

# Chemistry of aluminium(I)

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In this article, we discuss the synthesis of tetrameric and monomeric aluminium(I) compounds. These compounds are prepared by reduction of the respective Al–X (X = halide) bond containing precursor. The tetrameric aluminium(I) compounds are synthesized by using sterically bulky ligands whereas a stable monomeric aluminium(I) compound is obtained using a monovalent chelating ligand. Theoretical studies are carried out on the monomer to understand the Lewis basicity. The presence of a lone pair of electrons plays an important role in the preparation of aluminium containing heterocyclic compounds, main group–main group and transition metal–main group compounds having donor–acceptor bonds by carrying out reactions with unsaturated compounds and Lewis acids.

## Introduction

Aluminium is the third most abundant element in the earth's crust (7.4%). It never exists free in nature and it is usually bound to oxygen (alumina) or to other elements like fluorine (cryolite ( $\text{Na}_3\text{AlF}_6$ )). It is one of the major constituents of naturally available minerals like feldspars, zeolites, and micas. The majority of aluminium compounds known have a formal oxidation state of +3 for the aluminium atom and this can be attributed to the high stability of +3 oxidation state. The Hall–Héroult process, which involves electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in cryolite, is the widely employed process in the production of aluminium metal.<sup>1,2</sup> The area of low valent aluminium chemistry although less explored is quite intriguing and exciting from the perspective of synthetic methodology, structure and theoretical implications. On account of these factors a significant increase in the synthesis of these low

valent aluminium compounds has been observed in the past decade.<sup>3–5</sup> In this feature article we report the development of aluminium(I) chemistry in the last decade as well as the paradigm shift in the synthesis of monomeric aluminium(I) compounds from tetramers and its utility in the preparation of aluminium heterocycles hitherto not possible in conventional ways.

## Chemistry of aluminium(I) compounds

The field of Al(I) chemistry has been developed to a much lesser extent than that of Al(III) compounds owing to the low stability of the +1 oxidation state of the aluminium atom but in the last few years there has been an enhancement in the study of aluminium(I) chemistry. Aluminium behaves like beryllium and when subjected to anodic oxidation at high current densities sub-valent aluminium ions are formed.<sup>2</sup> There is ample evidence for the existence of aluminium(I) compounds like  $\text{AlH}$ ,  $\text{Al}_2\text{O}$ ,  $\text{Al}_2\text{S}$ ,  $\text{Al}_2\text{Se}$ , and  $\text{AlX}$  (X = F, Cl, Br, and I).<sup>6</sup>  $\text{AlH}$  is formed when aluminium is subjected to heating with hydrogen at 1500 °C and at atmospheric pressure.  $\text{Al}_2\text{O}$  is

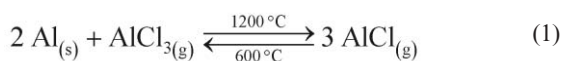
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obtained by heating a mixture of Al<sub>2</sub>O<sub>3</sub> and silicon at 1800 °C in a high vacuum. Both Al<sub>2</sub>S and Al<sub>2</sub>Se are prepared by heating a mixture of aluminium shavings and Al<sub>2</sub>S<sub>3</sub> and Al<sub>2</sub>Se<sub>3</sub>, respectively, at 1300 °C. Aluminium(I) halides are synthesized when metallic aluminium is heated with the appropriate aluminium trihalide. If AlF<sub>3</sub> and Al are heated to 650–850 °C, which is below the sublimation temperature of AlF<sub>3</sub> (1291 °C), a white sublimate is obtained, which upon X-ray examination revealed however only AlF<sub>3</sub> and Al. AlF can also be prepared by passing CF<sub>3</sub>H over molten aluminium at 1000 °C.<sup>7</sup> In 1948, Klemm and co-workers reported the preparation of AlCl by the reaction of elemental chlorine with aluminium at 1000 °C.<sup>8</sup> AlCl is also obtained by reacting aluminium and AlCl<sub>3</sub> under reduced pressure and high temperatures [eqn. (1)]. The formation of AlCl has been thoroughly studied and its use in purifying aluminium has been proposed.



AlF and AlBr are also prepared using a similar strategy. Tacke and Schnöckel followed a completely different approach in the synthesis of AlCl.<sup>9</sup> High yields of AlCl are obtained by reacting aluminium and hydrogen chloride at low pressure (less than 0.2 mbar) [eqn. (2)]. The IR spectrum shows a broad absorption band with a maximum at 320 cm<sup>-1</sup> and a half-width of about 100 cm<sup>-1</sup>. The stability of AlCl in coordinating solvents like ether is known but in weakly coordinating solvents like toluene they are highly unstable.

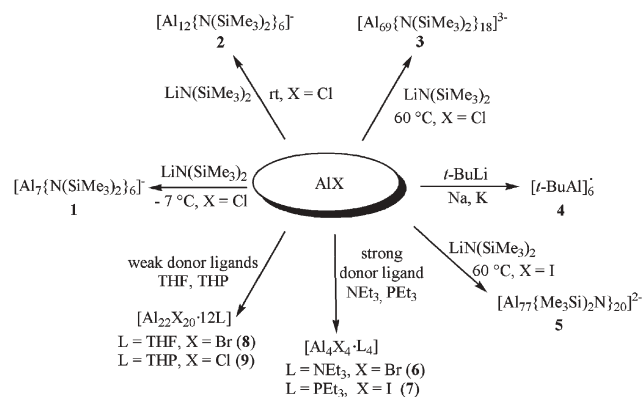


The reactivity of monovalent aluminium halides was investigated by Schnöckel and co-workers by carrying out matrix isolation experiments in solid argon.<sup>7</sup> The matrix induced reactions of AlCl with HBr and AlF with HCl and HBr resulted in the formation of adducts AlCl·HBr, AlF·HCl, and AlF·HBr, respectively. The formation of these species gives insight into the mechanism of the formation of aluminium(III) halides. Peroxo and bis-superoxo complexes of aluminium XAlO<sub>2</sub> and XAl(O<sub>2</sub>)<sub>2</sub> are also reported when AlX (X = F, Cl, and Br) is treated with dioxygen in an argon matrix upon photoexcitation.<sup>10,11</sup>

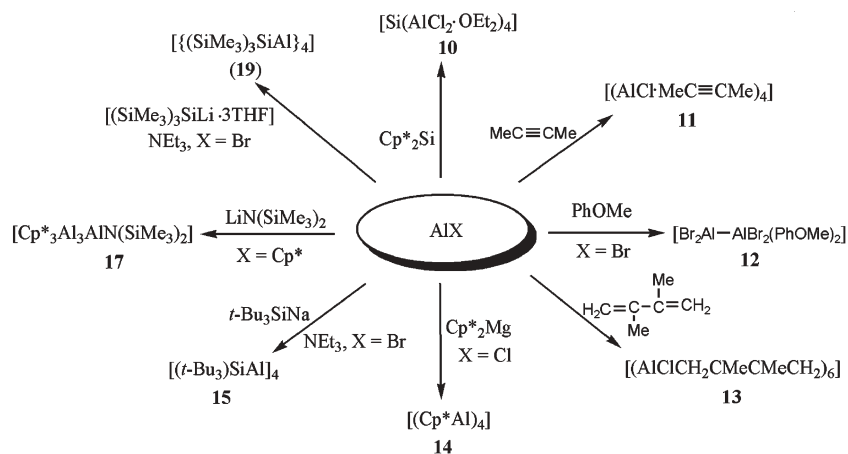
Due importance is given to the synthesis of aluminium metalloid clusters<sup>12</sup> as they show close similarity with the topology of aluminium metal. These clusters contain a large number of (naked) aluminium atoms having a minimum number of donor ligands. The formation of aluminium metalloid is directly dependent on the temperature. A rise in temperature can increase the size of cluster and *vice versa*. For example, AlCl solution when treated with LiN(SiMe<sub>3</sub>)<sub>2</sub> at -7 °C, room temperature, and 60 °C yields the metalloids [Al<sub>7</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>6</sub>]<sup>-</sup> (**1**),<sup>13</sup> [Al<sub>12</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>6</sub>]<sup>-</sup> (**2**),<sup>14</sup> and [Al<sub>69</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>18</sub>]<sup>3-</sup> (**3**),<sup>15</sup> respectively, whereas the reaction of *t*-BuLi with AlCl solution followed by reduction with Na/K alloy results in stable radical [t-BuAl]<sub>6</sub><sup>•</sup> (**4**).<sup>16</sup> However, [Al<sub>77</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>20</sub>]<sup>2-</sup> (**5**) is obtained when an AlI solution is

used.<sup>17</sup> Tetrameric halides ([Al<sub>4</sub>Br<sub>4</sub>·(NEt<sub>3</sub>)<sub>4</sub>] (**6**)<sup>18</sup> and [Al<sub>4</sub>I<sub>4</sub>·(PEt<sub>3</sub>)<sub>4</sub>] (**7**)<sup>19</sup>) of monovalent aluminium halides are prepared by co-condensation of AlX (X = Br and I) with strong donor ligands NEt<sub>3</sub> and PEt<sub>3</sub>, respectively. Both the compounds have a four-membered Al<sub>4</sub> ring with terminally arranged halide atoms and donor ligands. In the presence of weak donor ligands like THF and THP (tetrahydropyran) clusters of the type [Al<sub>22</sub>X<sub>20</sub>·12L] (L = THF, X = Br (**8**);<sup>20</sup> L = THP, X = Cl (**9**)<sup>21</sup>) are obtained (Scheme 1).

