The unique β-diketiminate ligand in aluminum(i) and gallium(i) chemistry

Mingdong Zhong, Soumen Sinhababu and Herbert W. Roesky

Over the past few decades, β-diketiminate ligands have been widely used in coordination chemistry and are capable of stabilizing various metal complexes in multiple oxidation states. Recently, the chemistry of aluminum and gallium in their +1 oxidation state has rapidly emerged. NacNacM(\(\text{M} = \text{Al, Ga, NacNac} = \beta\text{-diketiminate ligand}\)) shows a two coordinate metal center comparable with singlet carbene-like species. The metal center also possesses a formally vacant p-orbital. In this article we present an overview of the last 10 years for aluminum(i) and gallium(i) stabilized by β-diketiminate ligands that have been widely explored in bond breaking and forming species.

1. Introduction

Complexes containing a low-oxidation metal center is a key topic in modern organometallic chemistry as it leads to the development of new systems. A number of transition metal complexes were synthesized in a broad range of oxidation states to activate small molecules or used as catalysts in organic reactions. It was not until 1991 that the first structurally characterized molecular aluminum(i) compound was reported. Since then, the chemistry of Group 13 metals, and lanthanide and actinide metal complexes, have been observed in a range of main group elements, transition metals, and lanthanide and actinide metal complexes. The general M′R unit (M = Al, Ga) can be considered isolobal with singlet carbenes, CO, and CNR.

β-Diketiminate ligands have found widespread application as supporting ligands in metal-mediated catalysis. The stochiometric transformations of NacNacAl(i) and NacNacGa(i) have also been explored widely owing to the lone pair of electrons and a formally vacant p-orbital on aluminum affording high electrophilic and nucleophilic reactivity. A comparison between main group elements and transition metals was drawn when main group species were found to have reactivity towards small molecules under ambient conditions. This was rationalized by main group species possessing donor/acceptor frontier orbitals which are separated by modest energy gaps, thus drawing comparisons with open-shell transition metal species. In 2000, Roesky et al. chose the β-diketiminate ligand to synthesize a more kinetically stable monomeric aluminum(i) compound Al[HC(C(Me)NDipp)₂] (Dipp = 2,6-Pr₂C₆H₃) (1). This was the first stable dicoordinate aluminum(i) compound to be prepared and structurally characterized in the solid-state. Later, Cui et al. also reported a β-diketiminate ligand stabilized aluminum(i) compound Al[HC(C(μ-Bu)NDipp)₂] (2). Computational studies of β-diketiminate stabilized heavier group metal complexes have shown that their metal lone pairs are associated with the HOMO-2. As a result, they are good σ donor ligands and poor π acceptors like N-heterocyclic carbenes (NHCs), and thus have the potential to display carbene-like chemistry. Inoue et al. reported the first neutral Al(i) compound containing an Al=Al double bond, which was achieved through the reductive dimerization of the corresponding N-heterocyclic carbene (NHC)-stabilized silyl substituted aluminum(iii) dihalide (I, Fig. 1), and its reactivity toward the fixation and selective reduction of CO₂, both of which can be accessed in a stoichiometric and catalytic fashion. In 2018, Aldridge and Goicoechea et al. reported the first isolation of a nucleophilic aluminium anion [NON][Al]⁻ by employing a chelating ligand (NON = 4,5-bis(2,6-diisopropylamido)-2,7-di-tert-butyl-9,9-dimethylxanthene) (II, Fig. 1), which acts as an unprecedented aluminum(i) nucleophile (e.g., in reactions with Bu₃P), and which effects the formal oxidative addition of the C=C bond in benzene. After that, Coles and co-workers also synthesized a two-coordinate N-heterocyclic aluminium anion K[NON⁺][NON⁺] = [O(SiMe₂NDipp)₂]⁺, Dipp = 2,6-Pr₂C₆H₃, which is able to undergo further reactions such as activation of elemental selenium to form an...
aluminum complex containing an aluminum–selenium multiple bond and with 1,3,5,7-cyclooctatetraene (COT) to give the first aluminum complex containing a reduced COT-ligand with a strong aromatic character, respectively. Both aluminyl anion complexes reacted with two abundant greenhouse gases (CO₂ and N₂O) via cycloaddition to generate a monoalumoxane anion. The first isolable example of a room temperature stable monomeric cyclopentadienylaluminum(I) derivative was reported by Braunschweig and co-workers, which was supported by a bulky 1,2,4-tri-tert-butylcyclopentadienyl (Cp₃t) ligand (IV, Fig. 1). The same group also reported the first example of a monomeric Lewis base stabilized Al(I) hydride that can be isolated and handled under ambient conditions (V, Fig. 1). Very recently, Yamashita’s group reported an alkyl-substituted aluminum anion that exhibits very strong basicity and nucleophilicity (VI, Fig. 1). These species have been observed to form both covalent and donor–acceptor bonds, revealing both the reducing and nucleophilic properties of these novel complexes.

