

Free Aluminylenes: An Emerging Class of Compounds

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Dedicated to Professors Hansgeorg Schnöckel, Herbert W. Roesky, and Philip P. Power

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Abstract: Aluminylenes (R–Al) are aluminium analogs of carbenes. In contrast to isolable carbenes, aluminylenes are extremely rare species. In the past years, pioneered by Schnöckel, Roesky and Power, a few free aluminylenes and their complexes have been reported. Such compounds have the aluminium atom in the oxidation state +I, which contrasts with classical organoaluminium derivatives that contain the element in the +III oxidation state. Aluminylenes, either in their free state or in the coordination sphere of a Lewis base, are capable of coordinating to transition metals and activating inert chemical bonds. Free aluminylenes are emerging as potent synthetic platforms for unusual aluminium species.

1. Introduction

Aluminium is the most abundant metal in the Earth's crust and the third most abundant element.^[1] The aluminium compounds that are often encountered feature aluminium in the +III oxidation state. They have found a diverse range of applications in organic/inorganic synthesis, catalysis, and industrial processes, for example, the well-known Friedel–Crafts reactions and Ziegler–Natta polymerization.^[2–4] In stark contrast, compounds that have aluminium in the +I oxidation state are much less understood. Nonetheless, recent years have seen the thriving of Al(I) chemistry.^[5–13]

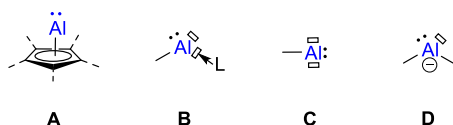


Figure 1. Representations of Cp-ligated Al(I) compounds **A**, di-coordinate Al(I) compounds **B**, mono-coordinate Al(I) compounds **C**, and aluminyl anions **D**.

According to the coordination numbers at Al (Figure 1), neutral Al(I) species can be classified into three broadly defined categories, namely Cp-ligated Al(I) compounds **A**,^[14–15] di-coordinate Al(I) compounds **B**,^[16–18] and mono-coordinate Al(I) compounds **C**.^[19–21] Representative compounds of **A** and **B** are Schnöckel's (Cp*Al)₄ (Cp* = pentamethylcyclopentadienyl) and Roesky's [HC(CRNDipp)₂Al] (R = Me or ^tBu; Dipp = 2,6-diisopropylphenyl), respectively, which have been reviewed extensively^[6–13] and are not covered by this concept. In addition, an intriguing class of nucleophilic anionic aluminyl compounds **D**^[22–27] (Figure 1) has been rapidly developed and recently reviewed.^[5] This concept focuses on the achievements of an emerging class of compounds **C**, namely free aluminylenes^[28] or alanediylys (R–Al), as well as recent advances in their Lewis base complexes of type **B**.^[29–33]

2. Free aluminylenes

The stability of mono-coordinate compounds of group 13 elements in the oxidation of +I increases from B to Tl due to the increasing inertness of the ns² valence electrons on descending the group. Compounds of the types R–E (E = Ga, In, Tl) are well documented.^[34–39] Simple aluminylenes, such as AlX (X = F, Cl, Br, I), AlH and Al₂O, are highly fleeting and have only been detected in the gas phase.^[40–43] Nevertheless, it has been proved that with right substituents, two examples of free aluminylenes are bottle-able at room temperature (Figure 2).^[19–21] Such free aluminylenes contain an Al(I) atom featuring a lone pair of electrons and two vacant orbitals,^[19–21] thereby exhibiting tri-active ambiphilicity.^[20]

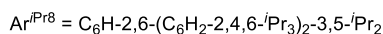
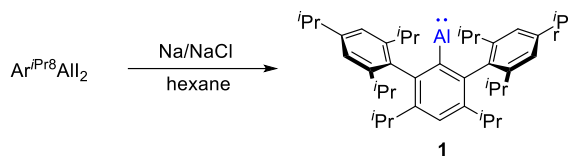
2.1 Synthesis and characterization

