

Account

Organoaluminum chemistry with low valent aluminum — recent developments

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The chemistry of mono and divalent aluminum has progressed very significantly in the last decade. Many fascinating and unusual results and novel structures of products have been realized. The monomeric form of divalent aluminum does not exist but dimers are well known and characterized. Stable Al(I) derivatives in both monomeric and tetrameric forms have been synthesized and structurally characterized. A common feature in these compounds is the use of bulky organic substituents. The chemistry of some of these compounds has also been explored. The monomeric Al(I) derivative, $[\text{HC}(\text{MeCNAr})_2]\text{Al}$, very recently synthesized, exhibits interesting addition and insertion reactions with alkyne, carbon dioxide and silyl azide at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Low valent chemistry of polyvalent elements is a topic of considerable research interest in recent years. For a long time, it was a formidable challenge to prepare compounds with subvalent elements in a laboratory. Thanks to the advent of new and sophisticated synthetic methodologies, nowadays more success stories are reported on solutions to difficult synthetic problems. Recent isolation and structural characterization of organometallic hydroxides [1], nonafluoromesityl telluride [2], metallasiloxanes from discrete silanetriols as building blocks [3] and a stable cyclootrimerenyl radical [4] are only a few examples of this development. However, for most new developments the design and details of the synthesis of the desired target are still dependent on the skill of the chemist.

Aluminum, the most abundant metal in the earth's crust, is known to have a vast chemistry in its normal

trivalent state [5,6]. Several organoaluminum compounds have found extensive use as selective reagents for a wide variety of organic transformations. On the industrial side, their most prominent applications are as polymerization cocatalysts, ceramic precursors and specialty chemicals in electronic devices. Further, compounds of the type $\text{R}_{3-x}\text{AlE}_x$ (where R is an organic group and E is halogen or hydrogen) have stimulated substantial interests for studies on structure and bonding concepts as well. The discovery that trialkyl aluminum compounds play an important role in the Ziegler–Natta process of olefin polymerizations has given tremendous boost to the research and developmental work in aluminum chemistry. It currently runs almost parallel to organolithium and organomagnesium chemistry in terms of its versatility and usefulness.

2. Interests and importance of low valent aluminum

Aluminum, a member of the main group metals, uses all the valence electrons ($3s^2, 3p^1$) for its trivalent chemistry. Its low valent chemistry is therefore to be characterized by the *restricted use of its valence electrons* in

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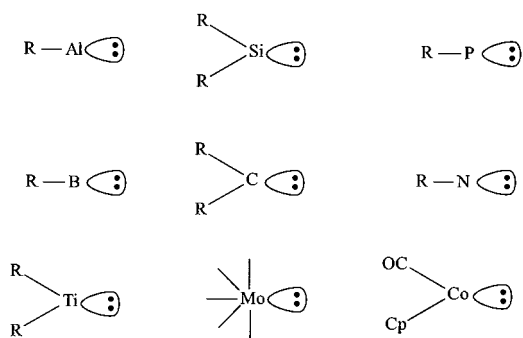


Fig. 1. Isolobal analogues of RAl(I).

compound formation. As one of the Group 13 elements, one might expect it to afford the monovalent state far more readily in compounds than the divalent state. The progress made in this direction can be perceived as an opportunity to add a new dimension to the chemistry of aluminum. A brief coverage of this topic has appeared in the latest edition of the book by Cotton et al. [7]. It is to be noted that Al(I) and (II) species have been often invoked as possible intermediates in photochemical and free radical reactions of organo aluminum(III) reagents [5]. It is therefore imperative that their isolation and characterization offer greater credibility to the proposal of such species made in reaction mechanisms.

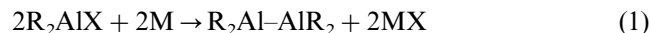
The pursuit of compounds of low valent aluminum has a long history of over 50 years. However, most of the fascinating progress has occurred only in the last decade, especially in the case of Al(I) which may prove to be of much consequence in the near future. Also, the isolobal analogy of RAl(I) that exists with a variety of other systems such as carbene or CO (Fig. 1) implies tremendous synthetic potential in this chemistry. This review is an attempt to set the pace for this fast moving and exciting aspect of aluminum chemistry by consolidating the available literature on both Al(I) and (II) as well as highlighting the recent developments of aluminum(I) compounds, in particular.

3. Divalent aluminum

Relatively little has been developed on this topic so far though some aluminum(II) compounds have been referred to in the literature for several decades. The divalent halogeno aluminums, 'AlX₂', have been proposed as reactive intermediates in the Hall–Nash reaction, which involves an olefin, Al, and AlX₃ [8]. Olah et al. [9] who have reinvestigated this reaction could only furnish spectroscopic evidence for the same. AlX₂ which undergoes room temperature disproportionation to Al(I) and Al(III) due to its greater kinetic instability has not been isolated pure so far [10]. However, ethene

is found to trap AlX₂ in a viscinal fashion [11]. Adducts of AlX₂ (X = Br, I) with anisole are stable solids at room temperature and have been isolated and structurally characterized [12]. Later, several donor stabilized compounds with AlX₂ (X = Cl, Br, I), like aqua, amino and other ether solvents, were also known [13]. The formation of the radical species R₂Al (R = phenyl and ethyl) from the reduction reactions of the corresponding dimeric Al(III) compounds, (R₂AlCl)₂, with alkali metals have been claimed [14–16].