A metastable solution of AlCl when reacted with SiCp\*<sub>2</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) in diethyl ether gave compound [Si(AlCl<sub>2</sub>·OEt<sub>2</sub>)<sub>4</sub>] (**10**),<sup>22</sup> which contains four Si–Al bonds and each AlCl<sub>2</sub> unit is further coordinated by a diethyl ether molecule. The most interesting reaction between AlCl and dimethylacetylene MeC≡CMe yields the dimeric 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (**11**).<sup>23</sup> The dimerization of **11** is due to the π-stacking of the two monomers. A unique and fascinating compound [(Cp\*Al)<sub>4</sub>] (**14**) is obtained from the reaction of AlCl solution and Cp\*<sub>2</sub>Mg (Scheme 2).<sup>24–26</sup> We followed a different strategy in the synthesis of **14** by reduction of [Cp\*AlX(μ-X)<sub>2</sub>] (X = Cl, Br, I) with a Na–K alloy or K.<sup>27</sup> We observed that the lower reaction temperature and the decrease in the bond energy of the Al–X bond (AlCl (331 kJ mol<sup>-1</sup>) > AlBr (256 kJ mol<sup>-1</sup>) > AlI (172 kJ mol<sup>-1</sup>)) result in high yields of product **14** (Fig. 1).<sup>28</sup> The starting material [Cp\*AlX(μ-X)<sub>2</sub>] is prepared from Cp\*SiMe<sub>3</sub> and aluminium trihalide (Scheme 3). Compound **14** decomposes around 205 °C and in the <sup>27</sup>Al NMR spectrum a singlet is observed at δ -80.8 ppm. Compound **14** is a tetramer with the aluminium atoms in tetrahedral environment. The bond length between two aluminium atoms is 2.769 Å. Each aluminium atom is coordinated to one Cp\* (Cp\* = C<sub>5</sub>Me<sub>5</sub>) ligand in an η<sup>5</sup>-fashion with Al–C bond length of 2.334 Å. In addition to [(Cp\*Al)<sub>4</sub>] (**14**), only few neutral Al(I) organometallic compounds [t-Bu)<sub>3</sub>SiAl]<sub>4</sub> (**15**),<sup>29</sup> [(SiMe<sub>3</sub>)<sub>3</sub>CAI]<sub>4</sub> (**16**) (Fig. 2),<sup>30</sup> [Cp\*<sub>3</sub>Al<sub>3</sub>AlN(SiMe<sub>3</sub>)<sub>2</sub>] (**17**),<sup>31</sup> [(t-BuCH<sub>2</sub>)Al]<sub>4</sub> (**18**),<sup>32</sup> [(SiMe<sub>3</sub>)<sub>3</sub>SiAl]<sub>4</sub> (**19**),<sup>33</sup> and [2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>)Al]<sub>4</sub> (**20**)<sup>34</sup> are reported and this is primarily due to the tendency of (RAl)<sub>4</sub> to disproportionate into elemental aluminium and AlR<sub>3</sub>. Compound **17** is obtained by the substitution of one of the Cp\* with N-based ligand. The reaction between Cp\*Al and LiN(SiMe<sub>3</sub>)<sub>2</sub> at 60 °C leads to the formation of **17**.



Scheme 1 Reactions of AlX compounds.



Scheme 2 Reactions of AIX compounds.

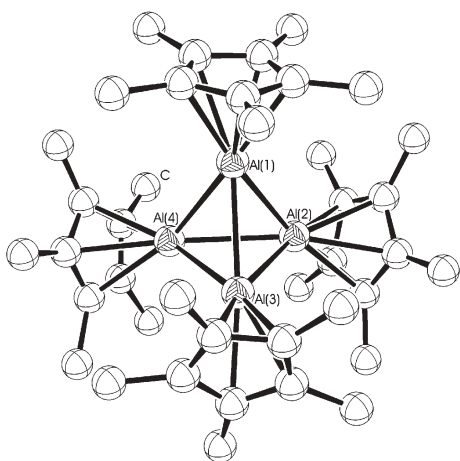


Fig. 1 Molecular structure of [(Cp\*Al)<sub>4</sub>] (14).

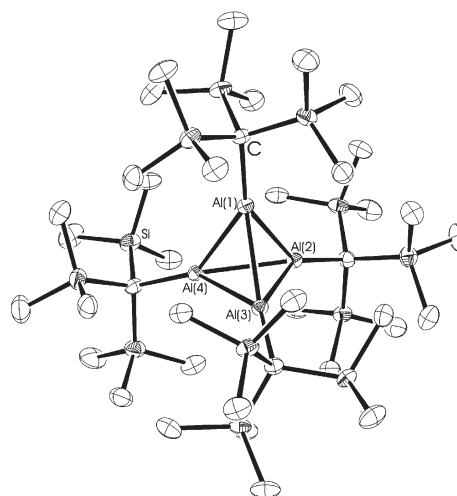
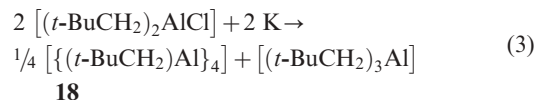


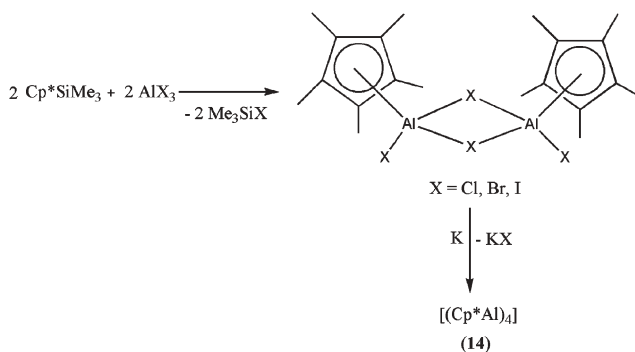
Fig. 2 Molecular structure of [(SiMe<sub>3</sub>)<sub>3</sub>CAI)<sub>4</sub>] (16).

Triethylamine coordinated aluminium(I) iodide and bromide solutions react with *t*-Bu<sub>3</sub>SiNa and [(SiMe<sub>3</sub>)<sub>3</sub>SiLi·3THF], respectively to yield [(*t*-Bu)<sub>3</sub>SiAl]<sub>4</sub> (15) and [(SiMe<sub>3</sub>)<sub>3</sub>SiAl]<sub>4</sub> (19) (Scheme 2). The reduction of [(*t*-BuCH<sub>2</sub>)<sub>2</sub>AlCl] with potassium led to aluminium(I) tetramer [(*t*-BuCH<sub>2</sub>)Al]<sub>4</sub> (18) and [(*t*-BuCH<sub>2</sub>)<sub>3</sub>Al] [eqn. (3)]. Compound [2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>)Al]<sub>4</sub> (20) which is exclusively nitrogen based is prepared by reacting [2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>3</sub>)AlI<sub>2</sub>]<sub>2</sub> with Na/K alloy in hexane

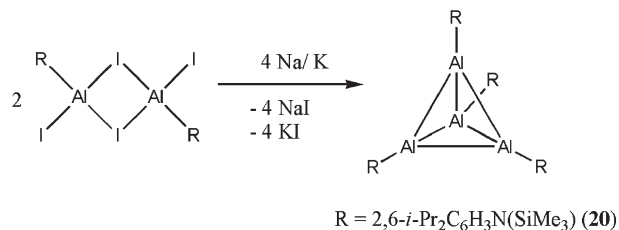
(Scheme 4). These compounds possess tetrahedral arrangement in the solid-state.