Gallium(I) compounds are often driven by the thermodynamic preference for the metal center to exist in the +3 oxidation state. Having said this, much of the reported chemistry of monomeric gallium(i) compounds is derived from the significant basicity of the metal through its lone pair of electrons. Gallium(i) compounds are generally more stable towards disproportionation than the corresponding aluminum(i) compounds. So far, several gallium(i) N-heterocycles have been reported. Bi- and tridentate ligand systems have been used in the preparation of a variety of neutral and anionic gallium(i) heterocycles (e.g., five-membered anionic complexes VII–VIII, a guanidinate complex IX and a monomeric tris(pyrazolylborate) complex X, see Fig. 2). These compounds have been prepared either by salt-metathesis reactions between alkali metal salts of the ligands and “GaI” or by alkali metal reduction of Ga III precursors. The monomeric example of Ga I amide (XI, Fig. 2) can be considered to be having a quasi one-coordinate metal center, which also exhibits weak intramolecular arene interactions in the solid state. Recently, a pincer-type gallylene ligand has been successfully synthesized utilizing bis(phosphino)-terpyridine as an efficient scaffold for the Ir–Ga I bond, which enabled various reactions at the Ir center by keeping the gallylene ligand intact. The β-diketiminate ligands typically provide monoanionic, bidentate support for metal complexes and offer a much higher degree of steric control through the choice of N-substituents. By tuning the steric and electronic properties of the supporting β-diketiminate ligands, the reactivity of the compounds can be significantly improved. Thus, complexes with a low-valent metal could be stabilized by the employment of sterically encumbering β-diketiminate ligands. It is interesting to note that with a redox-inactive metal bound and appropriate substituents, β-diketiminate ligands become redox-active ligands. Herein we present an overview that is of relevance to the corresponding bond

![Fig. 1](image1.png)

Di-tert-butyl(dimethyl)silyl-substituted dialumene (I), anionic group 13 analogues of N-heterocyclic carbenes (II–III), monomeric 1,2,4-tri-tert-butylcyclopentadienylaluminum(i) (IV), Lewis base stabilized aluminum(i) hydride (V) and an alkyl-substituted aluminum anion (VI).

![Fig. 2](image2.png)

Reported examples of gallium(i) N-heterocycles.
activation by aluminum(i) and gallium(i) with β-diketiminate ligands.

2. Chemistry of DippNacNacAl(i) and DippNacNacGa(i)

The monomeric aluminum carbenoid DippNacNacAl(i) (1) was prepared through reduction of the corresponding DippNacNacAlI₂ with potassium (Scheme 1). At the same time, Power and co-workers reported a β-diketiminate stabilized Ga(i) monomer DippNacNacGa(i) (2) (Scheme 1). It was obtained by the reaction of [Li{HC(CMeNDipp)₂}] with “Gal”. The remarkable thermal stability of the compounds toward disproportionation reaction (decomp. >150 °C) can be attributed to the steric bulk of the β-diketiminate ligand, which provides kinetic protection to the metal center. X-ray crystal structure analysis showed that compound 2 is monomeric and isostructural with its aluminum counterpart. With a singlet lone pair and formally empty p-orbital on the metal, the neutral heterocycles DippNacNacAl(i) and DippNacNacGa(i) have the potential to exhibit both nucleophilic and electrophilic characteristics.

2.1. Small-molecule activation

CO and CO₂ activation by transition-metal complexes has been studied extensively for many years. However, the activation of CO and CO₂ with Group 13 metal elements and their compounds has been explored scarcely. In 2018, Crimmin et al. reported carbon chain growth from C₁ to C₃ and to C₄ by sequential reactions of CO and CO₂ with a transition metal carbonyl complex in the presence of an aluminum(i) complex (Scheme 2). Warming a frozen suspension of [W(CO)₆] with 2 equiv. of 1 under 1 atm of CO from −78 °C to r.t. in a benzene-d₆ solvent results in the formation of the C₃ homologated product 3. Heating the isolated and purified sample of 3 under one atmosphere of CO leads to the formation of the chain growth product 4. Further chain growth of C₃ to a C₄ fragment could be achieved upon the reaction of 3 with one atmosphere of CO₂. Although the reaction of CO₂ with 3 at 25 °C initially produces 5, when the sample 3 is heated at 100 °C for 48 h, it completely converts to 6. No reaction occurs between 1 and CO in the absence of [W(CO)₆]. The gallium products of these reactions are not reported.

The [2.2.1] metallobicyclic compound 7 was synthesized by the cycloaddition of complex (1) with low-valent aluminum and 1,3-cyclohexadiene. The exposure of a C₆D₆ solution of 7 to one atmosphere of CO generated the insertion product 8. As shown in Scheme 3 the reaction mixture is reversible, when 8 is heated for longer time. Compound 9 was also studied in the reaction with CO, and the insertion of CO into the Al–C bond was observed. However, compound 10 decomposes at 25 °C within 12 h into an intractable mixture of products. Crimmin and co-workers documented the first reversible addition of ethylene to aluminum(i) 1. The monomeric molecular aluminum(i) complex reacted with a series of terminal and strained alkenes including norbornene, ethylene, propylene, hex-1-ene, 3,3-dimethyl-1-butene, allylbenzene and 4-allylanisole. Remarkably all these reactions are reversible under mild conditions (Scheme 4).

2.2. Cleavage of the M–X single bond

Aluminum(i) 1 has been developed to act as a synthon for the preparation of aluminum–metal bonded compounds via oxidative insertion of the Al center into metal-halogen linkages. Jones et al. reported the first example of molecular complexes
containing an unsupported Be-Al bond. The Be-Al bonded complexes 17 and 18 were obtained as yellow crystalline solids from the reaction of DippNacNacAl(i) (1) with [BeX2(tmeda)] (X = Br or I, tmeda = tetramethylethylenediamine) in 1 : 1 stoichiometry (Scheme 5). The Be-Al bond distances in 17 and 18 are 2.474(1) Å and 2.432(6) Å, respectively. They are significantly longer than the sum of single bond covalent radii of the elements (2.44 Å). DFT calculations reveal that the compounds are 2.474(1) Å and 2.432(6) Å, respectively. They are significantly longer than the sum of covalent radii of the elements (2.44 Å).