In recent years, many new developments have taken place on the dimeric form of R₂Al, which is formally an Al(II) compound possessing an Al–Al bond. Schleyer and coworkers [17] have also supported the dimeric form through theoretical studies on the model compound, (H₂Al)₂. A fairly strong Al–Al bond was indicated (262 pm) in this case. Hereby, we are mentioning a few examples of the dimeric divalent aluminum that are known and have been structurally characterized: [(Me₃Si)₂CH)₂Al]₂ (**1**), [(2,4,6-*i*-Pr₃C₆H₂)₂Al]₂ (**2**), [(*t*-Bu₃Si)₂Al]₂ (**3**), [RAl(Cl)–Al(I)R] (**4**), R = [(Me₃Si)₂CC(C₆H₅)CN(Me₃Si)]. Hoberg's claim on the synthesis of [(*i*-Bu)₂Al]₂ in the late 1970s [18,19] was reinvestigated by Uhl and coworkers [20,21], who prepared the first authentic sample of compound **1** in 1988 [22,23]. The general method for the preparation is given in Eq. (1).

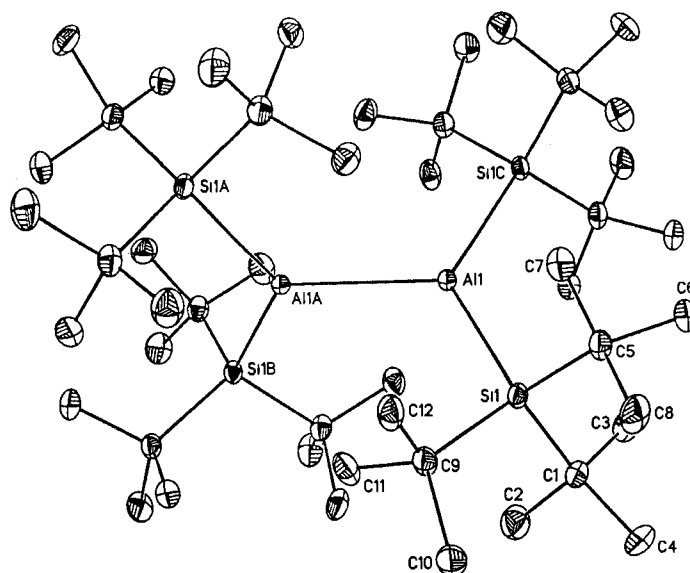


The reaction seems to proceed well with the halogens, X = Cl, Br, I, and the alkali metal M is usually potassium [24,25]. The supersilyl analogue (R = *t*-Bu₃Si) **3** was obtained as an unexpected product from the reaction of AlX₃ (X = Cl, Br) with *t*-Bu₃SiNa [26]. Its structure (Fig. 2) reveals the longest known Al–Al distance (275.1 pm).

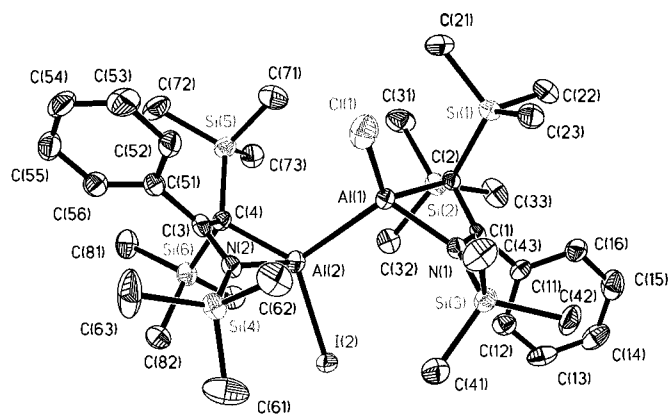
Contrary to **1**, **2**, and **4**, the dimer **3** is found to be more intensely colored and less thermally stable. Some of its reactions have been explored. Recently, we have prepared and structurally characterized a dimer **4** that contains both organic and halogen substituents [27] (Fig. 2). Tetracoordinate aluminum centers and a short Al–Al bond length (259.3 pm) are some of its interesting structural features. With its reactive halogen substituents it can be regarded as an ideal precursor for the synthesis of novel polynuclear derivatives.

4. Monovalent aluminum

To date, the progress made in Al(I) chemistry is much greater compared to that of Al(II). Several novel and significant results have emerged in the last decade. They can be categorized as: (i) monomeric aluminum halide, AlX (X = F, Cl, Br, I); (ii) monomeric organoaluminum, RAl (R = Me, Ph, Cp, Cp*); (iii) tetrameric



(a)



(b)

Fig. 2. X-ray single crystal structures of Al(II) dimers: (a) $[(t\text{-Bu}_3\text{Si})_2\text{Al}]_2$ (3) and (b) $\text{RAl}(\text{Cl})\text{-Al}(\text{I})\text{R}$ (4) [$\text{R} = (\text{Me}_3\text{Si})_2\text{CC}(\text{C}_6\text{H}_5)\text{CN}(\text{Me}_3\text{Si})$].

