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Main-group metal complexes of α-diimine ligands: structure, bonding and reactivity

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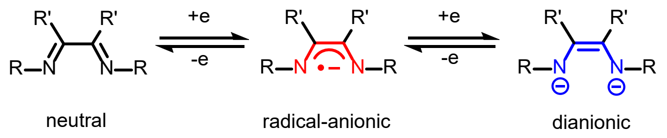
α-Diimine ligands, in particular 1,4-diazabutadiene (**dad**) and bis(iminoacenaphthene) (**bian**) derivatives, have been widely used for coordination with various metals, including main-group, transition, and lanthanide and actinide metals. In addition to their tunable steric and electronic properties, the **dad** and **bian** ligands are redox-active and can readily accept one or two electrons, converting into the radical-anionic ($L^{\bullet-}$) or dianionic (enediamido, L^{2-}) form, respectively. This non-innocence brings about rich electronic structures and properties of the ligands and complexes thereof. For example, the **dad** ligands in their three redox levels can effectively stabilize a series of metal centers in different oxidation states, including low-valent metals. Moreover, these ligands can serve as electron reservoirs and can participate in reactions toward other molecules with or without metals. Therefore, such ligands are extremely useful in the areas of low-valent complexes and small molecule activation. Herein, we will discuss the use of **dad** (and **bian**) ligands in the stabilization of metal–metal-bonded compounds, in particular those of main-group metals, as well as small molecule activation by these (low-valent) metal coordination species where the non-innocence of the ligands plays a key role.

1. Introduction

α-Diimine ligands have been widely used for coordination with metals, including most main-group, transition, and *f*-block metals. These *N*,*N*′-donor ligands have a stable N=C−C=N backbone, such as 1,4-diazabutadiene (**dad** or **dab**), bis(iminoacenaphthene) (**bian**), *o*-benzoquinonediimine (dianion of 1,2-phenylenediamine), imino-pyridine, and 2,2′-bipyridine, etc., which can chelate to a metal centre to form a five-membered metallocycle. While the complexes of all these ligands display rich chemistry and applications in many areas, herein only those with the **dad** (and in some cases **bian**) species are discussed.

The most notable application of **dad** (and **bian**) species is perhaps their use as ligands for late transition metal (Pd^{II} and Ni^{II}) catalysts for olefin polymerization, as discovered by Brookhart and coworkers in 1995.[1] Owing to the easily modified steric and electronic effects of **dad** species available by attaching variable substituents at the carbon and nitrogen atoms, it is convenient to control the properties at the metal centre, thereby changing the polymerization activity of the catalyst. As a result, much research has been done in olefin polymerization catalysed by late transition metal α-diimine systems, which has been well-documented in a couple of excellent reviews[2-5] and will therefore not be included in this article.

Besides the steric and electronic properties, the **dad** ligands possess another favourable characteristic, that is, they are redox active and have adjustable valence states. These species have a low-lying LUMO orbital and can readily accept one or two electrons upon reduction, thereby converting into the radical-anionic ($L^{\bullet-}$) or dianionic (enediamido, L^{2-}) form, respectively (Scheme 1). This non-innocence of α-diimine ligands, on the one hand, causes problems in assigning the oxidation levels of both metal and ligand; but on the other hand, it brings about rich electronic structures and properties of the ligand and complex. Firstly, the **dad** ligands in their three redox levels can effectively stabilize a series of metal centres in different oxidation states, including low-valent metals and those in metal–metal-bonded compounds. Secondly, it is possible to form electron-transfer complexes with novel optical and magnetic properties. Thirdly, these ligands can serve as electron reservoirs and donate/accept electrons when needed, thus making them capable of participating in reactions toward other molecules together with metals. Therefore, such ligands are of great interest in the areas of low-valent complexes and small molecule activation.



Scheme 1. The three oxidation levels of α-diimine (**dad**) ligands.

The redox non-innocence of α-diimine ligands and their transition metal complexes (such as Cr, Mn, Fe, Co, Ni, etc.) has been extensively investigated by Wieghardt's and other groups.[6-10] Due to the existence of both transition metal and α-diimine ligands that have many possible valence states, the clear assignment of the electronic structure of such complexes is highly challenging. Nevertheless, by a combination of several experimental techniques, including EPR, magnetic susceptibility, Mössbauer spectroscopy, X-ray diffraction, etc., as well as theoretical calculations, the electronic structures of a large number of homo- and heteroleptic complexes containing α-diimine ligands have been thoroughly

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elucidated.[7, 11] On the other hand, complexes of *s*-, *p*-, and *f*-block metals with the dianionic enediamido form (L^{2-}) of **dad** (and related diimine) ligands have been summarized recently by Cui *et al.*[12] Very recently, **dad** (in the reduced forms) complexes of earlier transition metals and *f*-block metals (groups 3, 5, 6) have been reviewed.[13] An earlier perspective article summarized the coordination chemistry of **bian** ligands with *s*- and *p*-block elements,[14] while a more recent review presented the synthesis and catalytic properties of *p*-block complexes with **bian** derivatives.[15] These specific areas are largely excluded here with only small portions being covered in this current article.

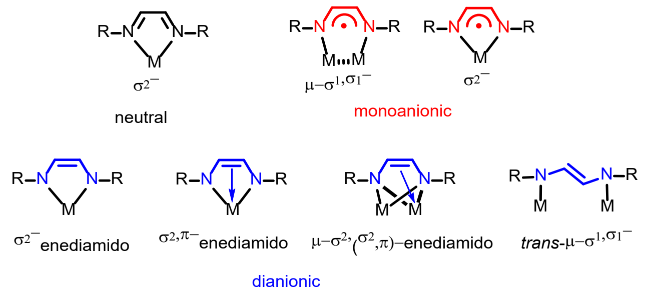
Herein, we intend to focus on the use of **dad** (and **bian**) ligands in the stabilization of metal–metal-bonded compounds, in particular those of main-group metals, as well as on the small molecule activation by these (low-valent) metal coordination species where the non-innocence of the ligands plays a key role. Recent progress in the study of heavier main-group elements not only reveals new structural and bonding features, but also demonstrates that these species can display similar chemistry to the transition metals with respect to their ability to catalyse many organic reactions and to promote chemical transformations.[16] These features, together with the advantages of α-diimine ligands, result in unique fundamental and practical advances in this field.

2. Non-innocence of α-diimine ligands

As mentioned above, when the LUMO of the neutral α-diimine is filled with one or two electrons, the ligand is reduced to the radical monoanion ($L^{\bullet-}$) or dianion (L^{2-}), respectively. This can be achieved by a variety of reducing agents, especially metals such as Li, Na, K, Mg, Al, Zn, Ga, etc., accompanied by the formation of the corresponding metal complexes/salts. On populating electron(s), the C–C and C–N bond lengths of the initial N=C–C=N backbone of the **dad** molecule gradually change. The neutral ligands display a typical C=N double bond (*ca.* 1.29 Å) and a C–C single bond length (*ca.* 1.50 Å). In the monoanion ($L^{\bullet-}$), the single electron is delocalized over the central C_2N_2 backbone, and the CN distance is elongated while the CC distance is shortened, resulting in averaged bond lengths (N⋯C⋯C⋯N) in between a single and a double bond (both can vary over a relatively wide range). When the ligand acquires two electrons to become dianionic (L^{2-}), the CN distance is further lengthened and the CC length shortened, consequently displaying a "long-short-long" $(N–C=C–N)^{2-}$ mode. Besides the internal bonds within the ligand, the metal–ligand bond lengths are also dependent on the redox form of the ligands, as the M–N bond with dianionic ligand is covalent in character and normally is shorter than the dative coordination bond with the neutral ligand. Such features are well-established in the literature for **dad** complexes, which can be conveniently judged from the respective crystal structures.[4,5] Therefore, single-crystal X-ray diffraction is a reliable and most important method in the assignment of the redox levels of α-diimine ligands (and subsequently the oxidation state of metal centre). Nevertheless, other techniques such as NMR and EPR spectroscopy, magnetic susceptibility measurements, UV-Vis spectra, and DFT computations are also necessary to provide complementary evidence for the elucidation of the electronic structures of such complexes. For example, EPR spectroscopy and magnetic studies can help to establish the paramagnetic nature of the species and to localize the radicals as well as their interactions, while theoretical studies may give some clue about the bond order, charge distribution, spin status, etc.

3. Various complexes of α-diimine ligands

All of the three states of the α-diimine ligand can coordinate to various metal centres. As mentioned above, the neutral ligands normally coordinate in the *N*,*N*′-chelating fashion (Scheme 2) to metal ions in the common oxidation states (e.g. Ni^{II} and Pd^{II}) to yield typical Werner-type complexes, such as LMX_2.[4, 5] In a few cases, neutral **dad** ligands can also bond to low-valent metal centres, such as in Ni(0) complexes with alkenes, $L'Ni(C_2H_4)_2$ [17] and LNi(alkene),[18] which may be facilitated by back bonding to the alkene thereby depleting the electron density at nickel(0). For the monoanionic and dianionic **dad** ligands, there are several coordination modes, including the normally seen σ^2-, σ^2,π- and μ-$(\sigma^2)(\sigma^2,\pi)$ in which the two N atoms are arranged in a *cis* (chelating) conformation, and the uncommon bridging modes, either *cis*-μ-σ^1,σ^1- [19-21] or *trans*-μ-σ^1,σ^1-coordination[22-24] where the two N atoms adopt a *cis*- or *trans* orientation, respectively, and each of them coordinates to one metal centre (Scheme 2). These two reduced forms of **dad** ligands are found to be able to stabilize low-valent metal centres. For example, the Cr-Cr quintuply bonded compound [LCrCrL] with Cr(I) centres is stabilized by the radical monoanionic form of the α-diimine ligand dpp-^{H}**dad** (dpp-NCHCHN-dpp) in the bridging *cis*-μ-σ^1,σ^1-mode.[21]



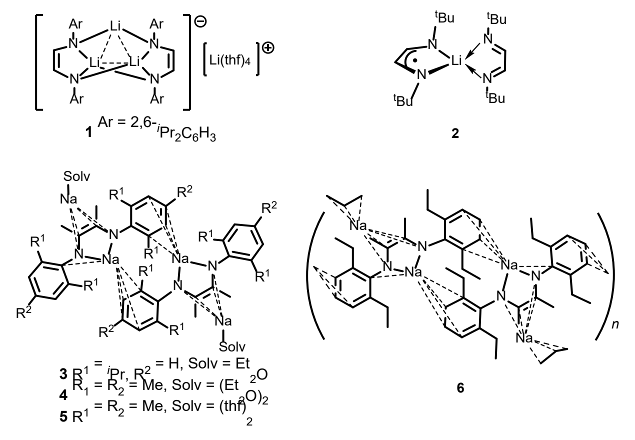
Scheme 2. Coordination modes of α-diimine (**dad**) ligands in the three oxidation levels.