The reactions of metal bonds have a high s-character. This is consistent with similar Pauling electronegativities between Al and Be. The isostructural Mg-Al (19) and Zn–Al (20) analogues of these complexes have been isolated in the 1 : 1 reaction of DippNacNacAl(I) (1) with [MgI2(tmeda)] and [ZnBr2(tmeda)], respectively (Scheme 5).

The composition of compound 20 was confirmed by means of single-crystal X-ray structural analysis (Fig. 3). Compound 20 has distorted tetrahedral Al and Zn centers. The Zn–Al bond distance is 2.471(1) Å, which is longer than the sum of covalent radii of the elements (2.44 Å). DippNacNacGa(i) (2) shows no reactivity towards [BeX2(tmeda)], even at elevated temperature. Roesky et al. reported unsymmetrical dianilumines by the disproportionation of DippNacNacAl(i) (1) with (Me2eAAC)AlX3 (X = Cl, I) adducts (Scheme 5). The Al–Al bond lengths in compound 21 (2.6327(11) Å) and compound 22 (2.5953(16) Å) are slightly shorter than those of symmetric Al–Al bond lengths, owing to the relaxation of the electrostatic repulsion between the Al atoms.

The reactions of DippNacNacAl(i) (1) with AgX (X = OCN, SCN) resulted in compounds 23 and 24 containing two pseudohalide groups coordinated to the aluminum(m) center. The reactions proceed via oxidative addition of the pseudohalides and elimination of the silver metal.

Harder et al. reported a combined attack of [[DippNacNac]Ca−(C6H4)][B(C6F5)4]− and DippNacNacAl(i) (1), which led to the complete dearomatization of benzene to give C6H62− that chelates to the Al(m) center (Scheme 6).

The molecular structure of 25, however, showed a heterobimetallic complex in which the C6H62− fragment is bridging to Ca and to the Al center.28 Very recently, Harder et al. have described the stoichiometric reactions of DippNacNacAl(i) (1) with [[DippNacNac]MgH]2 and (DippNacNac)ZnH, respectively in benzene, where the Al center inserts into the metal hydride bond, which results in (DippNacNac)Al(H)M(DippNacNac) complexes (M = Zn 26, Mg 27) (Scheme 7). However, the reaction of the calcium hydride complex with 1 in benzene followed a different course leading to benzene C–H alumination. The cleavage of the sp2 C–H bond in unactivated arenes (benzene, toluene and xylene) into C–Al bonds and proposed a mechanism by which the C–H bond is activated by an unusual Al–Pd intermetallic complex.28b

Scheme 6 Activation of benzene using Al(i) and Ca2+.
Orange crystals of compound 33 were isolated from hexane at −30 °C, and slowly decompose in solution with the formation of BiEt3 and elemental Bi. The analogous reaction of DippNacNacGa(I)(2) with E2Et4 is fully reversible and temperature dependent. Analytically pure compounds 34 and 35 were isolated from the 1:1 mixture of DippNacNacGa(I)(2) and E2Et4, respectively (Scheme 9). By changing the molar ratio of DippNacNacGa(I)(2) and Bi2Et4 into a 1:2 ratio, 35 can be isolated in good yield. Fischer et al. have achieved the reaction of DippNacNacGa(I)(2) with Bi(OSO2CF3)3 and [{Bi-(OC6F5)3(toluene)}2] to yield [(RfO)(DippNacNac)GaBi(OTf)2] (Tf = SO2CF3, C6F5). The dibismuthenes show short Bi–Bi bond lengths of 2.8111(2) and 2.8182(4) Å, respectively (Fig. 4). The reaction proceeds via oxidative addition of the Bi–O bond to DippNacNacGa(I)(2) and concomitant elimination of DippNacNacGaOTf. Finally, Bi(OTf)3 adds to another equiv. of 2 with subsequent dimerization to form a new type of dibismuthene stabilized by NHC-related ligands. Schulz et al. described a similar insertion reaction of DippNacNacM with BiEt3 that leads to DippNacNacMeBi(BiEt2) (M = Al 38 and Ga 39) (Scheme 9). The consecutive second activation proceeds at a higher temperature through the reductive elimination of DippNacNacMeBi, elemental Bi and BiEt3.31

Heavy-metal complexes containing gallium-lead and gallium-mercury bonds were derived from the oxidative addition of DippNacNacGa(I)(2) with the corresponding metal precursors. The reaction of Me3PbCl with DippNacNacGa(I)(2) in THF at ambient temperatures afforded compound [{(DippNacNac)Ga(Cl)}PbMe3] (40) in high yield. In addition, the reaction between [Pb(OSO2CF3)2] and DippNacNacGa(I)(2) (two equiv.) leads to the complex 41 containing a Ga–PbII–Ga linkage (Fig. 5). When two equiv. of DippNacNacGa(I)(2) were treated with [Pb(OSO2CF3)2·2H2O] in THF, deep red crystals of 42 were formed in very poor yield (Scheme 10). The structure of the compound consists of a bent Ga–Pb–Ga backbone with a bridging triflate group between the Ga–Pb bond and a
weakly interacting water molecule at the gallium center. Similarly, the reaction of mercury thiolate Hg(SC$_6$F$_5$)$_2$ with DippNacNacGa(I)$_2$ (two equiv.) produced the bimetallic homoleptic compound 43 (Scheme 10). The linear cationic complex [(DippNacNac)Ga$_2$Cu][OTf]·2C$_6$H$_5$F (44), $\text{OTf}=\text{SO}_2\text{CF}_3$] was obtained from the reaction of DippNacNacGa(I)$_2$ (two equiv.) with Cu[OTf]-4CH$_3$CN.$^{33}$

