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 in the +1 oxidation state has played a great part in the development of p-block chemistry. The synthesis of compounds with aluminum and gallium in the +1 oxidation state is experimentally challenging and consistently hampered by their high reactivity and pronounced tendency towards disproportionation. The lone pair of electrons in MR (R = β-diketiminate) (M = Al, Ga) compounds can act as a basic site towards a range of Lewis acids, forming a σ donating bond. Donor–acceptor bonds 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 stoichiometric 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[MeNDipp]2] (Dipp = 2,6-iPr2C6H3) (1). This was the first stable dicordinate 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(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(m) 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 aluminyl anion (NON)Al− by employing a chelating ligand (NON = 4,5-bis(2,6-diisopropyl-phenyl)-2,7-di-tert-butyl-9,9-dimethylxanthene) (I, Fig. 1), which acts as an unprecedented aluminum(i) nucleophile (e.g., in reactions with Bu3PAuI), 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 aluminyl anion [Al(NON2)] (NON2 = [O(SiMe2NDipp)2]) (2), Dipp = 2,6-iPr2C6H3, III, Fig. 1), 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 (CO\textsubscript{2} and N\textsubscript{2}O) via cycloaddition to generate a monoalumoxane. 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 (Cp\textsubscript{3}t) 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 “Gal” or by alkali metal reduction of Ga\textsuperscript{III} or Ga\textsuperscript{III} precursors. The monomeric example of Ga\textsuperscript{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\textsuperscript{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.
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).8 At the same time, Power and co-workers reported a β-diketiminate stabilized Ga(I) monomer DippNacNacGa(I) (2) (Scheme 1).20 It was obtained by the reaction of [Li{HC(CMeNDipp)2}] with “GaI”. 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 π-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.21 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).22 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.23

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,24a 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).24b

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 with metal–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).25 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 dialumanes by the disproportionation of DippNacNacAl(i) (1) with (Me2cAAC)AlX3 (X = Cl, I) adducts (Scheme 5).27 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.26 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.27 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+·(C6H6)] [B(C6F5)4] and DippNacNacAl(i) (1), which led to the complete deaeromatization 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.28a Crimmin et al. reported the first catalytic method for the transformation of C–H bonds 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 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).28c 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) by the low valent Al(i) complex 1 at room temperature has been achieved by the catalytic presence of [(DippNacNac)CaH]2 (Scheme 8). The possible pathway is the combined action of nucleophilic Al and arene activation by π-coordination to a Lewis acidic Ca center, which is parallel to the first alminyl anions.11c

Schula et al. reported that a solution of DippNacNacAl(i) (1) reacts with E2Et4 (E = Sb, Bi) in toluene to insert DippNacNacAl(i) (1) into the E–E bond with the formation of DippNacNacAl([EEt]2)
(E = Sb 32, Bi 33) (Scheme 9). 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.29 Fischer et al. have achieved the reaction of DippNacNacGa(I)(2) with Bi(OSO2CF3)3 and [Bi–(OC6F5)3(toluene)2] to yield [(R’O)(DippNacNac)GaBi(DippNacNac)(OTf)] (Tf = SO2CF3 36, C6F5 37). 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 DippNacNacGa(OTf)2. 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.30 Schulz et al. described a similar insertion reaction of DippNacNacGa with BiEt3 that leads to DippNacNacMer(BiEt3) (M = Al 38 and Ga 39) (Scheme 9). The consecutive second activation proceeds at a higher temperature through the reductive elimination of DippNacNacMeT3, 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–PbIII–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...
In addition, Schulz et al. showed that $^\text{DppNacNacGa}\text{(i)}$ (2) inserted into the In–C bond of InEt$_3$ resulted in the formation of $^\text{DppNacNacGaEt(InEt}_3\text{)}$ (45). The solution of 45 in benzene and toluene tends to decompose slowly at ambient temperature. But the reaction of $^\text{DppNacNacGa}\text{(i)}$ (2) with $^\text{i'Bu} \rightarrow \text{InEt}_3$ ($^\text{i'Bu} = [\text{C(\text{Nt}-\text{Bu}_2\text{CH})}_2]$) resulted in a stable compound 46, where the carbene coordinates to the indium atom. The reaction of InEt$_3$ with 2 equiv. of $^\text{DppNacNacGa}\text{(i)}$ (2) resulted in a double insertion product $[^\text{DppNacNacGa(Et)}_2]\text{InEt}$ (47) (Scheme 11), while further insertion of $^\text{DppNacNacGa}\text{(i)}$ (2) into the remaining In–Et bond does not occur. Complex 57 gradually decomposes at 80 °C in C$_6$D$_6$, resulting in $^\text{DppNacNacGa}$ (2) and $^\text{DppNacNacGaEt}_2$ (48). A similar reaction between $^\text{DppNacNacGa}\text{(i)}$ (2) and Cp*InEt$_2$ (Cp* = C$_5$Me$_5$) leads to the production of $^\text{DppNacNacGaEt}_2$ (48). These reactions proceeded via the oxidation of $^\text{DppNacNacGa}\text{(i)}$ (2) with the In–Et bond and subsequent reductive elimination of $^\text{DppNacNacGaEt}_2$ from the indium(III) center.