Thanks to the bulky terphenyl substituent Ar^{iPr8} (Ar^{iPr8} = C₆H-2,6-(C₆H₂-2,4,6-ⁱPr₃)₂-3,5-ⁱPr₂),^[44–45] Power and Tuononen succeeded in the isolation of an arylaluminylene Ar^{iPr8}Al (**1**) at the end of 2020 (Figure 2a).^[19] This species was synthesized by reduction of the corresponding monomeric arylaluminium diiodide. Shortly thereafter, employing a bulky carbazolyl substituent,^[46] we^[20] and Hinz^[21] groups independently prepared a carbazolylaluminylene **2** (Figure 2b). The key to isolating **2** on a preparative scale was the use of 5% w/w K/KI^[47] at low temperature.^[20] Other reducing agents (i.e. KC₈, Cp*₂Co) only gave **2** in very low yield.^[21] It is noteworthy that, with a less bulky terphenyl Ar^{dipp} (i.e. Ar^{dipp} = C₆H₃-2,6-Dipp) Power reported in 2003 that reduction of Ar^{dipp}AlI₂ with KC₈ in toluene led to a transient dialuminene, which reacted with the solvent toluene to give a dialane(4) product.^[48]

Compounds **1** and **2** were characterized by multi-nuclear NMR spectroscopies and single-crystal X-ray diffraction. In both cases, the Al atoms located nearly symmetrical between the two flanking aryl rings and no strong secondary bonding interaction between them was observed.^[19–21] In the solid state of **1**, the aluminum atoms are only bound to the ipso carbon of the aryl ligand with a C–Al bond length of 1.988(4) and 2.003(4) Å in two crystallographically independent molecules.^[19] The X-ray diffraction study of **2** revealed that the N atom adopts a planar environment (sum of angles: 359.3°).^[20] The Al–N bond length (1.913(9) Å) is slightly shorter than the standard value for an Al–N single bond (1.970 Å), while much longer than the standard value for an Al–N double bond (1.730 Å).^[49] This indicates the presence of a weak N-to-Al π-donation. Natural bond orbital (NBO) calculations suggested that this π-donation is stronger than that

for the monomeric aluminum monoamide $t\text{Bu}_2\text{AlNMe}_2$ ^[50] (Mes = mesityl).^[20]

(a)



(b)

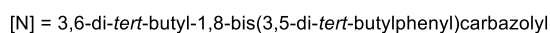
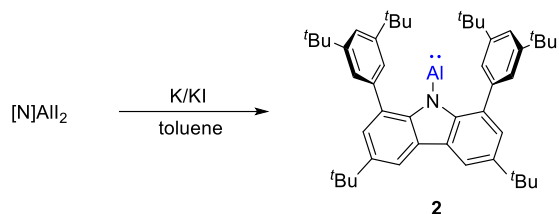


Figure 2. Synthetic methods for **1** (a) and **2** (b).

2.2 Electronic structures

The electronic structures of **1** and **2** have been analyzed by computational methods (Figure 3). For **1**, the HOMO is the Al nonbonding lone pair, while the LUMO and LUMO+1 are mainly in-plane and out-of-plane 3p orbitals of Al, respectively (Figures 3a-3c).^[19] However, these results are different from those calculated for **2**. The HOMO of **2** is composed of the lone pairs at both Al and N atoms and some π -bonding orbitals over the carbazoyl substituent, while the HOMO-1 is mainly the Al nonbonding lone pair (Figures 3d and 3e). The LUMO and LUMO+6 are mainly the out-of-plane and in-plane empty 3p orbitals of Al, respectively (Figures 3f and 3g), showing the dramatic influence of N-substitution on the electronic properties of free aluminylenes.^[20]