Thus, steric and electronic factors of the R group coupled with the easy synthesis of aluminium halides are the essential requirements in the synthesis of (RAl)<sub>4</sub> compounds. Synthesis of few more tetramers from aluminium(I) compounds are



Scheme 3



Scheme 4

**Table 1** Characteristic features of aluminium(I) tetramers

Compound	Mp/ <sup>o</sup> C (decomp.)	Space group	Al–Al distance/Å
[(Cp*Al) <sub>4</sub> ] ( <b>14</b> ) <sup>a</sup>	205	Triclinic, <i>P</i> $\bar{1}$	2.769
[{(t-Bu) <sub>3</sub> SiAl} <sub>4</sub> ] ( <b>15</b> )	—	Monoclinic, <i>C</i> 2/ <i>c</i>	2.604
[{(SiMe <sub>3</sub> ) <sub>3</sub> CAI} <sub>4</sub> ] ( <b>16</b> )	282	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	2.739
[Cp* <sub>3</sub> Al <sub>3</sub> AlN(SiMe <sub>3</sub> ) <sub>2</sub> ] ( <b>17</b> ) <sup>a</sup>	>180	Triclinic, <i>P</i> $\bar{1}$	2.758 <sup>b</sup>
[{(t-BuCH <sub>2</sub> )Al} <sub>4</sub> ] ( <b>18</b> )	—	—	—
[{(SiMe <sub>3</sub> ) <sub>3</sub> SiAl} <sub>4</sub> ] ( <b>19</b> )	>250	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	2.607
[2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(SiMe <sub>3</sub> )Al] <sub>4</sub> ( <b>20</b> )	>270	Triclinic, <i>P</i> $\bar{1}$	2.635

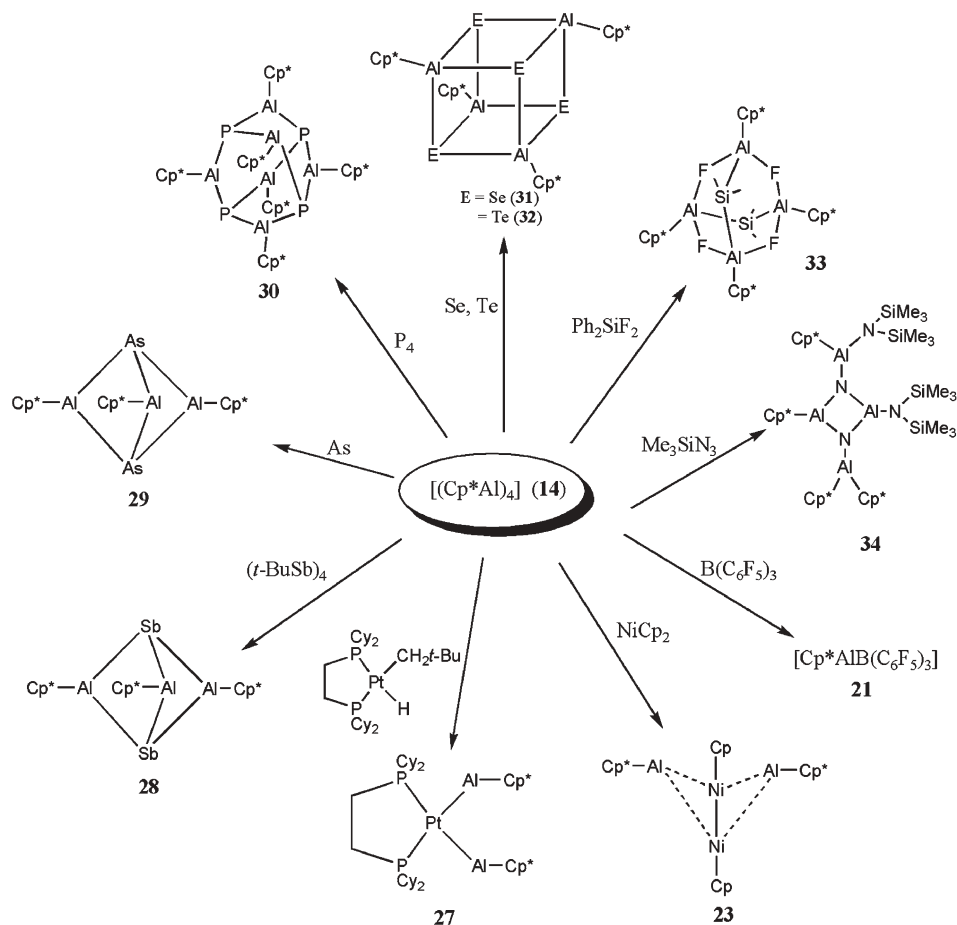
<sup>a</sup> Cp\* = C<sub>5</sub>Me<sub>5</sub>. <sup>b</sup> The distance between two aluminium atoms bound to Cp\* ligands.

depicted in Scheme 2. Some characteristic features of tetrameric aluminium(I) compounds are described in Table 1.

### Chemistry of [(Cp\*Al)<sub>4</sub>] (**14**)

Tetramer [(Cp\*Al)<sub>4</sub>] (**14**) undergoes dissociation in solution and in the gas phase with formation of the monomeric Cp\*Al species.<sup>35</sup> The monomeric Cp\*Al has been thoroughly investigated by <sup>27</sup>Al NMR spectroscopy.<sup>31</sup> The monomer exists in singlet state with a lone pair of electrons on the aluminium atom and its molecular structure was determined using gas phase electron diffraction. Cp\*Al is isolobal to singlet carbene and its reactivity is demonstrated in the presence of Lewis acids like B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to give the Lewis acid–base adduct of composition [Cp\*AlB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**21**)<sup>36</sup> whereas

the reactions with BBr<sub>3</sub> and AlCl<sub>3</sub> yield completely different products. When the reaction is carried out with BBr<sub>3</sub> exchange of Cp\* takes place to give an ionic compound [Cp\*BBr][AlBr<sub>4</sub>] (**22**)<sup>37</sup> and formation of [Cp<sub>2</sub>\*Al]<sup>+</sup> takes place in the presence of AlCl<sub>3</sub>. [Cp<sub>2</sub>\*Al]<sup>+</sup> has a sandwich-like structure isoelectronic with Cp<sub>2</sub>\*Mg.<sup>38</sup> Cp\*Al acts as an efficient ligand in transition-metal complexes L<sub>n</sub>M–AlCp\* (L<sub>n</sub> = ligand).<sup>39</sup> For instance, [(Cp\*Al)<sub>4</sub>] (**14**) in the presence of transition metal complexes [NiCp<sub>2</sub>], [Co<sub>2</sub>(CO)<sub>8</sub>], [Cr(CO)<sub>5</sub>COT] (COT = cyclooctene), [Fe(CO)<sub>5</sub>], and [(dcpe)Pt(H)(CH<sub>2</sub>*t*-Bu)] (dcpe = 1,2-bis(dicyclohexylphosphino)-ethane) yields [(CpNi)<sub>2</sub>(μ–AlCp\*)<sub>2</sub>] (**23**),<sup>40</sup> [Co(CO)<sub>3</sub>]<sub>2</sub>(μ–AlCp\*)<sub>2</sub> (**24**),<sup>41</sup> [(CO)<sub>5</sub>CrAlCp\*] (**25**),<sup>42</sup> [(CO)<sub>4</sub>FeAlCp\*] (**26**),<sup>43</sup> and [(dcpe)Pt(AlCp\*)<sub>2</sub>] (**27**),<sup>44</sup> respectively (Scheme 5). The Pt–Al bond distance (2.33 Å) in **27** is shorter in comparison to that in an alloy of platinum and

**Scheme 5**

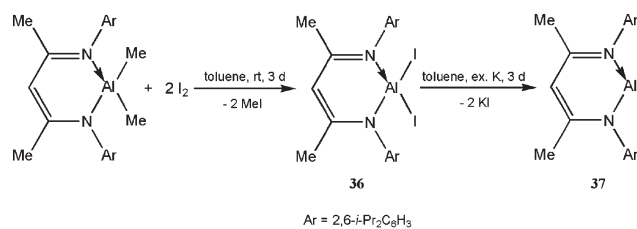
aluminium (2.52 Å).<sup>45</sup> In the above-discussed reactions the aluminium atom retains a formal oxidation state of +1.

The reactions of [(Cp\*Al)<sub>4</sub>] (**14**) with main group element compounds result in the formation of rings, cages, and clusters and a change in oxidation state from +1 to +3 is also observed. Treatment of **14** with (*t*-BuSb)<sub>4</sub> gave a polyhedral [(Cp\*Al)<sub>3</sub>Sb<sub>2</sub>] (**28**)<sup>46</sup> that has two fused four-membered rings. Polyhedral compounds [(Cp\*Al)<sub>3</sub>As<sub>2</sub>] (**29**)<sup>47</sup> and [(Cp\*Al)<sub>6</sub>P<sub>4</sub>] (**30**)<sup>48</sup> are also obtained when [(Cp\*Al)<sub>4</sub>] (**14**) reacts with arsenic and P<sub>4</sub>, respectively. Moreover, reactions are also carried out using Group 16 elements like selenium and tellurium. Colorless crystals of [(Cp\*AlSe)<sub>4</sub>] (**31**)<sup>27</sup> and pale green shiny crystals of [(Cp\*AlTe)<sub>4</sub>] (**32**)<sup>27</sup> are obtained when a solution of **14** in toluene is treated with an excess of selenium and tellurium, respectively. Both compounds possess tetrameric geometry with a deviation in bond angles at Al, Se, and Te centers (av Se–Al–Se 94.6°, Te–Al–Te 95.0°, Al–Se–Al 85.2°, Al–Te–Al 84.7°). The reaction of **14** with Ph<sub>2</sub>SiF<sub>2</sub> resulted in the formation of cage compound **33** instead of Cp\*AlF<sub>2</sub>. Compound **33** has two Al–Si–Al units while the bridging positions are occupied by the fluorine atoms.<sup>46</sup> **14** reacts with alkylsilylazides Me<sub>3</sub>SiN<sub>3</sub> and (*t*-Bu)<sub>3</sub>SiN<sub>3</sub> by an oxidative addition to give imidoalanes [Cp\*AlN{(Cp\*)AlN(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (**34**)<sup>49</sup> and [Cp\*AlNSi(*t*-Bu)<sub>3</sub>]<sub>2</sub> (**35**),<sup>50</sup> respectively. In the synthesis of **35** silyl group migration and Cp\* rearrangement takes place simultaneously. Both compounds **34** and **35** have nearly planar four-membered Al<sub>2</sub>N<sub>2</sub> rings. Moreover, both aluminium and nitrogen atoms have coordination number three (Scheme 5).

