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Syntheses and structural characterisation of some heteroleptic aluminium(III) formamidinates

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Abstract: A range of heteroleptic aluminium(III) formamidinate/formamidine complexes have been prepared involving metathesis reactions between AlX_3 (X = Cl, Br, I) and alkali metal formamidinates. The mononuclear, *bis*-substituted complexes of the composition [Al(XylForm)$_2$Cl] (XylForm = N,N'-*bis*(2,6-dimethylphenyl)formamidinate) (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (DippForm = N,N'-*bis*(2,6-diisopropylphenyl)formamidinate) (**3**), [Al(DippForm)$_2$I] (**4**), *mono*-substituted complexes of [Al(DippForm)Cl$_2$(thf)] (**5**), [Al(DippForm)ClBr(thf)] (**6**), [Al(XylFormH)Br$_3$] (**7**) and [Al(DippFormH)Br$_3$] (**8**) were synthesised. [Al$_3$(XylForm)$_2$(μ$_3$-O)(OH)Cl$_4$]$_2$·PhMe (**9**), was isolated in the reaction between K(XylForm) and AlCl$_3$ as a trinuclear compound.

1. Introduction

Significant attention has been paid to the coordination chemistry of the four-electron donor, monoanionic ancillary amidinate ligands [RNC(R')NR] as suitable replacement ligands for the ubiquitous cyclopentadienyl ligand. This class of ligand features readily substitutable groups bound to the nitrogen atoms and backbone carbon centres, potentially modifying the coordination environment at the metal centre.[1,2] A considerable range of transition- and lanthanoid-metal amidinate complexes have been synthesised by different methods.[3-6] Amidinate complexes of the main group elements,[7-8] especially those of the group 13 elements have attracted much attention due to their potential applications as precursors to low valent complexes,[9] as catalysts or as precatalyst for CO_2-epoxide copolymerization,[10] and hydride complexes.[11] A convenient synthetic approach to amidinato complexes of group 13 elements is treatment of a series of bulky amidinate salts M[RC(NAr)$_2$] (M = Li, Na or K; R = H, Fiso; Me, Aiso; tBu, Piso; Ar = 2, 6-iPr$_2$C$_6$H$_3$) with group 13 halides.[12] Alternatively, a facile approach to amidinates of group 13 elements is reported by the reactions of guanidines, triazenes, amidines, and lithium amidinates with trimethylamine alane ([AlH$_3$(NMe$_3$)]), lithium tetrahydridoaluminate, trimethylaluminium, aluminium trichloride, and indium trichloride.[13]

Reactions of the formamidine RN(H)C(H)NR (R = 2,6-diisopropylphenyl) with AlMe$_3$, AlMe$_2$Cl, GaMe$_3$ and ZnEt$_2$ were investigated in 2010.[14] Furthermore, many N,N'-bis(aryl)formamidinate (ArForm) ligands have been used in the synthesis of group 13 elements complexes, because the ligands can be easily synthesised with varying the substituents within the aryl groups and they have various coordination flexibility within the amidinate family. In a reported study involving Al and Ga, treatment of formamidines [FormH (ArNCHN(H)Ar) = EtFormH (N,N'-*bis*(2,6-diethylphenyl)formamidine) or DippFormH (N,N'-*bis*(2,6-diisopropylphenyl)formamidine)] with AlMe$_3$ in a 1:3 reaction stoichiometry led to dialuminium formamidinate complexes [Me$_2$Al(μ-Form)(μ-Me)AlMe$_2$] in good yields, while protolysis reactions of MMe$_3$ (M = Al, Ga) with (FormH) in a 1:1 stoichiometry resulted in [M(Form)Me$_2$] (M = Al, Form = DippForm, EtForm; M = Ga, Form = DippForm).[15] Concentration of the thf/n-hexane solution of [Me$_2$Al(μ-DippForm)(μ-Me)AlMe$_2$] to dryness yielded [Al(DippForm)Me$_2$], which can also be achieved from reaction of AlMe$_3$ with [Ga(DippForm)Me$_2$].[15] Complexes of the general formula [Al(Form)$_2$X] [Form = XylForm (N,N'-

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bis(2,6-dimethylphenyl)formamidinate), EtForm, DippForm] (X = Me, Cl) were produced from the reactions of N,N'-bis(aryl)formamidines/ates with half an equivalent of AlMe$_3$/AlCl$_3$.[13]

Here we report the successful syntheses of heteroleptic aluminium(III) formamidinate complexes from AlX$_3$ (X = Cl, Br, I) and alkali metal formamidinates. Two formamidines N,N'-*bis*(2,6-dimethylphenyl)formamidine)   [XylFormH] and *N,N'*-bis(2,6-diisopropylphenyl)formamidine) [DippFormH] (XylFormH has moderate bulkiness, while DippFormH is significantly bulkier) were used, and a considerable number of Al(Form)$_n$X$_{3-n}$ (Form = XylForm, DippForm; X = Cl, Br, I; n = 1, 2) have been prepared in moderate crystalline yields.

