with good yields of about 80 % was developed, especially for ligands carrying aromatic imine substituents. In that case, the reaction was accomplished by imine formation of 2,4-pentadienone with the desired *ortho*-/*para*-substituted aniline derivative in an ethanolic solution over several days. After aqueous workup with sodium carbonate solution, the corresponding protonated nacnacH ligands could be isolated (see Scheme 1-4). [9, 10] For the implementation of further increased steric bulkiness at the backbone of the nacnac ligands, *t*Bu groups were introduced, starting from pivaloyl chloride and the corresponding primary amine and followed by lithiation reactions for coupling.[11] The *N*-terphenyl substituted nacnac ligand should also be mentioned in this series, because the super-sized imine residues are protecting the metal complexes from oligomerization,[12] which will be a part of the following chapter as well.

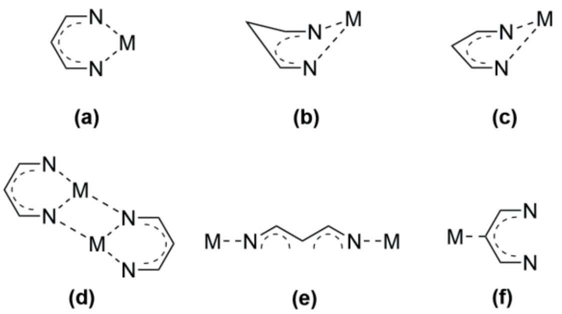


Scheme 1-4: Synthesis of the aryl substituted nacnacH ligands.

1.2 Group 13 Metal Diketiminato Complexes

Since the first transition metal complexes of the nacnac ligand were mentioned in 1968,[2b, 6, 13] in the past two decades also many *β*-diketiminate structures containing main group metals were synthesized and fully characterized.[14] These complexes embrace aluminium(III), gallium(III) and indium(III) compounds. The former range from the alkyl over the hydride to halide substituted metal centres. Furthermore, the dialkylaluminium *β*-diketiminates show catalytic activities towards ring-opening polymerisation.[15]

After deprotonation of the backbone of these nacnac ligands, a monoanionic *π*-system containing six electrons is generated, where a complete delocalization of the electrons is achieved. These ligands behave mostly as redox-inactive spectator ligands.[16] Usually these nacnac systems carry an aliphatic organic residue like Me or *t*Bu at the backbone imine carbon atom, as described earlier, and mostly some bulky moieties like Dipp, adamantyl or mesityl groups at the imine nitrogen atom (see Scheme 1-4).

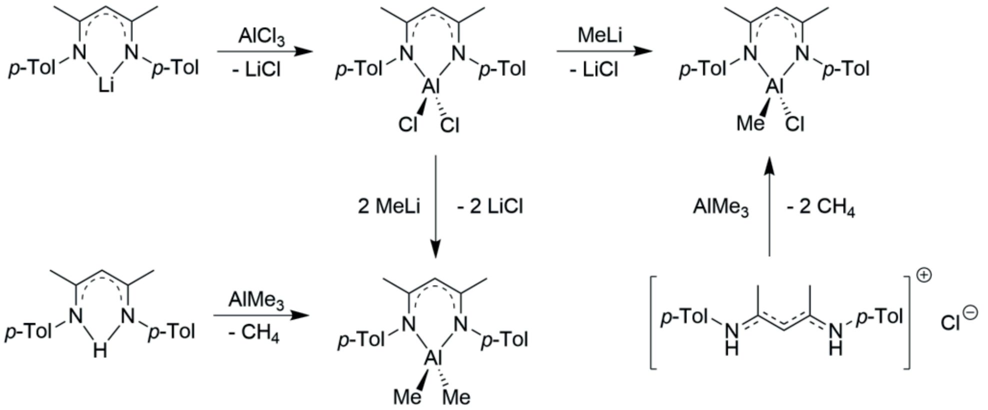


Scheme 1-5: Possible bonding motives observed for metal complexes of the nacnac ligand (the organic imine residues are omitted for clarity).

In Scheme 1-5, some different bonding modes of the deprotonated monoanionic nacnac ligand are shown, which have been structurally characterized and verified in the corresponding solid state structures. Mode **(a)** corresponds to the most common and also expected one, in which the six-membered metalla heterocycle is planar and the metal coordination is accomplished by the two imine nitrogen atoms in a terminal chelating fashion. In principle, the variants **(b)** and **(c)** show the same coordination motif as in **(a)**, but in these cases a boat-like conformation of the metalla heterocycle results.[17] Either the bridging methylene moiety as well as the coordinated metal fragment can bend out of plane **(b)** or just the metal cation is dislocated from the corresponding chelating plane, whereas the rest stays almost planar **(c)**. Motif **(d)** shows the presence of a dimeric species in which the metal cations are also coordinated in a chelating way similar to the previously mentioned binding modes, but two nitrogen atoms also operate as bridging donors to the neighbouring metal centre.[18]

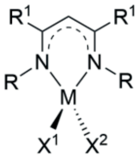
Two further interesting binding motifs can be described by means of **(e)** and **(f)**: the coordination in **(e)** is still achieved by the nitrogen donors, but here the ligand itself does not act as a chelate. In contrast to the other binding modes, the ligand is arranged in an open chain, so that each terminal nitrogen atom can coordinate a metal centre. By this the ligand acts as a bridge in between two metal centres.[19] Apart from the mostly nitrogen-centred coordination complexes obtained for the nacnac ligand, some examples for the coordination via the methylene bridge **(f)** are also observed.[20] In those quite rare cases, the metal cation is preferably coordinated in the solid state by the particular carbanionic centre instead of the more common nitrogen donors.

