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Alkynyl aluminium compounds: bonding modes and structures†

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Alkynyl aluminium compounds and the method of hydroalumination of multiple bonds are very useful tools in the hands of a synthetic chemist. The different reactions of alkynyl aluminium compounds as well as hydroalumination have resulted in versatile applications in organic synthesis, thereby various functionalities can be selectively transformed under mild reaction conditions. However, the bonding situation of alkynyl aluminium compounds and the structures of the intermediates formed by hydroalumination of different alkyne systems were only understood within limits. From the point of view of coordination chemistry the features of bonding and the structures of aluminium complexes in addition to their utilities in preparative chemistry are of significant interest. In this perspective, the chemistry of alkynyl aluminium and hydroalumination is traced back to its origin and is accentuated with respect to bonding and structures. A few recent results in alkynyl aluminium chemistry and the successful structural determination of the intermediates of hydroalumination gives insight into the unique properties of alkynyl aluminium compounds and opens a route to a new class of aluminium clusters.

1 Introduction

Since K. Ziegler discovered the synthetic and catalytic potential of organoaluminium compounds and the low pressure polymerization of olefins with organoaluminium/transition metal catalysts, organoaluminium chemistry has gained great interest.[1] For the past five decades a variety of reactions and reagents involving organoaluminium compounds have been developed.[2] There are a number of books, articles and reviews that cover the broad range of aluminium chemistry from practical aspects and synthetic strategies to theoretical investigations.[3] In particular the chemistry of aluminium alkynes and the hydroalumination of multiple bond systems as well as

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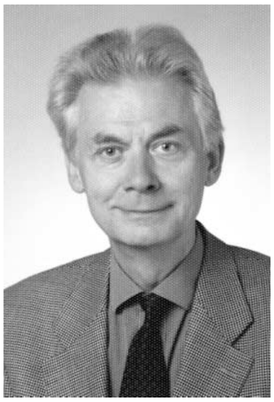

Herbert W. Roesky

Professor Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontiers lecturer at Texas A&M University at College Station, University of Texas at Austin and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists 'Leopoldina' in Halle, and the Academia Europaea in London. He served as the vice president of the German Chemical Society during 1995, and presently he is the president of the Academy of Sciences of Göttingen. He has received many awards, e.g., the Dr.rer.nat.h.c. of Bielefeld, and French Alexander-von-Humboldt award. More than 850 publications, articles, patents, and books record his research activity in the areas of inorganic chemistry and materials sciences.

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† Dedicated to Professor George M. Sheldrick on the occasion of his 60th birthday.

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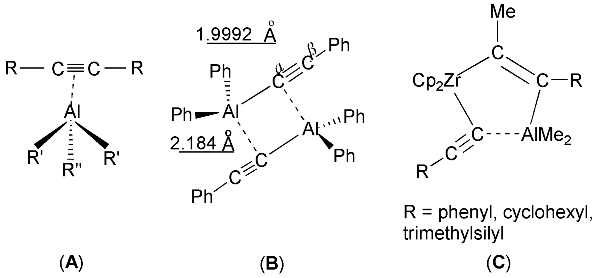
oligomerization of olefins and alkynes by catalysts containing aluminium species have been of significance since they are broadly applied to organic synthesis for efficient stereoselective transformations and polymerizations.[3,4] Hence, the study of the bonding situation of alkynyl aluminium compounds as well as the exploration of intermediate structures of hydroalumination are of particular interest to chemists in understanding the processes of related reactions. Within the scope of this micro review recent progress in the bonding features of alkynyl aluminium compounds will be introduced. Particularly, the hydroalumination with $H_3Al{\cdot}NMe_3$ and multiple bond systems (HC≡CR, N≡C–R and C≡N–R) and the unique structures of the intermediates will be summarized.

2 Bonding situation of neutral alkynyl aluminium compounds

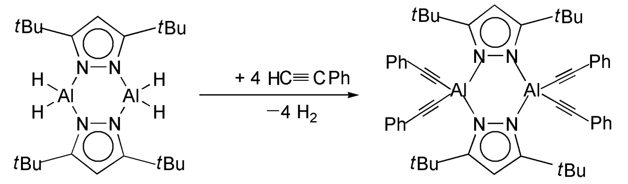
Metal alkynyl complexes have been well documented in organometallic chemistry.[5] The first synthesis and accurate description of an alkynyl aluminium compound, $Et_2Al–C≡CEt$, was reported by Wilke and Müller many years ago.[6a–c] This thermally stable compound was conveniently synthesized by salt-metathesis reaction from diethylaluminium chloride and NaC≡CEt in a 80–90% yield. Afterwards, several other alkynyl aluminium compounds were prepared by metallation of CH-acidic terminal alkynes with dialkylaluminium hydride or with trialkyl(triaryl)aluminium.[6d,e] Since then, alkynyl aluminium compounds, prepared mainly following Wilke's method, have been employed in selective organic synthesis such as reactions of dialkylalkynyl aluminium in 1,2-, 1,4- or homoconjugate addition of enones.[7] Especially the favourable stereospecific and regiochemical controlled reaction of alkynyl aluminium compounds with epoxides is of considerable significance because epoxides are highly resistant to attack by alkynyl Grignard and lithium reagents.[8]

Nevertheless, even though alkynyl aluminium complexes were widely applied to organic synthesis, the bonding situation between aluminium atoms and alkynyl groups was poorly understood due to the lack of structures in early days. It seemed that Eisch *et al.* made contributions to the bonding situation of alkynyl aluminium compounds as well as their reactions.[4f] Based on the fact that organoaluminium reagents add more readily to alkynes than to olefinic linkages,[9] along with other information on the stereochemistry observed in the hydroalumination and oligomerization of alkynes, it was postulated that a π-complex intermediate is initially involved (Scheme 1 (**A**)).[10] However, no direct evidence for such a π-complex or an analogue was acquired until the dimeric structure of an alkynyl aluminium complex $[PhC≡CAlPh_2]_2$ was reported by Stucky *et al.* in 1974 (Scheme 1 (**B**)).[11] The arrangement of $[PhC≡CAlPh_2]_2$ presented in the crystal structure indicated that C_α forms a σ-bond to one Al atom and a π-donor bond to the other. This feature was strongly supported by the Al–C bond lengths (1.9992 and 2.184 Å, respectively). This bonding character is reminiscent of the σ/π-bridges which occur for transition metal carbonyls. The alkynyl ligand may be viewed as a donor of three electrons (1σ-e, 2π-e) that provides alkynyl bridges which are more electron sufficient than alkyl bridges, thereby accounting for their robust nature. Further examples were aluminium/transition metal containing heterodimetallic complex systems which were established by Erker *et al.*,[12] whereby the alkynyl group serves as a bridge between an aluminium and a transition metal (Scheme 1 (**C**)).[12a] The bridging alkynyl group binds with metals in a manner similar to that observed in **B**. In light of the analysis of the above two systems, it seems to be general that in a combination of a σ/π-system, two electron deficient metal atoms (two Al atoms or one Al and one transition metal) and an electron sufficient alkynyl or olefinic system that rendered the necessary delocalizing π-donor properties, bimetallic complexes could be stabilized and might exist ubiquitously. However, arguments in favour of a completely σ-bridging feature of an alkynyl group have also been proposed since the μ-(σ/π-alkyne) component in the bridge leading to almost equal Al–C^α and Al–C^β bond lengths cannot be observed in **B** and **C**.[12b]



Scheme 1 Assumed alkynyl aluminium intermediate (**A**); alkynyl aluminium featuring a dimeric structure with a bridging alkynyl ligand between two aluminium centres (**B**) or between one aluminium atom and one early transition metal atom (**C**).