In this part, representative complexes of α-diimine ligands, particularly in the radical anionic and dianionic form, will be introduced. These include the main groups 1 (Li, Na, K), 2 (Be to Ba), 12 (Zn), 13 (Al, Ga, In), 14 (Ge, Sn), and 15 (As, Sb, Bi) metals. It is worth noting that most of these complexes are comprised of dianionic (enediamido) ligands. Moreover, besides the conventional solution-based synthesis, recently **bian** ligands and their complexes have also been synthesized by mechanochemical techniques.[15,25-27] The structure and bonding of selected complexes are presented herein, while their reactivity will be discussed in Part 4 with emphasis on the effects of ligand non-innocence.

3.1. Complexes of groups 1 and 2 metals

Group 1 metals are most commonly used as reducing agents to generate the anionic α-diimine ligands. The reduction of α-diimines by the alkali metals Li, Na or K gives the monoanionic or dianionic form as metal complexes (or salts). A couple of alkali metal complexes have been structurally characterized, which generally act as intermediate reagents in the synthesis of organometallic compounds through metathesis with other metals. The lithium complexes of both radical monoanionic and dianionic **dad** ligands (complexes **1** and **2**; Fig. 1) are known.[28-30]

The Yang group synthesized a series of sodium complexes with the doubly reduced, enediamido ligands by reduction of the neutral ligands with Na metal.[31] In the dimeric complexes **3**–**5**, the two Na^+ ions bonding to a same **dad**$^{2-}$ ligand show different coordination modes {μ-(σ^2)(σ^2,π)}, *i.e.* one of them is chelated by the two N donors (σ^2-), while the other is bonded by the N−C=C−N moiety (σ^2,π-) of the same ligand (and solvent molecules), the latter of which deviates significantly from the ligand plane. When the non-coordinating solvent toluene was used, a polymeric compound (**6**) was obtained, in which the Na^+ ions are not solvated but interact with aryl rings and bridge two ligands to form an infinite structure (Fig. 1). In these sodium complexes, the C_2N_2 moiety displays obvious “long-short-long” enediamido character (C–N bond lengths are in the range 1.402~1.430 Å and C–C bonds in the range 1.356~1.366 Å).



1 Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

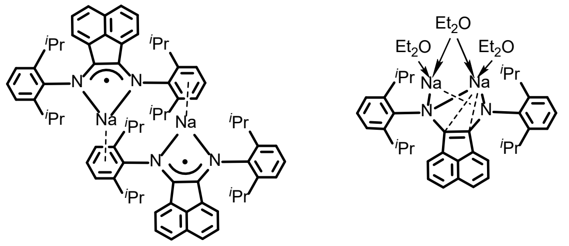
2

3 R^1 = ^{i}Pr, R^2 = H, Solv = Et_2O
4 R_1 = R_2 = Me, Solv = $(Et_2O)_2$
5 R^1 = R_2 = Me, Solv = $(thf)_2$

6

Fig. 1 Alkali metal complexes of mono- and dianionic **dad** ligands.

As a sub-group of α-diimines, bis(imino)acenaphthene (**bian**) derivatives have been well studied because of the applications of their complexes in catalysis.[4,5,32-34] These ligands combine both the α-diimine and robust naphthalene π systems in a single conjugated system, thus exhibiting specific redox properties.[35] In 2003, Fedushkin *et al*. reported that the dpp-substituted ligand 1,2-bis[(2,6-diisopropylphenyl)imino] acenaphthene (dpp-**bian**) can accept up to four electrons in a step-by-step reduction by Na metal, forming the mono-, di-, tri-, and tetra-anions (complexes **7**–**10**), where the first two electrons are placed on the α-diimine backbone (to yield **7** and **8**; Fig. 2), while the other two electrons are mainly delocalized over the naphthalene part.[36] The Fedushkin group has extensively studied the complexes of this ligand with main group and lanthanide metals, some of which will be discussed later in this review.



7 **8**

Fig. 2 Sodium complexes of mono- and dianionic dpp-**bian** ligand.

The chemistry of group 2 complexes with α-diimine ligands has been well developed. These alkaline earth metal complexes can be obtained either by salt metathesis of the above alkali metal complexes with MgX_2 (M = Mg, Ca, Sr, Ba), or by direct reduction of the neutral **dad** ligands with alkaline earth metals. A series of magnesium complexes bearing either monoanionic or dianionic **dad** ligands, including $[L^{2-}Mg^{II}(thf)_n]$ (**11**, **12**), $[Mg^{II}(L^{\bullet-})_2]$ (**13**, **14**), and $[K]_2[Mg^{II}(L^{2-})_2]$ (**15**) (Fig. 3), have been synthesized through the reduction of **dad** ligands by K metal followed by reaction with $MgCl_2$. Notably, the complexes $[Mg^{II}(L^{\bullet-})_2]$ display typical diradical character as proved by EPR spectroscopy, and the C–C (L^{iPr}, 1.403(5) Å; L^{Mes},

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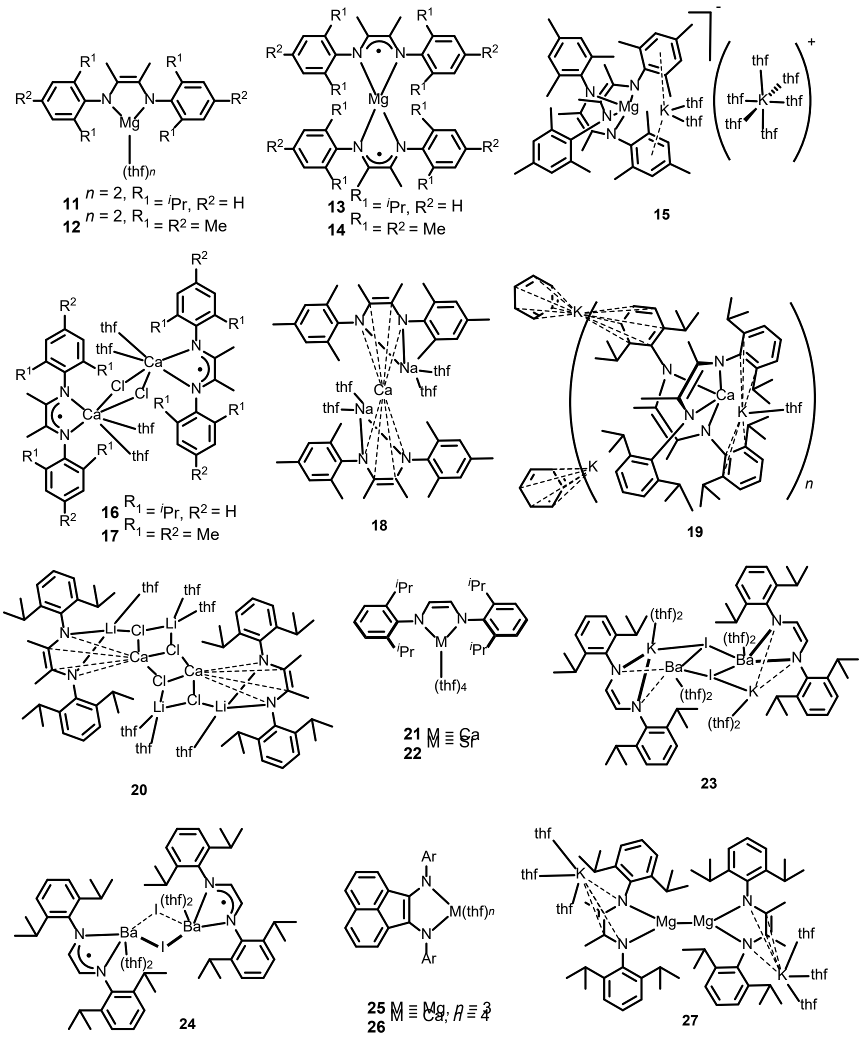


Fig. 3 Alkaline earth metal complexes of mono- and dianionic **dad** and **bian** ligands.

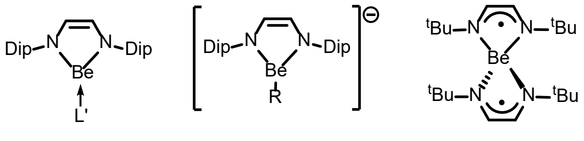
1.460(3) Å) and C–N (L^{iPr}, 1.358(4), 1.367(4) Å; L^{Mes}, 1.344(3), 1.342(3) Å) bond lengths of the α-diimine backbone are consistent with averaged single and double bonds of the radical monoanionic ligands.[37] Similarly, calcium complexes **16**–**20** have also been obtained from the reduced ligands (by Li, Na, or K) and $CaCl_2$,[38] while analogous complexes **21**–**24** of heavier group 2 congeners have been accessed by both salt metathesis and direct metalation of different **dad** ligands with metallic Ca, Sr, and Ba.[39] These complexes display mono- or binuclear structures with two reduced forms of the **dad** ligands, and (solvated) alkali metal ions are frequently incorporated to balance the charge.

Alkaline earth metal complexes of the **bian** ligands have also been studied by the Fedushkin group. Reaction of the neutral ligands with the corresponding metals afforded the mononuclear Mg(II) and Ca(II) complexes with the dianionic ligand, $[L^{2-}M(thf)_n]$ (**25**, **26**; Fig. 3),[40] in which the Mg or Ca centre is coordinated by one σ-*N*,*N′* ligand and solvent (thf) molecules. These complexes exhibit versatile reactivities towards a series of substrates, which will be presented later.