The first lithium containing nacnac complexes were reported in 1994 by reaction of bis-(trimethylsilyl)-methyl lithium and *tert*-butyl nitrile or benzonitrile in diethyl ether.[17a, 17c, 18b] In this kind of reaction, the first step covers the C–C coupling. Afterwards a 1,3-migration of an organic residue from a carbon to a nitrogen atom takes place. Besides this synthesis route, the most widespread preparation of lithium β-diketiminates is accomplished by simple deprotonation of the corresponding parent diketimine with alkyllithiums like *n*BuLi. In case of the Dipp-substituted nacnac ligand and in absence of donating solvents, two different crystal structures were observed for the resulting [Li{(N(Dipp)C(Me))$_2$CH}] and could be described as follows:[10b] one form appears as a dimeric species, in which the lithium cations are furthermore addressed by one aryl substituent of the second molecule. The other form is a dodecamer showing a slipped ladder structure also associated with the interactions of the Li$^+$ with one or two aryl carbon atoms. In the presence of diethyl ether or THF, monomeric complexes were observed, which exhibit a three coordinate lithium cation by means of the two imine nitrogen atoms and one additional oxygen donor from the Lewis-donating solvent.[10b] These lithiated compounds are commonly used as ligand transfer reagents for the synthesis of other metal complexes by simply adding different metal halides. Due to the resulting salt elimination reaction of the corresponding lithium halide, the desired transmetallated complex can be gained. For more practical reasons of separating the resulting salts, the sodium or potassium β-diketiminates were also used, because NaCl or KCl are less soluble in common organic solvents in comparison to LiCl, which facilitates the separation of this side product.[16b]



Scheme 1-6: Synthesis route for different exemplary Al(III) nacnac complexes.[14l]

Since the transition metal complexes of the nacnac ligand and the associated tuning of the ligand itself are playing a vital role in current research and catalytic applications,[4d, 4f, 9, 21] the corresponding research area of main group metal complexes became more and more interesting. Continuing with the group 13 metal complexes of the nacnac ligand, at this point the focus of this section lies on the corresponding aluminium, gallium and indium compounds due to the better connection to the scope of this work. The first aluminium complex $[Cl_2Al\{(N(Me)C(Me))_2CH\}]$ was published in 1991 by preparation from the corresponding ligand, triethylamine as a base, and $AlCl_3$ for metallation.[22] In 1998, the reactivity of the *p*ara-toloyl substituted nacnac ligands was studied in detail and a series of Al(III) complexes could be characterized sufficiently in solution and in the solid state (see Scheme 1-6).[14l] The $AlCl_2$ containing complex was prepared by reaction of the lithiated ligand with $AlCl_3$ under formation of LiCl as the driving force. The remaining chlorido residues at the chelated aluminium atom can easily undergo nucleophilic substitution reactions: by adding methyllithium in different molar equivalents, it is possible to obtain the single or double methyl substituted AlMeCl or $AlMe_2$ bearing complexes, while salt elimination of LiCl is occurring. These two species can also be synthesized in another approach by just adding the alkylaluminium reagent $AlMe_3$ directly to the parent ligand or the corresponding hydrochloride adduct. The basicity of $AlMe_3$ is sufficient to deprotonate the bridging methylene moiety of the ligand's backbone under evolution of gaseous methane, and thus the aforementioned AlMeCl or $AlMe_2$ bearing complexes can be obtained. Furthermore, the synthesis of complexes which contain a MMeCl metal fragment can be achieved by two different approaches: either a transmetallation reaction can take place by using the lithiated species and adding $MMeCl_2$ as reagent, or by simply treating the parent nacnacH ligand with MMe_2Cl to generate methane as side product.[23]



Scheme 1-7: General substitution pattern of the group 13 metal complexes of the nacnac ligand.

Table 1-1: Selected group 13 metal *β*-diketiminato complexes.

R	R^1	M	X^1	X^2	Ref.	R	R^1	M	X^1	X^2	Ref.
Me	Me	Al	H	H	[14h, 24]	Dipp	Me	Al	H	H	[25]
Me	Me	Al, Ga	Cl	Cl	[14j]	Dipp	Me	Al	Me	Me	[14k, 14l, 26]
Me	Me	Al	I	I	[14f]	Dipp	Me	Al	Et	Et	[26]
*i*Pr	Me	Al	H	H	[24]	Dipp	Me	Al	*i*Bu	*i*Bu	[26]
*i*Pr	Me	Al, Ga	Cl	Cl	[14j]	Dipp	Me	Al	Me	Cl	[14d, 27]
*i*Pr	Me	Al	I	I	[14f]	Dipp	Me	Ga, In	Me	Cl	[14d]
*t*Bu	Me	Al, Ga	Cl	Cl	[14j]	Dipp	Me	Ga	H	H	[14d]
Ph	Me	Al	H	H	[24]	Dipp	Me	Ga	Me	H	[14d]
p-Tol	Me	Al	Me	Me	[14l]	Dipp	Me	Al, Ga	F	F	[14d]
p-Tol	Me	Al	Me	Cl	[14l]	Dipp	Me	Al, Ga, In	Cl	Cl	[14i]
p-Tol	Me	Al	Cl	Cl	[14l]	Dipp	Me	Ga	Br	Br	[14d]
C_6F_5	Me	Al	Me	Me	[14e]	Dipp	Me	Al, Ga, In	I	I	[14i]
C_6F_5	Me	Al	Me	Cl	[14e]	Dipp	Me	Ga, In	Me	Me	[14i]
C_6F_5	Me	Al	Me	I	[14e]	Dipp	*t*Bu	Al	Et	Et	[28]
C_6F_5	Me	Al	Br	Br	[14e]	Dipp	*t*Bu	Al	I	I	[28]

Analogue to this synthetic approach, in the last two decades many nacnac metal complexes of aluminium, gallium and indium carrying either alkyl and/or halide substituents were described in the literature. For giving a short overview over these different compounds (see general substitution pattern depicted in Scheme 1-7), some examples for the group 13 metal β-diketiminato complexes are listed in Table 1-1.