The unique configuration of the dimeric structures with a bridging alkynyl ligand between two aluminium centres[11] or between one aluminium atom and one early transition metal atom[12] likely arises from the combination of the π-donor ligand and the free coordination site of the metal. If this is the case, the non-associated alkynyl aluminium complexes could be presumably favoured when the potential coordination sites of metals were filled by σ-donor ligands and consequently might result in structurally interesting compounds. Indeed, it was not until recently that the first structurally characterized terminal alkynyl complexes of aluminium were prepared following this strategy.[13] For instance, an N-containing bulky 3,5-di-*tert*-butylpyrazolato (3,5-*t*Bu_2pz) ancillary ligand was carefully chosen for preparing the objective compounds. The reaction of the aluminium dihydride [(μ,η^1,η^1-*t*Bu_2pz)(μ-Al)H_2]$_2$ (**1**)[14] and excess of phenylethyne (HC≡CPh) smoothly leads to the formation of a non-associated alkynyl aluminium compound [(μ,η^1,η^1-*t*Bu_2pz)(μ-Al)(C≡CPh)$_2$]$_2$ (**2**), in which covalent and coordinative bonds between aluminium and nitrogen atoms are formed and accordingly each aluminium atom generating two σ-bonds from carbon atoms of alkynyl groups gains an octet configuration (Scheme 2).[13]



1 **2**

Scheme 2 Synthesis of the terminal alkynyl aluminium compound **2**.

The X-ray structural analysis of **2** shows that the six-membered Al_2N_4 ring is in a twisted conformation and four phenylethynyl groups coordinate to aluminium atoms terminally (Fig. 1).[13] The twisted structural feature is in sharp contrast to other dimeric pyrazolato complexes.[15] Most interesting, two of the terminal Al–C≡C units are markedly deviated from linearity (Al–C≡C 160.2°). *Ab initio* calculations were carried out to gain a better understanding of this phenomenon. The driving force seems to be the strong reluctance of aluminium atoms for π-bonding, thereby converting these contributions to a higher σ-character. The vibronic energy gain accompanying such excitations determines the distortion. Hence the observed bonding and twisted character in **2** seems to be induced by the pyrazolato ligands rather than by the electronic structure of the alkyne ligands.[13]

To evaluate the influence of donor ligands on the bonding character, another terminal alkynyl aluminium complex

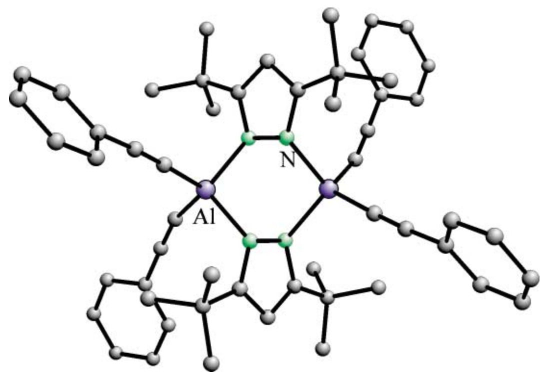
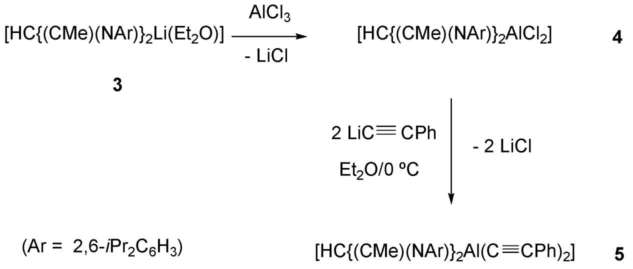


Fig. 1 Molecular structure of **2**. The twisted conformation of the six-membered Al_2N_4 rings is shown and two of the terminal Al–C≡C units are markedly deviated from linearity (Al–C≡C 160.2°). The hydrogen atoms are omitted for clarity.



Scheme 3 Preparation of compound **5**.

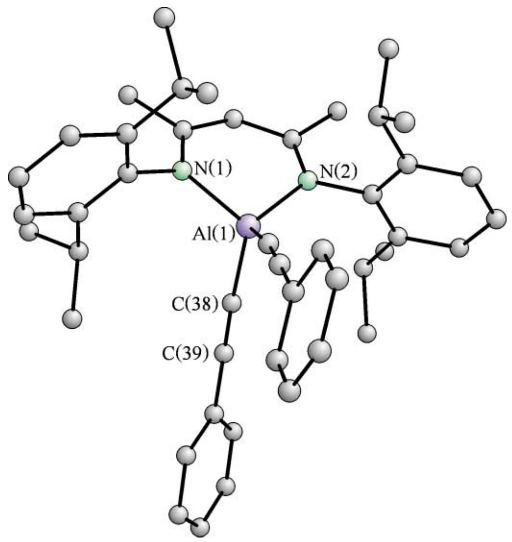
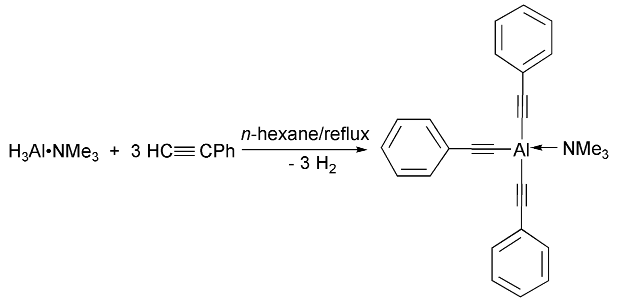


Fig. 2 The molecular structure of compound **5**. The tweezers-like terminal alkynyl groups are shown. The hydrogen atoms are omitted for clarity.

$[HC\{(CMe)(NAr)\}_2Al(C{\equiv}CPh)_2]$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (**5**) was recently prepared using LiC≡CPh and $[HC\{(CMe)(NAr)\}_2AlCl_2]$ (**4**) by salt-metathesis reaction in Et_2O (Scheme 3).[16]

Likewise in **2**, the aluminium atom in **5** (Fig. 2) acquired an octet configuration from both N-atoms of the bidentate ligand and the C-atoms of two alkynyl ligands. The bending of one Al–C≡C backbone from linearity is smaller (166.2(6)°) compared to that in **2** (Al–C≡C 160.2°). This feature is apparently attributed to the steric influence of the bulky ligands. It should be pointed out that, although the octet configuration of this alkynyl aluminium complex is structurally comparable with that of compound **2**, it is reminiscent of the tweezer-shaped transition metal alkynyl complexes.[17] Inasmuch as deviation of both Al–C≡C backbones from linearity is concerned it makes these two groups much closer in space (bite angle of C–Al–C 107.71(10)°) than those observed in **2** (C–Al–C 116.99(12)°). It is known that a transition or alkali metal ion can be embedded between two terminal alkynyl groups in tweezer-shaped transition metal alkynes through π-coordination.[18] Such complexes merit increasing interest for the prospect of finding materials with non-linear optical properties[19] and building blocks for molecular electronics as well as being found to be the catalytic intermediates in the head-to-tail dimerization.[20] Although no interaction between electron sufficient triple bonds and cationic alkali metal Li^+ was found in this instance, it could be envisaged that a suitable metal ion might be embedded between two alkynyl groups to form aluminium tweezer complexes.