Although the oxidation state of alkaline earth metals in their complexes and reagents is dominated by +2, as has been found in above complexes with **dad** ligands, the synthesis of the first stable molecular Mg(I) compounds containing an Mg–Mg bond ligated by β-diketiminate or guanidinate ligands[41] has expanded this chemistry to the subvalent Ae(I) (Ae = alkaline earth metals) species. Yang *et al*. reported that the dpp-substituted enediamido ligand can also effectively stabilize the Mg–Mg bond.[42] The centrosymmetric dimer $[K(thf)_3]_2[L^{2-}Mg^{I}-Mg^{I}L^{2-}]$ (**27**, Fig. 3) was prepared by a one-pot reduction of the ligand dpp-**dad** and $MgCl_2$ with excess potassium metal in tetrahydrofuran, in which the initial Mg^{II} ion is reduced to Mg^{I}, while the neutral ligand is reduced to the dianion L^{2-}. The compound is air- and moisture-sensitive but thermally stable in solution and the solid state. Following these examples, a few more Mg–Mg-bonded compounds have been synthesized by using other *N*,*N'*-donor ligands.[43-47] Computations revealed that in these Mg^{I} species, the metal–metal bond is formed mainly by the 3s orbitals of magnesium. These species display excellent reactivity and some of their reactions will be discussed in this article (*vide infra*).

Inspired by these results, attempts have been made to synthesize metal–metal-bonded species of other group 2 metals by using different types of ligands. However, up to now, no analogous dimetallic compounds with a metal–metal bond could be isolated other than for Mg, although theoretical calculations predict that some of these low-valent alkaline metal compounds should be stable.[48, 49] In the case of α-diimine ligands, computations also indicated that the [LMML] dimer (M = Be to Ba) can be stabilized by the dianionic **dad** ligand,[50] but attempts to synthesize the possible dimeric calcium(I) compound yielded the Ca(II) complexes (**16**–**20**) as mentioned above.

Very recently, a series of beryllium complexes with **dad** derivatives, namely the Lewis base adducts $[L^{2-}BeL']$ (L' = Lewis base, **28**), the alkyl complexes $[L^{2-}BeR]^{-}$ (R = alkyl, **29**) as well as a diradical complex $[Be(L^{\bullet-})_2]$ (**30**) have been synthesized (Fig. 4).[51] In all cases, the formal oxidation state of Be is +2, while efforts to obtain the subvalent $Be^{I}-Be^{I}$-bonded species have been unsuccessful. Notably, recent studies have resulted in a few low-valent alkaline earth species, such as novel Be(0),[51-53] Ca(I),[54, 55] and Mg(0)[56] complexes.



28 **29** **30**

L' = Lewis base, R = alkyl, Dip = 2,6-diisopropylphenyl

Fig. 4 Beryllium complexes with mono- and dianionic **dad** derivatives.

3.2. Complexes of group 12 metals (Zn)

Having the $3d^{10}4s^2$ valence electron configuration, zinc displays very similar coordination properties to group 2 metals. In recent years, one of the most important findings in zinc chemistry is perhaps the synthesis of the first Zn–Zn-bonded compound Cp*Zn–ZnCp* (Zn–Zn: 2.305(3) Å) in 2004,[57] which was followed by a number of dimeric zinc(I) species ligated by a wide variety of ligands, including α-diimines **dad** and **bian**, thus indicating that the Zn–Zn bond has greater tolerance of the supporting ligands than does the Mg–Mg bond. The structure, bonding, and reactivities of such species have been thoroughly studied.[58-60]

The dpp-**dad** stabilized Zn–Zn-bonded compounds $[M(thf)_2]_2[L^{2-}Zn^{I}-Zn^{I}L^{2-}]$ (**31**, M = Na, Zn–Zn: 2.393(1) Å; **32**, M = K, Zn–Zn: 2.399(1) Å) were synthesized by Yang *et al*. via the reduction of the dihalide L^0ZnCl_2 by Na or K metal.[61, 62] Indeed, the synthesis and structure of the aforementioned Mg–Mg-bonded compound **27** [44] greatly resembles those of the Zn–Zn analogues, except that the former is prepared from a one-pot reaction of $MgCl_2$, L, and alkali metal (K), while in the latter case, the $LZnCl_2$ precursor was isolated first and then reduced by Na or K. In both cases, the initial divalent metal ion is reduced to the subvalent M(I), while the neutral ligand is doubly reduced to the dianion. The structures of the two compounds are centrosymmetric, with M(I) centres being three-coordinated by the N donors of the ligand and another M atom. Interestingly, there are two solvated alkali metal ions, which reside over the central N–C=C–N ligand backbone and interact with the moiety in η^4-C_2N_2 fashion. Such an “alkali metal capped” feature is found to be characteristic for the enediamido ligands as required for charge balance. On the other hand, it may provide additional stabilization for the molecule from both an electronic and a steric viewpoint.

The effects of substituents of the **dad** ligand on the formation of Zn–Zn bond have been further explored by the Yang group. It has been found that 2,6-diisopropylphenyl (dpp) groups are essential for the stabilization of the low-valent complex, as other substituents such as mesityl or 2,6-diethyl- or 2,6-dimethylphenyl led to mononuclear Zn^{II} complexes (**33**–**36**; Fig. 5) rather than the dimeric Zn^{I} species.[63] Moreover, attempts to synthesize the Zn–Zn bond bearing the radical monoanion of the **dad** ligand starting from the L^0ZnCl_2 precursor have proven to be unsuccessful (complex **37**) despite attempts employing various amounts of the reducing agent (Na or K). Notably, complex **37** contains a ligand with a central C_2N_2 core in the *trans* conformation, acting as a μ-σ^1,σ^1 bridge between two zinc atoms (Scheme 2). Instead, through first reduction of the ligand to the dianion and then metathesis with $ZnCl_2$, the desired overall neutral compound $[L^{\bullet-}Zn-ZnL^{\bullet-}]$ (**38**) was eventually obtained, in which the ligand non-innocence played a key role, as the initial dianionic ligand acted as the electron donor to reduce the Zn^{II} to Zn^{I}.

A similar Zn–Zn-bonded compound with the radical anionic **bian** ligand, $[(dpp\text{-}\mathbf{bian})^{\bullet-}Zn-Zn(dpp\text{-}\mathbf{bian})^{\bullet-}]$ (**39**, Fig. 5), has been synthesized by Fedushkin *et al*. either from the reductive salt elimination of (dpp-**bian**)ZnI or by reaction of the reduced dianionic ligand with $ZnCl_2$.[64] The Zn–Zn bond length (2.3321(2) Å) is comparable to that of the **dad** analogue

(2.340(2) Å). However, the dianion-ligated dizinc(I) species was not reported, nor the Mg–Mg bond with either monoanionic or dianionic **bian** ligands. These results suggest that there are both similarities and differences between the **dad** and **bian** ligands, which are clearly reflected in the reactivity studies (*vide infra*).

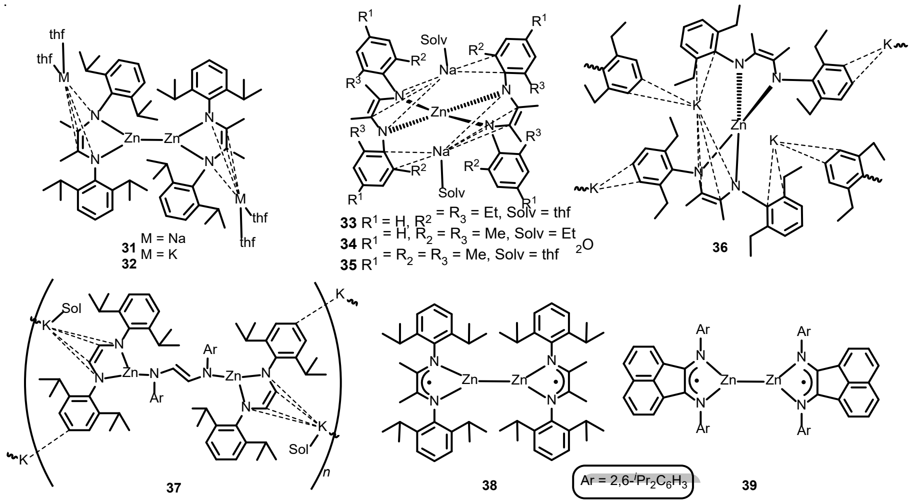


Fig. 5 Zinc(II) and -(I) complexes with mono- and dianionic **dad** and **bian** derivatives.

3.3. Complexes of group 13 metals (Al, Ga, In)

Organoaluminium compounds are widely used in organic synthesis and catalytic reactions. Over the past couple of decades, a number of low-valent group 13 metal complexes have been synthesized, such as the metal–metal-bonded species, dialumane and digallane, with Al^{II} and Ga^{II} centres respectively, and the N-heterocyclic carbene (NHC) analogues with formal Al^{I} and Ga^{I} heterocycles.[65-67] These compounds are ligated by Cp derivatives,[68] β-diketiminate (nacnac),[69] alkyls and silyls,[70,71] and α-diimines, etc. Such low-valent species display novel bonding and reactivities and have been extensively studied. In this section, the complexes of low-valent group 13 metals Al and Ga with reduced **dad** and **bian** ligands are summarized, while their reactivity will be described later in Part 4.

The development of aluminium and gallium complexes bearing **dad** or **bian** ligands largely parallels each other. In both cases, the Al–Al-bonded dialumane species have been prepared. The centrosymmetric dimer $[L^{2-}(thf)Al^{II}–Al^{II}(thf)L^{2-}]$ (L = dpp-**dad**, **40**, Al–Al bond length: 2.658(2) Å; Fig. 6) is the product of the reduction of the mixture $[Na_2L]$ (prepared *in situ*) and $AlCl_3$ by sodium metal in thf.[72] The Al atom is fourfold coordinated with the two N donors of a **dad** ligand, one thf molecule and the other Al atom.

In the case of dpp-**bian**, direct metalation of the neutral ligand with aluminium metal in the presence of $AlCl_3$ or AlI_3 in toluene or diethyl ether afforded the di- and mono-halide complexes [(dpp-**bian**)$^{\bullet-}Al^{III}Cl_2$] (**41**) and [(dpp-**bian**)$^{2-}Al^{III}X(OEt_2)$] ($X = Cl^-$, I^-) (**42**, **43**), respectively, bearing the radical anionic ($L^{\bullet-}$) or dianionic (L^{2-}) ligand, as reflected by the bond lengths within the C_2N_2 moiety.[73] On the other hand, a one-pot synthesis using dpp-**bian**, $AlCl_3$ and sodium (in 1:1:3 molar ratio) in toluene yielded the dialumane complex [(dpp-**bian**)$^{2-}Al^{II}–Al^{II}$(dpp-**bian**)$^{2-}$] (**44**) (Fig. 6).[74] The two dialumanes **40** and **44** show similar structures with Al^{II} centres and L^{2-} ligands, except that the **dad** analogue has one thf molecule coordinating to each Al centre.