2. Results and discussion

2.1. Synthesis and characterisation of compounds *1-9*.

The synthesis of compounds [Al(XylForm)$_2$Cl] (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (**3**), [Al(DippForm)$_2$I] (**4**), [Al(DippForm)Cl$_2$(thf)] (**5**), [Al(DippForm)ClBr(thf)] (**6**), [Al(XylFormH)Br$_3$] (**7**), and [Al(DippFormH)Br$_3$] (**8**) followed similar metathesis routes whereby a solution of M(N,N'-bis(aryl)formamidinate) (M(Form); FormH = N,N'-*bis*(2,6-dimethylphenyl)formamidine (XylForm); or N,N'-*bis*(2,6-diisopropylphenyl)formamidine (DippFormH); M = Li, Na, or K) in THF or PhMe was added dropwise to a stirred solution of AlX$_3$ (X = Cl, Br, I) in THF or PhMe at room temperature (Scheme 1). [Al(XylForm)$_2$Cl] (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (**3**) and [Al(DippForm)$_2$I] (**4**) were prepared in 2:1 ratios, and [Al(DippForm)Cl$_2$(thf)] (**5**), [Al(DippForm)ClBr(thf)] (**6**) in 1:1 stoichiometric ratios. In the 1:1 (FormH : AlBr$_3$) reactions involving the bromide species, Lewis adducts ([Al(XylFormH)Br$_3$] (**7**) and [Al(DippFormH)Br$_3$] (**8**) were isolated (Scheme 1). Similarly, in one reaction involving treatment of K(XylForm) with AlCl$_3$ in a 1:1 ratio the trinuclear compound [Al$_3$(XylForm)$_2$(μ$_3$-O)(OH)Cl$_4$]$_2$·PhMe (**9**) was isolated (Scheme 1). The compound ([Al(DippForm)$_2$I]) (**4**) was also obtained by [[La(η^6-MeC$_6$H$_5$)(AlI$_4$)$_3$] and K(DippForm) in a 1:2 ratio with a very small yield (few crystals).

Scheme 1
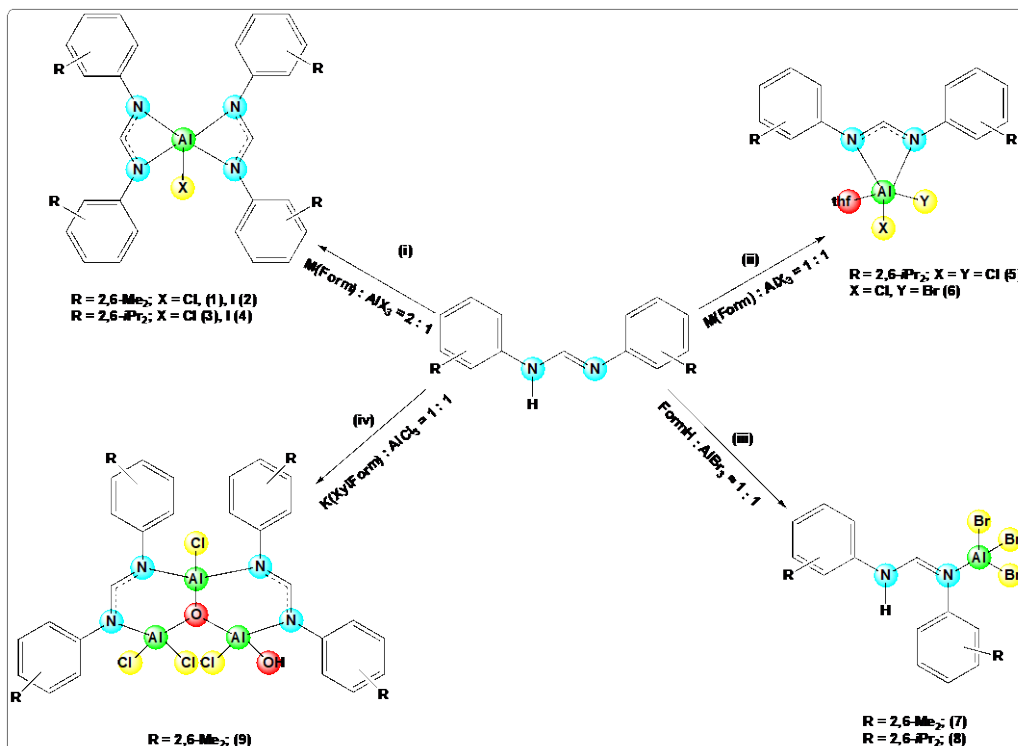
Infrared spectroscopic data of [Al(XylForm)$_2$Cl] (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (**3**), [Al(DippForm)$_2$I] (**4**), [Al(DippForm)Cl$_2$(thf)] (**5**), [Al(DippForm)ClBr(thf)] (**6**), [Al$_3$(XylForm)$_2$(μ_3-O)(OH)Cl$_4$]$_2$·PhMe (**9**) are devoid of an N–H stretch signal usually observed at 3300-3100 cm^{-1} in the parent formamidines, indicating complete deprotonation. IR spectra for all the formamidinate complexes showed that the N–H stretch at *ca*. 3300 cm^{-1} reappeared after the formamidinate complexes were exposed to air for two minutes. Crystalline compounds of [Al(XylFormH)Br$_3$] (**7**) and [Al(DippFormH)Br$_3$] (**8**) exhibit a sharp stretch in the IR spectrum at 3322 cm^{-1} (N–H), confirming presence of the parent formamidine.[16]