### Chemistry of [Al{HC(CMeNAr)<sub>2</sub>}] (**37**)

Although a good number of tetrameric aluminium(I) compounds of the type (RAl)<sub>4</sub> are known, a monomeric species of the composition of RAl has not been isolated. Spectroscopic evidence for the transient existence of MeAl in the gas phase has been provided by Schwarz *et al.*<sup>51</sup> Though PhAl is not isolated, it is considered as an intermediate in organic transformations under photolytic conditions.<sup>52</sup> Schnöckel and co-workers made many attempts to synthesize CpAl but were unsuccessful and this is possibly due to its high thermal sensitivity and decomposition within seconds above –60 °C.<sup>53</sup> However, they were able to characterize and determine the structure of Cp\*Al in the gas phase using electron diffraction.<sup>31,35</sup> This species exists in equilibrium in solution with its tetramer **14**.

We followed different routes to synthesize more kinetically stable aluminium(I) compounds. Considering the fact that bulkiness of the ligand plays a crucial role in the synthesis of aluminium(I) compounds we have chosen the β-diketiminato ligand. Aluminium diiodides were prepared using the chelating monovalent β-diketiminato ligand followed by reduction of [I<sub>2</sub>Al{HC(CMeNAr)<sub>2</sub>}] (**36**) with potassium which resulted in the formation of monomeric aluminium(I) carbenoid [Al{HC(CMeNAr)<sub>2</sub>}] (**37**) (Scheme 6).<sup>54</sup> This was the first stable dicoordinate aluminium(I) compound to be prepared and structurally characterized in the solid-state. Compound **37** (Fig. 3) is a thermally stable red crystalline solid, which has a decomposition point above 150 °C. It is soluble in non-polar



Scheme 6

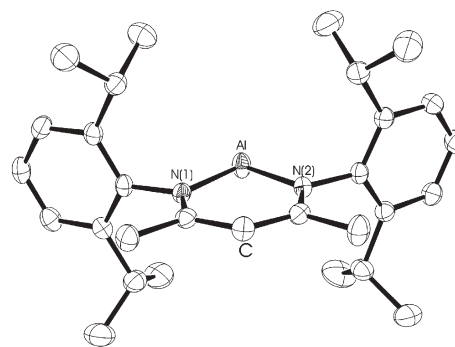
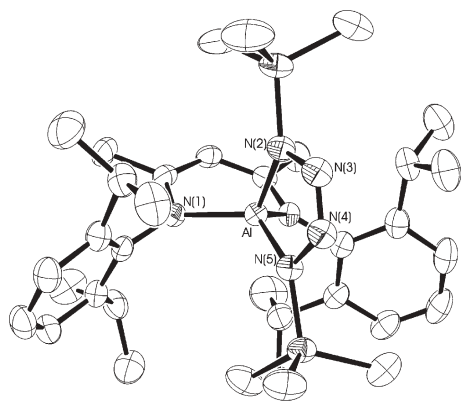


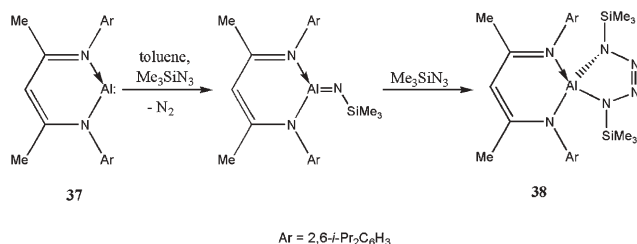
Fig. 3 Molecular structure of [Al{HC(CMeNAr)<sub>2</sub>}] (**37**).

solvents like toluene and benzene, respectively. The aluminium atom in **37** is a part of the six-membered heterocycle. The Al–N bond length (1.957 Å) is longer than that in the corresponding Al(III) compounds [Me<sub>2</sub>Al{HC(CMeNAr)<sub>2</sub>}] (av 1.922 Å) and [(SeH)<sub>2</sub>Al{HC(CMeNAr)<sub>2</sub>}] (1.899 Å).<sup>55</sup> Similarly, an acute bond angle is observed at the aluminium center (N–Al–N 89.86(8)°). The long Al–N bond and small N–Al–N bond angle lower the possibility of multiple Al–N bond character. The fascinating aspect of this molecule is the dual Lewis acid and Lewis base character. On the basis of *ab initio* calculations,<sup>56</sup> the stereochemically active lone pair of electrons on the aluminium atom and the possibility of quasi-trigonal-planar orientation are observed by analyzing the Laplacian of electron density<sup>57</sup> within the plane, which clearly describes the Lewis basicity of compound **37**. Moreover, charge depletion close to the aluminium atom into the semiplane of the six-membered ring was also observed indicating the Lewis acidity of **37**.

Main group heterocyclic compounds have found wide application in pharmaceutical, agrochemical, and material science.<sup>58</sup> There is a tremendous increase in the synthesis of Group 13 heterocycles in recent years. In the following paragraphs, we describe our work in the synthesis of aluminium containing heterocycles. Taking advantage of the lone pair of electrons on the aluminium atom, compound **37** is treated with Me<sub>3</sub>SiN<sub>3</sub> in the synthesis of tetrazole [{HC(CMeNAr)<sub>2</sub>}]Al[(NSiMe<sub>3</sub>)<sub>2</sub>N<sub>2</sub>] (**38**) (Fig. 4).<sup>59</sup> The intermediate [Me<sub>3</sub>SiN=Al(CMeNAr)<sub>2</sub>CH] which may have formed in the course of the reaction undergoes [2 + 3] cycloaddition reaction with Me<sub>3</sub>SiN<sub>3</sub> to yield **38** (Scheme 7). The formation of **38** precludes the dimerization of the intermediate and it can be attributed to the presence of the bulky chelating β-diketiminato ligand. Compound **38** has a nearly planar AlN<sub>4</sub> heterocycle and the geometries at the two



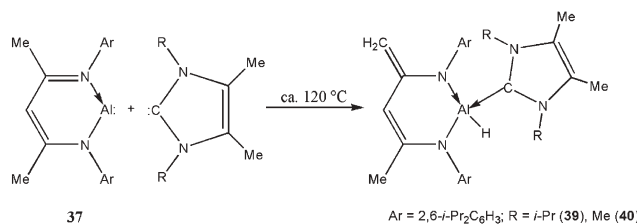
**Fig. 4** Molecular structure of  $[\{HC(CMeAr)_2\}Al[(NSiMe_3)_2N_2]]$  (**38**).



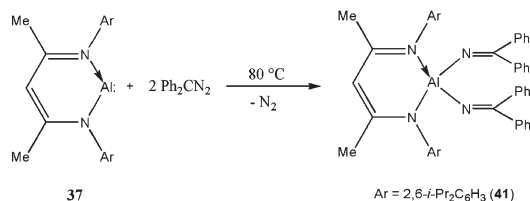
**Scheme 7**

nitrogen atoms connected to the aluminium atom are both trigonal planar. A similar five-membered  $AlN_4$  heterocycle is formed when the reaction is carried out with  $Ph_3SiN_3$ .