Notably, further reduced carbene-like Al^{I} species $[LAl:]^-$ have not yet been isolated for either **dad** or **bian** ligands. In contrast, a couple of either neutral (e.g. NacnacAl: with the β-diketiminate[69] and ArAl: with terphenyl[75]) or anionic Al^{I} compounds have been reported and demonstrated good reactivities.[76-80] Nevertheless, the Ga^{I} analogues of both **dad** and **bian** derivatives have been isolated (see below). This may be due to the reason that the **dad** and **bian** Al^{I} species are too reactive to be captured, and transform further during the small molecule reactions as described later in this article.

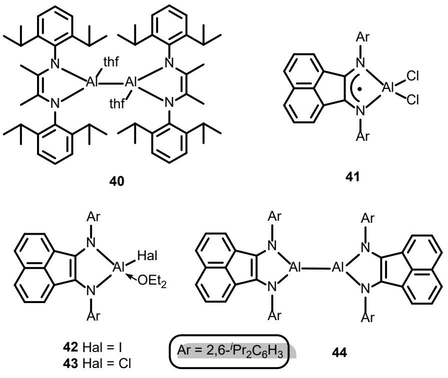


Fig. 6 Aluminium complexes including dialumanes (**40**, **44**).

Gallium complexes of α-diimine ligands have also been synthesized with the gallium centre in the formal oxidation states of +3, +2 and +1, with the ligands as both radical monoanion and dianion forms. Examples include the paramagnetic gallium(III) complex **45** that contains a dianion and a radical anion (to yield an overall neutral complex),[81] the diamagnetic gallium(II) complex **46**,[82] and the anionic gallium(I) heterocycle **47**.[83] Jones *et al*. synthesized the anionic Ga^I heterocycle and obtained the Zn–Ga-bond compounds **48** and **49** (Fig. 7) by reactions with two *N*,*N*-chelated zinc chloride complexes.[84] In these complexes, the $[LGa\text{:}]^-$ species can be viewed as a Lewis base donor that coordinates to the zinc(II) centre.

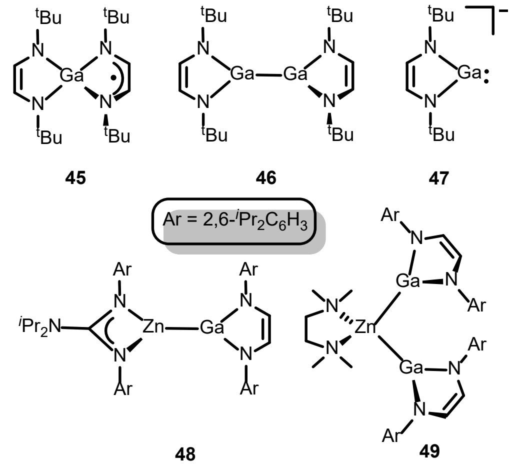


Fig. 7 Gallium(III), -(II) and -(I) complexes with mono- and dianionic **dad** derivatives.

Fedushkin *et al*. synthesized the homonuclear Ga–Ga-bonded [(dpp-**bian**)Ga–Ga(dpp-**bian**)] (**50**) and heteronuclear Ga–Zn-bonded [(dpp-**bian**)Zn–Ga(dpp-**bian**)] (**51**) compounds with the dpp-**bian** ligand. The former was obtained either by reaction of the trianionic ligand K_3(dpp-**bian**) with $GaCl_3$ at room temperature in Et_2O/thf,[85] or by direct reaction of the ligand with metallic gallium in toluene at reflux.[86] The latter [GaZn] compound was synthesized starting with the dimeric zinc iodide, [(dpp-**bian**)ZnI]$_2$, which was prepared from the neutral ligand with zinc metal and iodine (I_2), through reaction with $GaCl_3$ and the tetraanion K_4(dpp-**bian**).[85] In the digallium(II) compound, both ligands are in the dianionic form, while in the heteronuclear Zn–Ga species there is a radical anionic and a dianionic ligand present.

Moreover, the digallane **50** was further reduced by groups 1 and 2 metals, which afforded molecular compounds containing Ga–M bonds, [(dpp-**bian**)Ga–M(Solv)$_n$] (M = Li, Na, K; Solv = solvent molecules; **52**–**54**) and [(dpp-**bian**)Ga]$_2$–M'(Solv)$_n$ (M' = Mg, Ca, Sr, Ba; **55**–**58**) (Fig. 8).[44] The reduction generated the formal oxidation state of $Ga\text{:}^I$, which bonds to the alkali metal or alkaline earth metal ions through lone pair donation. Similarly, the digallane and carbene-like gallylene species of the analogous **dad** ligand have been reported by the Yang group (Fig. 9). The precursor $[(L)^{\bullet-}GaCl_2]$ (**59**), which contains a Ga^{III} centre and a radical-anionic ligand, was prepared by the reaction of anhydrous $GaCl_3$ with the monoanion [NaL] (in 1:1 ratio).[87] The digallane **60** was obtained from reduction of the dichloride precursor **59** by 2 equivalents of Na, which reduced the Ga^{III} centre to Ga^{II} and the ligand $L^{\bullet-}$ to L^{2-}.[88] Then, further reduction of the $[(L)^{\bullet-}GaCl_2]$ complex by 3 equivalents of alkali metal (Na, Li, K, and KC_8) afforded a series of Ga–M complexes **61**–**63**.[87] During the latter reaction process, the trivalent Ga^{III} was reduced to the monovalent Ga^I, while the radical anion of the α-diimine ligand acquired one electron to form the dianion. In these alkali metal adducts of the $[LGa\text{:}]^-$ moiety, Ga–M bonds are also formed by donation of the lone-pair electrons on Ga to the alkali metal ions.

Going down the group 13 elements to indium, related studies on its α-diimine complexes are much rarer. While both of the four- (with amidinate or guanidinate backbone) and six-membered (with β-diketiminate ligand) heterocycles of indium(I) are known, the (anionic) five-membered analogues (with α-diimine) are yet to be synthesized although they were theoretically predicted to be similar to their Al and Ga congeners.[65] Only a few examples of indium α-diimine halides have emerged recently, including investigations of the synthesis, optical and electrochemical properties of a series of indium(III) complexes (**64**–**68**) which consist of neutral Ar-**bian** ligands coordinating to indium(III) centre via dative bonds (Fig. 10).[27,89]

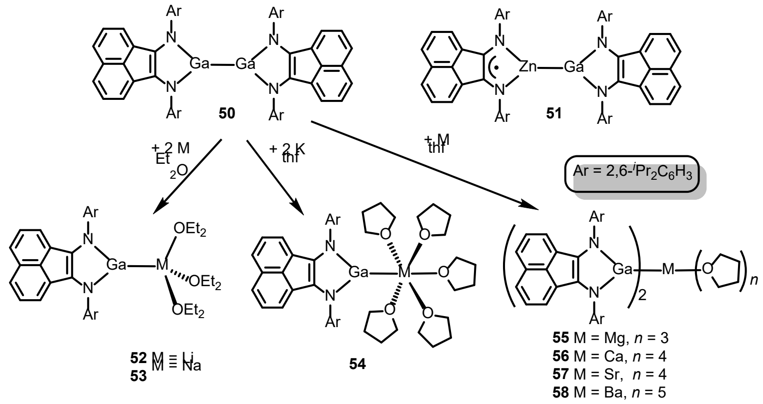
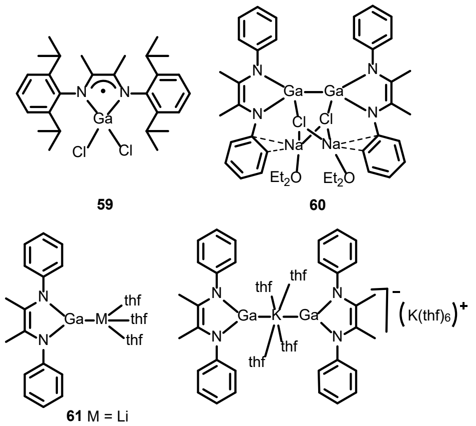


Fig. 8 Gallium(III), -(II) and -(I) complexes with dianionic dpp-**bian** ligand.

Zhang, R., Wang, Y., Zhao, Y., Redshaw, C., Fedushkin, I. L., Wu, B., & Yang, X. (2021). Main-group metal complexes of α-diimine ligands: structure, bonding and reactivity. Dalton transactions : an international journal of inorganic chemistry. Royal Society of Chemistry, https://doi.org/10.1039/d1dt02120f



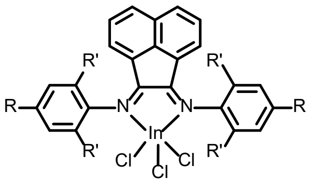
59

60

61 M = Li
62 M = Na

63

Fig. 9 Gallium(III), -(II) and -(I) complexes with mono- and dianionic dpp-**dad** ligand (the *i*Pr groups have been omitted in **60**–**63**).



64 R' = ^{i}Pr, R = H
65 R' = Me, R = H
66 R' = H, R = NO_2
67 R' = H, R = NMe_2
68 R' = H, R = OMe

Fig. 10 Indium(III) complexes with neutral **bian** derivatives.