It is noteworthy to mention that a trimethylamine adduct of an homoleptic alkynyl aluminium complex **6** was synthesized very recently by the reaction of excess HC≡CPh and $H_3Al{\cdot}NMe_3$ in boiling hexane (Scheme 4).[21] Compound **6** has been fully characterized and is structurally unique (Fig. 3). Like the electron configuration in **2** and **5** an octet shell at the aluminium atom avoids dimerization of **6**, thereby leading to the terminal feature of this alkynyl aluminium complex. The aluminium centre of **6** shows a slightly distorted tetrahedron. The backbones of Al–C≡C are almost linear. This reaction, on the other hand, together with other evidences of interaction between aluminium hydride and a variety of precursors further manifests that the three hydrides at the aluminium centre are all highly reactive and easily replaceable. Moreover, it could be inferred from this reaction that a substitution reaction of aluminium hydride and CH-acidic alkynes is more favourable than an addition reaction (*vide infra*, section 6). In comparison with the analogous R_3Al (R = alkyl group), in which only the first alkyl group is readily substituted,[22] aluminium hydrides, regardless of substituents, have shown excellent reactivity and are ideal starting materials for preparing some unique compounds which were difficult to synthesize by other routes.[23,24]



6

Scheme 4 Facile synthesis of compound **6**.

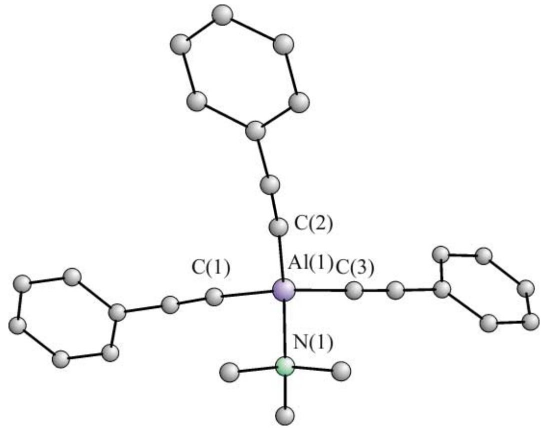
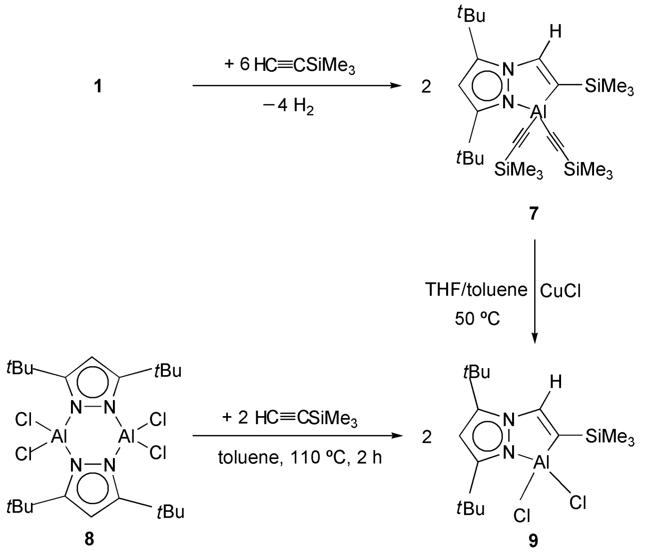


Fig. 3 The molecular structure of compound **6**. The hydrogen atoms are omitted for clarity.

3 An unusual [2 + 3] cycloaddition reaction between aluminium compounds and trimethylsilylethyne

The reaction of $[(\mu,\eta^1,\eta^1\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})\text{H}_2]_2$ (**1**) and $\text{HC}\equiv\text{C-SiMe}_3$ in toluene under stringent conditions (110 °C) results in a neutral monomeric chelating complex $[(3,5\text{-}t\text{Bu}_2\text{pz-}N\text{-CH=C(SiMe}_3))\text{Al(C}\equiv\text{CSiMe}_3)_2]$ (**7**) (Scheme 5).[13] The formation of this terminal alkynyl aluminium compound is unusual. We suppose that all the hydride atoms in **1** are initially replaced by $\text{C}\equiv\text{CSiMe}_3$ groups to yield a compound similar to **2** as an intermediate and then an insertion of $\text{HC}\equiv\text{CSiMe}_3$ follows between the aluminium and nitrogen bonds to afford **7**. This assumption can be evidenced by the substitution reaction of $\text{HC}\equiv\text{CPh}$ and $\text{H}_3\text{Al}\cdot\text{NMe}_3$ (Scheme 4) as well as the mass spectrometry data (molecular ion of the intermediate similar to **2** can be found from the MS (EI) spectrum, $\text{M}^+(m/z) = 800$ for $\text{C}_{42}\text{H}_{74}\text{Al}_2\text{N}_4\text{Si}_4$, 100%) when the reaction proceeds under mild conditions in *n*-hexane. In addition, the reaction of a dimeric pyrazolato aluminium dichloride $[(\mu,\eta^1,\eta^1\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})\text{Cl}_2]_2$ (**8**)[25] and $\text{HC}\equiv\text{CSiMe}_3$ readily leads to the chelating aluminium dichloride $[(3,5\text{-}t\text{Bu}_2\text{pz-}N\text{-CH=C(SiMe}_3))\text{AlCl}_2]$ (**9**).[26] The latter reaction might occur similarly to the second step described for **7**. Compound **9** was also formed in low yield (about 30%) when **7** was treated with CuCl in a mixture of THF and toluene at 50 °C, obviously *via* a metathesis reaction.[26] Fortunately, substitution of the chlorine atoms under elimination of hydrogen chloride was not observed so that the transformation of **8** and $\text{HC}\equiv\text{CSiMe}_3$ into **9** is in almost quantitative yield. The reactions forming **7** and **9** demonstrate that the AlCl_2 as well as the $\text{Al(C}\equiv\text{CSiMe}_3)_2$ groups stablized by pyrazolato units are able to activate the triple bond in the Me_3Si substituted alkyne. Therefore, pyrazolato aluminium complexes might be potential co-catalysts.



Scheme 5 Formation of compounds **7** and **9** from alternative routes.

The X-ray crystal structural analyses show the framework of **7** and **9** to be isostructural. They are mononuclear aluminium complexes with a metal atom coordinated by the $[3,5\text{-}t\text{Bu}_2\text{-}N\text{-CH=C(SiMe}_3)\text{pz}]$ chelating unit and two terminal $\text{C}\equiv\text{CSiMe}_3$ groups (**7**) or two Cl atoms (**9**) (Fig. 4). Compound **9** represents their typical structural features. The geometry of the aluminium atom in **9** is distorted tetrahedral (N1–Al1–C5 88.03(9)° and Cl1–Al1–Cl2 109.87(4)°) due to the constraint imposed by the chelate ring. The two fused five-membered AlN_2C_2 and pyrazolato rings are approximately coplanar. The $\text{C}\equiv\text{C}$ bond length of the inserted $\text{HC}\equiv\text{CSiMe}_3$ molecule is significantly increased (C=C (on the metallic ring), 1.323(4) Å) but is slightly shorter than those of the C=C double bonds of the σ-complex of the reaction of AlCl_3 with tetramethylcyclobutadiene (1.387(3) Å)[27] and the 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (1.367(3) Å),[28] respectively. The Al(1)–C (on the ring) bond length (1.954(2) Å) is slightly shorter than those in tetramethylcyclobutadiene (Al–C 1.979(5) Å)[27] and in 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (Al–C 1.990(av.) Å).[28]