It is indeed fascinating to study the reactivity of electron rich aluminium(I) compound **37** in the presence of other electron rich compounds like singlet N-heterocyclic carbenes and diphenyldiazomethane, a precursor to  $:CPh_2$ .<sup>60</sup> The reaction between **37** and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene is carried out at 120 °C to yield adduct **39** (Scheme 8). During the course of the reaction a proton migration from one of the methyl groups of the  $\beta$ -diketiminato ligand to the aluminium atom takes place to generate an Al–H bond. The exact mechanism of the migration is not clear but



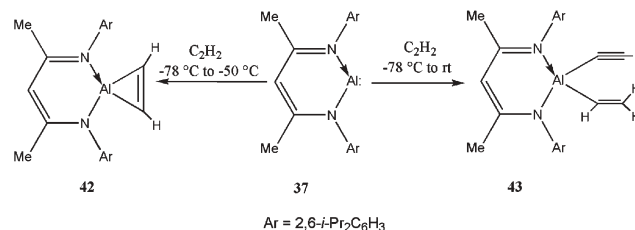
**Scheme 8**



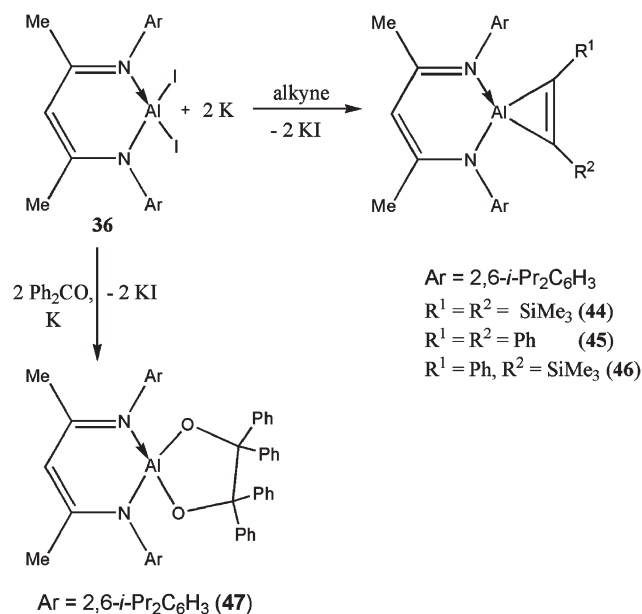
**Scheme 8**

from the IR and NMR spectra the formation of the Al–H bond is confirmed ( $\tilde{\nu}(Al-H)$  1809  $cm^{-1}$  and  $\delta$  4.8 ppm, respectively). 1,3-Dimethyl-4,5-dimethylimidazol-2-ylidene also reacts with **37** in similar fashion to give **40**. Treatment of **37** with two equivalents of diphenyldiazomethane  $Ph_2CN_2$  under heating affords the first example of diiminylaluminium compound  $[(Ph_2C=N)_2Al\{HC(CMeAr)_2\}]$  (**41**) in quantitative yield (Scheme 8). The formation of **41** proceeds *via* the oxidative addition of  $[Al\{HC(CMeAr)_2\}]$  (**37**) and the initially generated  $Ph_2C=N-N=CPh_2$ . The X-ray crystal structure shows a short Al– $N_{iminyl}$  bond length (1.774(4) and 1.785(4) Å) comparable to Al–N bond lengths of three-coordinated aluminium complexes  $[(trip)_2Al\{N(H)dipp\}]$  (1.784(3) Å),  $[MeAl(Ndipp)_3]$  (1.782(4) Å), and  $[Al\{N(SiMe_3)_2\}_3]$  (1.78(2) Å). C–N bond lengths of the iminyl groups (1.249(6) Å) are also found to be shorter than ideal C=N bond length. The short C–N bond may be due to the electron delocalization over the phenyl rings.

Synthesis of cyclopropene derivatives is mainly centered on Group 14 elements. They are prepared by the reaction of carbenes  $R_2C:$  or carbene analogues  $R_2M:$  ( $M = Si, Ge,$  and  $Sn$ ) with alkynes. The chemistry of Group 13 cyclopropene derivatives is mainly focussed on boron<sup>61</sup> but due to the high reactivity exhibited by the heavier main group cyclopropene compounds<sup>62</sup> we can see an upsurge in the synthesis of Al, Ga and In based cyclopropene compounds. Like carbenes,  $[Al\{HC(CMeAr)_2\}]$  (**37**) undergoes [1 + 2] cycloaddition reaction with unsubstituted and substituted alkynes to give three-membered aluminacyclopropene containing derivatives. Compound **37** in the presence of excess acetylene yields an enyne  $[\{HC(CMeAr)_2\}Al\{C\equiv CH\}(CH=CH_2)]$  (**43**) but when the reaction temperature is kept below –50 °C  $[\{HC(CMeAr)_2\}Al(\eta^2-C_2H_2)]$  (**42**) is exclusively formed (Scheme 9). The formation of **42** follows a [1 + 2] cycloaddition reaction and further reaction, with acetylene results in the formation of **43**, which proceeds through a donor–acceptor intermediate due to the Lewis acidic aluminium center in **42**.<sup>63</sup> The X-ray crystal structure of **42** reveals a three-membered aluminacyclopropene  $Al(\eta^2-C_2H_2)$  with short Al–C (1.882(2) Å) and C–C (1.358 Å) bond lengths while **43** has terminal acetylene and ethylene groups. Similarly, heterocyclic three-membered ring containing compounds  $LA[\eta^2-C_2(SiMe_3)_2]$  (**44**),  $LA[\eta^2-C_2Ph_2]$  (**45**), and  $LA[\eta^2-C_2(SiMe_3)Ph]$  (**46**) ( $L = \beta$ -diketiminato) are synthesized in modest yield by carrying out a reductive coupling reaction of  $[I_2Al\{HC(CMeAr)_2\}]$  (**36**) with respective disubstituted alkynes ( $(SiMe_3)_2C_2$ ,  $Ph_2C_2$ , and  $(SiMe_3)(Ph)C_2$ , respectively) (Scheme 10).<sup>64</sup> A possible mechanism is suggested in the formation of compounds **44**, **45**, and **46**. It is assumed that

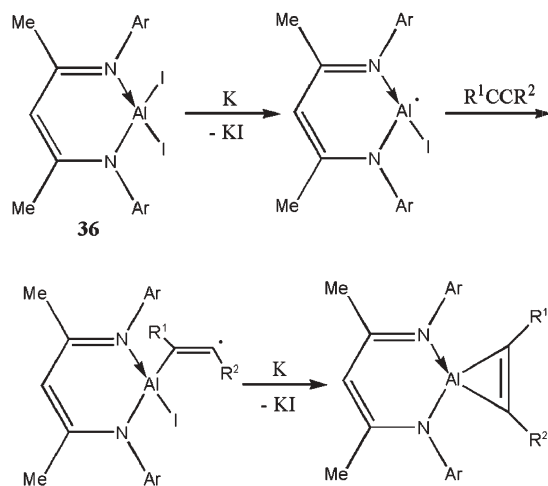


**Scheme 9**



Scheme 10

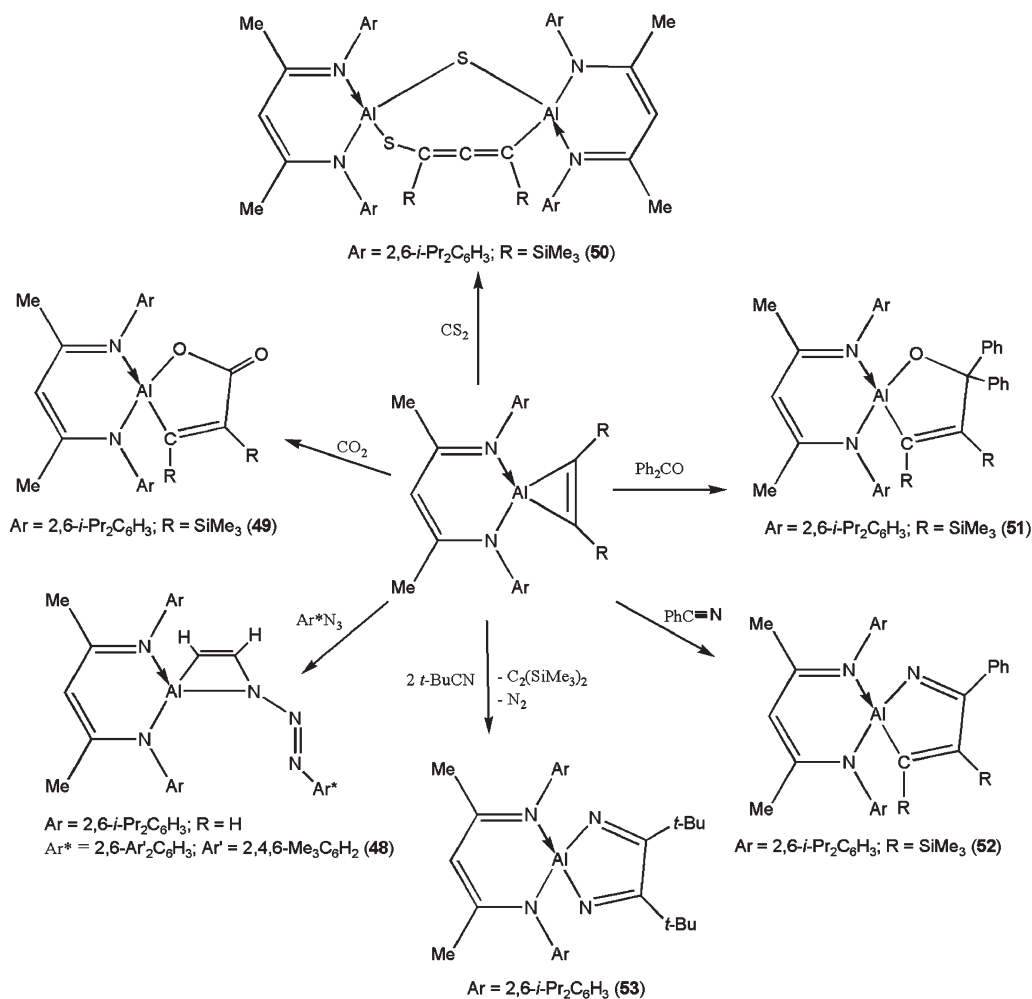
aluminium iodide radical ( $\text{LAlI}^\bullet$ ), generated from compound **36** in the presence of potassium, couples with alkynes followed by electron transfer to yield the desired products (Scheme 11). To understand the mechanism, **36** is treated with benzophenone ( $\text{Ph}_2\text{CO}$ ) in the presence of Na/K at room temperature. The reaction yields aluminium pinacolate  $\{\text{HC}[(\text{CMeNAr})_2]\text{Al}[\text{O}_2(\text{CPh}_2)_2]\}$  (**47**) which is formed *via* the dimerization of the ketyl  $[\text{K}^+(\text{OCPh}_2)^{\bullet-}]$ <sup>65</sup> radical followed by the elimination of KI (Scheme 11). The variable temperature  $^1\text{H}$  NMR spectrum of **44** shows the strong bonding between aluminium and C=C unit. In the  $^{27}\text{Al}$  NMR spectrum of **44**, aluminium atom resonates in the range  $\delta$  90 ppm. Compounds **44** and **45** have highly strained three-membered rings ( $\text{C-Al-C}$   $42.57^\circ$  (**44**) and  $42.02^\circ$  (**45**)) with a short Al-C bond length (1.899 Å (**44**) and 1.875 Å (**45**)). Both the six-membered rings and the three-membered rings are nearly perpendicular to each other.