3.4. Complexes of group 14 metals (Ge, Sn)

Heavier group 14 elements have been reported to form low-valent, metal–metal-bonded compounds (including multiple bonds) ligated by some ligands such as terphenyls.[16] However, the chemistry of α-diimines with these metals is dominated by the N-heterocyclic carbene (NHC) analogues, tetrylenes [LE:] (E = Ge, Sn, Pb), with a dianionic (enediamido) ligand and an E^{II} centre, which can form adducts with a variety of groups or fragments due to the presence of both lone-pair electrons and empty *p* orbitals.[12,65]

A series of germylenes (**69**–**73**) bearing **dad** ligands have been obtained by the reaction of $GeCl_2$ with lithium metal and **dad** ligands or with the lithium salt of the radical anionic ligand.[90-94] The corresponding **dad** stannylenes (**74**, **75**) were prepared by *trans* amination of the α-amino aldimines with $[Sn(N(SiMe_3)_2)_2]$.[95] Several N-heterocyclic germylenes with dianionic **bian** derivatives, [(Ar-**bian**)Ge:] (**76**–**78**, Fig. **11**) were prepared by firstly the reduction of the corresponding bian ligands with activated Mg to afford the Mg complexes (Ar-**bian**)Mg(thf)$_3$, followed by reaction with $GeCl_2$(1,4-dioxane). The complex [(dpp-**bian**)Ge:] can also be obtained by the reaction of $GeCl_4$ with [(dpp-**bian**)Na_4] in Et_2O.[96]

Fedushkin *et al.* also synthesized the three-coordinate, pyramidal complex [(dpp-**bian**)GeCl] (**79**) by the reaction of $GeCl_2$(1,4-dioxane) with either dpp-**bian** or the sodium salt of the radical anionic ligand.[97] Compounds **80** and **81** were the products of **79** with 2 or 3 equiv of HCl, which led to protonation of the ligand. The Ge–N bond lengths in **4** (2.0058(19) and 2.004(2) Å) indicate that the bonding between the Ge(II) cation and the (dpp-**bian**) radical anion is weaker than those to the dianionic ligand in **76** (1.896(3) and 1.885(3) Å).

Cowley *et al.* synthesized the Sn(IV) complexes [(dpp-**bian**)$SnCl_4$] (**82**) from the neutral dpp-**bian** ligand and $SnCl_4$, and [(mes-**bian**)$SnCl_4$] (**83**) from mes-**bian** and $SnCl_2$ (via an apparent Sn(II) to Sn(IV) process).[98,99] Contrary to this latter case, the reaction of dtb-**bian** with $SnCl_2$ yielded the Sn(II) complex [(dtb-**bian**)$SnCl_2$] (**84**).[100] These compounds display N→Sn donor-acceptor bonds and can be regarded as neutral α-diimine-ligated complexes.

3.5. Complexes of group 15 metals (As, Sb, Bi)

A few group 15 element complexes with **bian** ligands have been reported. The arsenium salt [(dpp-**bian**)As][$SnCl_5$•thf] (**85**) was synthesized from the reaction of $AsCl_3$ with $SnCl_2$ in thf and then treatment with dpp-**bian**.[101] In the complex, the arsenic is in the +3 oxidation state, whilst the AsN_2C_2 ring is planar. The C–N and As–N bond distances compare well to those in previously reported cyclic arsenium cations.[102]

The mononuclear antimony(III) compound [(dpp-**bian**)$SbCl_3$] (**86**) was isolated from the reaction of $SbCl_3$ with the dpp-**bian** ligand.[98] The Sb atom is penta-coordinated with a distorted square-pyramidal geometry, where the antimony-based lone pair is located at the equatorial position. Similarly, reactions of $BiCl_3$ with the corresponding Ar-**bian** ligands afforded the compounds [(dpp-**bian**)$BiCl_3$] (**87**) and [(mes-**bian**)$BiCl_3$] (**88**).[98] Different from **86**, complexes **87** and **88** are unsymmetrically μ$_2$-chloride-bridged dimers, with Bi–Cl distances of 2.6976(11) and 3.0488(18) Å. However, the reaction of dpp-**bian** or mes-**bian** with $AsCl_3$ was unsuccessful, which may be due to the weaker Lewis acidity of the arsenic(III) halides in comparison to their heavier congeners.

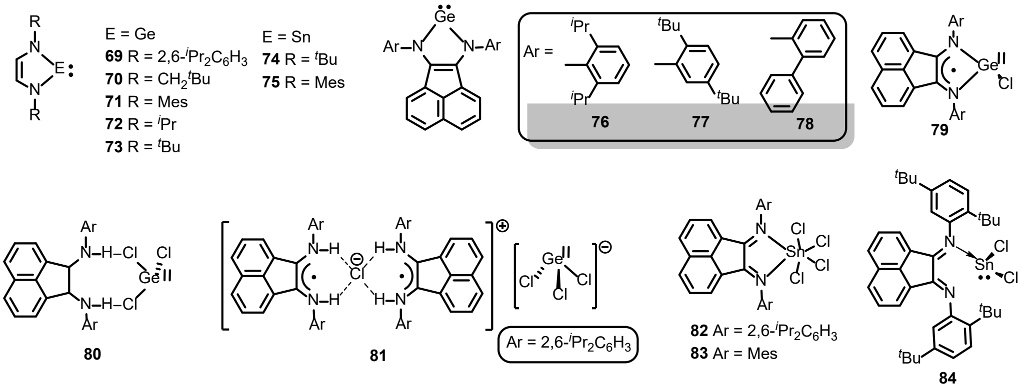


Fig. 11 Germanium and tin complexes with **dad** and **bian** ligands.

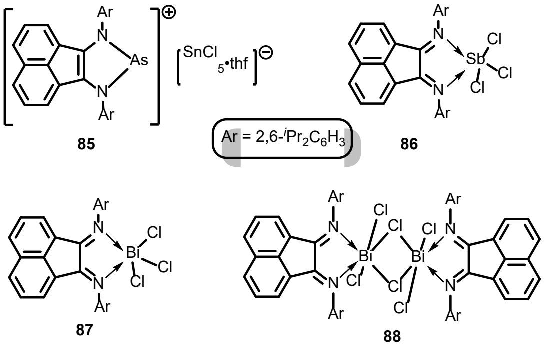


Fig. 12-Arsenic, antimony, and bismuth complexes with **dad** and **bian** ligands.

4. Reactivity of α-diimine-ligated complexes

Small molecules, which are ubiquitous in nature or are produced in industrial processes, are useful stock materials for further transformation into value-added products, in which the activation of chemical bonds is a necessary step. Traditionally, the activation and transformation of small molecules are mostly mediated by transition metals, but the use of main-group metals has increased in recent years because the heavier main-group elements can exhibit transition metal-like behaviour when forming suitable complexes.[16] For example, the low-valent main-group species, in particular metal–metal-bonded compounds, have been found to be able to activate a variety of inorganic and organic small molecules.[103, 104]

In this part, we will collect some representative examples of the studies on small molecule reactivity of selected main-group metal–metal-bonded compounds, with emphasis on the work of the Fedushkin and Yang groups on the reactivity of group 13 metal (Al and Ga) α-diimine complexes towards various small substrates. In addition, some related studies on small molecule activation properties of magnesium and zinc compounds with α-diimine ligands will be included.

For the metal–metal-bonded compounds, the activation of small molecule can occur cooperatively between the metal centers,[105] behaviour which is also observed in biological processes.[106] On the other hand, the non-innocent α-diimine ligands can endow their complexes with unique reactivities that cannot be realized without these ligands, because such ligands can actively participate in small molecule activation processes through several routes. Firstly, it has been proven that the reduced forms of the α-diimine ligands can support low-valent metal centres, thus evoking special reactivity of the metals. Secondly, they can act as electron reservoirs and participate in the electron transfer processes either alone or cooperatively with the metal centre. Thirdly, these ligands possess the ability to undergo transformations themselves or to bond with the substrates, thus providing a possible method to form new bonds. Therefore, the α-diimine-ligated metal–metal-bonded compounds have exhibited unusual reactivities.

As typical examples, the main-group metal complexes of **dad** and **bian** ligands (mostly in the enediamido form) display surprisingly diverse reactions with a wide variety of substrates. They can act as reducing agents and promote oxidative additions,[107] cycloaddition or reductive coupling of unsaturated molecules such as alkynes,[108-111] isocyanates,[112] isothiocyanates,[113] alkenes,[114] SO_2,[115] azabenzene derivatives,[72] nitriles and isocyanides,[42, 116] and so on.[117] Herein, some examples will be given and the non-innocent behaviour of the α-diimine ligands will be discussed.

4.1 Reactivity of magnesium complexes

Fedushkin *et al*. prepared the magnesium complex [(dpp-**bian**)Mg(thf)$_3$] (**25**)[40] by the reduction of dpp-**bian** with metallic magnesium in thf and studied the reactivity of this complex (Fig. 13). In the reactions with Ph_2CO, anthracenone,[118, 119] iodine,[119] and RS–SR,[120] the dianionic ligand provided one electron and became the radical-anionic form (in products **89**–**95**). When complex **25** was reacted with ethyl halides EtX (X = Cl, Br, I) in thf, oxidative addition occurred via a single-electron transfer process, wherein the ethyl group is bonded to the carbon atom of the ligand, and an X^- ion is coordinated to the magnesium atom (**96**–**98**).[121] Moreover, reactions with PhCCH, enolisable ketones,[118] and Ph_2CHCN [122] proceeded via protonation of the ligand at the basic nitrogen atom, leading to the transfer of protons to yield products **89**–**93**.

Yang *et al*. reported that the Mg–Mg bond compound **27** exhibits good reactivity toward a series of nitriles (Fig. 14).[42] Reaction of the Mg(I) dimer with 2.0 equiv. of Me_3SiCN proceeded through reductive Si–C(CN) bond cleavage to generate the cyanide ion (CN^-), which acts as a bridge to link the tetrameric complex **104**. When increasing the molar amount of Me_3SiCN or *t*BuCN to 3 equivalents, both Si–C (or C–C) bond cleavage and terminal coordination of the nitriles occurred, leading to the tetramers **105** and **106**. Moreover, the Mg(I) compound can promote the reductive deprotonation of the α-H (through release of H_2) of isobutyronitrile (*i*PrCN) or cyclohexyl nitrile (CyCN) to form the dinuclear products (**107**, **108**) with two bridging ketimine (R'C=C=N) ligands. In these reactions, the Mg(I) centres act as electron donors and are oxidized to Mg(II), while the **dad** ligand remains in the dianionic form during the reaction processes.