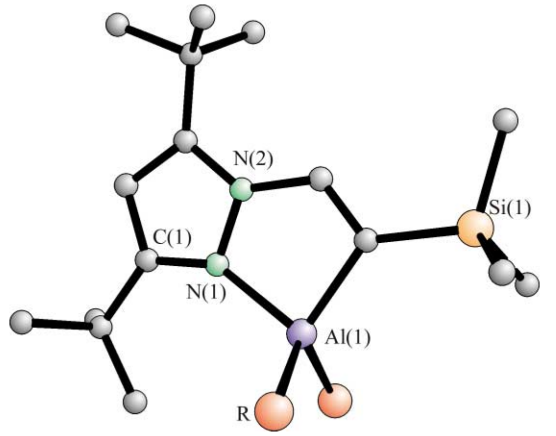


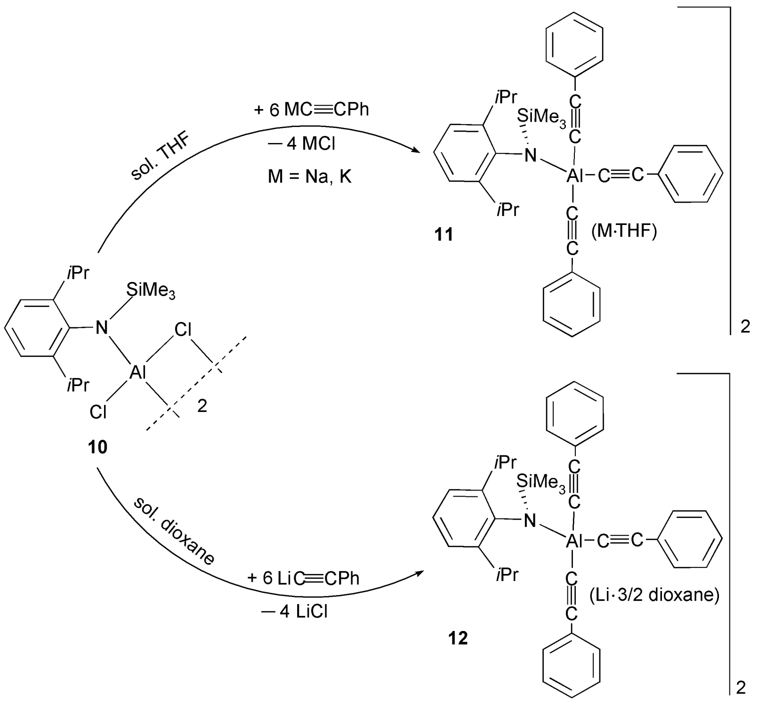
Fig. 4 Structures of compounds **7** ($\text{R} = \text{C}\equiv\text{CSiMe}_3$) and **9** (R = Cl).

The formation of **7** and **9** may proceed *via* a [2 + 3] cycloaddition reaction with the aluminium pyrazolato species functioning as the dipolar component. Namely, the process resulting in **9** may be rationalized by dissociation of **8** prior to the reaction with $\text{HC}\equiv\text{CSiMe}_3$. The different nucleophilicities of the carbon atoms and the N_2Al dipole are probably responsible for the regioselectivity of the cycloaddition forming exclusively isomer **9**. Whether such cycloaddition occurs in a general way is worthwhile investigating since this type of reaction may be of general significance in the preparation of heterocyclic compounds and in aluminium catalysed enantioselective reactions.[29] Interestingly, compound **9** has been confirmed to be an ideal precursor for broader applications due to its excellent solubility in most common organic solvents. The chlorine atoms in **9** can be partly or completely substituted by electrophilic groups such as the pyrazolato,[26] methyl, and hydride[30] whereas the metallic ring seems rather stable during these transformations even under harsh reaction conditions.

4 Anionic alkynyl aluminium compounds

Further exploration of the novel nature of alkynyl aluminium complexes was performed by utilizing a monodentate N-containing ligand $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3)^-]$. We reasoned that versatile alkynyl aluminium complexes might be formed using such types of ligand. Certainly, three terminal alkynyl anionic aluminium complexes $[\text{M}^+\cdot\text{THF}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3))\text{Al(CCPh)}_3{}^-]_2$ (M = Na (**11a**), K (**11b**)) and $[\text{Li}^+\cdot 3/2\text{dioxane}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3))\text{Al(CCPh)}_3{}^-]_2$ (**12**) were recently prepared by the reaction of the aluminium dichloride dimer $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3)\text{AlCl}_2]_2$ (**10**) with a bulky monodentate ligand $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N(SiMe}_3)^-]$ and $\text{M–C}\equiv\text{CPh}$ (M = K, Na, Li) by salt-metathesis reactions (Scheme 6).[31] Due to the low solubility of **11** in organic solvents it can only be separated by recrystallization from a mixture of *n*-hexane and THF while **12** was readily obtained as a colourless crystalline solid after treating the oily residue of the reaction with dioxane. On the basis of their components, these three anionic alkynyl aluminium complexes may be regarded as analogues to the ate complexes of composition $[\text{M}^+\text{AlR}_4{}^-]$ (M = Li, Na, K).[32a]

To understand the bonding, X-ray diffraction analyses of molecules **11** and **12** were carried out and three remarkable configurations were revealed. Compounds **11a** and **11b** are isostructural. All three compounds are actually dimers joined by two alkali metal cations through the electron rich triple



Scheme 6 Syntheses of compounds **11** and **12**. The starting material **10** was prepared by the reaction of Li[2,6-iPr$_2$C$_6$H$_3$N(SiMe$_3$)] and AlCl$_3$.

bonds of phenylethynyl groups. Their typical structural features can be depicted from the plot of **11a**. Each aluminium atom in **11a** is coordinated by three terminal phenylethynyl and one bulky ancillary ligand. The geometry of the four coordinated aluminium atom is distorted tetrahedral (N(1)–Al(1)–C(2) 113.34(15), C(4)–Al(1)–C(2) 106.13(16), C(3)–Al(1)–C(2) 103.72(15)°). The electronic shell of each aluminium atom including one negative charge gained an octet configuration. Four triple bonds of alkynyl groups are involved in a π-fashion and additionally, one oxygen of the THF molecule is coordinated to a sodium cation to form a novel five-fold coordination sphere. Likewise, two triple bonds of alkynyl groups bind to one Li$^+$ cation to assemble another aluminium ate species **12**. The distances of Na$^+$ and the carbon atoms of the triple bonds in **11a** are in the range of 2.651(4) to 2.968(4) Å, which is significantly longer than that of the ionic radii due to the high coordination number around the sodium atoms.[32b] Interestingly, only two Al–C≡C units are considerably deviated from linearity (164.2(3)°) whereas the remaining four Al–C≡C ligands are almost linear (172.2(3), 176.7(3)°). A π-bonding interaction of the alkali metal cations with the C≡C- triple bonds in alkynyl aluminium compounds such as in **11** and **12** is rare[33] (see Figs. 5 and 6) whereas a number of structures of transition metal ate complexes with alkali or transition metal cations are well documented.[34] Although aluminium ate complexes such as MAlH$_4$ (M = Li, Na) are well known, the terminal alkynyl aluminium bimetallic compounds **11** and **12** in which embedded metal ions are coordinated by the C≡C- triple bonds in a π-fashion, to the best of our knowledge, are structurally unique.