Schulz and co-workers have also reported a stibinyl radical $[^\text{DppNacNac(Cl)Ga}]_2\text{Sb}^\prime$ (49) by the reaction of two equiv. of $^\text{DppNacNacGa}\text{(i)}$ (2) with Cp*SbCl$_2$ (Scheme 12), and the traces of $^\text{DppNacNac(Cl)GaSb(H)Cp}^\ast$ (50) were formed as a byproduct. Similarly, the equimolar reaction yielded $^\text{DppNacNac(Cl)GaSb(Cl)}_2\text{Cp\ast}$ and the antimony metal. The analogous reaction of $^\text{DppNacNacGa}\text{(i)}$ (2) with Cp*BiCl$_2$ yielded a bis-bismuthyl radical $[^\text{DppNacNac(i)Ga}]_2\text{Bi}^\ast$ (52) (Scheme 12). Their formation illustrates the stepwise insertion of $^\text{DppNacNacGa}\text{(i)}$ 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-
turally characterized compound containing a Ga=Sb double bond (Scheme 13). In contrast, the equimolar redox reaction of 2 with the single-electron oxidant \([\text{NO}]\,[\text{BF}_4]\) occurred with the formation of \(\text{DippNacNacGaClF}\) (54).\(^{36}\)

The \(\text{Cp}^*\text{AsCl}_2\) (\(\text{Cp}^* = \text{C}_5\text{Me}_5\)) reacted with one equiv. of \(\text{DippNacNacGa(I)}_2\) with the insertion of \(\text{DippNacNacGa(I)}_2\) into one As–Cl bond and the subsequent formation of \(\text{DippNacNacGaAs(Cl)Cp}^*\) (55) (Scheme 14). In contrast, the reaction of two equiv. of \(\text{DippNacNacGa(I)}_2\) with \(\text{Cp}^*\text{AsCl}_2\) proceeds with the formation of gallaarsene \(\text{DippNacNacGaAsCp}^*\) (56) with a Ga=As double bond and \(\{\text{DippNacNacGaCp}^*\}\) (\(\text{DippNacNacGa}\)[\(\eta^1,\eta^2,\mu^3\text{As}_3\)] (57), containing a central GaAs$_3$ butterfly type core. The central structural motif of 57 is the bridging As$_3$ 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 \(\text{DippNacNacGa(I)}_2\) in detail, Schulz et al. studied the reactions of \(\text{DippNacNacGa(I)}_2\) with other Sb$^{III}$ reagents. \(\text{DippNacNacGa(I)}_2\) reacted with Sb$^\text{III}$ reagents in a 2 : 1 molar ratio to form Ga-substituted distibenes \([\text{DippNacNacGaX)}_2\text{Sb}_2\] (X = NMe$_2$ 58, Cl 59) (Scheme 15). Heating a toluene solution of 58 at 120 °C for 24 h yielded \([\text{DippNacNacGaNMe}_2)_2(\mu_\text{η}^1\text{η}^1\text{Sb}_4]\) (60). But complex 59 required 7 days of heating at 130 °C to give \([\text{DippNacNacGaCl}_2(\mu_\text{η}^1\text{η}^1\text{Sb}_4]\) (61). Compound 58 can react with GaCl$_3$ to form 59; in addition, 59 reacts with Li amide to form 58. The central Sb$_4$ unit in 60 and 61 adopts a butterfly type conformation (Fig. 7). Interestingly, compound 60 reacted with GaCl$_3$ in an amide/Cl exchange reaction with the subsequent formation of 61.\(^{38}\)