Scheme 11

Highly strained three-membered rings undergo facile ring opening reactions. This is clearly evident in cyclopropene containing compounds. In order to expand further the scope of the ring opening chemistry, reactions are carried out on aluminium containing three-membered cyclopropene compounds **42** and **44** with unsaturated molecules. Treatment of **42** with organic azide  $\text{N}_3\text{Ar}^*$  ( $\text{Ar}^* = 2,6\text{-Ar}'_2\text{C}_6\text{H}_3$ ,  $\text{Ar}' = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) exhibits an unusual end-on azide insertion resulting in a four-membered aluminiumazacyclobutene  $\{\text{HC}(\text{CMeNAr})_2\text{Al}(\text{CH}=\text{CH})(\text{NN}=\text{NAr}^*)\}$  (**48**).<sup>63</sup> The reaction of **44** with  $\text{CO}_2$  proceeds smoothly at room temperature to generate aluminium bound  $\alpha,\beta$ -unsaturated lactone  $\text{LAl}[\text{OC}(\text{O})\text{C}_2(\text{SiMe}_3)_2]$  (**49**) *via* C-C bond coupling. In the IR spectrum a strong absorption band corresponding to the C=O unit is observed at  $1666 \text{ cm}^{-1}$ . A similar reaction with  $\text{CS}_2$  did not result in a five-membered heterocyclic ring; instead an allene unit present in a seven-membered  $\text{Al}_2\text{C}_3\text{S}_2$  ring containing compound **50** is obtained by carrying out the reaction with **44** at  $-78^\circ\text{C}$ .<sup>66</sup> During the course of the reaction the color of the solution changes from red-black to yellow. The formation of the allene unit in the final product is quite unique and unexpected. It is possible that an intermediate analogous to compound **49** may have formed in the reaction medium that reacts further with the second molecule of **44** to give **50**. The bond angle of  $122.57^\circ$  for Al-S-Al is the widest among dinuclear aluminium sulfides or thiolates. Benzophenone also undergoes C-C bond coupling with **44** to give aluminadihydrofuran  $\text{LAl}[\text{OC}(\text{Ph})_2\text{C}_2(\text{SiMe}_3)_2]$  (**51**). The reaction is carried out at room temperature in diethyl ether. This is a first example of an aluminium bound dihydrofuran structure. The reactivity of **44** with PhCN is monitored in diethyl ether at room temperature to give aluminium containing pyrazole structure  $\text{LAl}[\text{NC}(\text{Ph})\text{C}_2(\text{SiMe}_3)_2]$  (**52**). Crystal structures of **51** and **52** show the tetrahedral geometry for the aluminium atom. The Al-O bond length in **51** (1.727 Å) is comparable to that of **47** (1.730 Å) whereas a bond length of 1.867 Å is observed for an Al-N bond in **52**, which is shorter in comparison to Al-N bond length in the aluminium iminato complex  $\{\textit{i}\text{-Bu}\}_2\text{Al}[\mu\text{-N}=\text{C}(\text{H})(\text{C}_6\text{H}_3\text{-}2,6\text{-Me}_2)]_2$  (1.946 Å).<sup>67</sup> Aluminium bis(iminato) complex  $\text{LAl}[\text{N}_2(\text{C}t\text{-Bu})_2]$  (**53**) is obtained *via* the replacement of the alkyne moiety when compound **44** is treated with *t*-BuCN (Scheme 12).

It is often observed that synthesis of imidoalanes occurs at elevated temperatures and involves the elimination of alkanes, alkenes, or dihydrogen from imidoalanes. The elimination of substituents results in a decrease in the steric crowding around the imidoalane and thereby increases the possibility of association leading to the formation of dimers, tetramers, hexamers *etc.*<sup>68</sup> On the other hand organoazides<sup>49,69</sup> play a significant role in the synthesis of unassociated rings having Al-N bonds. The reaction between  $\beta$ -diketiminato stabilized aluminium(I) compound **37** and  $\text{N}_3\text{-}2,6\text{-Dipp}_2\text{C}_6\text{H}_3$  results in the formation of two different isomers **54** and **55**.<sup>70</sup> They are formed *via* a monomeric imidoalane (**A**) which exhibits latent reactivity. The formation of the intermediate species **A** is confirmed by  $^1\text{H}$  NMR kinetic study. Two different reaction pathways are followed in the synthesis of **54** and **55**. A [2 + 2] cycloaddition reaction of the Al=N bond and a phenyl ring of the Ar' substituent on the nitrogen leads to **54** (path "a"). The



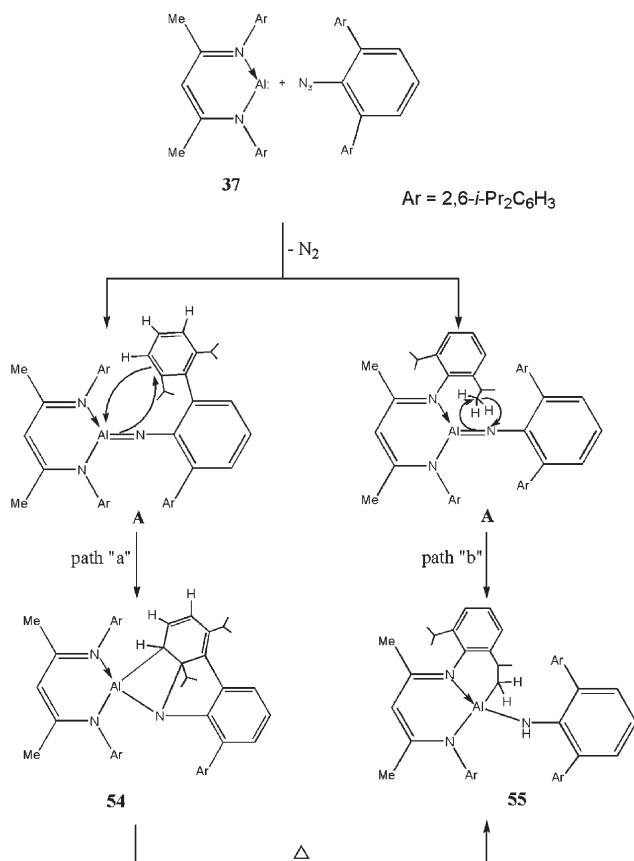
Scheme 12

X-ray crystal structure reveals the formation of quasi-planar AlNC<sub>2</sub> ring ( $\Delta = 0.0680 \text{ \AA}$ ) with an Al–N bond length of 1.867(2)  $\text{\AA}$ . The phenyl ring after the cycloaddition reaction is nonplanar. Intramolecular C–H bond activation of the isopropyl group of the Ar substituent generates **55** (path “b”). In the IR spectrum an absorption band at 3298  $\text{cm}^{-1}$  assignable to the N–H stretching frequency is observed. The crystal structure of **55** shows the formation of a new six-membered AlN<sub>2</sub>C<sub>3</sub> ring with aluminium in tetrahedral geometry. Moreover, **54** can be transformed to **55** under thermal conditions (Scheme 13).