The ^{1}H-NMR spectral studies of the bulk vacuum dried compounds (**1-6**) show the lack of the signal attributed to the N–H resonance, again demonstrating clean deprotonation of the parent formamidine. The NC(H)N resonances in the ^{1}H NMR spectra (in C$_6$D$_6$) at δ = 7.50 (**5**) and 7.57 ppm (**6**) are almost close to the values for reported the corresponding ligands.[15] The ^{1}H NMR spectrum of compound (**7**) [Al(XylFormH)Br$_3$] shows a broad resonance at 5.63 ppm confirming the presence of N–H, while the spectrum of compound (**8**) [Al(DippFormH)Br$_3$] has a signal at

8.24 ppm attributable to the backbone hydrogen of the DippFormH and a slightly broad resonance at 6.25 ppm confirms the presence of N−H.

An OH stretch for (**9**) was confirmed in the infrared spectrum at 3712 cm^{-1}, which is slightly different to that recorded in related complexes.[17,18] The ^{1}H-NMR spectrum of (**9**) exhibits three sets of methyl resonances in a 1:2:1 ratio and a well-defined formamidinate NCHN resonance at δ = 7.29 ppm. The terminal hydroxyl group is identified by ^{1}H-NMR with signal at 0.41 ppm that is in the normal range of other reported Al–OH signals.[17,18] The incorporation of O^{2-} and OH$^-$ in the trinuclear (**9**) presumably arises from adventitious moisture leading to partial hydrolysis, and highlights the extreme moisture sensitivity of these compounds as compound (**9**) was obtained in moderately high yield (65%). However, the source of O^{2-} and OH$^-$ could possibly be from the ring opening of thf, but no other products of ring-opened thf were evident.

It is worth mentioning that many aluminium compounds used in this study react rapidly towards air and moisture, [19-24] and satisfactory microanalyses could only be obtained for the compounds (**3**), (**5**), (**6**) and (**7**). Generally, values were lower than expected, indicative of decomposition during international travel to the microanalytical service in London, despite crystals being submitted sealed under N$_2$. Problems with microanalysis of reactive main group compounds, e.g. alkaline earth organometallics are well documented in the literature.[25,26] The yields of crystalline products were in the moderate range 40 – 70%.


2.2. Structural discussion

*2.2.1. Discussion of [Al(XylForm)$_2$Cl] (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (**3**) and [Al(DippForm)$_2$I] (**4**).*

The monomeric complexes [Al(XylForm)$_2$Cl] (**1**), [Al(XylForm)$_2$I]·PhMe (**2**), [Al(DippForm)$_2$Cl] (**3**) and [Al(DippForm)$_2$I] (**4**) crystallized in the space groups monoclinic *P2$_1$/c*, triclinic *P-1*, monoclinic *P2$_1$/n* and monoclinic *P2$_1$/c* respectively, each with one molecule within the asymmetric unit. A poor quality X-ray crystal structure of Compound (**3**) was previously published and was reported as "for connectivity only".[13] Here we present a more precise dataset for this compound. Compounds (**1**) to (**4**) are all structurally similar with a five-coordinate aluminium centre with two chelating formamidinates and one terminal halide. Interestingly, these compounds have similar

coordination environments observed for the bismuth(III) complex [Bi(DippForm)$_2$Bu^n].[27] The geometry about the aluminium atom in compounds (**1**) to (**4**) is a distorted trigonal bipyramid with nitrogen atoms at the axial positions (N$_{ax}$-Al-N$_{ax}$ angles for (**1**) to (**4**) range from 154.97(8) to 161.81(7)) °) and two nitrogens and one halide in the equatorial positions (angles about the equatorial sites in compounds (**1**) to (**4**) all sum to 360° within three e.s.d.s). The distortion arises due to the tight chelation imposed by the formamidinate ligands. In all four compounds (**1**) to (**4**) there is asymmetric binding of the chelating formamidinate (see Figure 2 caption) where Al-N$_{eq}$ are all close to 0.1 Å shorter than Al-N$_{ax}$ and this is a recurring feature among five coordinate aluminium complexes being supported by chelating amidinates, e.g. [Al{MeC(NiPr)$_2$}$_2$Me],[28] [Al{MeC(NiPr)$_2$}$_2$Cl],[29] [Al(XylForm)$_2$Me],[13] and [Al{HC(ND$i$pp)$_2$}Me].[14] Likewise the related aluminium structures [{MeC(NiPr)$_2$}$_2$AlCl],[29] [{MeC(NiPr)$_2$}$_2$AlMe],[28] [{PhC(NSiMe$_3$)$_2$}$_2$AlH],[30] and [{HC(ND$i$pp)$_2$}$_2$AlH].[31]