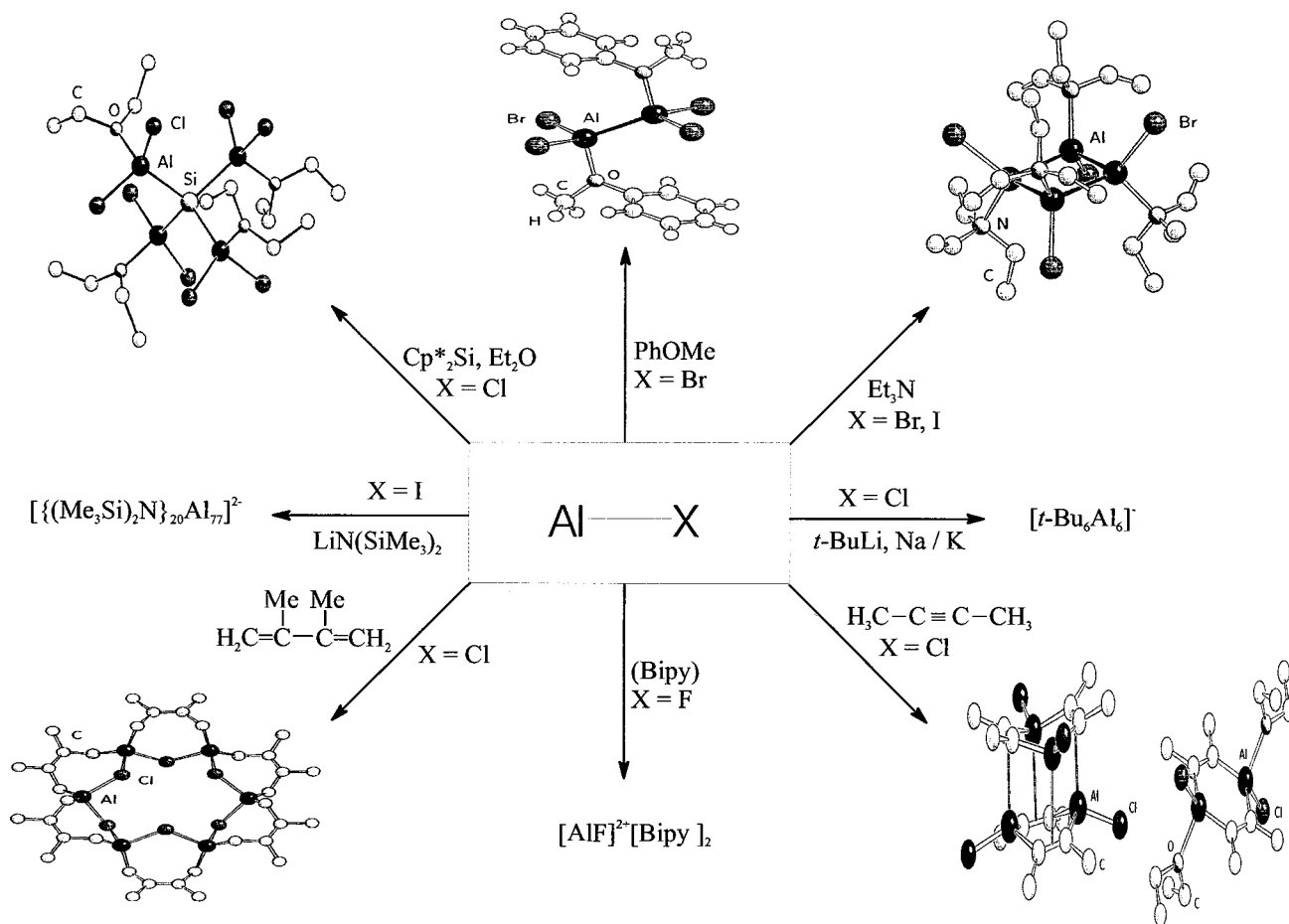
organoaluminum(I), $(\text{RAI})_4$; (iv) first room temperature stable monomer, RAI ; and (v) theoretical studies.

Monochloro aluminum, $\text{AlCl}(\text{I})$, is the first among these to be reported in 1948 by Klemm et al. [29]. Elemental chlorine and aluminum metal were reacted at 1000°C to get this species. Since that time, considerable progress has been made and all the monohalo aluminum species, AIX , are known. Schnöckel and coworkers have done pioneering work in this area and have covered various aspects of this chemistry in some detail in a recent review [13]. Recently, they have also reported structurally characterized adducts of some AIX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) compounds [13]. AIX species have been shown to exist in the monomeric form in the gas phase [30] and as metastable species in solution [31,32]. Regardless of the high sensitivity of AIX to disproportionation

reaction, Schnöckel et al. have demonstrated the merit of employing matrix isolation techniques as well as cryogenic facilities for the synthesis of AIX and their conversion to structurally novel products (Scheme 1).