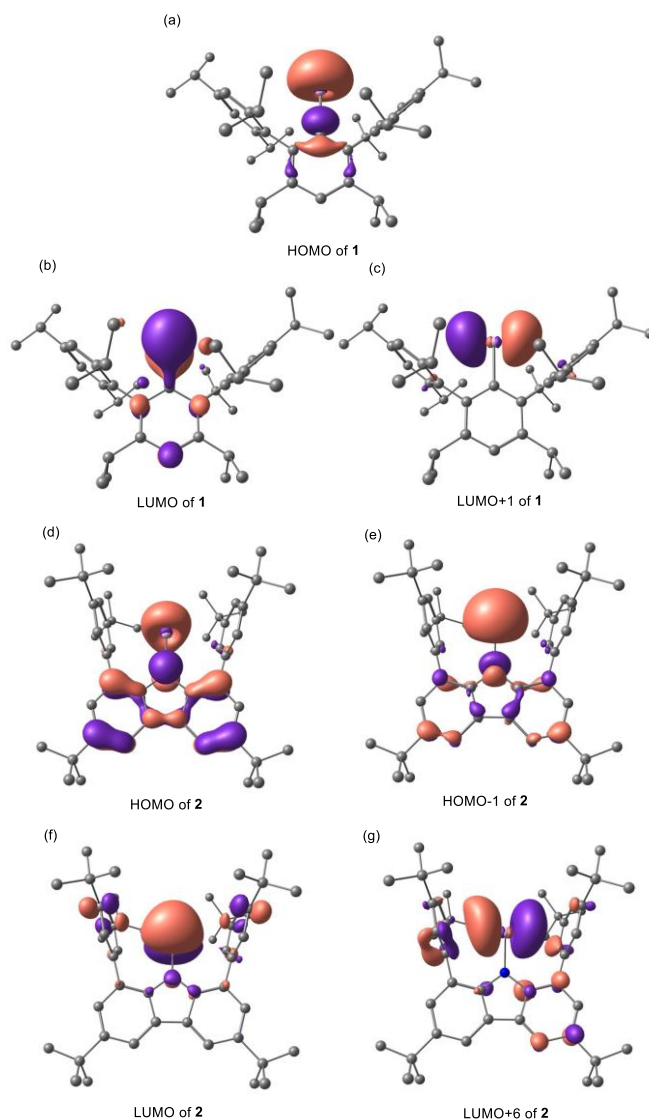


Figure 3. Frontier molecular orbital analysis of **1** (a-c) and **2** (d-g).

2.3 Reactivity

On the basis of conceptual density functional theory calculations, free aluminylenes feature predominantly electrophilic behavior.^[18] This is in stark contrast to the main nucleophilic behavior observed for their Lewis base complexes and aluminyl anions.^[5, 18] Free aluminylenes are capable of activating inert chemical bonds via oxidative insertion into saturated and unsaturated bonds.^[19, 51-52] With a lone pair and two empty p orbitals on Al, featuring electron donating and doubly electron accepting properties, free aluminylenes can function as versatile Al ligands in coordination chemistry.^[20] Most strikingly, **2** is a synthon for accessing an acyclic mono-base-stabilized aluminylene.^[18]

2.3.1 Redox reactions

As previously demonstrated for neutral Al (I) compounds, the two-electron oxidation of Al (I) to Al (III) is typically a thermodynamically favorable process.^[10-11] Indeed, **1** reacted rapidly with H_2 in C_6D_6 , giving the hydrogenation product $[\text{AlH}(\mu\text{-H})\text{Ar}^i\text{Pr}^8]_2$ **3** (Figure 4).^[19] Computations indicate that the direct

reactivity of **1** with H_2 involve a very high-energy transition state. Thus, a weak association of two molecules of **1** to generate the ensuing dialuminene could be essential for the observed reactivity. Further explorations showed the unusual reactivity of **1** toward organic azides, resulting in trivalent Al compounds **4-6**.^[51] Compound **6** is the first iminoalane with an $Al=N$ triple bond. Our group found that the Al center in **2** can undergo oxidative insertion with $IDippCuCl$, which afforded a rare terminal Cu-alumanyl complex **7** (Figure 4).^[20] In addition, the strong reducing ability of **2** was reflected by the reaction of **2** with $(THT)AuCl$ ($THT = \text{tetrahydrothiophene}$), which ended up with the formation of the carbazolyl-substituted aluminum dichloride **8** as well as Au mirror.^[20]

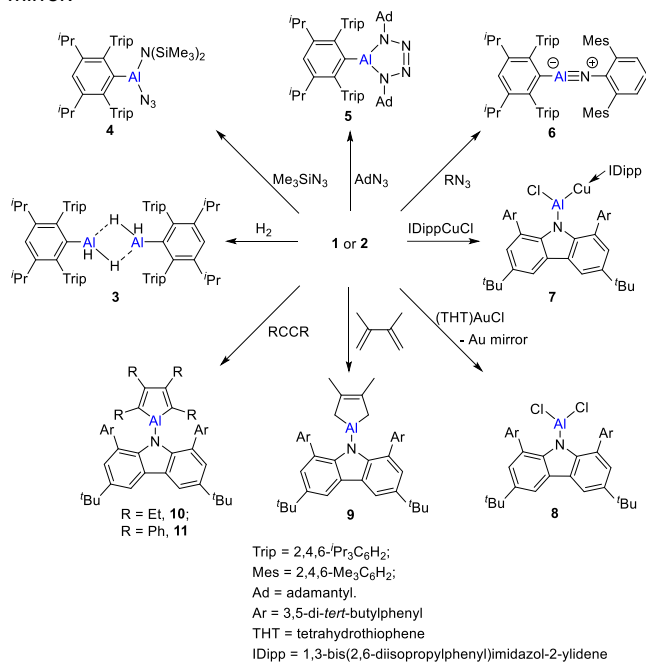


Figure 4. Redox reactions of aluminynes **1** and **2**.