The Al–Cl bond lengths in (**1**) (2.1327(14) Å) and (**3**) (2.1531(11) Å) are unexceptional compared with the Al–Cl bond length (2.141 (15) Å) reported for [Al(EtForm)$_2$Cl][13] but on the lower end of Al–Cl bond lengths (2.16 – 2.20 Å) for those of seven reported [Al(Form)$_2$Cl] complexes (Form = chelating amidinate).[13,32-34] In (**2**) (2.5443(9) Å) and (**4**) 2.5653(14) Å), the Al–I bond lengths are in the reported range[5,12,29,33] but is slightly longer than those of [Al(Priso)I$_2$] (2.50, 2.51 Å)[35] and [Al(CGiso)I$_2$] (2.50 Å).[13]
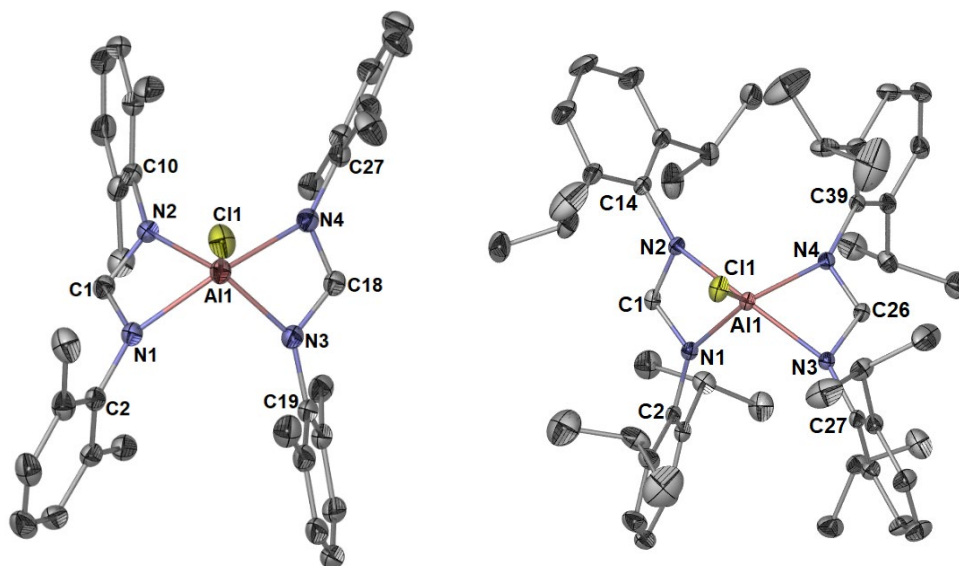
Figure 1. (a) Molecular structure of (**1**) ([Al(XylForm)$_2$Cl]) (the structure of (**2**) is similar). (b) Molecular structure of (**3**) ([Al(DippForm)$_2$Cl]) (the structure of (**4**) is similar). Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Compound (**1**): Al(1)-N(1) 2.010(3), Al(1)-N(2) 1.905(3), Al(1)-N(3) 1.910(3), Al(1)-N(4) 2.016(3), Al(1)-Cl(1) 2.1327(14); Compound (**2**): Al(1)-N(1) 2.035(2), Al(1)-N(2) 1.923(2), Al(1)-N(3) 1.924(2), Al(1)-N(4) 2.032(2), Al(1)-I(1) 2.5443(9); Compound (**3**): Al(1)–N(1) 1.9169(17), Al(1)–N(2) 2.0415(17), Al(1)–N(3) 2.0603(17), Al(1)–N(4) 1.9143(17), Al(1)–Cl(1) 2.1531(11), N(1)–C(1) 1.334(2), N(2)–C(11) 1.305(3), N(3)–C(26) 1.309(3), N(4)–C(26) 1.338(2);; Compound (**4**): Al(1)-N(1) 2.052(4), Al(1)-N(2) 1.932(4), Al(1)-N(3) 1.929(4), Al(1)-N(4) 2.047(4), Al(1)-I(1) 2.5653(14).

2.2.2. X-ray structural characterisation of [Al(DippForm)Cl$_2$(thf)] (**5**) and [Al(DippForm)ClBr(thf)] (**6**),

In order to compare the structural nature of 1:1 (Al:formamidinate) complexes with the 2:1 complexes presented above, [Al(DippForm)Cl$_2$(thf)] (**5**) and [Al(DippForm)ClBr(thf)] were isolated and crystallised (Scheme 1). The monomeric complexes of (**5**) and (**6**) are isostructural and crystallised in the triclinic space group *P-1*. The five-coordinate aluminium centre in each of (**5**) and (**6**) is ligated by two nitrogen atoms from the formamidinate ligand, and the other three sites are occupied by two halide atoms and a thf ligand (Figure 3). The coordination environment for the Al atom in (**5**) and (**6**) are as expected identical, except one chloride ligand in (**5**) is replaced by a bromide ligand in (**6**). The formamidinate moieties in (**5**) and (**6**) serve as bidentate N,N'-chelating ligands and they are almost similar to the structures observed for the corresponding [GaMe$_2$(PhNCPhNPh)],[36] [E{RC(NR')$_2$}Cl$_2$] [E = Sb, R = *t*Bu, R' = *i*Pr, Cy, 2,6-*i*Pr$_2$C$_6$H$_3$ (DippForm); R= *n*Bu, R' = *i*Pr; E = Bi, R = *t*Bu, R' = *i*Pr , DippForm][37a] and [Sb(Form)X$_2$] [X = F, N$_3$; Form = *t*BuC(N*i*Pr)$_2$ or *t*BuC(N{2,6-*i*Pr$_2$C$_6$H$_3$})$_2$].[37b]