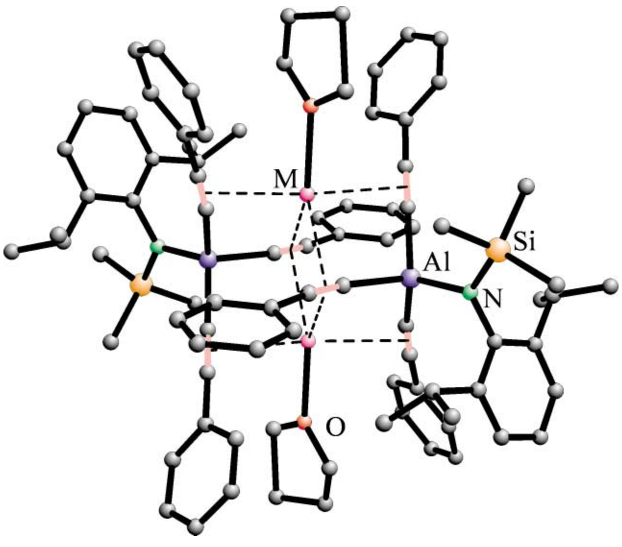
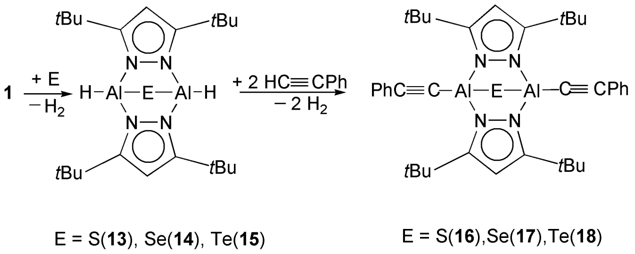


Fig. 5 The molecular structure of compound **11** exhibits dimers joined by two alkali metal cations (M = Na$^+$ or K$^+$) through the electron rich triple bonds of phenylethynyl groups. The hydrogen atoms are omitted for clarity.



Scheme 7 Preparation of compounds **13**–**18**.

5 Fused aluminium chalcogenide complexes with terminal alkynyl groups

We have reported that the reaction of aluminium hydride [(μ,η^1,η^1-tBu$_2$pz)(μ-Al)H$_2$]$_2$ (**1**) with the congeners E (E = S, Se, Te) of oxygen afforded the related aluminium chalcogenide hydrides [(μ,η^1,η^1-3,5-tBu$_2$pz)$_2$(μ-E)(μ-Al)$_2$H$_2$] (E = S (**13**), Se (**14**), Te (**15**)) (Scheme 7).[23] Generally, these three complexes can be readily prepared. However, it is crucial to use strictly equivalent amounts of starting materials and the mixture of the solvent system THF–toluene for preparing **13** since otherwise insoluble polymeric materials would be formed. X-Ray crystallography reveals that compounds **13**–**15** are isostructural (Fig. 7).

It was of interest that the remaining hydrogen atoms on each aluminium atom in these chalcogenide compounds (**13**–**15**) are still highly reactive. Developing a system in which aluminium atoms are functionalized by both terminal phenylethynyl and

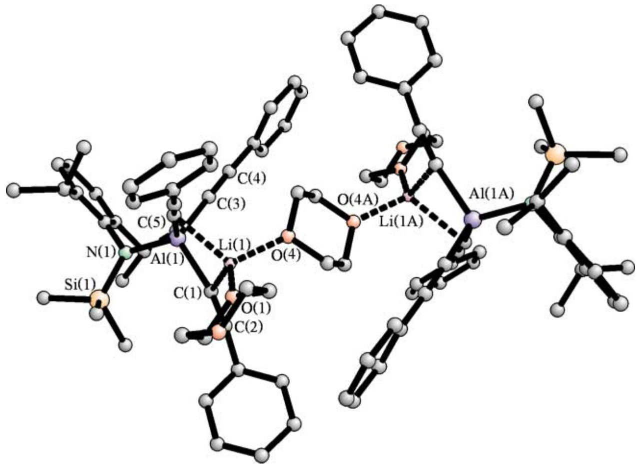


Fig. 6 The molecular structure of compound **12**. Two triple bonds of the alkynes bind to one Li^+ cation to assemble dimeric species. The hydrogen atoms are omitted for clarity.

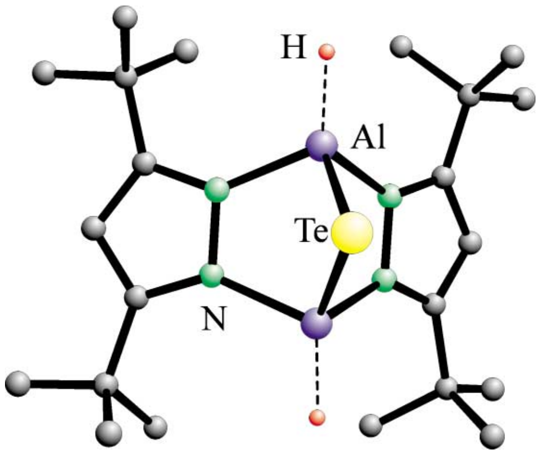


Fig. 7 The molecular structure of **15**. The compounds $[(\mu,\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu\text{-E})(\mu\text{-Al})_2H_2]$ (E = S (**13**), Se (**14**), Te (**15**)) are isostructural. The hydrogen atoms are omitted for clarity.

chalcogenide atoms is of significance. The aluminium chalcogenide complexes with terminal alkynyl groups $[(\mu,\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bupz})_2(\mu\text{-E})(\mu\text{-Al})_2(C{\equiv}CPh)_2]$ (E = S (**16**), Se (**17**), Te (**18**)) were readily prepared when an excess of phenylethyne was reacted with $[(\mu,\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz})_2(\mu\text{-E})(\mu\text{-Al})_2H_2]$ (E = S (**13**), Se (**14**), Te (**15**)) in toluene (Scheme 7).[25] These three compounds, especially **18**, are extremely sensitive to moisture. For instance, the exposure to air will immediately lead to decomposition of **18**.

The crystal structures of compounds **16** and **17** are shown in Figs. 8 and 9. Compounds **16** and **17** are isostructural and crystallize in the monoclinic system, space group $P2_1/c$. Both compounds adopt boat-shaped six-membered ring geometries due to the strain imposed by the chalcogenide bridges (S for **16**, Se for **17**) between the two Al-atoms. The interesting features are that the two phenyl groups on both sides of the molecule are perpendicular and the phenylethynyl groups arrange terminally. The Al–C≡C angle is 174.3(3)° showing a nearly linear arrangement of the ethynyl ligands. Although the structure of compound **18** was not determined it can be concluded to be isostructural to **16** and **17** due to the similarities of their physical data.[25]

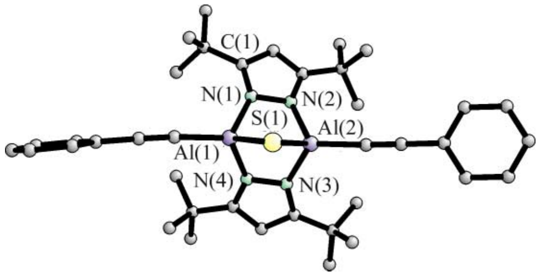


Fig. 8 The molecular structure of compound $[(\mu,\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bupz})_2(\mu\text{-S})(\mu\text{-Al})_2(C{\equiv}CPh)_2]$ (**16**). The two phenyl groups on both sides of the molecule are perpendicular and the phenylethynyl groups arrange terminally. The hydrogen atoms are omitted for clarity.