In addition to the aforementioned ligand systems, which usually exhibit just a remaining hydrogen atom at the deprotonated methylene bridge in the backbone, there are also compounds available which are substituted at this position with aryl moieties[14c] or for example phosphino functionalities.[29] It is obvious from the examples given in Table 1-1 that the majority of the investigated nacnac ligands are carrying methyl groups at the imine carbon atoms and 2,6-diisopropylphenyl moieties at the imine nitrogen atoms. Even if there are also alkyl or other aryl substituted β-diketiminates present in ongoing research, the Dipp-substituted nacnac ligands are still the most wide-spread ones and of great interest because of their good shielding abilities. Upon metal coordination, a six-membered metalla heterocycle is formed and the phenyl entities are twisted nearly perpendicular with respect to this metalla heterocycle. By means of this, the *i*Pr groups of the Dipp residues can embrace the coordinated metal atom in an adequate manner, so that neither an oligomerization of the metal fragments in low oxidation state nor electrophilic attacks can occur (*vide infra* in the next chapter).[30] It is known that the scaffold tends to deviate from a planar arrangement within metal coordination by means of twisting or bending, and merely the backbone remains in plane. This deviation is caused by the flexible but bulky organic substituents at the imine moieties. They are twisted nearly perpendicular with respect to the chelating C_3N_2M-plane, which causes the metal atoms to be most protected. To visualize this bonding situation, the crystal structures of the corresponding $AlMe_2$[14l] and the higher congener $GaMe_2$[14i] Dipp substituted nacnac complex are shown in Figure 1-2.

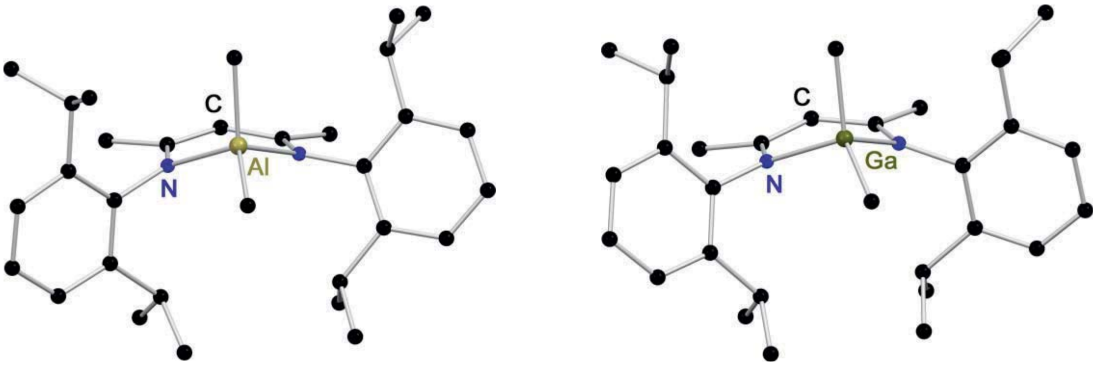
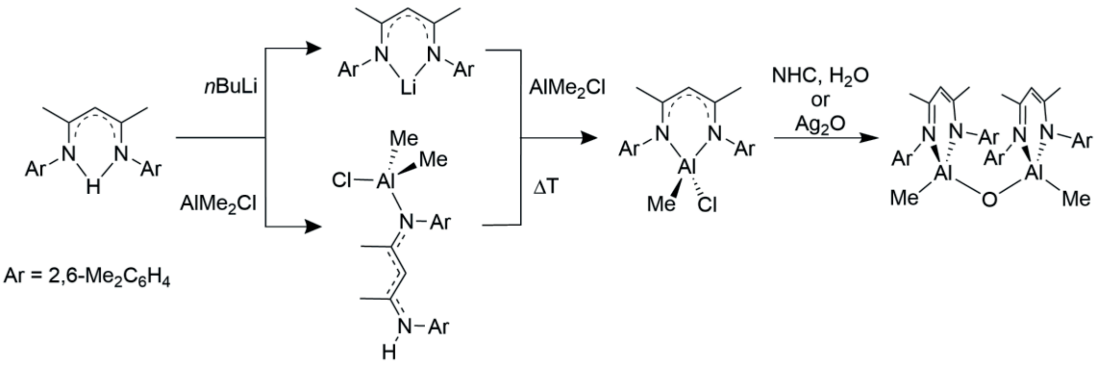


Figure 1-2: Crystal structures without anisotropic displacement parameters of some already known nacnac complexes: *left*: $[Me_2Al\{(N(Dipp)C(Me))_2CH\}]$;[14l] *right*: $[Me_2Ga\{(N(Dipp)C(Me))_2CH\}]$.[14i] Hydrogen atoms are omitted for clarity reasons.