Compound **2** has proved to be a potent synthon for Al-heterocycles (Figure 4).^[52] It underwent a facile [4+1] cycloaddition reaction with 2,3-dimethyl-1,3-butadiene to produce **9**. Moreover, alumole derivatives **10** and **11** were synthetically accessible upon treating **2** with an excess amount of internal alkynes. The formation of **10** and **11** involved a [2+1] cycloaddition followed by a ring expansion reaction. These reactions represent the first examples of alumole syntheses using simple unsaturated hydrocarbons. Interestingly, the combination of tetraphenyl-alumole with the carbazolyl group in compound **11** gives rise to unique dual emissive molecules. This preliminary result showcased huge potentials of free aluminynes for construction of Al-containing functional materials. It is worth noting that the similar reaction of Power's organogallium(I) compound Ar^*Ga ($Ar^* = C_6H_3-2,6-Trip_2$) with 2,3-dimethyl-1,3-butadiene gave a digallamacrocycle,^[53-54] which was probably formed via dimerization of a five-membered Ga-heterocycle analogous to **9**.

2.3.2 Synthon for di-coordinate aluminynes

Whereas one of the extreme bonding situations of $[HC(CRNDipp)_2]Al$ ($R = Me$ or tBu) can belong to type **B** (Figure 1), stable genuine mono-base-stabilized aluminynes were long-sought-after objects. In 2021, Krämer and Cowley disclosed the transient existence of an amidophosphine-supported aluminylene **14** (Figure 5a).^[31] This species was in equilibrium with its dimeric dialumene **13** in solution although direct observation of **14** was unsuccessful.^[31-32]

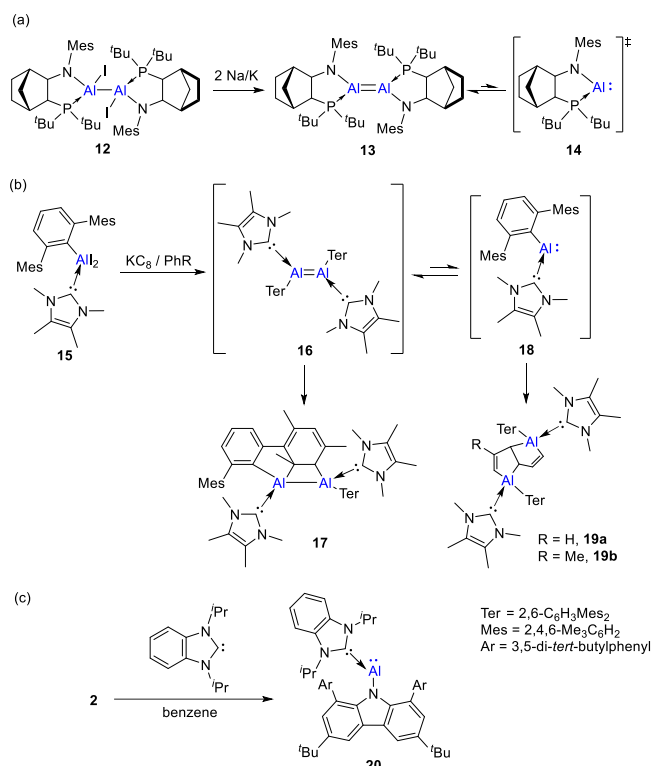


Figure 5. Formation of transient di-coordinate aluminynes **14** (a) and **18** (b) and a stable di-coordinate aluminylene **20** (c).

More recently, Braunschweig presented that reduction of **15** generated a highly fleeting N-heterocyclic carbene (NHC) coordinated aluminylene **18**, as evidenced by cleavage of solvents (i.e. benzene and toluene) furnishing dialuminene derivatives of pentalene **19a** and **19b**, respectively.^[33] The dimerization of **18** to **16** is thermodynamically favored. The dimer **16** was not stable either and underwent an intramolecular [2 + 2] cycloaddition between the $Al=Al$ double bond and the peripheral mesitylene ring affording **17** (Figure 5b).^[33] Of note, employing a different NHC stable dialuminene derivatives were achieved by the group of Inoue.^[29-30]

We also sought to tame mono-base-stabilized aluminynes. Gratifyingly, simple addition of 1,3-di-isopropyl benzimidazole-2-ylidene ($Pr_2\text{-bimy}$) to a benzene solution of **2** gave rise to a dark solution, in which **20** was isolated and thoroughly characterized (Figure 5c).^[18] Compound **20** represents the first example of a stable genuine noncyclic mono-base-stabilized aluminylene. Although Lewis bases are well known to stabilize electron-deficient species, compound **20** revealed much higher redox reactivity towards inert aromatic systems, in comparison to that of **2**. Computations showed that the coordination of **2** with $Pr_2\text{-bimy}$ significantly shrunk the HOMO–LUMO gap, thereby enhancing the redox behavior.