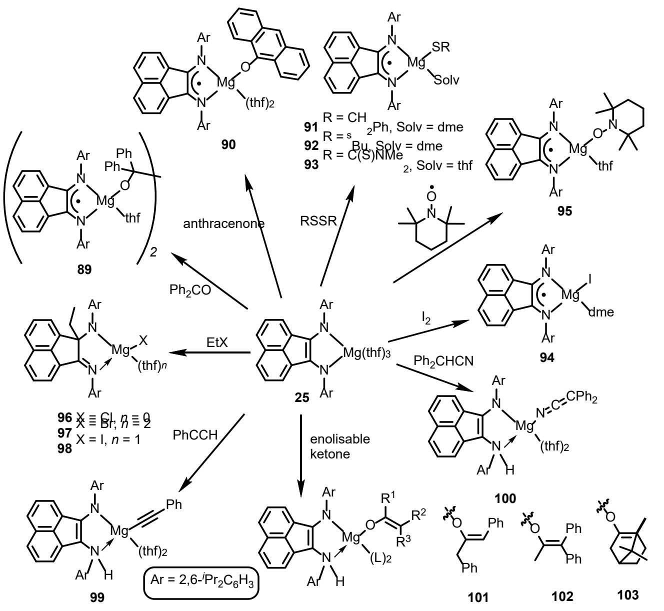


Fig. 13 Reactions of [(dpp-**bian**)Mg(thf)$_3$] (**25**) with various organic molecules.

4.2 Reactivity of zinc complexes

In addition to the Zn–Zn-bonded species **31** and **32** of the dianionic ligand (L^{2-}) and **38** of the radical monoanion ($L^{\bullet-}$), Yang *et al*. reported three related Zn(I) compounds **109**–**111**, in which the initially η^4(C_2N_2)-bonded alkali metal ions (Na^+ or K^+) are captured by crown ethers (Fig. 15).[123] Removal of the alkali metal ions from the ligand central backbone results in elongated Zn–Zn bonds. Then, the reactions of all the three types of Zn–Zn-bonded compounds with phenylacetylene (PhCCH) were carried out, which proceeded through different redox processes and gave three types of alkynylzinc products.

For the monoanion-ligated precursor [$L^{\bullet-}$Zn–Zn$L^{\bullet-}$] (**38**), reactions with different amounts of alkyne afforded two products, the bis(alkynyl)-bridged dinuclear complex [$L^{\bullet-}$Zn(μ-CCPh)$_2$Zn$L^{\bullet-}$] (**112**) and the mononuclear complex [L^0Zn(CCPh)$_2$] (**113**). In both cases, the Zn(I) centres are oxidized to Zn(II), while the initial radical monoanionic ligands either remain intact (in **112**) or, rather surprisingly, are oxidized to the neutral form L^0 (in **113**). In the latter case, both of the Zn(I) centres and the monoanionic ligands participate in the reductive dehydrogenation of phenylacetylene (to form H_2), leading to the simultaneous activation (deprotonation) of 4 equivalents of alkyne molecules.

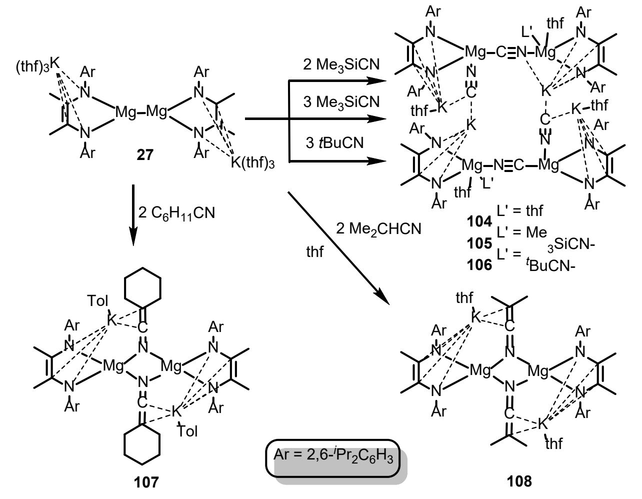


Fig. 14 Reactions of Mg–Mg bonded compound **27** with nitriles.

On the other hand, the (15-crown-5)-containing **110** also reacted with phenylacetylene through a disproportionation of the Zn^{2+} units to give the homoleptic tetraphenylethynyl zincate **114**, in which the **dad** ligands are dissociated as the free neutral form and the Zn(II) centre is coordinated solely by (four) alkynyl anions (Fig. 15). Also, the **bian** analogue **115** has been isolated from the reaction of [(dpp-**bian**)$^{\bullet-}$Zn–Zn(dpp-**bian**)$^{\bullet-}$] (**39**) with PhCCH.[124] In these reactions, different redox processes are observed, in which the non-innocent **dad** ligand plays important roles in receiving or donating electrons.

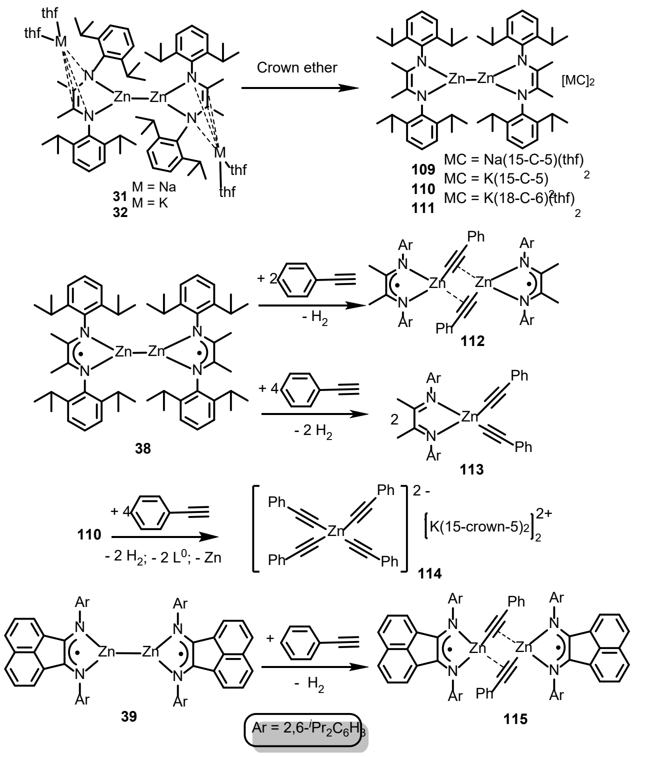


Fig. 15 Reactions of Zn–Zn-bonded compounds with various substrates.

4.3 Reactivity of aluminium and gallium complexes

The low-valent complexes of aluminium and gallium in the formal oxidation states of +2 and +1 display very rich reactivities toward inorganic and organic small molecules. In this section, the recent progress in the reactions of dialumanes (Al^{II}) and digallanes (Ga^{II}) bearing **dad** and **bian** ligands, respectively, as well as of the corresponding Al^{I} and Ga^{I} species, with various substrates will be summarized.

The dialumane of dpp-**dad**, [L(thf)Al–Al(thf)L] (**40**), which contains dianionic ligands and Al(II) ions, has been shown to be an excellent electron donor that is capable of providing multiple electrons to substrates. A good example of metal-ligand cooperative reduction of small molecules is the reaction of **40** with azobenzene derivatives to give bis(imido)-bridged dinuclear complexes **116**–**118** (Fig. 16). During the reaction, the dialumane behaves as a four-electron reductant, leading to complete reductive cleavage of the N=N double bond, while the initially dianionic ligands are oxidized into monoanions and the Al(II) centers to Al(III). Notably, when the asymmetric azobenzenes (4-methoxyazobenzene and 4-dimethylaminoazobenzene) were used, asymmetric products were obtained, thus proving the cooperation of the metal–metal bond in the reaction process. Overall, all components, the two metal centres and two ligands, simultaneously participated in the reactions, resulting in the multi-electron transfer products.

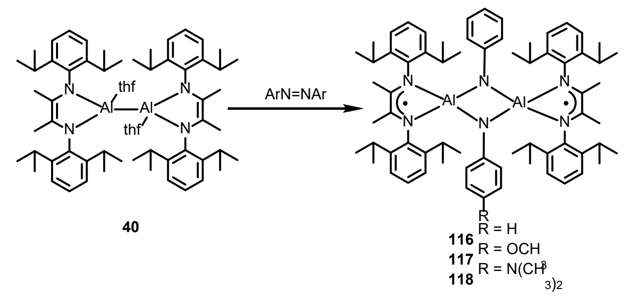


Fig. 16 Reactions of dialumane **40** with azobenzene derivatives to afford the bis(imido)-bridged products.

Another characteristic metal-ligand cooperation in such systems is exemplified by the cycloaddition reactions of the α-diimine-ligated Ga(II) and Al(II) species with a variety of unsaturated bonds, such as alkynes (C≡C) and cumulated C=C and C=E bonds (*vide infra*).

In 2010, Fedushkin *et al*. reported the reversible cycloaddition of alkynes to the Ga–N–C fragments of the digallane [(dpp-bian)Ga–Ga(dpp-bian)] (**50**).[109] The triple bond of an alkyne can add to each metal–ligand moiety by forming both carbon–carbon and carbon–gallium bonds at room temperature, while at elevated temperatures the alkyne molecules can dissociate (Fig. 17). In the cycloaddition products (**119**–**122**) of different alkyne substrates, regio-selectivity was observed in that a bulkier substituent at the triple C≡C bond (e.g. Ph group) is oriented away from the metal, but the smaller ester group is oriented toward the metal.

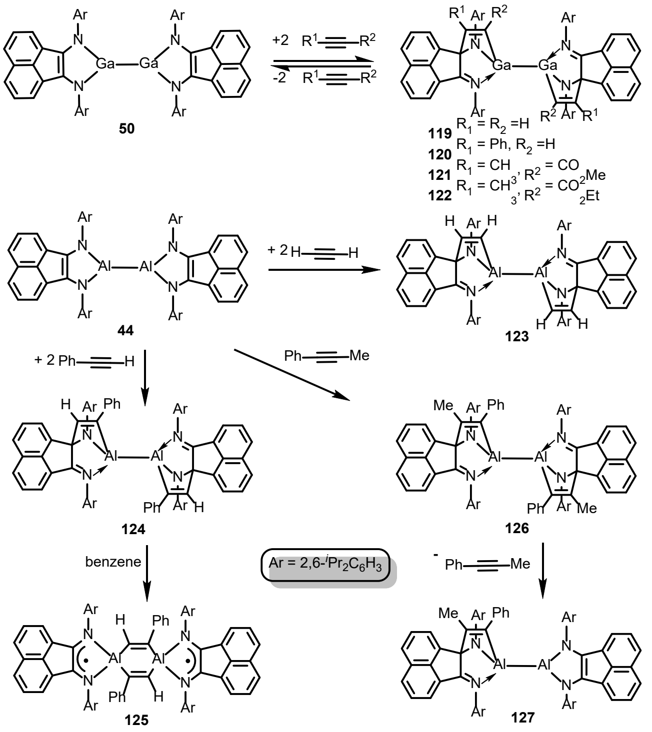


Fig. 17 Cycloaddition of alkynes to the metal-ligand moieties in digallane (**50**) and dialumane (**44**) of dpp-bian ligand.