Furthermore, partially hydrolyzed derivatives of the aluminium β-diketiminates are known, which exhibit terminal or bridging hydroxy functionalities or bridging oxides in the case of the corresponding alumoxanes.[4e, 23, 31] Referring to the popular methyl alumoxane (MAO), which is also generated by partial hydrolysis of trimethyl aluminium and a very potent cocatalyst in the Ziegler-Natta polymerization of ethylene and propylene,[32] and related partially hydrolyzed group 13 metalorganics,[33] the investigations on nacnac supported alumoxanes is of high interest in current research. For example, the formation of such a dialumoxane was achieved in 2012 by controlled NHC-assisted hydrolysis[14e, 31b] of the corresponding organoaluminium chloride [MeClAl{(N(2,6-$Me_2C_6H_4$) C(Me))$_2$CH}] and by an anhydrous approach using Ag_2O as an oxygen source (see Scheme 1-8).[23] Interestingly, the synthesis of the organoaluminium chloride precursor starting directly from the parent nacnacH ligand and dimethyl aluminium chloride yielded the Lewis acid-base-adduct at room temperature, where the aluminium is further coordinated by one imine nitrogen donor of the nacnacH ligand. The deprotonation of the ligand, the associated release of methane and thus the final formation of the AlMeCl complex were achieved in a second step, when the reaction mixture was heated up to the boiling point of toluene.

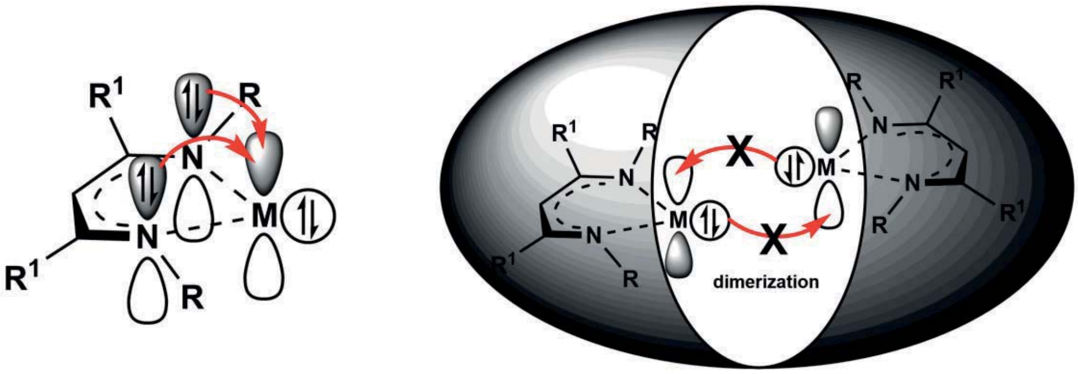


Scheme 1-8: Formation of a nacnac-supported dialumoxane.[23]

1.3 Low-Valent Group 13 Species – Metallylenes

As a further topic in the context of the omnipresent nacnac ligand, its low-valent group 13 metal complexes will be discussed in this section. Following the above-mentioned species in Table 1-1, in the cases of Al, Ga, In and Tl also the reduced species in the oxidation state +I are accessible by using the Dipp-substituted nacnac ligand system, which forms a six-membered metalla heterocycle.[28, 34] These so-called metallylenes, analogues of *N*-heterocyclic carbenes, are rare and offer interesting prospects as reagents in organic syntheses or as ligands in catalysis, where they might replace other commonly utilized *N*-heterocyclic carbenes or phosphanes.[35]

These low-valent group 13 metal centres combine two unifying properties: on the one hand, the low-valency leads to the presence of formally vacant π-orbitals, which causes the metal cation to also incorporate electrophilic reactivity behaviour. On the other hand, the coordinated metal cation carries an electron lone pair, which enables the metal centre to act as a nucleophile or simply as a Lewis donor like NHCs. This lone pair has a quasi-trigonal planar orientation in a *sp*-like hybrid orbital within the plane of the metalla heterocycle, which exhibits an increasing *s*-character for heavier metal atoms because of a lower affinity for hybridization.[34c, 35, 36] Due to those main features, the metallylenes are highly reactive species and their stabilization represents a challenging goal in current research.[35] Hence, the low-valent metal cation is stabilized by the mesomeric effect of the adjacent coordinating nitrogen donors. The electron density of their lone pairs, which are located in a *p*-orbital perpendicular to the chelating C_3N_2M plane within the π-system of the delocalized ligand system, is pushed towards the electrophilic metal centre and the electron deficiency of the low-valent group 13 element can be partially compensated (see Scheme 1-9 *left*).[35b]



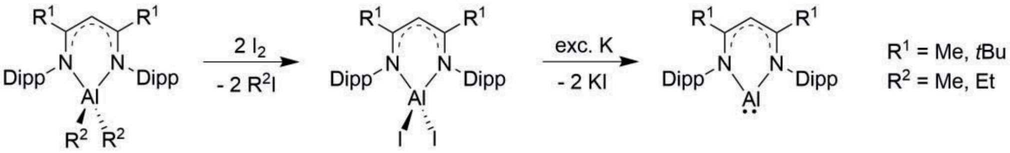
Scheme 1-9: *left:* Stabilization of the singlet ground state in six-membered metallylenes (M = Al, Ga, In, Tl; R^1 = Me, *t*Bu; R = Dipp); *right*: Suppression of self-dimerization due to the bulky nacnac ligand.[35b]

Theoretical calculations for the reactivity of neutral six-membered carbene analogues $[M\{(N(Ph)C(Me))_2CH\}]$ (M = B, Al, Ga, In, Tl) revealed that the singlet-triplet splitting is increasing significantly from boron to the higher homologues.[30] Whereas the splitting for the boron carbenoid is just about 3.5 kcal/mol, the values for the aluminium and gallium derivatives are 45.7 kcal/mol and 54.5 kcal/mol, respectively. These values are highlighting that in the cases of Al and the higher congeners, a singlet ground state can be assumed, in which both electrons are paired in the *sp*-hybrid orbital. On the contrary, in the case of the boron carbenoid, which could not be synthesized successfully yet, a dimerization reaction is predicted to take place easily at room temperature, because also the triplet state (one electron in *p*-orbital and the second in the hybrid orbital) is populated. The dimerization of the heavier carbenoids is accordingly energetically unfavoured from a thermodynamic and kinetic point of view, so that the monomers can be isolated at room temperature. Hence, the reactivity of the group 13 metallylenes towards C–H bond insertion, cycloaddition and dimerization decreases with increasing atomic number of the incorporated metal cation in the order B > Al >> Ga > In > Tl.[30b]