In addition, Schulz et al. showed that DippNacNacGa(i) (2) inserted into the In–C bond of InEt$_3$ resulted in the formation of DippNacNacGaEt(InEt$_3$) (45). The solution of 45 in benzene and toluene tends to decompose slowly at ambient temperature. But the reaction of DippNacNacGa(i) (2) with tBu $\rightarrow$ InEt$_3$ (tBu = [C(Nt-Bu$_2$CH)$_2$]) resulted in a stable compound 46, where the carbene coordinates to the indium atom. The reaction of InEt$_3$ with 2 equiv. of DippNacNacGa(i) (2) resulted in a double insertion product [DippNacNacGa(Et)$_2$]InEt (47) (Scheme 11), while further insertion of DippNacNacGa(i) (2) into the remaining In–Et bond does not occur. Complex 57 gradually decomposes at 80 °C in C$_6$D$_6$, resulting in DippNacNacGa (2) and DippNacNacGaEt$_2$ (48). A similar reaction between DippNacNacGa(i) (2) and Cp*InEt$_2$ (Cp* = C$_5$Me$_5$) leads to the production of DippNacNacGaEt$_2$ (48). These reactions proceeded via the oxidation of DippNacNacGa(i) (2) with the In–Et bond and subsequent reductive elimination of DippNacNacGaEt$_2$ from the indium(III) center.$^{35}$

Schulz and co-workers have also reported a stibinyl radical [DippNacNac(Cl)Ga]$_2$Sb (49) by the reaction of two equiv. of DippNacNacGa(i) (2) with Cp*SbCl$_2$ (Scheme 12), and the traces of DippNacNac(Cl)GaSb(H)Cp* (50) were formed as a byproduct. Similarly, the equimolar reaction yielded DippNacNac(Cl)GaSb (Cl)Cp* (51), which slowly decomposed to DippNacNacGaCl$_3$, decamethylfulvalen (Cp$_2$) and the antimony metal. The analogous reaction of DippNacNacGa(i) (2) with Cp*Bi$_2$ yielded a bismuthinyl radical [DippNacNac(i)Ga]$_2$Bi (52) (Scheme 12). Their formation illustrates the stepwise insertion of DippNacNacGa(I) into the E–X bond of Cp*EX$_2$ followed by the homolytic bond cleavage of the E–Cp* bond and elimination of Cp*$_2$. Theoretical calculations showed the significant electron delocalization of the Sb and Bi unpaired radicals onto the Ga ligands. Compounds 49 and 52 adopt V-shaped geometries with Ga–E–Ga bond angles of 104.89(1)° (49) and 106.68(3)° (52), respectively. Compound 53 was isolated by the direct reaction of 49 with KC$_8$ in benzene, which gives the first struc-

**Fig. 5** X-ray single crystal structure of compound 41; the THF molecule attached to lead is omitted for clarity.
naturally characterized compound containing a Ga=Sb double bond (Scheme 13). In contrast, the equimolar redox reaction of \( \text{I} \) with the single-electron oxidant \([\text{NO}][\text{BF}_4]\) occurred with the formation of \( \text{IV} \) (Scheme 13). The reaction of two equiv. of \( \text{I} \) with \( \text{Cp}^*\text{AsCl}_2 \) proceeds with the formation of gallaarsene \( \text{V} \) with a Ga=Sb double bond and \( \text{V} \), containing a central GaSb butterfly type core. The central structural motif of \( \text{V} \) is the bridging Sb three-membered ring, which coordinates in an \( \eta^1 \) and \( \eta^2 \) fashion to two Ga atoms, respectively (Fig. 6).37

To evaluate the reduction potential of \( \text{II} \) in detail, Schulz et al. studied the reactions of \( \text{II} \) with other Sb\(^{IV}\) reagents. \( \text{II} \) reacted with Sb\(_X\) (\( X = \text{NMe}_2, \text{Cl} \)) in a 2:1 molar ratio to form Ga-substituted distibenes \( \text{VI} \) (Scheme 15). Heating a toluene solution of \( \text{VI} \) at 120 °C for 24 h yielded \( \text{VI} \). But complex \( \text{VII} \) required 7 days of heating at 130 °C to give \( \text{VII} \). Compound \( \text{VIII} \) can react with GaCl\(_3\) to form \( \text{VIII} \); in addition, \( \text{VIII} \) reacts with Li amide to form \( \text{VIII} \). The central Sb\(_4\) unit in \( \text{VII} \) and \( \text{VII} \) adopts a butterfly type conformation (Fig. 7). Interestingly, compound \( \text{VII} \) reacted with GaCl\(_3\) in an amide/Cl exchange reaction with the subsequent formation of \( \text{VIII} \).38

To better understand the reaction mechanism leading to compounds containing Sb=Sb and Ga=Sb double bonds, the reactions of SbCl\(_3\) with different equiv. of \( \text{II} \) at different temperatures were investigated. The \( \text{II} \) (X\(^{IV}\)NacNac (X = F \( 62\), Cl \( 63\), Br \( 64\), and I \( 65\) ) compounds were formed by a twofold insertion of \( \text{II} \) into two Sb–X bonds, followed by an intramolecular elimination of \( \text{II} \) (Scheme 16). The reactions of two equiv. of \( \text{II} \) with SbCl\(_3\) at 8 °C yielded cyclotristibine \( \text{IX} \). The Sb–Sb bond (2.8205(3)–2.8437(3) Å) in cyclotristibine \( \text{IX} \) is typical of the Ga–Sb single bond.39

---

**Scheme 12** Synthesis of compounds 49–52.

**Scheme 13** Single-electron oxidation and reduction reactions of compound 49.

**Scheme 14** The reaction of \( \text{II} \) with \( \text{Cp}^*\text{AsCl}_2 \).

**Scheme 15** Syntheses of compounds 58–61.

**Fig. 6** X-ray single crystal structure of compound 57.
The insertion reactions of two equiv. of DippNacNacGa(I) (2) with SbX3 (X = Cl, Br) at low temperature produced a double-inserted product (DippNacNacGaX)2SbX (X = Cl, Br). In addition, the reaction of isolated compounds and with strong σ-donating carbenes (IDipp(1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene), Me2cAAC) yielded four carbene-stabilized stibinidenes (69–72) (Scheme 17). The studies reveal that IDipp-stabilized stibinidenes 69 and 70 show Sb–Ccarbene single bonds, whereas the Me2cAAC-stabilized derivatives 71 and 72 exhibit Sb–Ccarbene π-backbonding character.