In 2012, the same group reported analogous cycloadditions of alkynes to the dialumane [(dpp-bian)Al–Al(dpp-bian)] (**44**) to give the products **123**–**127** (Fig. 17).[74] In contrast to the digallane species, the dialumane is reactive also toward the internal alkyne MeCCPh, where one or two alkynes can add to the Al–N–C moieties of dialumane. Notably, the cyclo-adduct of phenylacetylene can undergo rearrangement at elevated temperatures to form a bis alken-1,2-diyl-bridged dinuclear complex **125** upon Al–Al bond cleavage and transformation of the ligand to the radical-anionic form.

The reactivity of the **dad** dialumane [L(thf)Al–Al(thf)L] (**40**) toward alkynes has also been explored by Yang *et al.* (Fig. 18).[111] It is noted that this dialumane exhibits different reaction types from the **bian** analogue. Although **40** is also active to internal alkynes, the reaction with diphenylacetylene affords a unique dinuclear product **128**, wherein the C≡C triple bond inserts into the Al–Al bond, resulting in the cleavage of Al^{II}–Al^{II} with accompanying electron transfer from metal to substrate to form Al^{III} and reduction of the alkyne to a dianion (while the dianionic ligands remain unchanged). However, with phenylacetylene (or 4-ethynyltoluene) the cycloaddition of the alkyne to the AlN_2C_2 ring, as in the above cases, has occurred, yielding the bis(bicyclic) products **129** and **130** where the Al^{II}–Al^{II} core is retained. Thus, it is clearly seen that the dialumane **40** can behave as a multicentre electron donor, in which different redox centres (L^{2-} or Al^{II}) can be involved in the electron transfer processes. On the other hand, the Ga^{II} species of **dad** does not react with alkynes, which is also different from the **bian** analogue.

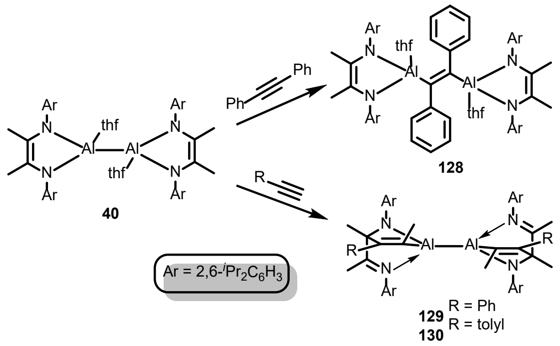


Fig. 18 Insertion or cycloaddition of alkynes to the Al–Al bond or metal-ligand moieties in dialumane (**40**).

The reactions of dialumane **40** with alkenes (C=C double bond) have also been studied,[114] which represent the first examples of reactions of an Al–Al bonded compound with alkenes (Fig. 19). The insertion of styrene or stilbene into the Al–Al bond occurs upon electron transfer from Al(II) to the alkene similar to the case of diphenylacetylene insertion, yielding two Al(III) centres bridged by the reduced alkene (**131**, **132**). In comparison, in the presence of metallic sodium, the reactions of **40** with butadienes yielded aluminium cyclopentenes as [1+4] cycloaddition products **133**, **134**, as well as the [2+4] cycloaddition product **135**. In these two reactions, it is proposed that the dialumane was actually reduced to the Al(I) species, as either the dinuclear "dialumene" $[Al{=}Al]^{2-}$ or the mononuclear carbene analogue $[LAl{:}]^{-}$ by the Na metal, as demonstrated by theoretical calculations, although these two species have not yet been isolated. In the products, the diene exists as the enediyl form, while the aluminium displays the formal oxidation state of +3.

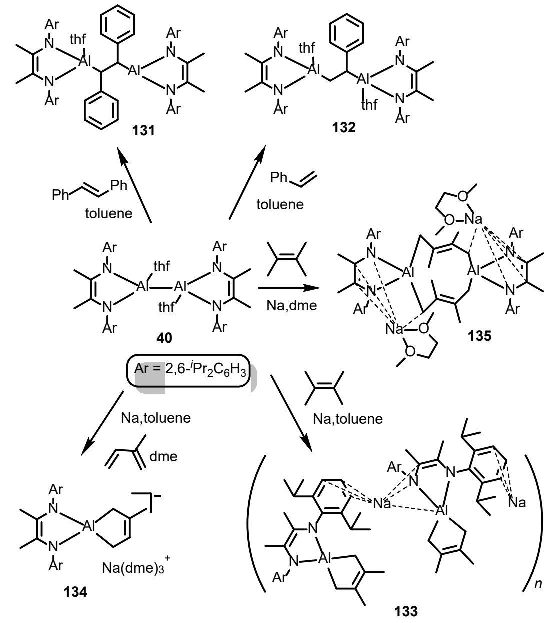


Fig. 19 Reactions of 40 with alkenes to afford insertion or cycloaddition products.

Fedushkin *et al*. studied the reactions of bian-ligated digallane **50** with various substrates, such as acenaphthene-quinone (AcQ), sulfur dioxide, and azobenzene,[115] which yielded the products **136**–**140** (Fig. 20). Owing to the existence of two types of redox-active centres in the molecule, either metal- or ligand-centred (or both) redox processes may occur, leading to diverse reactivities. For example, reactions with different equivalents of AcQ and SO_2 undergo different redox processes. First, with 1 equiv. of AcQ, the dianionic ligands donate electrons and become monoanionic, while the Ga^{II} centres and Ga–Ga bond remain intact (in **136**). However, with increasing amounts of substrate (2 equiv.), the Ga^{II} centres begin to participate in the electron transfer, resulting in metal–metal bond cleavage to give Ga^{III} (**137**). Similarly, in the reactions with sulfur dioxide, addition of 2 or 4 equiv. of the substrate gives different products (**138** and **139**) in which only the ligand or cooperative metal-ligand are involved, respectively, in the reduction process. In the case of azobenzene (**140**), both metal and ligand redox centres are involved in the four-electron reductive cleavage of N=N double bond as in the case of **dad** dialumane.[118]

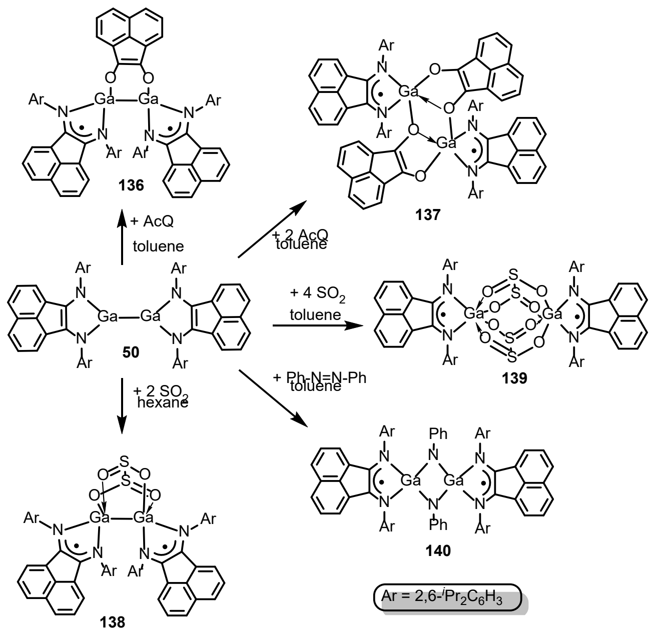


Fig. 20 Reactions of digallane **50** with various substrates.

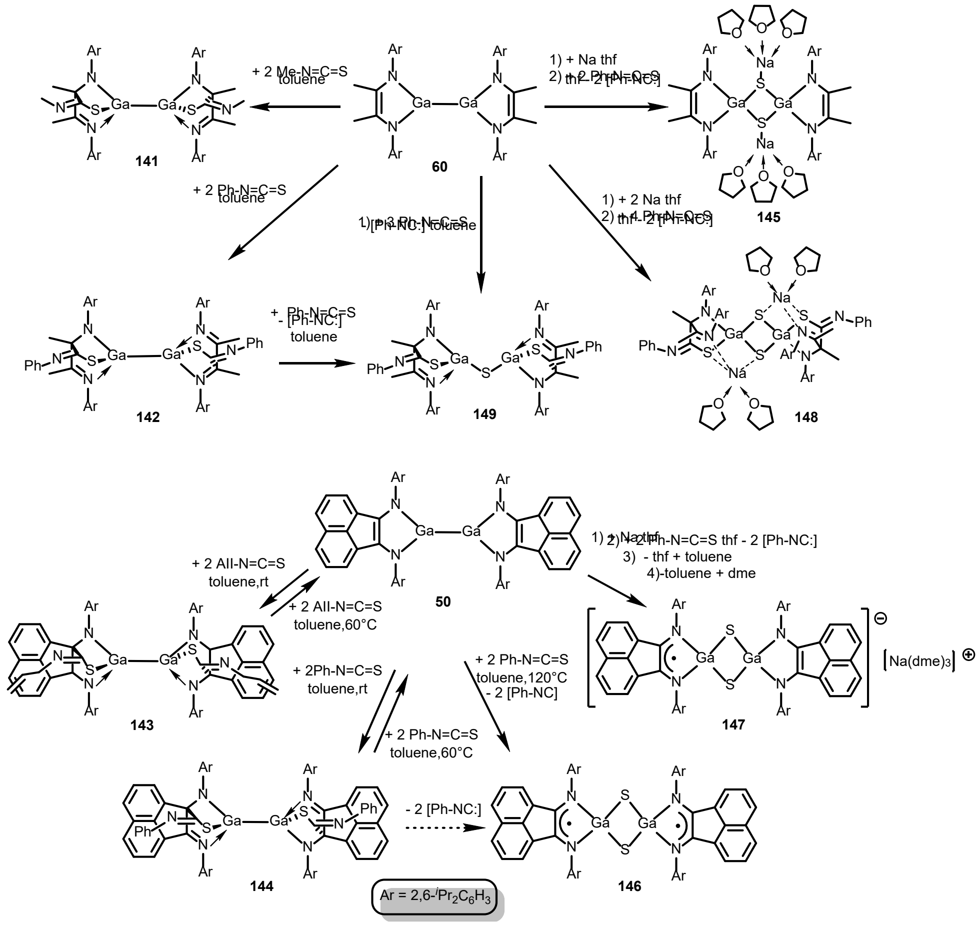


Fig. 21 Reactions of digallanes **60** and **50** with isothiocyanates.