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 \(\text{DippNacNacGa(I)}_2\) were investigated. The \(\text{DippNacNacGaSbGa}\) (X) \(\text{DippNacX} (X = \text{F} 62, \text{Cl} 63, \text{Br} 64, \text{and I} 65)\) compounds were formed by a twofold insertion of \(\text{DippNacNacGa(I)}_2\) into two Sb–X bonds, followed by an intramolecular elimination of \(\text{DippNacNacGaX}_2\) (Scheme 16). The reactions of two equiv. of \(\text{DippNacNacGa(I)}_2\) with SbCl$_3$ at 8 °C yielded cyclotristibine 66. The Sb–Sb bond (2.8205(3)–2.8437(3) Å) in cyclotristibine 66 is typical of the Ga–Sb single bond.\(^{39}\)
The insertion reactions of two equiv. of \( \text{DippNacNacGa(I)}(2) \) with \( \text{SbX}_3 \) (\( X = \text{Cl, Br} \)) at low temperature produced a double-inserted product \( \text{DippNacNacGaX}_2 \text{SbX} \) (\( X = \text{Cl, Br} \)). Additionally, the reaction of isolated compounds and with strong \( \sigma \)-donating carbenes (IDipp(1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene), Me\text{2cAAC}) yielded four carbene-stabilized stibinidenes (\( 69 \)–\( 72 \)) (Scheme 17). The studies reveal that IDipp-stabilized stibinidenes \( 69 \) and \( 70 \) show \( \text{Sb}–\text{Ccarbene} \) single bonds, whereas the Me\text{2cAAC}-stabilized derivatives \( 71 \) and \( 72 \) exhibit \( \text{Sb}–\text{Ccarbene} \) \( \pi \)-backbonding character.

A red-brown complex \( 73 \) was obtained by the reaction of the half-sandwich complex \( [\text{CpR}′\text{Ni(μ-Br)}]_2 \) (\( \text{CpR}′ = \text{C}_5(\text{C}_6\text{H}_4-4-\text{Et})_5 \)) with \( \text{DippNacNacGa(I)}(2) \) in THF (Scheme 18).