A red-brown complex 73 was obtained by the reaction of the half-sandwich complex [CpR′Ni(μ-Br)]2 (CpR′ = C5(C6H4-4-Et)5) with DippNacNacGa(I) (Scheme 18). The CpR′(centroid)-Ni-Ga linkage is bent, and the nickel atom is surrounded by an η5-coordinated CpR′ ligand and a σ-coordinated Ga(DippNacNac) ligand, while the bromide bridges the Ni-Ga bond. The reduction of 73 with KC8 afforded compound 74 where the “CpR′Ni(i)” fragment is trapped by DippNacNacGa. The reduction of [CpR′Ni(μ-Br)]2 with KC8 and the subsequent addition of DippNacNacGa(I) also resulted in compound 74 albeit in smaller yield (Scheme 18).

2.3. Cleavage of E’–E single and E’==E double bonds

To stabilize Ga-coordinated dipnictenes of the type [DippNacNac(X)Ga]2E2 (E = P–Bi), the reactions of DippNacNacGa(I) with PCl3 (X = Cl, Br) in toluene at ambient temperature produced a double-inserted product (DippNacNacGaX)2SbX (X = Cl, Br). In addition, the reaction of isolated compounds 67 and 68 with strong σ-donating carbenes (IDipp(1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene), Me2cAAC) yielded four carbene-stabilized stibinidenes (69–72) (Scheme 17). The studies reveal that IDipp-stabilized stibinidenes 69 and 70 show Sb–Ccarbene single bonds, whereas the Me2cAAC-stabilized derivatives 71 and 72 exhibit Sb–Ccarbene π-backbonding character.

The analogous reaction with Me2NAsCl2 yielded unsymmetrically-substituted diarsene [DippNacNac(X)Ga]As==As[Ga(NMe2)DippNacNac] (78) (Scheme 20). In contrast, the reaction of DippNacNacGa(i) (2) with As(NMe2)3 required much harsher reaction conditions. A mixture of DippNacNacGa(i) (2) and As(NMe2)3 heated at 165 °C for 5 days resulted in compound 79 (Scheme 19). Its analogous reaction with DippNacNacAl(i) (1) yielded [DippNacNac(Me3NEt)Al]As2 (80) after heating at 80 °C for one day (Scheme 20). Finally, the reaction of DippNacNacGa(i) (2) with Bi(NEt2)3 also occurred with the insertion and elimination of DippNacNacGa(NEt2) and resulted in the corresponding Ga-stabilized dibismuthene [DippNacNac(Et3N)Ga]2Bi2 (81) (Scheme 19). The reaction of 2 with elemental tellurium yielded the Te-bridged compound [DippNacNacGa-μ-Te]2 (82).
Moreover, the cleavage of the Te–Te and Te–C bonds upon reactions of 2 with Ph₂Te₂ and Pr₂Te resulted in the formation of DippNacNacGa(PhTe) (83) and DippNacNacGa(Pr)Te(Pr) (84), respectively (Scheme 20).⁴⁴

Nikonov and Crimmin groups separately reported the reactions of the monomeric Al(I) complex with various fluoralkenes and fluoroarenes, resulting in the breaking of strong sp³ and sp² C–F bonds. Aluminum(I) compound 1 undergoes a facile oxidative addition with aryl C–F bonds.⁴³ The reaction of 1 with an excess of hexafluorobenzene or pentafluorobenzene resulted in compounds 85 and 86, respectively (Scheme 21). A further decrease in the number of fluorine atoms in the starting arene necessitates an increase in the reaction temperature to cleave the C–F bond. The cleaving ability decreases in the order o– > p– > m–. The addition of 1-fluorohexane or fluorecyclohexane to 1 at room temperature yielded the corresponding aluminum alkyl 92 and 93, respectively (Scheme 22).⁴³ The reaction with (E)-1,3,3,3-tetrafluoro-propene(HFO-1234ze) resulted in the immediate formation of a 4 : 1 mixture of 94-E and 94-Z (Scheme 23). The addition of hexafluoropropene to 1 gave two products which were separated by fractional crystallization from hexane. 95 is formed from the internal sp² C–F bond cleavage, while 96 is the result of breaking the terminal sp² C–F bond trans to the CF₃ group. The reaction of 1 with 3,3,3-trifluoropropene yielded 97 by the formation of a metallocyclopropane intermediate followed by β-fluoride elimination (Scheme 23).⁴³

Streubel and co-workers described the reaction of monovalent compounds DippNacNacM (M = Al, Ga) with imidazole-2-thione based tricyclic 1,4-diphosphine, which produced the corresponding 7-metalla-1,4-diphosphanorbornadiene (98, 99) (Scheme 24).⁴⁴ Previously Nikonov et al. described the oxi-
hexafluoropropene and trifluoropropene, respectively.

![Scheme 23](image1)

Scheme 23 Reactions of 1 with (E)-1,3,3,3-tetrafluoro-propene, hexafluoropropene and trifluoropropene, respectively.