Al1–N1 and Al1–N2 distances in (**5**) and (**6**) were found to be 2.107(2)/1.928(2) and 2.101(3)/1.928(3) Å and are unexceptional.[5,14,28-29] The aluminium centre in these five coordinate compounds are in distorted trigonal bipyramidal geometry as for compounds (**1**) to (**4**) and have N(1) and O(1) in axial positions with N(1)-Al(1)-O(1) angles being 156.49(10) and

155.11(12)° in (5) and (6) respectively while the two halides and N(2) reside in equatorial positions (the sum of the equatorial angles in (5) and (6) are both 359.3°).

(a)   **(b)**
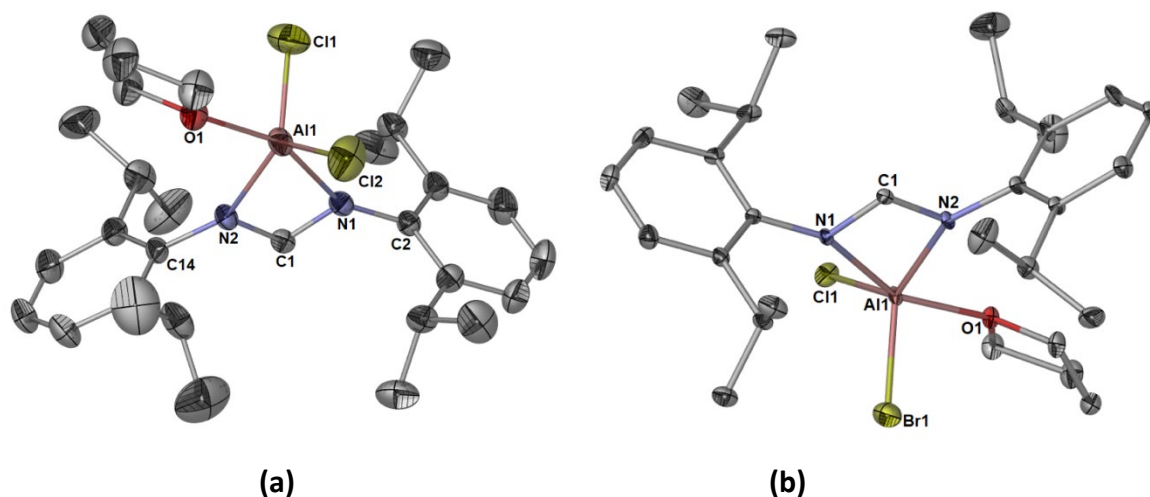
Figure 2. **(a)** Molecular structure of (5). **(b)** Molecular structure of compound (6). Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Compound (5): Al(1)-N(1) 2.107(2), Al(1)-N(2) 1.928(2), Al(1)-Cl(1) 2.1090(15), Al(1)-Cl(2) 2.0862(14), Al(1)-O(1) 1.999(2); Compound (6): Al(1)-N(1) 2.101(3), Al(1)-N(2) 1.928(3), Al(1)-Cl(1) 2.2206(14), Al(1)-Br(1) 2.3028(13), Al(1)-O(1) 2.004(3).

2.2.3. X-ray structural characterisation of (7) [Al(XylFormH)Br₃] and (8) [Al(DippFormH)Br₃]

The monomeric complexes [Al(XylFormH)Br₃]) (7) and ([Al(DippFormH)Br₃] (8) crystallised in the monoclinic space groups *P2₁/n* (7) and *P2₁/c* (8) respectively, with one molecule within the asymmetric unit. Structural determination revealed the aluminium centre is four coordinate tetrahedral, with a dative bond to nitrogen from the formamidine ligand (through κ^1(N1) XylFormH or DippFormH), and three terminal bromine atoms. Complexes (7) and (8) resemble the previously reported structure of [AlI₃(AisoH)].[12] The Al−N bond lengths [(7) 1.899(3) Å, (8) 1.885(3) Å] are much shorter than the dative Al−N bond, but are somewhat longer than the covalent Al−N bond.
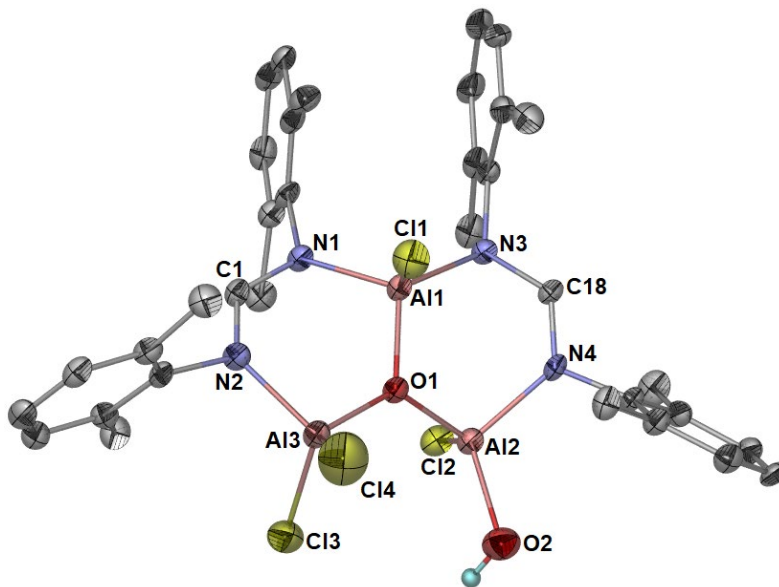
9