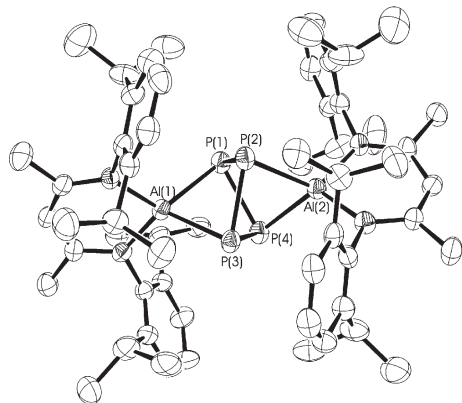
Organophosphorus compounds and sulfur containing compounds like metal sulfides, S<sub>8</sub>, P<sub>4</sub>S<sub>10</sub>, H<sub>2</sub>S, and organo polysulfanes have attracted a great deal of attention owing to their structural reactivity and due to their wide potential application.<sup>71</sup> Transition-metal sulfides are widely employed not only in catalytic reactions like HDS (hydrodesulfurization) of fossil fuels<sup>72</sup> but also as intermediates in enzymatic processes. Quite contrary to the availability of transition-metal sulfides [Cp<sub>2</sub>TiS<sub>5</sub>]<sup>73</sup> and [ $\{\eta^5\text{-MeC}_5\text{H}_4\text{Ru}(\text{PPh}_3)(\mu\text{-S}_3)\}_2$ ]<sup>74</sup> and phosphides [Cp\*<sub>2</sub>(CO)<sub>2</sub>Co<sub>2</sub>P<sub>4</sub>] (Cp\* = C<sub>5</sub>Me<sub>5</sub>)<sup>75</sup> Group 13 metal sulfides and phosphides are less explored. We investigated the reactivity of **37** in the presence of white

phosphorous (P<sub>4</sub>) and elemental sulfur (S<sub>8</sub>) in the successful synthesis of P<sub>4</sub><sup>4-</sup> and S<sub>6</sub><sup>4-</sup> unit containing aluminium phosphide [ $\{\text{HC}(\text{CMeNAr})_2\text{Al}\}_2\text{P}_4$  (**56**) (Fig. 5)<sup>76</sup> and sulfide [ $\{\text{HC}(\text{CMeNAr})_2\text{Al}\}_2\text{S}_6$  (**57**) (Fig. 6),<sup>77</sup> respectively (Scheme 14). During the reactions cleavage of two P–P and four S–S bonds is observed. The presence of excess **37** could not lead to the complete cleavage of the remaining P–P and S–S bonds. The <sup>31</sup>P NMR spectrum of **56** shows resonance at  $\delta$  78.6 ppm, which is downfield in comparison to the free P<sub>4</sub> molecule ( $\delta$  –519 ppm) and in the X-ray crystal structure cleavage of two P–P bonds is noticed. The Al–P bond length of 2.37  $\text{\AA}$  is in the range of the Al–P bond length of [(Cp\*Al)<sub>6</sub>P<sub>4</sub>] (**30**) (2.31–2.42  $\text{\AA}$ ). The charge distribution in the Al<sub>2</sub>P<sub>4</sub> unit was investigated using DFT calculations with RI-BP86/TZVP within TURBO-MOLE. A net charge transfer from the aluminium atoms to P<sub>4</sub> is observed when calculated Mulliken charges on the P atom (–0.22) are taken into consideration, which clearly demonstrates the formation of an ionic Al–P bond. The bond order of zero shows the cleavage of the P–P bonds whereas the binding energy of the order of 36.4 kcal mol<sup>–1</sup> ( $(E_{(\text{LM})2\text{-P}_4} - 2^*E_{\text{L-M}} - E_{\text{P}_4})/2$ ) indicates a strong interaction between aluminium atoms and P<sub>4</sub>. The synthesis of pale yellow crystals of [(LAl)<sub>2</sub>S<sub>6</sub>] (**57**) is carried out at –78 °C.

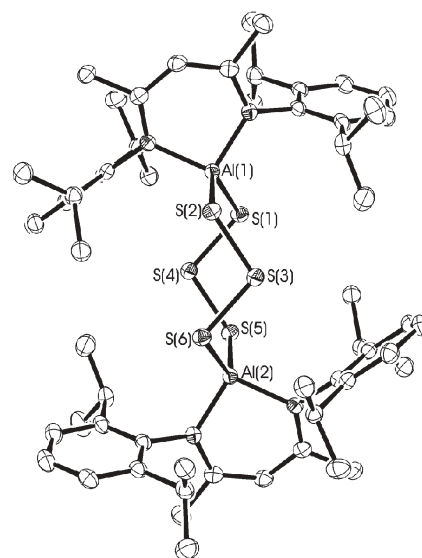




The crystal structure of **57** shows that the aluminium atoms are connected by two  $\mu$ -S<sub>3</sub> chains to form an aluminium hexasulfide Al<sub>2</sub>S<sub>6</sub>. The eight-membered Al<sub>2</sub>S<sub>6</sub> ring has a staggered conformation in contrast to the S<sub>8</sub> molecule's eclipsed conformation. The S–S bond length (av 2.08 Å) is longer than that in the S<sub>8</sub> molecule (av 2.05 Å) whereas the S–S–S bond angle (104.7°) is close to the bond angles found in transition-metal sulfides [({η<sup>5</sup>-MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Ti(μ-S<sub>3</sub>)<sub>2</sub>] (109.1°) and [({η<sup>5</sup>-MeC<sub>5</sub>H<sub>4</sub>)Ru(PPh<sub>3</sub>)(μ-S<sub>3</sub>)<sub>2</sub>] (105.2°). DFT calculations carried out on **57** using RI-BP86/TZVP within TURBO-MOLE shows more than one stable conformation for the



**Fig. 5** Molecular structure of [HC(CMeNAr)<sub>2</sub>]AlI<sub>2</sub>P<sub>4</sub> (**56**).

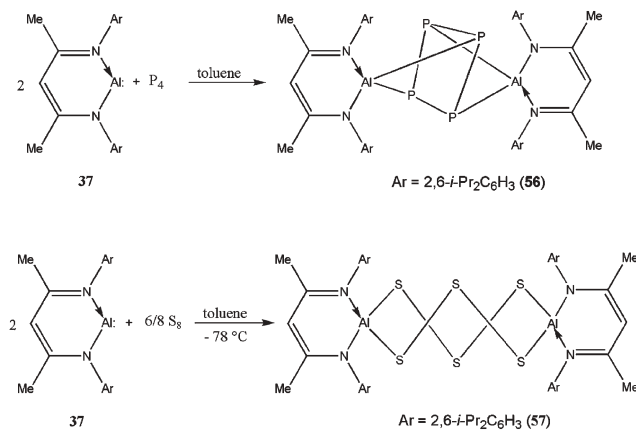


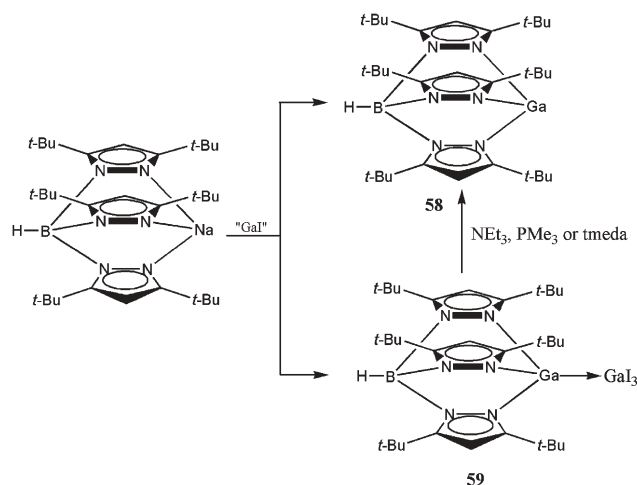
**Fig. 6** Molecular structure of [HC(CMeNAr)<sub>2</sub>]AlI<sub>2</sub>S<sub>6</sub> (**57**).

[L<sub>2</sub>Al<sub>2</sub>S<sub>n</sub>] (L = ligand; n = 2–8) species, which makes the isolation of the species difficult.