![Scheme 24](image2)

Scheme 24 Reaction of tricyclic 1,4-diphosphinine with DippNacNacAl(I) (1) and DippNacNacGa(I) (2) to get 7-metalla-1,4-diphosphanorbornadienes 98 and 99.

dative cleavage of the C=S bond at the metal center,44b while 98 and 99 undergo the [4 + 1] cycloaddition reaction, which is both kinetically and thermodynamically favorable.

The aluminum(i) compound DippNacNacAl(I) (1) reacted with diethyl sulfide at 50 °C, which resulted in the oxidative addition of the C(sp³)-S bond. This is the first example of C(sp³)-S bond activation by a main-group element.15 The groups of Nikonov, Crimmin, and Kinjo independently reported the reactions of monomeric Al(i) compound 1 towards C-O bonds. The oxidative addition reaction of tetrahydrofuran with DippNacNacAl(I) (1) smoothly occurred at room temperature to give complex 101,43b while the reaction between 1 and benzofuran upon heating at 80 °C slowly converted it to product 102.43a The reaction of 1 with an equiv. amount of L’PhB (103) (L’ = oxazol-2-ylidene) in toluene instantly occurred with the insertion of DippNacNacAl(I) (1) into the C-O bond, affording complex 104 involving an Al, N, and O mixed heterocyclic carbene or anionic (amino)(boryl) carbene derivative (Scheme 25).46

Treatment of DippNacNacAl(I) (1) with thiourea resulted in the first carbene-stabilized terminal aluminum sulfide complexes 105 and 106 by the oxidative cleavage of the C=S bond. In contrast, the mixing of compound 1 and triphenylphosphine sulfide in a 1 : 1 ratio afforded a mixture of terminal sulfide DippNacNacAl=S(S=PPh₃), unreacted 1, and free triphenylphosphine. The existence of the Al-S double bond in 105 and 106 was supported by DFT calculations. Complex 105 undergoes facile cycloaddition with phenyl isothiocyanate to form complex 107 along with zwitterion 108 obtained from the coupling between the liberated carbene and PhN=CS (Scheme 26).44b To investigate the oxidative cleavage of the unsaturated bond of the C=N unit, the reaction of DippNacNacAl(I) (1) with cyclic guanidine was accomplished and showed the unprecedented cleavage of the C-N multiple bond to give the carbene-ligated amido complex DippNacNacAl [NHTol][SIMe] (SIMe = C{N(Me)CH₂}₂) (109). The splitting of the C=N bond in 109 is the first example of the oxidative addition of the C=N double bond to any metal center.47 The DFT study supported that the production of 109 occurs via an intermediate of aluminum imide as a result of the oxidative cleavage of TolN=SIMe (SIMe = C{N(Me)CH₂}₂) by 1. The reactions of phosphine oxides with 1 occurred readily with the formation of hydroxyl derivatives DippNacNacAl(OH)(O=PR₃) (R = Ph 110, Et 111). The C=O bond (179 kcal mol⁻¹) is much stronger when compared with the P=O bond (110 kcal mol⁻¹). Therefore, the reaction of cyclic urea 1,3-dimethyl-2-imidazolidinone with 1 resulted in an unexpected aluminum hydride DippNacNacAlH(O=SIMe) (SIMe = C{N(Me)CH₂}₂) 112, with the deprotonation of the weakly acidic methyl group in the backbone of the DippNacNac ligand.48c In contrast, the reactivity of 1 towards benzophenone afforded a ketone species NacNacAl(η²(C=O)-OCPPh₃) (113) (Scheme 27). The latter compound undergoes easy cyclization reaction with an unsaturated substrate.48d

Recently Stephan et al. have reported the first heteroaluminineries DippNacNacAl[C(R)=P] (R = Bu or adamantyl) 114 and 115 via the [1 + 2] cycloaddition reaction of the aluminum(i) complex DippNacNacAl(I) (1) with phosphaalkynes, which feature moderate three-centered 2π-electron aromaticity.
The compounds containing the AlCP ring can be used as synthons to prepare a series of unprecedented Al- and P-containing heterocyclic frameworks. The Ga(I) compound easily undergoes cyclization with methacrolein at room temperature within 10 min to give gallium enolate. Unlike the aluminum congener, the gallium compound does not cleave the P=S bond of Et₃P=S, even upon heating to 80 °C. With Ph₃P=S, however, a slow reaction occurs upon heating to 80 °C to obtain the sulfide \((\text{DippNacNacGa})_2(\mu-S)(\mu-CNPh)\) at a ratio of 5:1. 