(a)   **(b)**
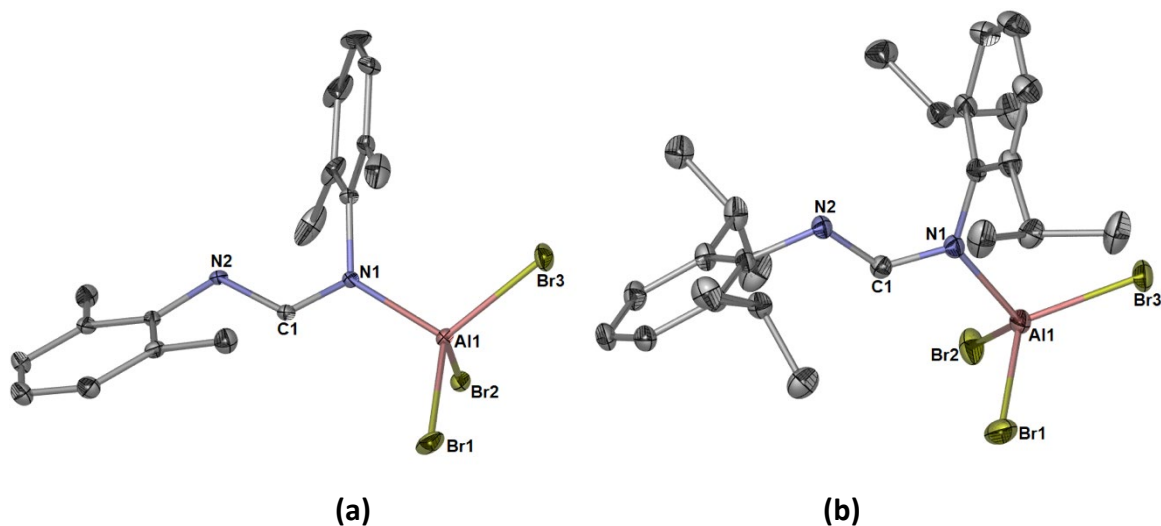
Figure 3. (a) Molecular structure of (**7**). (b) Molecular structure of compound (**8**). Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Compound (**7**): Al(1)-N(1) 1.899(3), Al(1)-Br(1) 2.2913(11), Al(1)-Br(2) 2.3043(11), Al(1)-Br(3) 2.2685(10); Compound (**8**): Al(1)-N(1) 1.885(3), Al(1)-Br(1) 2.2784(13), Al(1)-Br(2) 2.2800(12), Al(1)-Br(3) 2.2484(11).

2.2.4. X-ray structural characterisation of (*9*), [Al₃(XylForm)₂(μ₃-O)(OH)Cl₄]₂.PhMe

[Al$_3$(XylForm)$_2$(μ$_3$-O)(OH)Cl$_4$]$_2$·PhMe (**9**) crystallised in triclinic space group *P-1*. Two crystallographically unique molecules, with similar fundamental coordination geometries are present in the asymmetric unit. The X-ray crystallographic study for complex (**9**) showed that each of the two molecules has two deprotonated ligands supporting three aluminium centres through a *μ*-[κ^1-N: κ^1-N] mode, forming a trinuclear formamidinate bridged structure (Figure 5). A terminal chloride and a terminal OH⁻ group are present on each aluminium centre and the three Al centres are bound to a central oxide ligand. It is assumed that the occurrence of oxygen (O^{2-} and OH⁻) arises from adventitious H$_2$O highlighting the reactivity of (**9**) but thf being the source of oxygen cannot be ruled out.[38-41] Models of a three-coordinate oxygen centre with bonds to three aluminium atoms are exceptional but not unprecedented.[42-44] The best description for this structure is two merged six membered rings, that share Al1 and O1. The Al–N bond lengths are in the range between 1.891(5) – 1.935(5) Å, and together with NCN angles are similar to those reported in neutral chelated formamidinate complexes.[28,29] The Al–N metric parameters are

very comparable to those of the heteroleptic Al (III) amidinate complex reported by Lesikar and Richards.[14] Complex (**9**) exhibits Al1/Al2/Al3–O1 distances of 1.769(4), 1.805(4) and 1.794(4) Å, respectively, which correspond closely to the [{DippNCHDipp}$_2$Al$_3\mu_3$O(OH)$_2$(Cl/OH)ClMe] complex with distances of 1.782(4), 1.772(4) and 1.792(4) Å respectively.[14]