Indeed, **20** readily underwent intramolecular C–C bond cleavage of the flanking aryl group to yield **21** (Figure 6). This conversion was found to be reversible at 80 °C as treatment of **20** or **21** with naphthalene furnished the [1+4] cycloaddition product **22** at room temperature or 80 °C, respectively. Interestingly, **20** reacted with biphenylene at room temperature to give a [1+4] cycloaddition product **23**, while elevating the temperature led to **24** as a result of insertion of Al into the C(3)–C(4) bond of biphenylene. This remarkable reaction stands in contrast to reports by Crimmin and Kinjo groups, where the C(2)–C(3),^[55] C(4)–C(5)^[55] and C(1)–C(2)^[56] bonds of biphenylene were broken by highly reactive Al species.

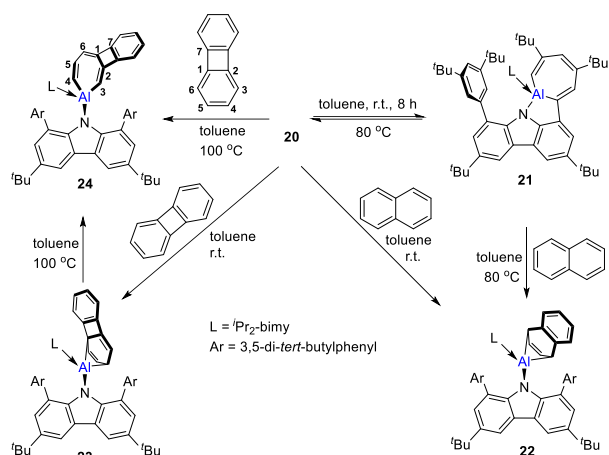


Figure 6. Reactivity of **20** towards inert aromatic systems.

2.3.3 Coordination chemistry

Ancillary ligands play essential roles in modern synthetic chemistry. Whereas metal carbonyl complexes ligated by aluminylenes can be dated back to the late 1990s,^[57] these species remains rare due to the lack of stable Al precursors. In 2014, Tokitoh synthesized platinum complexes of arylaluminylene **27** via the reaction of a dialumene-benzene adduct **25** with $[\text{Pt}(\text{PCy}_3)_2]$ or by the reduction of 1,2-dibromodialumanes **26** in the presence of $[\text{Pt}(\text{PCy}_3)_2]$ (Figure 7a).^[58] These reactions indicate the potential of dialumenes to deliver an aluminylene moiety.

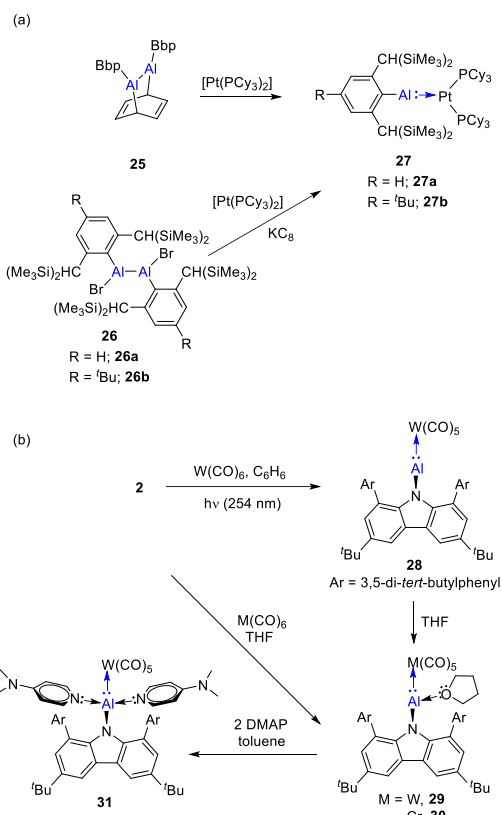


Figure 7. Syntheses of transition metal aluminylene complexes.