It is noteworthy that the reaction of AlCl with $t\text{-BuLi}$ followed by reduction gave a stable radical anion [33] and that of AlI with $(\text{Me}_3\text{Si})_2\text{NLi}$ resulted in the isolation of one of the largest metal clusters [34]. An illustration of the advantage of AlCl in organic synthesis [35,36] is also given in Scheme 2.

It is reported that hexamethyl benzene is the only organic compound of this reaction where AlCl seems to play a catalytic role. The use of ^{27}Al -NMR spectroscopy has been made and its merits in this field have been demonstrated.



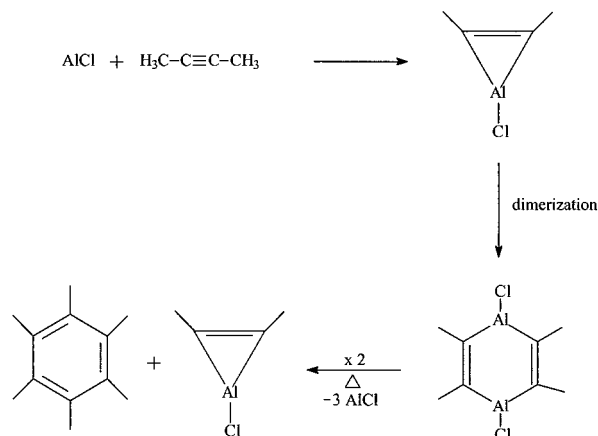
Scheme 1. Some representative reactions of aluminum(I) halides.

Srinivas et al. [37] have provided spectroscopic evidence for MeAl, which has only transient existence in the gas phase. Phenylaluminum, PhAl, has not been isolated but invoked as a feasible intermediate in the photolysis and other organic transformations of triphenyl aluminum [38]. Schnöckel et al. have tried different routes to synthesize ‘CpAl’ but met with only limited success [13]. This species, which could be evidenced by ^{27}Al -NMR spectral study [39], was found to be extremely thermally sensitive and decompose within seconds above -60°C . In contrast to CpAl, the monomeric Cp*Al does exist and has been characterized by ^{27}Al -NMR spectroscopy [39]. Cp*Al is known to equilibrate in solution with its tetramer [40]. A few reactions also provide supportive evidence to the monomeric Cp*Al (Scheme 3).

Recently, an organometallic approach for stabilizing the monomeric species of aluminum(I) and gallium(I) has been demonstrated [41–43]. Structurally characterized Cp*Al-Fe(CO)₄ was obtained from the reaction of Cp*AlCl₂ with K₂Fe(CO)₄ [42]. Similar reactions gave the opportunity to isolate (CO)₅Cr-ER(tmeda) (E = Al, Ga; R = Cl, C₂H₅) [41] and (dcpe)Pt(ECp*)₂ (E = Al,

Ga) [43]. Cp*Al, a two electron donor can be regarded as an isolobal partner to a carbene.

In more recent years, the chemistry of organoaluminum(I) has been developed primarily with the stable tetrameric compound **5** and the newly synthesized monomeric compound **10**. The following sections will therefore describe these results in more detail.



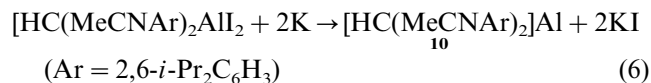
Scheme 2. Synthesis of hexamethylbenzene mediated by AlCl.

show any tendency to dissociate to its monomer in solution. Extensive use of ^{27}Al -NMR spectroscopic investigations indicated several other monomeric and tetrameric examples in solution [39]. A variety of substituted cyclopentadienyl moieties were studied which also gave the opportunity to characterize $[\text{CpAl}]_4$. $[(\text{Cp}^*\text{Al})_3(\text{CpAl})]$ is stable in solution, contrary to $[\text{CpAl}]_4$.

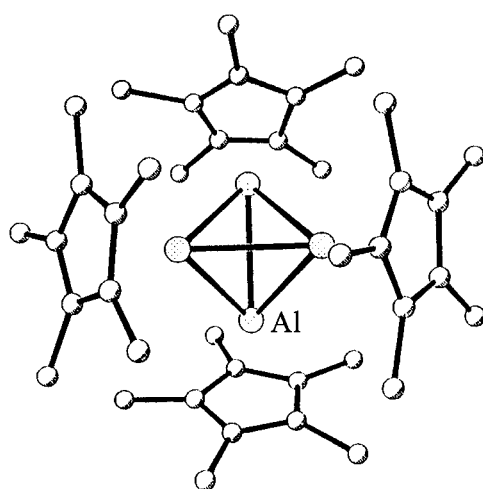
Compounds **5–9** are colored (yellow, brown, violet, orange and blue-violet, respectively), soluble in organic solvents, and stable as solids at room temperature in argon–nitrogen atmosphere. They are sublimable at high temperatures in vacuum.