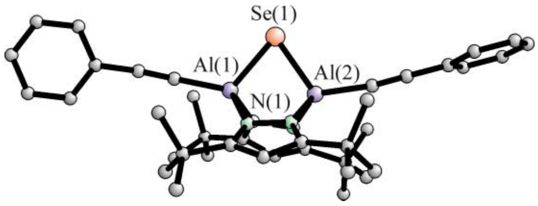


Fig. 9 The molecular structure of compound $[(\mu,\eta^1,\eta^1\text{-}3,5\text{-}t\mathrm{Bupz})_2(\mu\text{-Se})(\mu\text{-Al})_2(C{\equiv}CPh)_2]$ (**17**). Only the selenium atom is exposed. The hydrogen atoms are omitted for clarity.

As nucleophilic reagents chalcogenide compounds of composition $(RE)MR_2$ play an important role in organic synthesis (E = S, Se, Te, M = Al *etc.*, R = organic group) to prepare a series of intermediates.[35] They are highly reactive, soft nucleophiles that can be used in a variety of transformation reactions such as chalcogenoesters.[36] Aluminium compounds with fused functional transfer-groups, namely with both chalcogenide and alkynyl units were not known before and they might be unique reagents in organic synthesis since it is possible that both chalcogenide and alkynyl groups may be transferred simultaneously to prepare the expected compounds with two functionalities. Especially, compounds **16**–**18** with a symmetrical arrangement where only the chalcogenide is exposed may prove ideal regioselective reagents.

6 Hydroalumination of the H–C≡C–R system by $H_3Al{\cdot}NMe_3$ (R = Ph, CH_2SiMe_3)

Compared with the organometallics of other main group elements, aluminium organyls easily add to alkenes and alkynes. The regio- and stereo-selectivity of these carbaaluminations as well as the related hydroaluminations using R_2AlH is an additional asset to form carbon–aluminium bonds. Hence, the controlled hydroalumination of alkynyl compounds plays one of the most important roles. For example, the facile synthesis of stereo- and regio-defined alkynyl aluminium compounds *via* hydroalumination reactions provides an expedient route to a wide array of stereochemically pure olefinic derivatives.[3] Organic transformations of such addition intermediates containing carbon–aluminium bonds by undergoing facile protonation, oxidation and halogenation usually lead to the corresponding hydrocarbons, alcohols and alkyl halides, respectively. In addition, the generated organoaluminium complexes participate in a variety of carbon–carbon bond-forming reactions, including alkylation, carbonation, cyanation, addition to carbonyl compounds, conjugate addition to enones and epoxide ring-opening reactions.[4] From the point of view of coordination chemistry, structural determination of the intermediates of hydroalumination of alkynyl compounds would contribute to a better understanding of the mentioned reaction process and are of significant importance. It seemed that their real cluster structures, adamantane-like cage compounds compared to their analogous carbaboranes, were first inferred when Wilke and Schneider investigated the reactions between R_2AlH and $R_2Al\text{–}C{\equiv}C\text{–}R$ (R = Me, Et).[37] Such intermediates, obtained from the identical reactions of R_2AlH and $R_2Al\text{–}C{\equiv}C\text{–}R$ (R = Me, Et), were structurally characterized by Uhl *et al.* (Scheme 8).[38]

To date, there have been two different structural types of carbaalane compounds. One is highlighted by a cube of eight

$$11\ Me_2AlH + 5\ Me_2Al{-}C{\equiv}CPh \longrightarrow (AlMe)_8(CCH_2Ph)_5H + 8\ AlMe_3$$

(**19**)

$$10\ Me_2AlH + 6\ Me_2Al{-}C{\equiv}CPh \longrightarrow (AlMe)_8(CCH_2Ph)_5(CCPh) + 8\ AlMe_3$$

(**20**)

$$9\ Et_2AlH + 5\ Et_2Al{-}C{\equiv}CPh \longrightarrow (AlEt)_7(C{=}CH_2Ph)_2(CCH_2Ph)_3 + 7\ AlEt_3$$

(**21**)

Scheme 8 Preparation of carbaalanes **19**–**21**.

aluminium atoms and the six faces of the cube are occupied by five C–CH$_2$–R groups (for instance **19**) or the carbaalane has a structure with one vertex unoccupied and possesses only seven aluminium atoms.[38] The second type of carbaalane such as (AlMe)$_7$(CCH$_2$CH$_3$)$_4$H$_2$ holds a *closo*-conformation in the light of its structure and electron count and is a remarkable analogue of the *closo*-borate anion $[B_{11}H_{11}]^{2-}$.[39] The further investigation of carbaalanes is documented in a recent review.[40c] The bonding situation of these two types of carbaalanes has also been studied by quantum-chemical calculations.[40a]

Our interest in unsaturated organoaluminium compounds has prompted us to study the behaviour of the trimethylamine adduct of aluminium hydride AlH$_3$·NMe$_3$ toward alkynes.[13,14] Treatment of the HC acidic alkynes HC≡CR (R = Ph, CH$_2$SiMe$_3$)[41] with an excess of the alane trimethylamine adduct in boiling toluene leads to the formation of the carbaalane [(AlH)$_6$(AlNMe$_3$)$_2$(CCH$_2$R)$_6$] (R = Ph (**22**), CH$_2$SiMe$_3$ (**23**)) in good yields (Scheme 9).[42] The formation of compounds **22** and **23** obviously proceeds *via* a regioselective addition of the aluminium hydride to the C≡C– triple bond after the alkyne hydrogen atom is deprotonated. Compounds **22** and **23** could be readily separated by recrystallization in toluene.

$$8\ H_3Al{\bullet}NMe_3 + 6\ HC{\equiv}CR \xrightarrow[\substack{-6\ H_2\\ -6\ NMe_3}]{} (AlH)_6(AlNMe_3)_2(CCH_2R)_6$$

R = Ph (**22**)
R = CH$_2$SiMe$_3$ (**23**)

Scheme 9 Facile preparation of the aluminium cluster compounds **22** and **23**.

The X-ray crystallography reveals compounds **22** and **23** to be isostructural. The core of the structures is depicted by the bold line in Fig. 10 and the structure is a rhombic dodecahedron containing a cube of eight aluminium atoms with six carbon atoms and attached organic groups at each face of the cube. Each carbon atom of the core is connected to three AlH and one Al(NMe$_3$) units. Two aluminium atoms on opposite sides of the polyhedron (in 1,4 position) are bearing a trimethylamine ligand. As expected, the average bond distances from Al(NMe$_3$) atoms to the closest polyhedron carbon atoms (2.028 Å **22**, 2.024 Å **23**) are shorter than the corresponding distances from AlH atoms to the polyhedron carbon atoms (2.095 Å **22**, 2.086 Å **23**). The bonding properties in these polyhedrons can be probably regarded as a three-dimensional surface aromaticity. On the closed Al$_4$C faces of the cube four bonds are formed using three electron pairs consequently leading to a strong delocalization of the electrons. The theoretical analysis of the bonding nature of the core inside **22** and **23** was carried out on a modified structure (AlNH$_3$)$_2$(AlH)$_6$(CMe)$_6$, optimized under D_{3d} symmetry.[42] On the basis of *ab initio* (RHF and DFT) calculations the orbital scheme localized at one cubic face has an orbital sextet with a large HOMO–LUMO gap (≈8.8 eV) consistent with the criteria of aromaticity. The bonding nature of the core was also described by qualitative valence bond theory.[42] However, it must be mentioned, as one of the referees pointed out, that the NICS value (magnetic criteria by Schleyer *et al.*) is a better and generally accepted criteria for aromaticity rather than a large HOMO–LUMO gap. Actually, the interpretation of the bonding properties in these polyhedra is still a matter of debate.