Figure 4. Molecular structure of (**9**). Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.881(5), Al(1)–N(3) 1.883(5), Al(1)–O(1) 1.769(4), Al(1)–Cl(1) 2.080(3), Al(2)–N(4) 1.940(5), Al(2)–O(1) 1.805(4), Al(2)–O(2) 1.976(5), Al(2)–Cl(2) 2.165(3), Al(3)–N(2) 1.928(5), Al(3)–O(1) 1.794(4), Al(3)–Cl(3) 2.124(3), Al(3)–Cl(4) 2.035(3).

3. *Conclusions*

Metathesis reactions between the alkali metal salts of two differing formamidinates of varying steric bulk, (XylForm and DippForm) and AlX$_3$ (X = Cl, Br, I) have produced nine new complexes. Using either supporting ligand and with X = Cl, I, we were able to obtain the 2:1 complexes [Al(Form)$_2$X] while 1:1 complexes [Al(Form)X$_2$] were only isolable for the more sterically demanding ligand DippForm for both X = Cl, or Cl/Br. In attempts to synthesise 1:1 complexes using either XylFormH or DippFormH and X = Br, Lewis adducts [Al(XylFormH)Br$_3$] and [Al(DippFormH)Br$_3$] were isolated. In one attempt to synthesise the 1:1 complex using XylForm

as the supporting ligand and X = Cl, we obtained the trinuclear oxo-centred [Al$_3$(XylForm)$_2$(μ_3-O)(OH)Cl$_4$]$_2$.PhMe, that presumably arose from hydrolysis, but thf as an oxygen source is not ruled out. Overall, this work has enriched the knowledge regarding (formamidinato) aluminium halide (III) complexes particularly with respect to their solid state structures. These compounds would be suitable precursors to investigations towards low valent aluminium compounds after treatment with reducing agents such as KC$_8$.

4. Experimental

4.1 General

The two sterically bulky formamidine pro-ligands: XylFormH = N,N'-bis(2,6-dimethylphenyl)formamidine and DippFormH = N,N'-bis(2,6-diisopropylphenyl)formamidine, was synthesised according to a published procedure.[45,46] All aluminium complexes described herein are extremely air- and moisture-sensitive, therefore all the reactions were performed under oxygen- and moisture-free conditions using standard Schlenk-line and glovebox techniques. Hexane and toluene were dried by an LC solvent purification system. Sodium or sodium/benzophenone was used for refluxing and distillation of tetrahydrofuran (THF) to dry and deoxygenate it prior to use in reactions. Anhydrous $AlCl_3$, $AlBr_3$, AlI_3 and other starting materials such as lithium-/sodium-/potassium-bis(trimethylsilyl)amide and n-butyllithium, were purchased from Sigma Aldrich and used as received. Room temperature (25 °C) ^{1}H spectra were recorded at 400 MHz on a Bruker AVANCE III HD instrument with dry degassed deuterobenzene (C_6D_6) as the solvent, and resonances were referenced to the residual ^{1}H resonances of the deuterated solvent. Infrared spectra were obtained as Nujol mulls between with NaCl plates on a Nicolet-Nexus FTIR spectrophotometer within the range of 4000-500 cm^{-1} (samples were prepared in the dry box). Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory, Science Centre, London Metropolitan University, England, and samples were sealed under nitrogen. Elemental analyses for compounds **1, 2, 4, 8** and **9** consistently gave poor correlation with material obtained from Xray analysis and other characterisation, presumably due to decomposition during transport to the analysis centre, or due to incomplete combustion due to carbide formation. Melting points were obtained under nitrogen in sealed capillaries.

[Al(XylForm)₂Cl] (1)

XylFormH (0.50 g, 2.0 mmol) was dissolved in PhMe (20 ml). At room temperature LiN(SiMe₃)₂ (1.0 M solution in THF, 2.0 ml, 2.0 mmol) was added dropwise by syringe, forming the solution of Li(XylForm). This solution was added dropwise through a cannula to a solution of $AlCl_3$ (0.13 g, 1.0 mmol) in PhMe (10 ml) at room temperature with stirring. Stirring was maintained for 18 h and a yellow solution with a white precipitate of LiCl formed. All volatiles were removed in vacuo.

The filtrated solution was concentrated to ca. 10 ml and placed at −30 °C overnight giving colourless crystals of (**1**).

Yield = 0.20 g (40%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): 1.85, 2.13, 2.16, 2.31 (s, 24H, CH$_3$), 6.76-6.83 (m, 4H, *p*-Ar*H*), 6.84-6.95 (m, 8H, *m*-Ar*H*), 7.09 (d, 2H, NCHN). IR (*v*/cm^{-1}, Nujol mull): 1651 (s), 1632 (s), 1588 (w), 1547 (w), 1340 (w), 1309 (w), 1286 (m), 1203 (m), 1148 (w), 1092 (m), 1031 (m), 918 (w), 795 (m), 759 (m), 722 (m), 620 (w), 662 (w).