Because of the high electrophilicity of the M(I) species, steric protection is essential to maintain the monomeric carbene-like structural motif and prevent dimerisation or nucleophilic attacks.[30] Therefore, the issue of steric shielding of metal centres within the group 13 complexes in the oxidation state +I is an important aspect for the further applications and reactions. As depicted at the right hand side of Scheme 1-9, the steric demand of the

Dipp-substituted nacnac ligand is sufficient for the suppression of self-dimerization, which is also supported by the theoretical findings in the previous paragraph.

The low-valent aluminium metallylene can be synthesized by converting the corresponding dialkyl aluminium complex into its AlI_2 derivative with the help of two equivalents of elementary iodine. By this procedure, the former methyl groups at the metal centre are replaced by iodide residues and two equivalents of methyl iodide were formed as side product. Afterwards, a reduction step takes place by using potassium or potassium graphite to obtain the carbene-like Al(I) species (see Scheme 1-10) in good overall yields.[28, 34c] The driving force in this reduction approach is the generation of potassium iodide.



Scheme 1-10: Synthesis of the aluminium containing metallylenes.[28, 34c]

In contrast to the above-mentioned synthesis, the corresponding metallylenes encumbering the heavier congeners like Ga, In or Tl were gained easily by direct salt metathesis starting from the lithium or potassium nacnac complex and the stable low-valent metal iodide precursor. Because the higher congeners show an increasing stability of the metals in low oxidation states,[37] these metal halides are easily accessible in the oxidation state +I in contrast to the corresponding aluminium salt, which is not stable as Al(I) compound. For instance, the gallium metallylene is synthesized by using [Li{(N(Dipp)C(Me))$_2$CH}] and "GaI" and subsequent treatment with potassium to reduce the formed iodide species.[34d] The reactive starting material "GaI" represents a mixture of metalloid Ga and the low-valent species GaI, Ga_2I_3 and Ga_2I_4 and behaves like monovalent gallium iodide.[38] The corresponding In(I) and Tl(I) complexes were synthesized starting from the parent ligand, which is deprotonated by K[N(SiMe$_3$)$_2$] in a first step and undergoes salt elimination with InI[34a, 34b] or TlI[34a] in a one-pot-reaction.

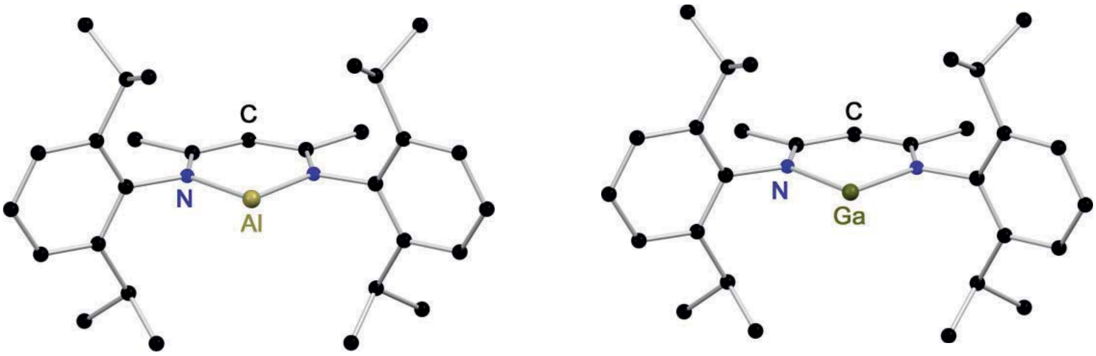
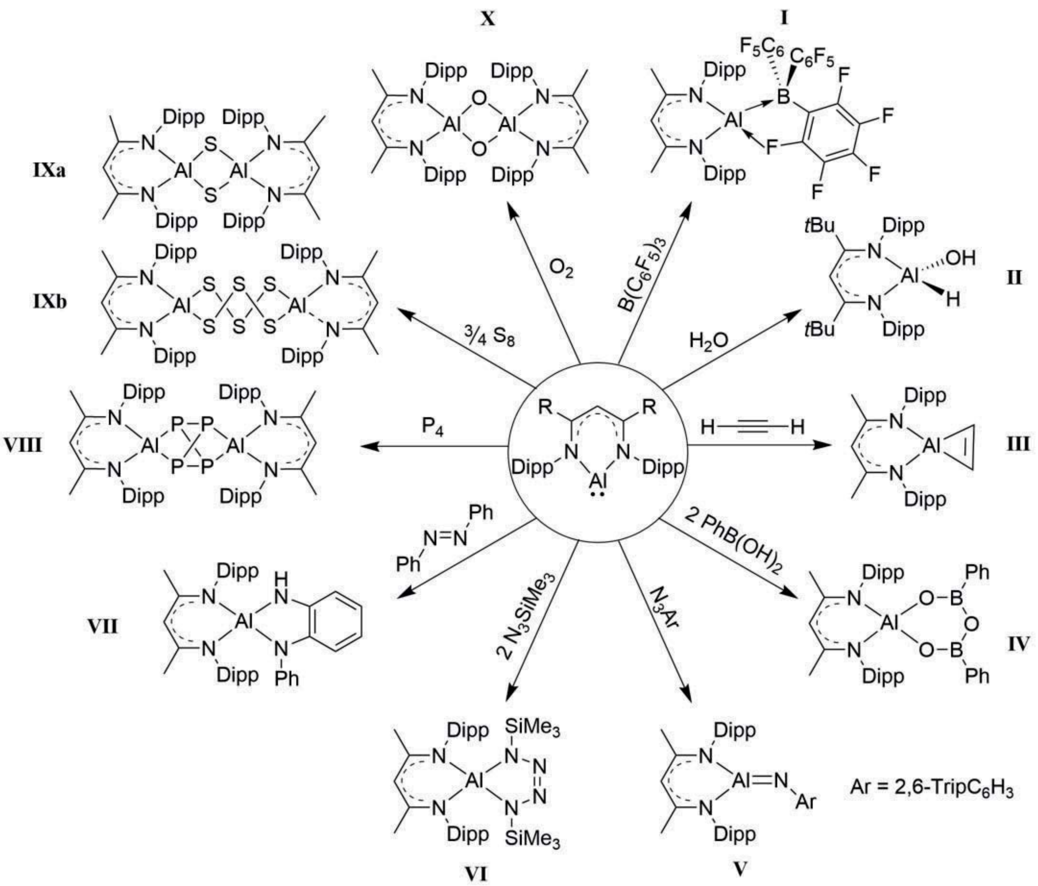