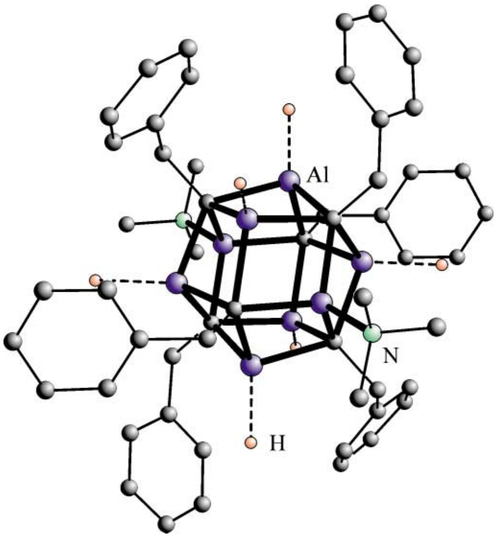


Fig. 10 The molecular structure of complex **22**. The structural frameworks of compounds **22** and **23** are identical (shown by the bold line).

In contrast to the preparation strategy established by Uhl *et al.* (Scheme 8), the starting materials for preparing **22** and **23** are commercially available or can be conveniently synthesized on a large scale in the laboratory. Moreover, each face of the cube contains one carbon atom yielding a closed stable configuration. Most important are six remaining reactive Al–H bonds in **22** and **23**. Both the facile synthesis and the remaining highly reactive Al–H bonds of complexes **22** and **23** will render possibilities that will probably lead to a series of interesting compounds containing the aluminium cluster core.

In fact, preliminary experimental results have shown that compound **23** smoothly reacts with stoichiometric amounts of BCl$_3$ to yield the metathesis product (AlCl)$_6$(AlNMe$_3$)$_2$(CCH$_2$CH$_2$SiMe$_3$)$_6$ (**24**).[42] Unexpectedly, when an excess of BCl$_3$ was employed, one methyl group of the SiMe$_3$ unit in **24** can be further replaced by a chlorine to generate (AlCl)$_6$(AlNMe$_3$)$_2$(CCH$_2$CH$_2$SiMe$_2$Cl)$_6$ (**25**).[42] The structures of compounds **24** and **25** have been fully characterized (Fig. 11). This experiment clearly demonstrates that the polyhedron can be stepwise functionalized both within the inner and outer sphere. However, the degradation of the Al$_8$C$_6$ core is not observed during this transformation, reflecting the high stability of the core. How the substitution on the outer sphere occurs is currently unknown but obviously the core influences the environment of compound **24**. The easy access of **24** and its further conversion to **25** show that unique substitutions at the core as well as at the periphery can be developed at different stages under a controlled amount of starting materials. Very recently, a fluorine substituted carbaalane (AlEt)$_7$(C=CHPh)$_2$(CCH$_2$Ph)$_3$F was also reported by the reaction of (AlEt)$_7$(C=CHPh)$_2$(CCH$_2$Ph)$_3$H and HBF$_4$.[43]

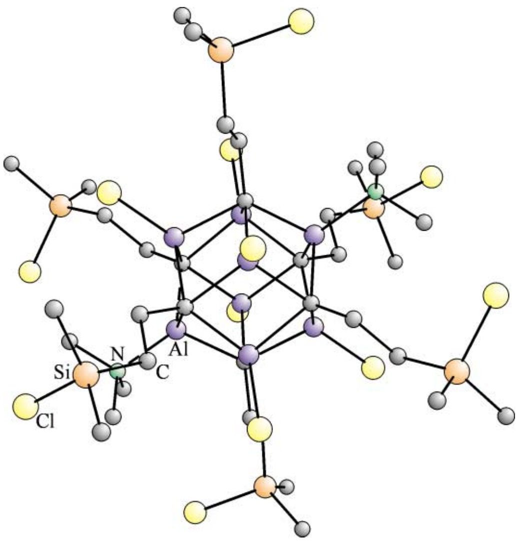


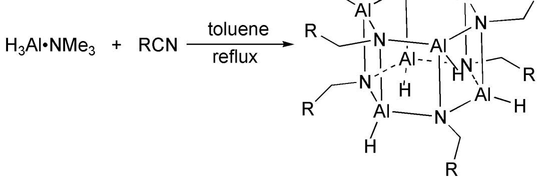
Fig. 11 The molecular structure of compound **25**. The hydrogen atoms are omitted for clarity.

7 Hydroalumination of the N≡C–R system (R = Ph, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$) by $H_3Al{\cdot}NMe_3$

Aluminium compounds containing the $(AlN)_n$ skeleton are potential precursors for a variety of applications.[44] The aluminium imides and amides, including those involving an Al_6N_6 core, can be prepared by the reaction of alanes and alanates with various amines.[45,46] It was reported that the reaction of methylamine and alane leads to an insoluble Al–N polymer in which an equivalent of hydride per Al was evidenced by elemental analysis but the product was not structurally characterized.[47] Although the formation of aluminium imides from the reaction of trialkylamine alanes with acetonitrile and propionitrile was investigated many years ago, no structural evidence for their products was presented.[48]

Obviously the lack of structural evidence hinders the better understanding of such types of reactions. The successful preparation of compounds **22** and **23** inspired us to study the reaction of $AlH_3{\cdot}NMe_3$ toward substituted heteroalkynes such as nitriles. We are particularly interested in the structural modes of intermediates involved in hydroalumination reactions.[49]

Several aluminium imides obtained by hydroalumination of substituted nitriles were recently structurally characterized. Addition of $AlH_3{\cdot}NMe_3$ to RCN (R = Ph, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$) in toluene results in a yellow solution. After refluxing the mixture for a while and keeping it at 0 °C overnight it yields colourless crystals of $(HAlNCH_2R)_6$ (R = Ph (**26**), *p*-MeC_6H_4 (**27**), *p*-$CF_3C_6H_4$ (**28**)) (Scheme 10).[49]



Scheme 10 Preparation of compounds **26**–**28**.

Compounds **26**–**28** were all structurally characterized (Fig. 12). The compounds contain a hexagonal drum with the top and bottom faces of the polyhedron being made of two six-membered $(AlN)_3$ rings, which are almost planar. These six-membered rings are joined by six transverse Al–N bonds forming six rectangular side faces of the drum. Similar to the previously studied structures, the Al–N bonds in the six-membered rings are significantly shorter than the transverse bonds joining the rings.[45a,b] The substituted groups on N-atoms are oriented toward each other blocking the top and bottom faces of the hexagonal drum thereby exposing the hydride atoms. The formation of **26**–**28** may proceed in a different way from that of **22** and **23**, presumably *via* an aluminium iminato intermediate,[50] which, under the reaction conditions, further gives the aluminium amides.

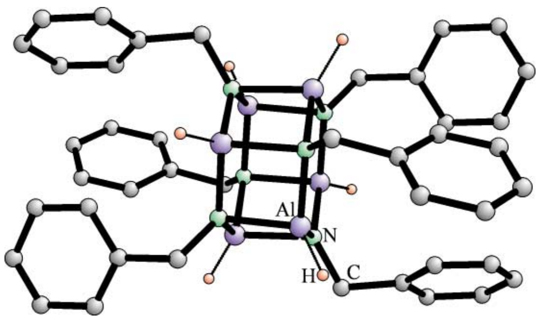
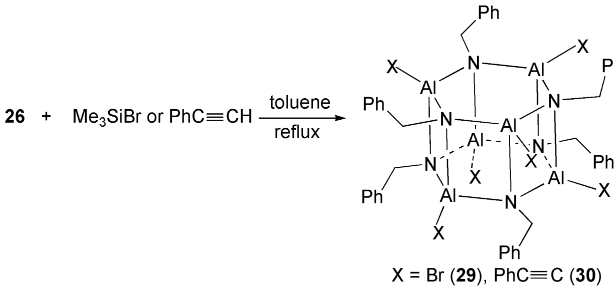


Fig. 12 The molecular structure of compound **26**. The structural cores of complexes **26**–**30** are identical.