2.3 Cleavage of E′–E single and E′==E double bonds
To stabilize Ga-coordinated dipnictenes of the type \( [\text{DippNacNac}(\text{X})\text{Ga}]_2\text{E}_2 \) (\( \text{E} = \text{P–Bi} \)), the reactions of \( \text{DippNacNacGa(I)}(2) \) with phosphorus, arsenic, and bismuth halides and amides were studied.\(^{42} \) Two equiv. of \( \text{DippNacNacGa(I)}(2) \) reacted with \( \text{PX}_3 \) (\( X = \text{Cl, Br} \)) in toluene at ambient temperature with the insertion of \( \text{DippNacNacGa(I)}(2) \) into two \( \text{P}–\text{X} \) bonds, which resulted in \( [\text{DippNacNac(X)Ga}]_2\text{PX} \) (\( X = \text{Cl, Br} \)) (Scheme 19). Similar twofold insertion reactions into \( \text{AsCl}_3 \) and the subsequent elimination of \( \text{DippNacNacGaCl}_2 \) resulted in the formation of the stable Ga-coordinated diarsene species, which was isolated as a green crystalline solid \( 77 \) (Scheme 20). The analogous reaction with \( \text{Me}_2\text{NAsCl}_2 \) yielded unsymmetrically-substituted diarsene \( [\text{DippNacNacCl(GaAs=As)Ga}]_2 \) (\( 78 \)) (Scheme 20). In contrast, the reaction of \( \text{DippNacNacGa(I)}(2) \) with \( \text{As(NMe}_2)_3 \) required much harsher reaction conditions. A mixture of \( \text{DippNacNacGa(I)}(2) \) and \( \text{As(NMe}_2)_3 \) heated at 165 °C for 5 days resulted in complex \( 79 \) (Scheme 19). Its analogous reaction with \( \text{DippNacNacAl(I)}(1) \) yielded \( [\text{DippNacNac(Me}_3\text{Al})_2\text{As}]_2 \) (\( 80 \)) after heating at 80 °C for one day (Scheme 20). Finally, the reaction of \( \text{DippNacNacGa(I)}(2) \) with \( \text{Bi(NEt}_2)_3 \) also occurred with the insertion and elimination of \( \text{DippNacNacGa(NEt}_2)_3 \) and resulted in the corresponding Ga-substituted dibismuthene \( [\text{DippNacNac(Et}_3\text{Bi})_2\text{Ga}]_2 \) (\( 81 \)) (Scheme 19). The reaction of 2 with elemental tellurium yielded the Te-bridged compound \( [\text{DippNacNacGa(μ-Te)}_2] \) (\( 82 \)).
Moreover, the cleavage of the Te–Te and Te–C bonds upon reactions of 2 with Ph₅Te₂ and Pr₅Te resulted in the formation of DippNacNacGa(TeXPh) (83) and DippNacNacGa(Pr)Te(Pr) (84), respectively (Scheme 20).³⁴

Nikonov and Crimmin groups separately reported the reactions of the monomeric Al[i] complex with various fluoroalkenes and fluoroarenes, resulting in the breaking of strong sp² and sp³ 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 fluorocyclohexane 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 metalloyclopropane intermediate followed by β-fluoride elimination (Scheme 23).²⁴

Streubel and co-workers described the reaction of monovalent compounds DippNacNacM (M = Al, Ga) with imidazole-2-thione based tricyclic 1,4-diphospinine, which produced the corresponding 7-metalla-1,4-diphosphanorbornadiene (98, 99) (Scheme 24).⁴⁴ Previously Nikonov et al. described the oxi-
The aluminum(i) compound DippNacNacAl(\(\text{I}\)) (1) reacted with diethyl sulfide at 50 °C, which resulted in the oxidative addition of the C(sp\(^3\))-S bond. This is the first example of C(sp\(^3\))-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(\(\text{I}\)) (1) smoothly occurred at room temperature to give complex 101.\(^{43a}\) 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\(_2\)PhB (103) (L' = oxazol-2-ylidene) in toluene instantly occurred with the insertion of DippNacNacAl(\(\text{I}\)) (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).\(^{16}\)

Treatment of DippNacNacAl(\(\text{I}\)) (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=PhP\(_3\)), 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 compound 107 along with zwitterion 108 obtained from the coupling between the liberated carbene and PhN=C=S (Scheme 26).\(^{44b}\) To investigate the oxidative cleavage of the unsaturated bond of the C=N unit, the reaction of DippNacNacAl(\(\text{I}\)) (1) with cyclic guanidine was accomplished and showed the unprecedented cleavage of the C-N multiple bond to give the carbene-ligated amidox complex DippNacNacAl(NH\(_2\))SIMe (SIMe = C{N(Me)CH\(_2\)}\(^2\)) (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.\(^{17}\) 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)CH\(_2\)}\(^2\)) by 1. The reactions of phosphine oxides with 1 occurred readily with the formation of hydroxyl derivatives DippNacNacAl(OH)\((\text{O} = \text{PR}_3\)) (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)CH\(_2\)}\(^2\)) 112, with the deprotonation of the weakly acidic methyl group in the backbone of the DippNacNac ligand.\(^{48b}\) In contrast, the reactivity of 1 towards benzophenone afforded a ketone species NacNacAl(\(\eta^2\)(C\(_6\)H\(_5\))(C\(_6\)H\(_5\))O=O)CPh\(_3\)) (113) (Scheme 27). The latter compound undergoes easy cyclization reaction with an unsaturated substrate.\(^{43a}\)