Figure 1-3: Crystal structures without anisotropic displacement parameters of some known nacnac assisted metallylenes: *left*: [Al{(N(Dipp)C(Me))$_2$CH}];[34c] *right*: [Ga{(N(Dipp)C(Me))$_2$CH}].[34d] Hydrogen atoms are omitted for clarity reasons.

In Figure 1-3, the crystal structures of the aluminium and gallium metallylenes, coordinated by the Dipp-substituted nacnac ligand, are depicted. In general, these two structures look quite identical: in both cases the imine substituents are twisted perpendicular with respect to the six-membered metalla heterocycle and the chelated Al(I) and Ga(I) cations are lying nearly ideally in the C_3N_2 plane. In contrast to the crystal structures of the dimethyl substituted M(III) fragments shown in Figure 1-2, it is obvious that there is a clear change in the bonding mode. While in the case of the M(I) species a planar coordination geometry is favoured (Scheme 1-5, case **(a)**), the corresponding M(III) compounds prefer a boat-like alignment in the solid state (Scheme 1-5, case **(b)**). Furthermore, all known group 13 metallylenes (Al, Ga, In and Tl), which are encumbered by the Dipp-substituted *β*-diketiminate ligand, are present as a monomeric species in the solid state. As a proof for the influence of the steric demand of the imine moieties on the aggregation, different indium compounds should be noted.[39] By decreasing the bulkiness of the moieties, changing from Dipp-residues in the monomers to mesityl or xylol substituents, dimeric species can be identified in the solid state.



Scheme 1-11: Exemplary reaction behaviour of [Al{(N(Dipp)C(Me))$_2$CH}] with different organic and inorganic substrates.[14b, 16a, 35a, 36]

The different reactions displayed in Scheme 1-11 underline the versatility of the aluminium carbenoid for the transformation of unsaturated organic compounds or inorganic material like P_4 or S_8. Starting clockwise with the top right structure, a very interesting Lewis acid-base adduct **I** of [Al{(N(Dipp)C(Me))$_2$CH}] and B(C_6F_5)$_3$ is shown. This compound highlights the electrophilic as well as nucleophilic character of the Al(I) centre: on the one hand, the lone pair at the aluminium is addressed to the boron atom (Al–B distance: 218.5 pm) and on the other hand, the aluminium cation is coordinated as Lewis acid (via its vacant *p*-orbital) by a fluoro substituent of one C_6F_5 moiety (Al···F distance: 215.6 pm).[40] The next molecule shows the hydrolysis product of [Al{(N(Dipp) C(*t*Bu))$_2$CH}], which is obtained upon oxidative addition of water to the low-valent aluminium centre. The resulting Al(III) complex **II** carries a hydroxido and a hydride substituent.[28] In analogy to NHCs, this carbenoid undergoes a [1+2]-cycloaddition reaction, when acetylene is added as reagent. The resulting metalla cyclopropene derivative **III** is shown at the right side of Scheme 1-11.[41] By adding two equivalents of phenylboronic acid to the metallylene, an unprecedented spirocyclic Al(III) complex **IV** with a six-membered B_2O_3Al ring is formed under dissociation of water and H_2.[42] The reaction with azides is dependent on the size of the covalently linked residue: while the reaction with bulky aryl substituted azides leads to the formation of a monomeric imide **V**,[43] the usage of two equivalents of N_3SiMe_3 promotes the formation of the corresponding metalla tetrazole derivative **VI**.[44] Furthermore, the reactivity towards *N*-unsaturated molecules like azobenzene should be mentioned in this context by means of **VII.** It is suggested, that after an intermediate [1+2]-cycloaddition reaction of the Al(I) centre and the N=N double bond, an *ortho*-C–H activation of one phenyl moiety takes place.[45] The compounds **VIII** and **IX** are prominent examples for representing the reducing properties of [Al{(N(Dipp)C(Me))$_2$CH}] in conjunction with inorganic substrates like P_4 or S_8. In compound **VIII**, an activated P_4^{4-} moiety is implemented in a bridging fashion between two Al(III) containing nacnac ligands. Formally, the aluminium centres are inserted into two opposing P–P edges of the white phosphorus to end up in the shown target molecule.[46] By adding elemental S_8 to the carbenoid species, two different (poly-)sulfide bridged molecules **IXa** and **IXb** could be isolated and structurally characterized. As the major product of that reaction, in the first case the two aluminium cations are linked by two μ-S entities,[47] whereas in the latter case as side product a S_3-bridged dimeric species was gained.[48] Finally, the reaction product with elemental O_2 is depicted as compound **X**. This compound shows the ability of the parent low-valent aluminium nacnac complex to activate small molecules by cleaving the O=O double bond under reducing conditions. This affords [(μ-O)Al{(N(Dipp)C(Me))$_2$CH}]$_2$ similar to the previously mentioned sulfide bridged dimer.[49]