Recently, we have obtained the first example of a

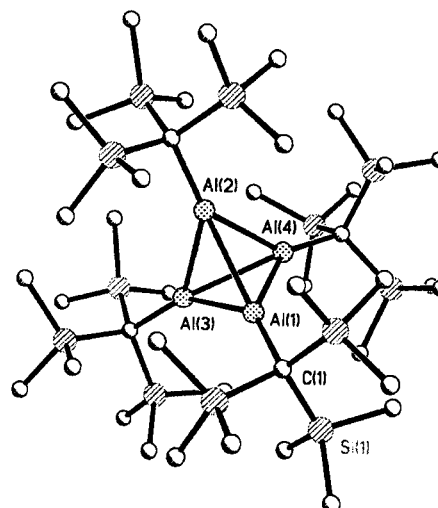
room temperature stable monomeric Al(I) compound $[\text{HC}(\text{MeCNAr})_2]\text{Al}$ (**10**) (Ar = 2,6-bis(isopropyl)phenyl) [50] (Eq. (6)).



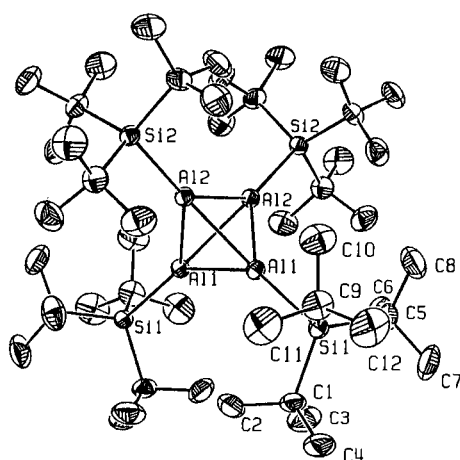
Steric protection provided by the chosen bulky substituent enabled a slow but facile reduction of the corresponding diiodide to yield monomer **10**. Red colored crystalline **10** is soluble in organic solvents (toluene, benzene, and hexane) and stable both thermally and in an inert atmosphere. Only above 150°C it decomposes to any noticeable extent.



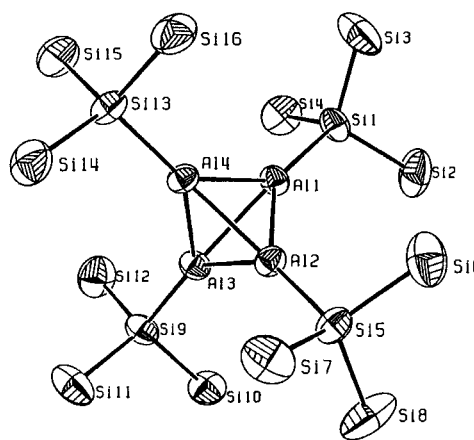
$[\text{Cp}^*\text{Al}]_4$
5



$[(\text{Me}_3\text{Si})_3\text{CAl}]_4$
8



$[(t\text{-Bu})_3\text{SiAl}]_4$
7



$[(\text{Me}_3\text{Si})_3\text{SiAl}]_4$
9

Fig. 3. Molecular structures of tetrameric compounds, **5–9**.

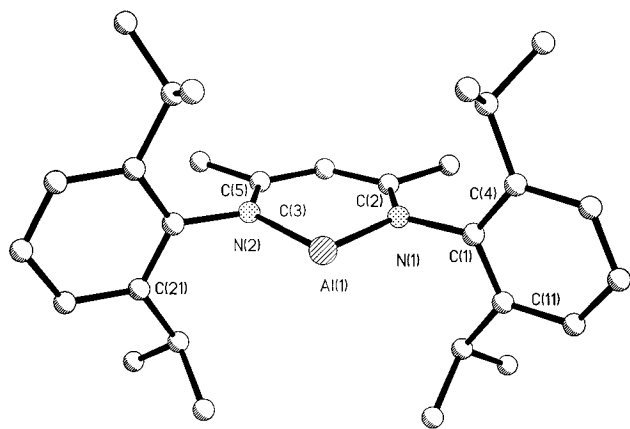
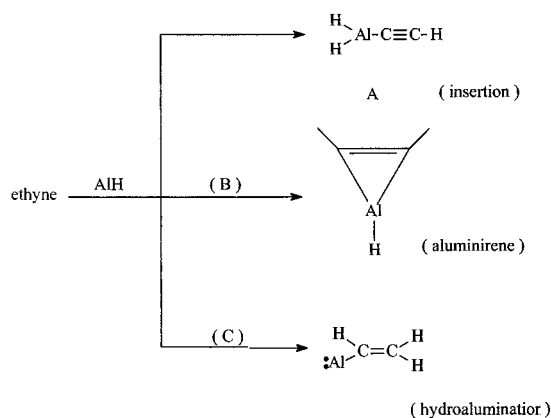


Fig. 4. Molecular structure of the monomer, **10**.



Scheme 4. Reactions of AlH with ethyne — possibility of isomeric products.