Recently Stephan et al. have reported the first heteroaluminiirennes DippNacNacAl[C(\(\text{R} = \text{Bu or adamantyl}\)] 114 and 115 via the [1 + 2] cycloaddition reaction of the aluminum(i) complex DippNacNacAl(\(\text{I}\)) (1) with phosphalkyenes, which feature moderate three-centered 2\(\pi\)-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 (DippNacNacGa–S)₂. Nevertheless, compound readily reacts with two equiv. of PhNCS to give product via C=S bond cleavage and cyclization, and also the dimer (DippNacNacGa)₂(μ-S)(μ-CNPh) at a ratio of 5:1 (3,5-Me₂C₆H₃)NCO and PhNCO, respectively, reacts with 2, readily to form the coupling products and . 1,3-Di-p-tolylecarbonodiimide and DippNacNacGa(i) formed the coupling product (Scheme 29). DippNacNacAl(I) reacted with diphenyl disulfide to afford the symmetrically substituted bis(phenyl sulfide) aluminum complex via the cleavage of the S–S bond in diphenyl disulfide. In a similar fashion, the reaction of 1 with bulky tetraphenyl diphosphine resulted in the cleavage of the P–P bond over the course of 3 d at 70 °C to produce the novel aluminum bis(diphenyl phosphido) complex (Scheme 30).

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,
HOiPr, H₂NtBu and H₂NPh with 1 proceeded smoothly at ambient temperature, while the reaction of bulkier silane (H₂SiMePh₂), H₂Cp⁺H with compound 1 required heating at 70 °C. The Al(I) compound reactivity toward the oxidative addition of DippNacNacAlH₂ is reversible, proving the possibility of reductive elimination from the species DippNacNacAlH₂(X) (X = H, B, C, Si, N, P, O). Linti et al. described that DippNacNacGa(i) (2) undergoes facile oxidative addition reactions towards H₂, HNSnPh₃, HNEt₂, H₂PPh₃, HOEt and H₂O, leading to a series of gallium hydrides, DippNacNacGaH(X) (X = H, Sn, O, N, P), substituted by hydride, tin, alkox, amido and phosphido groups. The oxidative addition of DippNacNacGa(i) (2) with HCCCH₂OH, Ph₂Si(OH)₂, (nBuO)₂P(O)(OH) and (4-Me-C₆H₄)S(O)₂(CH₂O) resulted in the formation of compounds DippNacNacGa(H)₄(μ-O)₂(CH₂C₆H₄-4-Me) (138), DippNacNacGa(H)(μ-O)SiPh₂(OH) (139), DippNacNacGa(H)(μ-O)P(O)(O²Bu)₂ (140) and DippNacNacGa(H)(μ-O)S(O)₂(C₆H₄-4-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 N₂O 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 pyridine oxide led to the C–H bond activation of pyridine oxide, yielding DippNacNacGa(OH)(η¹(C),κ¹(O)-o-C₆H₄-N-O) (142), and pyridine. A similar reaction between DippNacNacGa(i) (2) and N₂O in the presence of pyridine and cyclohexanone leads to DippNacNacGa(OH)(o-C₆H₄-N) (143) and DippNacNacGa(OH)(OC₆H₅) (144), respectively. The oxidation of DippNacNacGa(i) (2) in the presence of Ph₂C=O resulted in the isolation of compound DippNacNacGa(k²-O₂CPh₂) (145), formed from the sequential oxidation and cyclization. The in situ oxidation of the mixtures of DippNacNacGa(i) (2) with O═SMe₂ and O═PET₃ resulted in the sp³ C–H bond cleavage yielding compounds DippNacNacGa

In conclusion, we report monomeric aluminum and gallium carbene complexes supported by β-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 carbeneoid complexes undergo a series of oxidative addition reactions with σ 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 CO₂ 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.

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Notes and references