As a consequence of the previously discussed reaction products, [Al{(N(Dipp) C(Me))$_2$CH}] seems to be a very promising reagent for small molecule activation or transformation of organic substrates. These features are induced by its ability to act as reducing agent in combination with electrophilic and nucleophilic reaction behaviour at the Al(I) centre. In summary, the aluminium metallylene shows similar reactivity like in the cases of singlet carbenes.[50] In the context of the ongoing increasing demand in the activation of small molecules like H_2, N_2, NH_3 or CO_2, the development of new synthetic approaches for generating catalytic active species is of high interest. Even though this research area of catalytic activation is mostly focused on the field of transition metal complexes, the transfer to suitable main group metal complexes, which should adopt the same catalytic reactivity compared to the transition metals or even exceed them, plays a key role in current research.[51]

As figurehead for efficient small molecule activation, the FLP chemistry (frustrated Lewis pairs) developed to a promising research area over the last decade and is mentioned at this point for comparative reasons.[52] In this course, the usage of mainly phosphorus/boron, nitrogen/boron or carbon/boron FLP systems offers a simple access to the efficient splitting of dihydrogen[53] or ring opening of THF.[54] Aluminium-based FLP's were found to be advantageous for B–H or N–H bond activation,[55] polymerisation reactions of methyl methacrylate[56] and conversion of CO_2.[57] Furthermore, the nacnac ligand and the derived main group metal complexes, respectively, facilitate the stabilisation of metal ions in low oxidation states as mentioned previously. The synthesis of the first Mg(I) compound[58] and corresponding β-diketiminate Ca(II) complexes,[59] which were successfully applied for epoxide/CO_2 copolymerisation[60] or hydrogenation reactions of alkenes with H_2,[61] should be highlighted as alkaline earth metal complexes performing in catalysis.

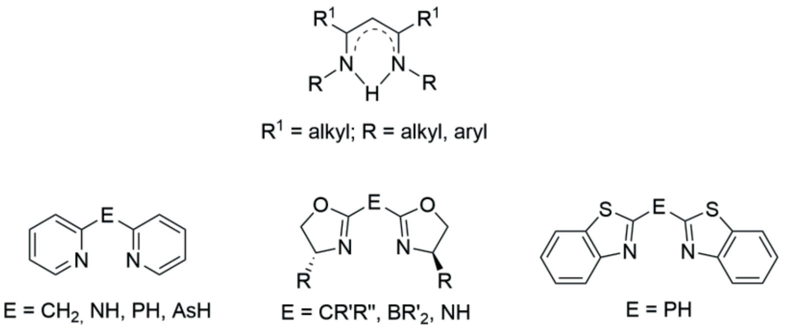
As already mentioned above, the low-valent Al(I)[14b, 28, 34c, 36, 62] and Ga(I)[34d] species employing the Dipp-substituted nacnac ligand are accessible. More recently, the catalytic activity of the related alumoxanes was studied in detail.[31a, 23, 25a, 63] In this context also other common ligand types including substituted terphenyls should be mentioned briefly, which are used for stabilisation of dimeric low-valent group 13 species involving metal-metal multiple bonds and are prone for interaction with small molecules like H_2.[64]

The coordination chemistry as donor Lewis base of the first aluminium metallylene, whose reaction behaviour was briefly described in Scheme 1-11, towards other (transition) metals is presently just barely investigated. For example, there are three palladium complexes described in the literature, in which $[Al\{(N(Dipp)C(Me))_2CH\}]$ acts as a σ-donor ligand in a terminal or bridging fashion at one or two Pd centres, respectively. In two cases, the palladium cations are further coordinated by dvds ligands (dvds = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane), and in another case, those siloxane ligands are replaced by monovalent $GaCp^*$.[65] Referring to the former mentioned palladium complexes bearing the dvds ligands, additionally a related complex was synthesized, which is terminally coordinated by a NHC instead of the Al(I) metallylene.[66] A structural comparison of those two complexes, one carrying a NHC and one a metallylene, reveals that the C–C bond lengths within the dvds ligands are nearly identical. This fact gives rise to the assumption that $[Al\{(N(Dipp)C(Me))_2CH\}]$ has comparable σ-donor abilities like the NHC.

In contrast to the Al(I) species, the metal coordination abilities of the corresponding Ga(I) complex are much more developed, although its utilization in the transformation of organic substrates compared to the aluminium counterpart is less investigated due to its weaker reducing nature.[35a] In the same context as described in the former paragraph, the Pd(0) complex of $[Ga\{(N(Dipp)C(Me))_2CH\}]$ and the dvds ligand was studied in detail. Additionally, different mono- and dinuclear Pt(0) complexes carrying two low-valent gallium ligands and carbonyl or isonitriles were synthesized and structurally characterized.[65a] To continue with further examples for derived transition metal complexes, the following compounds should be mentioned at this point: an iron complex was accessible via facile reaction of $Fe(CO)_5$ with a gallium metallylene[67] and two rhodium chlorido complexes could be obtained by substitution of a PPh_3 or cyclooctene ligand in the starting material.[68] Furthermore, several homo- and multinuclear nickel olefin complexes are known in the literature, in which the $[Ga\{(N(Dipp)C(Me))_2CH\}]$ acts as terminal or bridging Lewis donor ligand.[69]