The Yang and Fedushkin groups further studied the redox activity and reactions of both low-valent gallium and aluminium compounds (in the oxidation states of +2 and +1) towards a wide variety of small molecules, including isothiocyanates,[113] isocyanates,[112] carbodiimides,[125, 126] nitriles,[115] isocyanides,[116] and some nitrogen-rich compounds (organic azides, azo, diazo-compounds),[127] where many reaction pathways have been observed, yielding novel products. Both similarities and differences between the **dad**- and **bian**-ligated complexes are observed and discussed.

Herein, we only discuss the reactions of **dad** and **bian** digallanes with isothiocyanates as an example to demonstrate the rich reaction pathways possible (Fig. 21). Three types of reactions are observed for the reactions of the digallanes with isothiocyanates, including: (i) [2+4] cycloaddition with retention of the Ga−Ga bond (**141**−**144**), in which the C=S double bond of RN=C=S adds to the metal-ligand moiety (as in the case of alkyne cycloaddition), forming both Ga−S and new C−C bonds. Notably, this reaction is reversible for the bian-ligated digallane but not for the dad analogue, thus demonstrating the difference of the two systems with different ligands; (ii) complete cleavage of the C=S bond in the presence of Na metal, yielding the disulfide-bridged dinuclear compounds (**145**−**147**); and (iii) both cycloaddition and reductive cleavage of the C=S bond can occur (products **148** and **149**). These compounds are the first examples of the cycloaddition of isothiocyanates to the dianionic α-diimine ligands. In some of the reactions, the ligands are found to be active, transferring electrons to the substrate together with metals. For example, in the formation of the disulfide product **146**, both of the Ga(II) ions and dianionic ligand behave as electron donors, leading to the reductive cleavage of the C=S double bond to yield S^{2-} ions that bridge the two Ga(III) centres, while the bian ligand is oxidized to the monoanion.

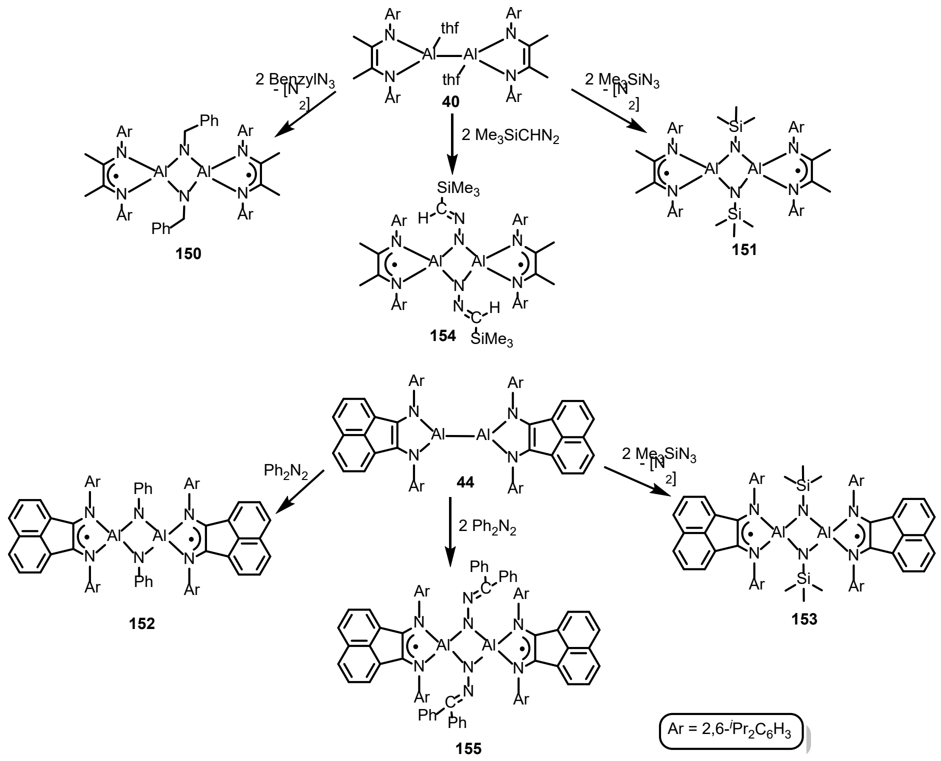


Fig. 22 Activation of nitrogen-rich substrates by dialumanes **40** and **44**.

Moreover, the two dialumanes (**40** and **44**) have been shown to be able to activate different kinds of nitrogen-rich substrates (Fig. 22), yielding the diimido-bridged dinuclear complexes (**150**–**153**) through bond cleavage of azides or azobenzene.[127] They can also doubly reduce the diazomethane derivatives to form the terminal N-bridged complexes **154** and **155**. In all these cases, the dialumanes act as four-electron donors through the cooperation of metal and ligand, leading to either N=N double bond cleavage or reduction of the substrates, while the metal and ligand are oxidized from Al(II) to Al(III) and L^{2-} to the radical anion $L^{\bullet-}$, respectively.

The **dad** ligated dialumane **40** was found to exhibit novel reactivity toward isocyanides, and both linear- and cyclo-trimerization of *tert*-butylisocyanide has been observed (**156**–**159**, Fig. 23), wherein the latter resulted in a unique three-membered ring system, namely the aromatic tris(*tert*-butylimino)deltate dianion **159**.[116] Moreover, **40** can effectively activate pyridines, resulting in an organometallic metallo-macrocycle (**161**) with six Al atoms bridged by six pyridine-4-yl carbanions formed by the reductive dehydrogenation of pyridine (Fig. 24).[128]

These studies clearly demonstrate the excellent ability of the complexes with α-diimine ligands (mostly in the reduced dianionic or monoanionic form) and low-valent metal centres to activate a wide variety of small molecules. In many cases, the redox non-innocent ligand actively participates in the reaction process, playing an important role in the transformation of the substrates and endowing the metal complex with specific reactivity.

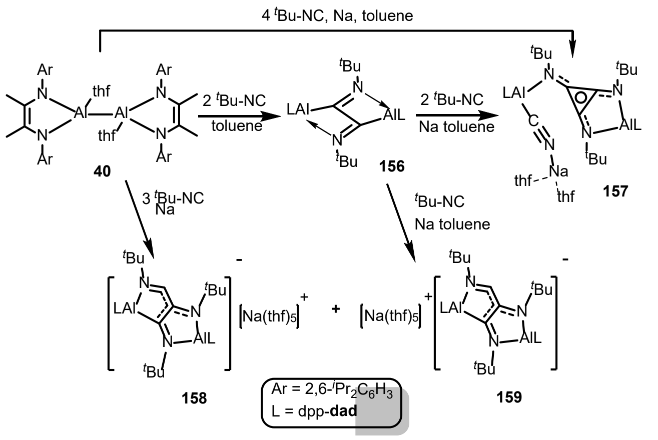


Fig. 23 Reactions of dialumane **40** with isocyanides.

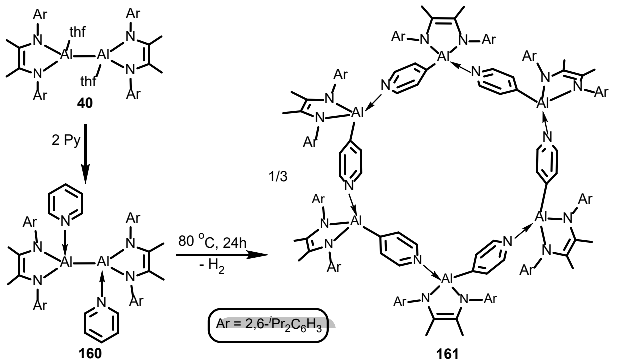


Fig. 24 Reactions of dialumane **40** with pyridine to yield a metallomacrocycle.

5. Conclusions and outlook

The non-innocent α-diimine ligands in the reduced forms (radical monoanion or dianion) have proven to be able to stabilize a rich variety of (low-valent) metal centres, including both main-group and transition metals. Herein, we summarized the synthesis, structure and bonding of α-diimine-ligated main-group (and in two cases transition) metal complexes, including metal–metal-bonded compounds such as the Mg(I), Zn(I), Cr(I), Al(II) and Ga(II) dimers featuring a single or a quintuple (in the case of Cr compound) bond between the two metal atoms.

Moreover, the non-innocence of such ligands enables rich reactivity of their metal complexes, wherein either metal-centred or ligand-centred, or metal-ligand cooperative processes can occur. For complexes with low-valent metals and reduced α-diimine ligands, one of the most commonly seen processes is the electron storage and transfer in their reactions. During these studies, the cooperation either between two metals (in metal–metal-bonded compounds) or between metal and ligand is observed, leading to unique reaction pathways, e.g. the four-electron transfer mentioned above for the reactions of dialumanes **40** and **44** with a couple of substrates (such as nitrogen-rich species).

In the future, it is reasonable to propose that the non-innocence of α-diimine ligands will continue to be a main focus. Research in this field will likely be directed to the following aspects: 1) expansion of metal complexes including new metal–metal bonds; 2) detailed study on the mechanism of small molecule activation to gain deeper insight into the reactivity of these metal complex systems; 3) expansion of ligands, e.g. to chiral species for possible catalysis applications; and 4) ultimately, the applications of such complexes in both stoichiometric and catalytic reactions with various substrates. Overall, novel complexes with intriguing structures and reactivity can be expected for metal complexes with such redox-active ligands.

Conflicts of interest

There are no conflicts to declare.

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