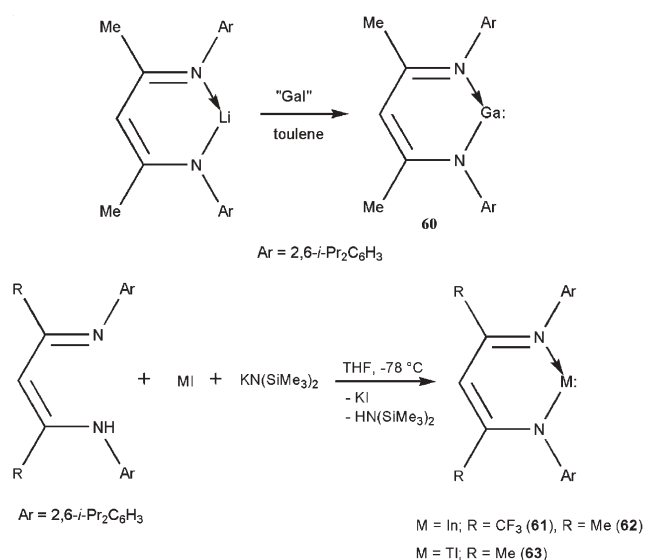
### Chemistry of heavier Group 13 carbenoids

It is interesting to know that Al(I) carbenoid was synthesized prior to the discovery of the analogous Ga(I), In(I), and Tl(I) carbenoids even though the stability of monovalent oxidation state increases as Group 13 is descended. In general low valent heavier Group 13 compounds containing a M–M bond (M = Ga, In, and Tl) exist as tetramers or hexamers that may dissociate to lower aggregates in the vapor or solution phase. Although the pentamethylcyclopentadienyl derivative of Ga(I) was structurally characterized as the monomer in the gas phase by electron diffraction, it is highly unlikely to exist as a monomer in solid state. Thus, the Ga(I) compound Ga(Tp<sup>t-Bu</sup>) (**58**) [Tp<sup>t-Bu</sup> = tris(3,5-di-*tert*-butylpyrazolyl)-hydroborato] was structurally characterized for the first time by Parkin and co-workers in the solid-state by carrying out the reaction between *in situ* generated GaI and Na(Tp<sup>t-Bu</sup>), which also gave the adduct Ga(Tp<sup>t-Bu</sup>)<sub>2</sub> → GaI<sub>3</sub> (**59**) (Scheme 15).<sup>78</sup>





Scheme 15



Scheme 16

The closest Ga...Ga distance is *ca.* 10.4 Å, which clearly indicates the absence of any kind of interactions between the monomers. The stability of this molecule is derived from the presence of bulky tridentate ligand  $\text{Tp}^{t\text{-Bu}}_2$ . In continuing efforts to synthesize monovalent gallium compounds Power and co-workers reported  $\beta$ -diketiminato stabilized Ga(I) monomer,  $[\text{Ga}\{\text{HC}(\text{CMeNAr})_2\}]$  (**60**), (Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (Scheme 16).<sup>79</sup> It was obtained by the reaction of  $[\text{Li}\{\text{HC}(\text{CMeNAr})_2\}]$  with GaI. During the course of the reaction any Ga(III) compound,  $[\text{I}_2\text{Ga}\{\text{HC}(\text{CMeNAr})_2\}]$  formed was subsequently reduced with excess potassium to generate the monovalent derivative. The Ga–N bond length (2.054(4) Å) in **60** is shorter than the corresponding bond length in **58** (2.230(5) Å) and indicates the absence of multiple Ga–N bond character which might have arisen from the delocalization of  $\pi$ -electrons within the six-membered ring. Recently, Schmidbaur and Jones have reported the anionic Ga(I) heterocycle.<sup>80–82</sup>

Observing these exciting results Hitchcock and co-workers gave impetus to the synthesis of monomeric indium and thallium compounds in their +1 oxidation state. The In(I) carbenoids  $[\text{In}\{\text{HC}(\text{C}(\text{R})\text{NAr})_2\}]$ ; (R = CF<sub>3</sub> (**61**),<sup>83</sup> Me(**62**)<sup>84</sup>), stabilized by the bulky  $\beta$ -diketiminato ligand, having a two-coordinate neutral In(I) singlet, is synthesized by carrying out a ‘one pot’ reaction of equimolar quantities of  $\text{K}[\text{N}(\text{SiMe}_3)_2]$ , readily available InI, and  $[\text{H}\{\text{HC}(\text{C}(\text{R})\text{NAr})_2\}]$ ; (R = CF<sub>3</sub>, Me) in THF at –78 °C. A similar strategy is employed in the preparation of Tl(I) carbenoid  $[\text{Tl}\{\text{HC}(\text{CMeNAr})_2\}]$  (**63**) (Scheme 16).<sup>83</sup> Compounds **61**, **62**, and **63** are isostructural

with the corresponding Al(I) and Ga(I) derivatives **37** and **60**, respectively. Although Cp\* bound gallium(I) and indium(I) compounds are extensively used in Lewis acid-Lewis base adducts<sup>85</sup> but the chemistry of  $\beta$ -diketiminato stabilized Ga(I), In(I), and Tl(I) monomers **60–63** is still in its infancy. Power and co-workers recently reported the synthesis of monomeric imides  $[\{\text{HC}(\text{CMeNAr})_2\}\text{GaN-2,6-Trip}_2\text{C}_6\text{H}_3]$  (**64**) by carrying out the reaction between bulky azide N<sub>3</sub>-2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and **60**.<sup>86</sup> The X-ray crystal structure shows a short Ga–N<sub>imide</sub> bond (1.742(3) Å) and a bent geometry for the imide nitrogen (Ga–N<sub>imide</sub>–C 134.6(3)°). The deviation from the linear alignment is attributed due to the presence of bulky ligands around the imide bond. A similar *trans* bent geometry is observed at the nitrogen center in the compounds Ar'MNAr'' (Ar' = 2,6-Dipp<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Dipp = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); Ar'' = 2,6(Xyl-4-*t*-Bu<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>; M = Ga (**65**) and In (**66**)), which are prepared by the reaction of gallium and indium dimers (Ar'M)<sub>2</sub> (M = Ga, In) with N<sub>3</sub>Ar''.<sup>87</sup> When the present manuscript was under preparation, Power *et al.* reported the synthesis of monomeric thallium(I) amide  $[\text{TlN}(\text{Me})\text{Ar}^{\text{Mes}}_2]$  (**67**)<sup>88</sup> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) by carrying out the reaction between TlCl and bulky lithium amide  $[\text{LiN}(\text{Me})\text{Ar}^{\text{Mes}}_2]$  but when the diethyl ether adduct of lithiated aryl compound 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li·Et<sub>2</sub>O is used 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Tl (**68**) (Trip = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) is obtained.<sup>89</sup> The characteristic features of monovalent monomeric Group 13 compounds are shown in Table 2.

Table 2 Characteristic features of monovalent monomeric Group 13 compounds

Compound	Mp/°C	Space group	M–N bond distance/Å	N–M–N bond angle (°)
$[\text{Al}\{\text{HC}(\text{CMeNAr})_2\}]$ ( <b>37</b> )	>150 <sup>a</sup>	Monoclinic, $P2_1/n$	1.957	89.86
$[\text{Ga}\{\text{HC}(\text{CMeNAr})_2\}]$ ( <b>60</b> )	202–204	Monoclinic, $P2_1/n$	2.054	87.53
$[\text{In}\{\text{HC}(\text{CMeNAr})_2\}]$ ( <b>61</b> )	203–205 <sup>a</sup>	Monoclinic, $P2_1/n$	2.268	81.12
$[\text{In}\{\text{HC}(\text{CF}_3\text{NAr})_2\}]$ ( <b>62</b> )	90 <sup>a</sup>	Triclinic, $P\bar{1}$	2.357	78.23
$[\text{Tl}\{\text{HC}(\text{CMeNAr})_2\}]$ ( <b>63</b> )	104–105 <sup>a</sup>	Monoclinic, $P2_1/n$	2.428	76.67

<sup>a</sup> Decomposition.

## Conclusions

The present review focuses on the development of aluminium(I) chemistry in the last decade.<sup>90,91</sup> It also lays emphasis on the synthesis of heavier analogous of aluminium like Ga, In, and Tl. The preparation of monomeric and tetrameric aluminium(I) compounds is possible only in the presence of an aluminium–halogen bond. Even though several tetrameric aluminium compounds are known, the ligands present on them are not suitable enough in the synthesis of monomeric species. The monovalent chelating  $\beta$ -diketiminato ligand plays a decisive role in the preparation of  $[\text{Al}\{\text{HC}(\text{CMeNAr})_2\}]$  (**37**). Thus, we have seen a gradual transition in the synthetic methodology in the synthesis of monomeric aluminium(I) compound **37** from tetrameric aluminium(I) compounds by using a bulky ligand. Tetramer  $[(\text{Cp}^*\text{Al})_4]$  (**14**) reacts with several main group element compounds and transition metal compounds and generates cages, clusters, and rings whereas the  $[\text{Al}\{\text{HC}(\text{CMeNAr})_2\}]$  (**37**) reacts with unsaturated compounds to afford aluminium containing heterocyclic compounds. The reaction between  $[(\text{Cp}^*\text{Al})_4]$  (**14**) and Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  results in the generation of a main group–main group donor–acceptor bond. The chemistry of aluminium(I) is still in its infancy but it has a great potential as it has already found wide application in materials and agrochemicals.

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