1.4 Related Bridged Bisheterocycles

Because of the very high interest and the associated research activities in the broad field of nacnac metal complexes (see Figure 1-1), other promising ligand platforms have come into play which are closely related to the ubiquitous *β*-diketiminato ligand. Most of them are mimicking its chelating coordination behaviour, so that upon metallation a six-membered metalla heterocycle with six delocalized *π*-electrons is formed, in which two imine nitrogen atoms are working as Lewis donors for the metal centre. The two $R^1C{=}NR$ moieties of the prototype nacnac ligand are replaced by fused heterocycles, which each also possess an endocyclic C=N imine moiety to retain the same coordination abilities. Formally, the residues at the backbone of the parent nacnac ligand are fixed to the imine nitrogen atom, while formation of a mostly five- or six-membered heterocycle occurs. Examples for the derived bridged bisheterocyclic compounds, which were studied in the past two decades intensively, are depicted in Scheme 1-12.



Scheme 1-12: Comparison of the nacnacH ligand (*top*) and related ligand systems carrying fused heterocyclic substituents (*bottom*).

Starting with the popular bis-(oxazolin-2-yl)-methanes, also abbreviated as BOX ligands, which is shown as the molecule in the middle of Scheme 1-12 (with E standing for a substituted methylene bridge), very fruitful ligand systems for asymmetric catalysis were developed in the beginning of the 1990s.[70] Those ligands consist of five-membered heterocycles, which are bearing a saturated C–C single bond in the backbone. This key feature is essential for the introduction of chiral centres at the ligand, mostly at the position adjacent to the nitrogen. Due to the coordination via the two imine nitrogen donors, the stereochemically active residues are in close proximity to the coordinated substrate, so that the chiral information can be transferred to that substrate, which enables efficient asymmetric catalysis.[71] In the most metal complexes, the neutral BOX ligand is involved, where the bridging methylene moiety carries two alkyl substituents.[71b, 72] Although the neutral ligand is more prominent in coordination chemistry, the monoanionic form of the BOX ligands with at least one remaining hydrogen atom in the backbone ($E = CH_2$ or CHR) can be achieved by facile deprotonation. The related methanide complexes are established as well.[70c, 73] In addition to the common BOX ligands, asymmetrically substituted methane derivates are known, where e.g. one oxazoline heterocycle is substituted by a NHC[74] or bis-(*N*-arylamino)-phosphane residue.[75] The formal substitution of the methylene bridge by a nitrogen atom yields in bis-(oxazoline)-amines,[76] 5-aza-semicorrins[77] and chiral bis-(2-pyridylimino)-isoindoles[78] with interesting comparable organic scaffolds. Furthermore, it is possible to link two oxazoline moieties via a BR_2 bridge.[79] Other catalytically active species were synthesized in the work group of Kempe. For instance, two obtained iridium complexes containing each functionalized amine moieties can be used as efficient catalyst for pyrrole synthesis[80] or for *N*-alkylation of amino pyridines and anilines.[81]

Another ligand class is depicted at the left hand side of Scheme 1-12, where two 2-pyridyl moieties were introduced as side arms instead of the above-mentioned oxazolines. In the case, that the bridging moiety is a methylene bridge, the resulting dipyridyl methane[82] and the corresponding methanides were investigated in the 1990s. In former publications, our workgroup synthesized a series of lithium and group 13 metal complexes of the bis-(pyrid-2-yl)-methanide and an associated structure-reactivity study was performed based on the results of X-ray diffraction experiments.[83] Representing the group 1 complexes, $[([12]\text{crown-4})_2Li][Li\{(2\text{-}NC_5H_4)_2CH\}]$ can be highlighted as a solvent separated ion pair, or $[(thf)_2Li\{(2\text{-}NC_5H_4)_2CH\}]$ as a monomeric lithiated compound, both solely yielding Li–N contacts.[83a, 83c] These two lithiated compounds were easily accessible via deprotonation reaction of the parent dipyridyl methane with equimolar amounts of *n*BuLi in either hexanes or THF as the solvent. As an intermediate of that deprotonation, it was moreover possible to isolate (at −80 °C) and characterize $[\{(2\text{-}NC_5H_4)_2CH_2\}Li\{(2\text{-}NC_5H_4)_2CH\}]$. In this complex, just one half of the starting material is deprotonated, whereas the other half equivalent remains untouched, so that a lithium complex with one monoanionic and one neutral ligand is formed.[83d] Additionally, some group 13 complexes like $[Me_2Al\{(2\text{-}NC_5H_4)_2CH\}]$ and $[Me_2Ga\{(2\text{-}NC_5H_4)_2CH\}]$, where the $(thf)_2Li$ unit is formally replaced by a Me_2Al or Me_2Ga moiety, were prepared by adding $AlMe_2Cl$ or $GaMe_2Cl$ to the lithiated compound, respectively.[83d, 84]

In further research on these ligand systems, the coordination abilities and electronic properties were affected by switching the bridging atom between the two heteroaromatic residues from a group 14 to a group 15 element. This means that the bridging CH_2 unit is isoelectronically replaced by NH,[85] PH[86] or AsH.[85c, 87] The corresponding investigated main group metal complexes of the derived monoanionic ligand systems will be described as follows: the dipyridyl amine, which contains a secondary amine functionality in the bridging position, reacts smoothly with the corresponding trimethyl organo metallic reagent MMe_3 (M = Al, Ga, In, Tl) to give the desired MMe_2 complex under formation of methane. In the case of the thallium complex, the reactive species $TlMe_3$ has to be gener-