### 2.4 H–X bond activation

In 2014, Nikonov et al. reported the first examples of oxidative addition of a series of robust H–X bonds (X = H, B, C, Si, N, P, O) to a single Al(i) center. The addition of H₃SiPh, HBPin, HPPPh₂,
HO\textsubscript{i}Pr, H\textsubscript{2}NtBu and H\textsubscript{2}NPh with 1 proceeded smoothly at ambient temperature, while the reaction of bulkier silane (H\textsubscript{2}SiMePh\textsubscript{3}), H\textsubscript{2}Cp*H with compound 1 required heating at 70 °C. The Al(I) compound reactivity toward the oxidative addition of DippNacNacAlH\textsubscript{3} is reversible, proving the possibility of reductive elimination from the species DippNacNacAlH\textsubscript{2}(X) (X = H, B, C, Si, N, P, O). Linti et al. described that DippNacNacGa(I) (2) undergoes facile oxidative addition reactions towards H\textsubscript{2}, HSnPh\textsubscript{3}, HNEt\textsubscript{2}, HPPh\textsubscript{2}, HOEt and H\textsubscript{2}O, leading to a series of gallium hydrides, DippNacNacGaH(X) (X = H, Sn, O, N, P), substituted by hydride, tin, alkoxy, amido and phosphido groups. The oxidative addition of DippNacNacGa(I) (2) with HCCCH\textsubscript{2}OH, Ph\textsubscript{3}Si(OH)\textsubscript{2}, (nBuO)\textsubscript{2}P(O)(OH) and (4-MeC\textsubscript{6}H\textsubscript{4})S(O)\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}-4-Me) resulted in the formation of compounds DippNacNacGaH(\mu-O)CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}C\textsubscript{6}H\textsubscript{4}S(O)\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}-4-Me) (137), DippNacNacGaH(\mu-O)SiPh\textsubscript{3}(OH) (139), DippNacNacGaH(\mu-O)P(O)(O\textsubscript{i}Pr)\textsubscript{2} (140) and DippNacNacGaH(\mu-O)S(O)\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}-4-Me) (141), respectively at very low temperature (Scheme 31). Very recently, Nikonov et al. have reported the in situ oxidation of DippNacNacGa(I) (2) by N\textsubscript{2}O or pyridine oxide which results in the generation of NacNacGa(O) as a monomeric oxide intermediate leading to the C–H bond activation (Scheme 32). The oxidation of DippNacNacGa(I) (2) by using pyridine oxide led to the C–H bond activation of pyridine oxide, yielding DippNacNacGa(OH)(\eta\textsuperscript{1}C),\eta\textsuperscript{1}O(o-C\textsubscript{6}H\textsubscript{4}N=O) (142), and pyridine. A similar reaction between DippNacNacGa(I) (2) and N\textsubscript{2}O in the presence of pyridine and cyclohexanone leads to DippNacNacGa(OH)(o-C\textsubscript{6}H\textsubscript{4}N) (143) and DippNacNacGa(OH)(OC\textsubscript{6}H\textsubscript{5}) (144), respectively. The oxidation of DippNacNacGa(I) (2) in the presence of Ph\textsubscript{3}C=O resulted in the isolation of compound DippNacNacGa \((k^2-O_2CPh_2) (145)\), formed from the sequential oxidation and cyclization. The in situ oxidation of the mixtures of DippNacNacGa(I) (2) with O=SM\textsubscript{2}E and O=PE\textsubscript{2} resulted in the sp\textsuperscript{3} C–H bond cleavage yielding compounds DippNacNacGa.

### Scheme 30

P–P and S–S bond cleavage by 1.

### Scheme 31

Oxidative addition of \(\sigma\)-bonds to Al(I) and Ga(I) compounds, respectively.

### Scheme 32

Sequential oxidation/C–H activation of Ga(I).

(Ch2S(=O)Me)OH (146) and DippNacNacGa(CH(Me)P(=O)Et\textsubscript{2}) OH (147), respectively.

3. Conclusions and perspectives

In conclusion, we report monomeric aluminum and gallium carbenoid complexes supported by \(\beta\)-diketiminate ligands which possess a lone pair of electrons and a formally vacant p orbital. These features afford high electrophilic and nucleophilic reactivity that could be used in bond activation and cleavage upon reactions with small molecules. The aluminum and gallium carbenoid complexes undergo a series of oxidative addition reactions with \(\sigma\) H–X and E–E bonds where E is an element from groups 13 to 16. These compounds also demonstrate the oxidative cleavage of multiple bonds and enthalpically strong bonds (M–X, E–E). An extension of the synthetic approach is presented in this review for the synthesis of Group 13 metalloid complexes that consist of an unsupported M–M' (M' = Al, Ga) bond. The oxidative cleavage of multiple bonds shows new and unusual reactivities. These reactivities have opened up a new realm in aluminum and gallium chemistry that could lead to many new products. Nevertheless, the compounds with low valent aluminum and gallium are still showing some limitations in catalytic applications.

However, dialumene (I) promoted both the catalytic and stoichiometric reduction of CO\textsubscript{2} to value added C1 products, which is the first example of catalysis using a homonuclear main-group multiple bond. It is important to explore reductive elimination of C–C bonds, which leads to reversible bond activation paving the way towards catalytic applications. Recent developments in the isolation of aluminyl complexes (II) will likely extend the low oxidation state Al chemistry that is used to activate the C–C bonds. We look forward to conducting
further studies of the Al(i) and Ga(i) complexes which will result in more unprecedented bond cleavage reactions and important future applications in catalysis.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
H. W. R. thanks the DFG for support of this work (RO 224/71-1). We also thank Prof. Z. Yang from the Beijing Institute of Technology for helpful discussions. This work is dedicated to Professor Reinhold Tacke on the occasion of his 70th birthday.