6. Structural features

Single crystal X-ray structures have been determined for **5**, **7**, **8** and **9** (Fig. 3). The structures reveal that in all of them, four Al centers exist in a tetrahedral arrangement and each of the aluminum atoms carry a corresponding substituent. In **5**, Cp* is found in η^5 -mode bonding, whereas *t*-Bu₃Si[−] in **7**, (Me₃Si)₃C[−] in **8** and (Me₃Si)₃Si[−] in **9** are bonded to aluminum in a sigma fashion to give rise to Al–Si and Al–C bonds. It is observed that the Al–Al bond length ranges from 259.2 to 277.3 pm. Compound **8** is the first structurally characterized neutral aluminum cluster having a sigma bonded alkyl substituent.

The single crystal X-ray structure of compound **10** is given in Fig. 4, which shows its monomeric nature and no observable close contacts in the unit cell. This is the first dicoordinate aluminum(I) compound to be prepared and structurally characterized. The most important structural feature is that the aluminum center finds itself as a part of a planar six-membered heterocycle with the skeletal atoms of the ligand (NCCCN). It possesses slightly longer endocyclic Al–N bonds (195.7

pm) and a relatively narrow angle at aluminum (ca. 90°).

7. Theoretical studies

Subvalent aluminum chemistry has attracted considerable attention for theoretical investigations from several different perspectives. A large number of studies, especially on Al(I) have been carried out and the type of compounds considered are AlX, RAl and (RAl)₄. The prime motivation has been to seek a reason for a variety of observations made in their chemistry, such as: (i) the highly unstable nature of AlX; (ii) the varying stability of Al₄ cluster and the substituent effects on it; (iii) the energetics and kinetics of monomer–tetramer equilibrium; and (iv) their unusual chemical behavior. Furthermore, this has been used to predict the most stable structures among the structural alternatives possible in specific cases and to calculate ²⁷Al-NMR chemical shifts of species to facilitate characterization.

For example, ab initio calculations carried out by Xie and Schäfer [51] showed that the reaction of ethyne with AlH can give rise to isomeric products (Scheme 4).

Their study indicates that though **A** is sufficiently stable (dissociation energy: 115.9 kJ mol^{−1}), **B** and **C** are comparatively more stable than **A** by 60.3 and 82.9 kJ mol^{−1}, respectively. Thus, in these reactions products of the type **B** and **C** appear to be thermodynamically more favored. It remains to be seen whether such species will be isolated in the near future.

In another study, the formation and stability of (Cp*Al)₄ and other unknown analogues (AlX)₄ (X = H, F, Cl) were considered [52]. It revealed that AlX showed a marked tendency for tetramerization. The stabilization energy of (CpAl)₄ was found to be 34 kJ mol^{−1} more than that of CpAl. The results also indicated that (CpAl)₄ would be weaker compared to (AlX)₄ (X = H, F, Cl) due to its pronounced degree of π -back bonding. Schneider et al. carried out an ab initio study [53] on (R₃SiAl)_n [*n* = 1 and 4; R = H, Me, *t*-Bu] much before (*t*-Bu₃SiAl)₄ **7** was structurally characterized and concluded that compound **7** exists as a tetramer and is more stable than (Cp*Al)₄. They deduced a stabilization energy of −430 kJ mol^{−1} for tetramerization of *t*-Bu₃SiAl. In accordance with their prediction, the X-ray structure of **7** showed a shorter Al–Al bond (260.4 pm) compared to that of (Cp*Al)₄ (277.3 pm). The fact that it could be sublimed in vacuum even at 180°C also reflects its high thermal stability. The study also concluded that the tetrameric form will be stable for R = H and methyl which are hitherto unknown.

On the basis of ab initio work [50], we sought a rationale for the novel structural features of the Al heterocycle, **10** (Fig. 5).

The lone pair of Al(I) is stereochemically active and possibly has a quasi-trigonal planar orientation, as shown in Fig. 5. Charge depletion of the aluminum atom into the semiplane of the ring is also noticed. These features provide scope for observing both Lewis acid and Lewis base behavior of **10**.

The surprising high stability of this monomer is possibly due to the presence of a nonbonded pair of electrons on the Al atom and the participation of an aluminum center in the ring delocalization, besides the steric protection offered by the bulky aryl moieties.

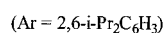
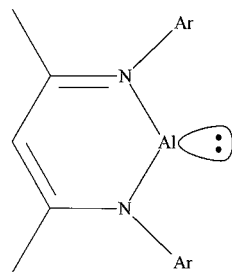
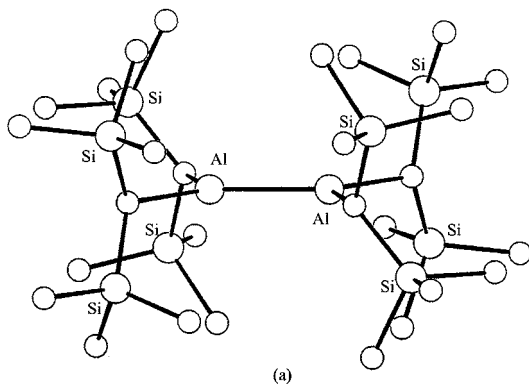
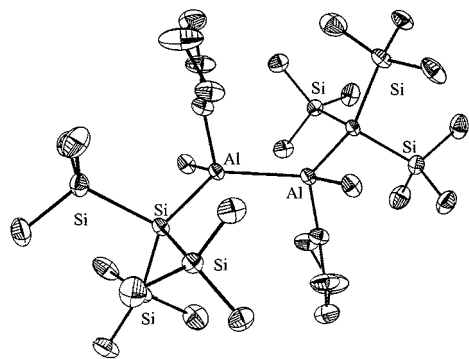