In 2021, we probed the coordination behavior of **2** to transition metals (Figure 7b).^[20] Compound **2** revealed diverse coordination modes. Irradiation (254 nm) of a benzene solution of **2** and

$\text{W}(\text{CO})_6$ cleanly produced complex **28**, which subsequently gave product **29** after THF coordination to Al. Alternatively, treatment of **2** with $\text{W}(\text{CO})_6$ or $\text{Cr}(\text{CO})_6$ in THF at room temperature afforded **29** and **30**, respectively. 4-Dimethylaminopyridine (DMAP) as a stronger Lewis base coordinated to the Al center of **29**, which ended up with the generation of **31**. It is documented that ligand exchange at the Al center of aluminylenes gave access to modulating of electronic properties of transition metals.

3. Summary and Perspectives

The chemistry of free aluminylenes is in its infancy but beginning to flourish. These species indeed showcased fascinating and diverse reactivities, including oxidative addition, cycloaddition and coordination. Taking advantage of the lowest electronegativity of Al ($\chi = 1.6$) among p-block elements, aluminylenes and their Lewis base complexes are potentially the strongest electron-releasing p-block ligands. This ability, coupled with easily tunable electronic properties of Al via ligand exchanges at Al, makes transition metal aluminylene complexes potential catalysts for unique organic transformations.

The isolation of free aluminylenes also provides a synthetic platform for unusual species (e.g. isolation of **20**). Further modulation of frontier molecular orbitals of aluminylenes may lead to activation of extremely inert small molecules like N_2 . With more research inputs, one can safely expected that many other elusive Al species (e.g. di-coordinate aluminium ions, aluminylene-based radical ions and aluminium carbonyls) will be synthetically achievable from free aluminylenes.

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Keywords: Aluminium; Aluminylene; Carbene Analog; Ligand; Small molecule activation

Conflict of Interest

The authors declare no conflict of interest.

Author Biographies:



Xin Zhang was born in 1991 and received his B.Sc. degree in Chemistry in 2015 from Lanzhou University, China. Then, he obtained his Ph.D. in 2020 at the Shanghai Institute of Organic Chemistry (Chinese Academy of Sciences) under the supervision of Prof. Zheng Huang in organometallics chemistry, where he focused on design, synthesis, and application of pincer iridium and ruthenium complexes. Since Sep. 2020, he has been a postdoctoral fellow in the group of Prof. Liu Leo Liu at SUSTech. He is currently working on low-valent boron and aluminum chemistry.



Yanbo Mei studied chemistry at the Zhengzhou University (China) and received his Ph.D. degree in 2020 from ETH Zürich under the supervision of Prof. Hansjörg Grützmacher. He joined the group of Liu in 2021 at SUSTech as a postdoctoral researcher. His research interests are focused on the synthesis and properties of main-group-element compounds and electrochemical activation of elemental phosphorus and arsenic for novel organic and inorganic molecules.



Liu Leo Liu is an Associate Professor at SUSTech. His group is developing the chemistry of multi-active ambiphilic centers and extremely electron-releasing

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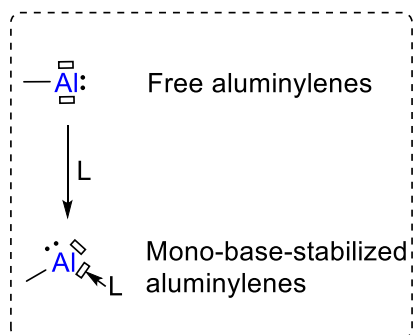
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- [28] We use the term "aluminumylene" to refer to systems containing aluminium in the +I oxidation state and generating complexes of the form, M-AIR, M-AIRL or M-AIRL₂, based on well established literature precedent for the related derivatives of other group 13 elements, namely borylene, gallylene and indylene for the boron, gallium and indium analogues. Although the terms boranylidene and aluminylidene are recommended by the IUPAC red book (R. M. Hartshorn, A. T. Hutton in *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005, IUPAC Red Book*, (Eds.: N. G. Connelly, T. Damhus), RSC Publishing, London, 2005) for the parent BH and AlH systems, this convention has not been followed in the naming of previous boron and aluminium systems of the types RB and RAl.
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CONCEPT

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Free aluminylenes and mono-base-stabilized aluminylenes are extremely reactive species. The ambiphilicity of these species allows facile activation of inert chemical bonds as well as coordination to transition metals in diverse modes. Free aluminylenes are potent synthons for unusual aluminium species.

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