Notes and references
1 (a) R. H. Holm, Chem. Rev., 1987, 87, 1401–1449; (b) N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457–2483; (c) E. M. McGarrigle and D. G. Gilheany, Chem. Rev., 2005, 105, 1563–1602; (d) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, Chem. Rev., 2010, 110, 890–931; (e) B. Sarkar, D. Schweinfurth, N. Deibl and F. Weisser, Coord. Chem. Rev., 2015, 293–294, 250–262.
2 (a) C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, Angew. Chem., Int. Ed. Engl., 1991, 30, 564–565, (Angew. Chem., 1991, 103, 594–595); (b) S. Schulz, H. W. Roesky, H.-J. Koch, G. M. Sheldrick, D. Stalke and A. Kuhn, Angew. Chem., Int. Ed. Engl., 1993, 32, 1729–1731.
3 (a) W. Uhl, Angew. Chem., Int. Ed. Engl., 1993, 32, 1386–1397, (Angew. Chem., 1993, 105, 1449–1461); (b) C. Dohmeier, D. Loos and H. Schnöckel, Angew. Chem., Int. Ed. Engl., 1996, 35, 129–149, (Angew. Chem., 1996, 108, 141–161).
4 A. H. Cowley, Chem. Commun., 2004, 2369–2375.
5 (a) L. Bourget-Merle, M. F. Lappert and J. R. Severn, Chem. Rev., 2002, 102, 3031–3066; (b) Y. Tsai, Coord. Chem. Rev., 2012, 256, 722–758; (c) C. Chen, S. M. Bellows and P. L. Holland, Dalton Trans., 2015, 44, 16654–16670.
6 (a) H. W. Roesky and S. S. Kumar, Chem. Commun., 2005, 4027–4038; (b) S. Nagendran and H. W. Roesky, Organometallics, 2008, 27, 457–492; (c) M. Asay, C. Jones and M. Driess, Chem. Rev., 2011, 111, 354–396; (d) W. Li, X. Ma, M. G. Walawalkar, Z. Yang and H. W. Roesky, Coord. Chem. Rev., 2017, 350, 14–29; (e) Y. Liu, J. Li, X. Ma, Z. Yang and H. W. Roesky, Coord. Chem. Rev., 2018, 374, 387–415; (f) T. Chu and G. I. Nikonov, Chem. Rev., 2018, 118, 3608–3680; (g) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, Chem. Rev., 2018, 118, 9678–9872; (h) P. Bag, C. Weetman and S. Inoue, Angew. Chem., Int. Ed., 2018, 57, 14394–14413.
7 (a) P. P. Power, Nature, 2010, 463, 171–177; (b) C. Weetman and S. Inoue, ChemCatChem, 2018, 10, 4213–4228; (c) R. L. Melen, Science, 2019, 363, 479–484.
8 (a) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, Angew. Chem., Int. Ed., 2000, 39, 4274–4276; (b) X. Li, X. Cheng, H. Song and C. Cui, Organometallics, 2007, 26, 1039–1043; (c) H. Zhu, R. B. Oswald, H. Fan, H. W. Roesky, Q. Ma, Z. Yang, H.-G. Schmidt, M. Noltemeyer, K. Starke and N. S. Hosmane, J. Am. Chem. Soc., 2006, 128, 5100–5108.
9 Y. García-Rodeja, F. M. Bickelhaupt and I. Fernández, Chem. – Eur. J., 2016, 22, 13669–13676.
10 (a) P. Bag, A. Porzelt, P. J. Altmann and S. Inoue, J. Am. Chem. Soc., 2017, 139, 14384–14387; (b) C. Weetman, P. Bag, T. Szilvási, C. Jandl and S. Inoue, Angew. Chem., Int. Ed., 2019, 58, 10961–10965.
11 (a) J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, Nature, 2018, 557, 92–95; (b) J. Hicks, A. Mansikkamäki, P. Vasko, J. M. Goicoechea and S. Aldridge, Nat. Chem., 2019, 11, 237–241; (c) J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, J. Am. Chem. Soc., 2019, 141, 11000–11003.
12 (a) R. J. Schwamn, M. D. Anker, M. Lein and M. P. Coles, Angew. Chem., Int. Ed., 2019, 58, 1489–1493; (b) M. D. Anker and M. P. Coles, Angew. Chem., Int. Ed., 2019, 58, 13452–13455.
13 (a) J. Hicks, A. Heilmann, P. Vasko, J. M. Goicoechea and S. M. Aldridge, Angew. Chem., Int. Ed., 2019, 58, 17265–17268; (b) D. Anker and M. P. Coles, Angew. Chem., Int. Ed., 2019, 58, 18429–18433.
14 (a) A. Hofmann, C. Pranckevicius, T. Tröster and H. Braunschweig, Angew. Chem., Int. Ed., 2019, 58, 3625–3628; (b) S. K. Mellerup, Y. Cui, F. Fantuzzi, P. Schmid, J. T. Goettel, G. Bélanger-Chabot, M. Arrowsmith, M. Krummenacher, Q. Ye, V. Engel, V. Engels and H. Braunschweig, J. Am. Chem. Soc., 2019, 141, 16954–16960; (c) S. Kurumada, S. Takamori and M. Yamashita, Nat. Chem., 2020, 12, 36–39.
15 (a) S. L. Choong, W. D. Woodul, A. Stasch, C. Schenkl and C. Jones, Aust. J. Chem., 2011, 64, 1173–1176; (b) C. P. Sindlinger, S. R. Lawrence, S. Acharya, C. A. Ohlin and A. Stasch, Dalton Trans., 2017, 46, 16872–16877; (c) A. L. Hawley, C. A. Ohlin, L. Fohlmeister and A. Stasch, Chem. – Eur. J., 2017, 23, 447–455.
16 (a) E. S. Schmidt, A. Jockisch and H. Schmidbaur, J. Am. Chem. Soc., 1999, 121, 9758–9759; (b) E. S. Schmidt, A. Schier and H. Schmidbaur, J. Chem. Soc., Dalton Trans., 2001, 505–507; (c) R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, J. Chem. Soc., Dalton Trans., 2002, 3844–3850; (d) I. L. Fedushkin, A. N. Lukoyanov, G. K. Fukin, S. Y. Ketkov, M. Hummert and H. Schumann, Chem. – Eur. J., 2008, 14, 8465–8468; (e) I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko and M. Hummert, Chem. – Eur. J., 2010, 16, 7563–7571; (f) I. L. Fedushkin, A. N. Lukoyanov, G. K. Fukin, S. Y. Ketkov, M. Hummert and H. Schumann, Chem. – Eur. J., 2008, 14, 8465–8468; (g) I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin,