Fig. 5. Compound **10** showing its lone pair orientation.

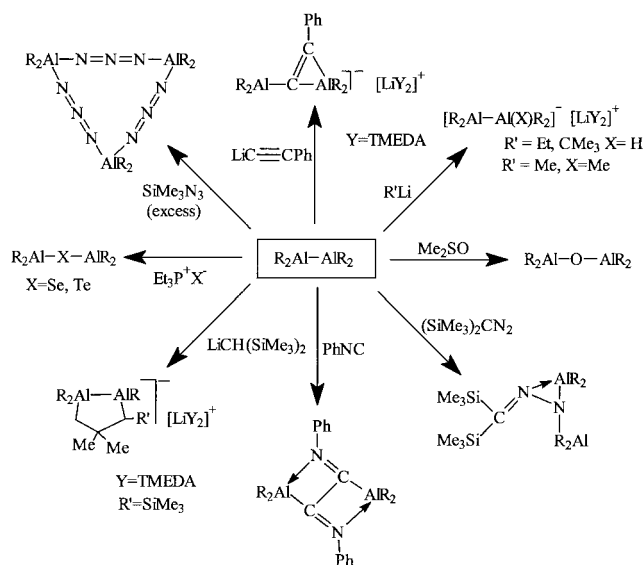


(a)



(b)

Fig. 6. X-ray single crystal structure of: (a) Al₂(CH(SiMe₃)₂)[Li(TMEDA)₂] (Li adduct is not shown in the figure) and (b) Al₂X₂[Si(SiMe₃)₃]₂·2THF.



Scheme 5. Some reactivity aspects of dimer **1**.

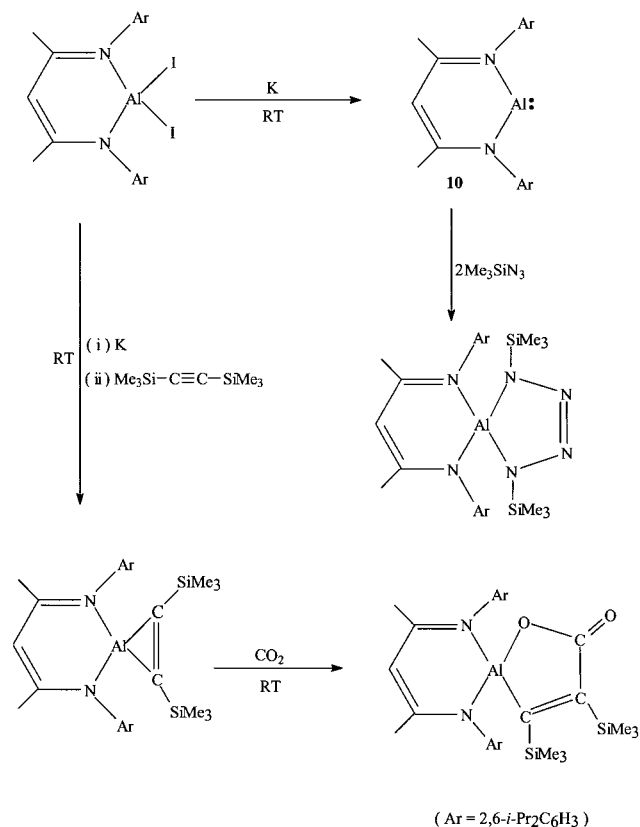
8. Reactivity aspects

The dimeric compounds **1** and **2** undergo an interesting and facile reduction with alkali metals at room temperature or below, to afford the corresponding radical anions of intense color and high thermal stability [25,28] (Fig. 6). Both of them have been structurally characterized and their Al–Al bond length is found to be significantly shorter (e.g. 264.7 pm changes to 247.0 pm in the latter) implying multiple bond character of the metal–metal bond. It is found that R₂Al moieties have an almost planar arrangement in the radical anions contrary to the corresponding neutral dimers where they are twisted with respect to each other. Uhl and coworkers have done further studies of compound **1**, a detailed report of these studies was reported in their recent papers [28a–f]. Compound **1** reacts with RLi forming a hydrido adduct (when R = Et, CMe₃) and methyl adduct (R = Me) on one of the two aluminum atoms. Further, compound **1** undergoes insertion reactions with DMSO to form an oxo bridged linear dialumoxane. The detailed study of compound **1** is described (Scheme 5). Recently, Schnöckel et al. have prepared a mixed organic and halide compound from Al₂X₄·2NMe₂SiMe₃ (X = Cl, Br) and LiSi(SiMe₃)₃ (Fig. 6) [28g].