The reactivity of Al–H bonds in **26** with nucleophilic reagents was also studied (Scheme 11).[49] Compound **26** smoothly reacts with an excess of Me_3SiBr in toluene to replace all the hydride atoms by bromine atoms, evidencing high reactivity of all remaining Al–H bonds on the core. The experimental results show that compound **29** is the only isolated product. The reaction of compound **26** with PhC≡CH is straightforward with the evolution of hydrogen to yield compound **30**.



Scheme 11 The reactivity of compound **26**.

Compounds **29** and **30** are both structurally characterized.[49] A comparison of bond distances and bond angles with those of **26** showed that the cage structure is not disturbed by the replacement of the hydrogen atoms by the bromine atoms or phenylethynyl groups (Fig. 12), indicating the hexagonal core is rather rigid.

8 A polyhedron with an $Al_4C_4N_4$ framework

Molecular compounds of composition AlCN are potentially important for generating CVD thin film of carbo-nitrides containing aluminium.[51] The hydroalumination of isonitriles probably leads to unique structures. Power *et al.* reported that the reaction of a primary alane $[(2,4,6\text{-}t\text{Bu}_3C_6H_2AlH_2)_2]$ and *tert*-butyl isocyanide affords a dimeric compound $[(2,4,6\text{-}t\text{Bu}_3C_6H_2AlCH_2N t\text{Bu})_2]$.[50]

Treatment of CN*t*Bu with $H_3Al{\cdot}NMe_3$ in toluene results in the formation of the polyhedron $[(\mu_3\text{-}AlH)(\mu_3\text{-}CH_2N t\text{Bu})]_4$ (**31**).[52] The X-ray structural analysis of **31** reveals a remarkable $Al_4C_4N_4$ cage configuration in which the C atoms adopt *exo* positions and thus may be formally considered as inserting into four Al–N bonds of an Al_4N_4 cube. The $Al_4C_4N_4$ core structure is shown in Fig. 13. The core of **31** consists of six faces formed by two boat-shaped six-membered $Al_2C_2N_2$ rings and four

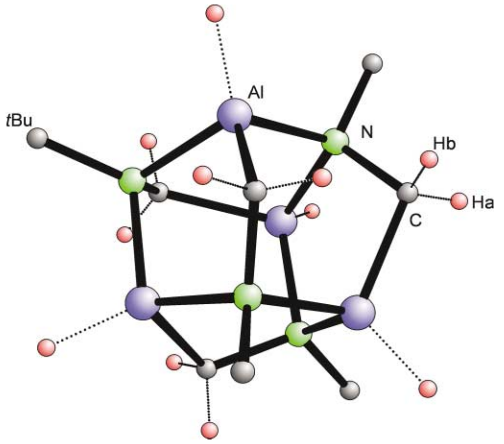


Fig. 13 The molecular structure of compound **31**.

puckered five-membered Al_2CN_2 rings. The two six-membered rings are crosswise located to each other and the four five-membered rings are arranged between the two. It is surprising that a significant difference in the arrangement of the atoms within the cage skeleton of **31** is found in comparison with other known aluminium compounds containing a twelve-membered core.[53] The molecular symmetry of **31** is quite close to S_4 whereas no further elements of symmetry exist in the molecule. The high reactivity of the remaining four Al–H bonds could be inferred on the basis of experimental results described in sections 6–7. As a result of the Laplacian analysis, the CH_2NtBu fragments of **31** can be regarded as μ_3-coordinating ligands. The unusual results of the dynamic NMR experiment of **31** were discussed and may be theoretically attributed to the promotion of rotational disorder around the C–N bond of the terminal fragments.[52]

The $Al_4C_4N_4$ core of **31** is unique and thus it could be considered as a fused carba-aminoalane. The exact mechanism for the formation of **31** is unknown, but probably an initial donor–acceptor intermediate is involved, where the isocyanide carbon coordinates to aluminium followed by hydrogen migration from aluminium to carbon to yield the CH_2 moiety.[52]

9 Summary and outlook

This contribution presents recent progress on the bonding of aluminium alkynes and the structural characterization of intermediates isolated following the reactions of a variety of unsaturated systems containing C≡C–, N≡C– as well as C=N– multiple bonds with $AlH_3 \cdot NMe_3$.

A comparison of the structures of compounds $[PhC{\equiv}CAlPh_2]_2$, **2**, **5**, **6**, **11** and **12** concludes that a sextet electron shell of the aluminium centre is very labile in formal monomeric aluminium alkynes. The dimeric structure of $[PhC{\equiv}CAlPh_2]_2$ results from the combination of a σ/π-system between electron deficient Al and electron rich alkynyl, consequently the aluminium centres comply with the octet rule. However, on treatment with a base such as donor ligands and organoalkali reagents, the coordinatively unsaturated aluminium atom is filled to yield the corresponding terminal alkynyl aluminium species **2**, **5**, **6** and the anionic compounds **11** and **12**, respectively. This will easily explain why **5** is a neutral compound containing a bidentate ligand, whereas **11** and **12** are anionic complexes even though the starting materials and the reaction conditions are almost identical. Therefore a variety of alkynyl aluminium compounds could be envisaged when different types of donor ligands are employed following the developed strategy.

Examination of the products derived from the addition reaction of $H_3Al \cdot NMe_3$ toward C≡C–, N≡C– and C=N– multiple bond systems reveals a striking preference for generating highly thermally stable polyhedral aluminium hydride clusters. The reaction of alkynes or heteroalkynes with an excess of $H_3Al \cdot NMe_3$ results in the formation of carbaalanes containing the Al_8C_6 core structure $[(AlH)_6(AlNMe_3)_2(CCH_2R)_6]$ (R = Ph (**22**), CH_2SiMe_3 (**23**)), iminoalanes $[HAlNCH_2R]_6$ (R = Ph (**26**), p-MeC_6H_4 (**27**), p-$CF_3C_6H_4$ (**28**)) involving the Al_6N_6 framework and a carbaaminoalane $[(\mu_3\text{-}AlH)(\mu_3\text{-}CH_2NtBu)]_4$ (**31**) holding the $Al_4C_4N_4$ skeleton. The reaction processes are apparently not the same due to the different electron nature between alkyne and heteroalkynes. However, the hydrides on the aluminium atoms of their products are highly reactive and readily replaceable by nucleophilic reagents while the core of the clusters seems to be rather stable. Facile syntheses and unique structural features of these polyhedrons are likely to open an avenue to new cluster aluminium compounds.

In light of our experimental experience, $H_3Al \cdot NMe_3$ is really an excellent starting material. All hydride atoms are very reactive and can be employed for metathesis reactions. Moreover, $H_3Al \cdot NMe_3$ is also capable of reacting with multiple bond systems to form additional products. The successful synthesis of three types of aluminium polyhedron (**22**, **23**; **26**–**28**; **31**) with unique structures by regioselective addition will undoubtedly facilitate the broad application of $H_3Al \cdot NMe_3$ in the near future.

10 Acknowledgements

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