Among the tetramers **5–9**, with the exception of one reaction of **7** [45], the chemical behavior of (Cp*Al)₄ **5** alone has so far been explored to some extent [49,54–58] and the results are presented in Scheme 3. The tendency of tetramers to convert to a variety of cages and clusters is noteworthy. For example, the reaction of **5** with Ph₂SiF₂ [55] afforded an unexpected cluster composition having novel structural features, instead of the oxidative addition product, Cp*AlF₂ (Scheme 3).

Moreover, Cowley et al. have prepared a Lewis acid–base adduct type $(\text{Cp}^*\text{AlB}(\text{C}_6\text{F}_5)_3)$ of compound with Cp^*Al [59]. It demonstrates the reactive nature of **5** and compositional and structural novelties of products possible from these reactions. Recently, Schnöckel et al. have made a neutral SiAl_{14} cluster from Cp^*Al and SiCl_4 [60]. Likewise, the reaction with organic azides [56,57] having bulky substituents gave unexpectedly novel four-membered cyclic products.

The study of the chemical behavior of the monomer **10** has just begun. The results of the first couple of reactions reported so far [61,62] reveal remarkable features (Scheme 6). The silylated alkyne, $(\text{Me}_3\text{SiC})_2$, adds smoothly to give rise to a three-membered ring which has a very acute C–Al–C angle of just $42.56(11)^\circ$ (Fig. 7). This red black compound, which is extremely sensitive to air and moisture, exhibits a facile room temperature insertion reaction with CO_2 . One CO_2 molecule adds across an Al–C bond to give rise to a five-membered ring as shown. Compound **10** affords an interesting cyclic tetrazole derivative with the silyl azide (Scheme 6), which may have been derived from the $[2+3]$ cycloaddition of a molecule of Me_3SiN_3 with the highly reactive iminoalane bond formed in the previous step. This is the first structurally characterized AlN_4 ring and the aluminum tetrazole part (AlN_4) is found to be essentially planar.



Scheme 6. Addition and insertion reactions of monomer, **10**.

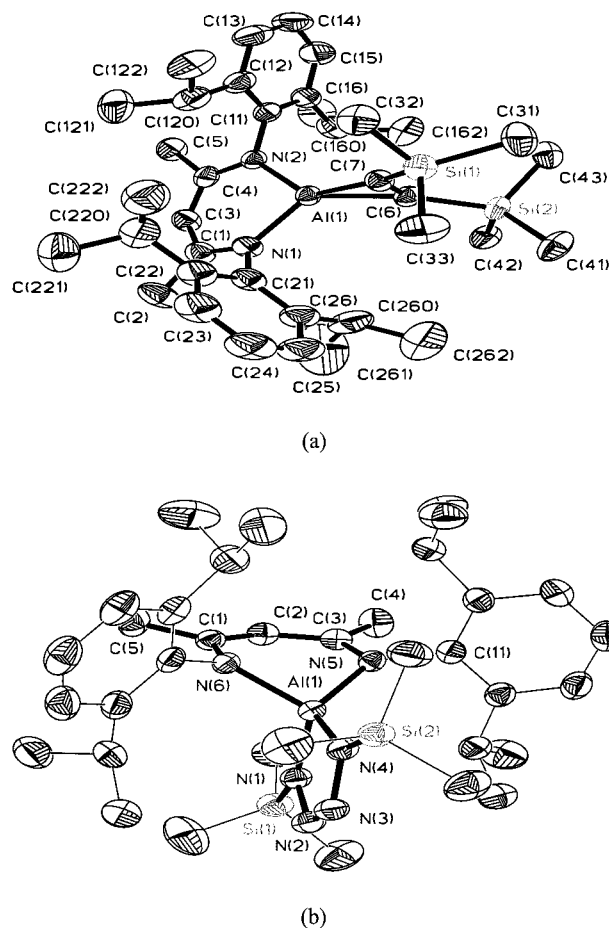


Fig. 7. X-ray single crystal structures of: (a) ' AlC_2 ' and (b) ' AlN_4 ' rings from **10**.

9. Conclusions

The account given in the preceding sections reveals convincingly that the chemistry of organoaluminum compounds with low valent aluminum has evolved very significantly in the last decade. These are very fascinating results and promise much for more fruitful and exciting compounds for the future. As organoAl(I) compounds are now available as stable solids in good yield at room temperature and are reactive both in monomeric and tetrameric forms, several synthetic transformations of interest involving them will become a reality soon. Furthermore, RAl(I) with its donor properties and isolobal analogy to a huge variety of structural moieties of different elements (both metals and nonmetals) clearly offers tremendous potential and scope for notable contribution to preparative and structural inorganic chemistry. The successes and the possibilities of this emerging topic of research, shown in this article, are sure to trigger and take this domain of aluminum chemistry into a more active phase in the not too distant future.

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