[Al(XylForm)$_2$I]·PhMe (2)

A solution of K(XylForm), prepared from XylFormH (0.50 g, 2.0 mmol) in PhMe (20 ml) and KN(SiMe$_3$)$_2$ (0.5 M solution in PhMe, 4 ml, 2.0 mmol) at room temperature, was added dropwise through a cannula to a solution of AlI$_3$ (0.41 g, 1.0 mmol) in PhMe (10 ml) at room temperature with stirring. The reaction mixture was continued stirring for 18 h to yield a yellow solution with a white precipitate of KI. Filtration, concentration and slow cooling to −30 °C overnight of this solution giving light yellow crystals of (**2**).

Yield = 0.31 g (62%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.96, 2.06, 2.41, 2.46 (s, 24H, C*H*$_3$), 6.71-7.03 (m, 12H, Ar*H*), 7.08 (s, 2H, NC*H*N). IR (v/cm^{-1}, Nujol mull): 1648 (s), 1612 (w), 1578 (m), 1304 (m), 1262 (m), 1203 (w), 1092 (w), 891 (m), 799 (m), 672 (m).

[Al(DippForm)$_2$Cl] (3)

Li(DippForm) was prepared from DippFormH (0.72 g, 2.0 mmol) and LiN(SiMe$_3$)$_2$ (1 M solution in thf, 2.0 ml, 2.0 mmol) in THF (20 ml) at room temperature. This solution was added dropwise via a cannula to a solution of AlCl$_3$ (0.13 g, 1.0 mmol) in THF (10 ml) at room temperature with stirring. The reaction mixture was subsequently continued stirring for 24 h. Volatiles were removed in vacuo and the residue was extracted into PhMe (25 ml) and filtered. The filtrate was concentrated to ca. 10 ml and placed at −30 °C for 48 h yielded white crystals of (**3**).

Yield = 0.51 g (70%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.14 (d, 48H, CH(C*H*$_3$)$_2$), 3.36 (m, 8H, C*H*(CH$_3$)$_2$), 6.81-7.09 (m, 12H, Ar*H*), 7.68 (d, 2H, NC(*H*)N). Elemental analysis calcd. (%) for C$_{50}$H$_{70}$AlClN$_4$ (*M* = 789.56 g/mol): C 76.06, H 8.93, N 7.09; found: C 75.35, H 8.76, N 6.66. IR (v/cm$^-$

[Al(DippForm)$_2$I] (4)

Method 1: Li(DippForm) (0.148 g, 0.4 mmol) was dissolved in 5 ml thf and added slowly to a solution of AlI$_3$ (0.082 g, 0.2 mmol) in PhMe (5 ml) in ice bath via a cannula. The reaction mixture was stirred overnight. The filtrate was concentrated to ca. 5 ml and placed at -20 °C overnight yielded colourless crystals of **4**.

Yield = 0.14 g (80 %). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.17 (d, 48H, CH(CH$_3$)$_2$), 3.44 (sept, 8H, CH(CH$_3$)$_2$), 6.92-7.12 (m, 12H, ArH), 7.53 (d, 2H, NC(H)N). IR (v/cm^{-1}, Nujol mull): 1667 (s), 1587 (w), 1333 (w), 1288 (w), 1260 (w), 1234 (w), 1181 (m), 1074 (s), 913 (s), 799 (m), 753 (w), 723 (w), 671 (w).

Method 2: Treatment of a toluene solution of [La(η^6-MeC$_6$H$_5$)(AlI$_4$)$_3$] (1.52g, 0.83mmol) with KDippForm (0.67 g, 1.67 mmol) and heating for 12 h at 100 °C provided a colourless solution and white precipitate. The solution was filtered and concentrated to ca. 10ml and stored at ambient temperature for 2 days whereupon a few colourless crystals were obtained.

[Al(DippForm)Cl$_2$(thf)] (5)

A solution of Li(DippForm), was prepared from DippFormH (0.36 g, 1.0 mmol) and *n*-BuLi (1.6 M solution in hexanes, 0.6 ml, 1.0 mmol) in THF (20 ml) at room temperature. After 2 h stirring, the solution was added dropwise through a cannula to a stirred solution of AlCl$_3$ (0.13 g, 1.0 mmol) in THF (10 ml) at 0 °C. The reaction mixture was continued stirring for 16 h. The reaction mixture was dried under vacuum to the point of dryness and extracted into PhMe (20 ml), forming a precipitate of LiCl. Filtration and concentrated to ca. 10 ml, followed by cooling −30 °C overnight resulted in white crystalline samples of (**5**).

Yield = 0.15 g (42%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.03 (br m, 4H, CH$_2$-thf), 1.25 (d, 24H, CH(CH$_3$)$_2$), 3.56 (br m, 4H, OCH$_2$-thf), 3.77 (sept, 4H, CH(CH$_3$)$_2$), 6.99 (br m, 2H, *p*-ArH), 7.10 (br m 4H, *m*-ArH), 7.50 (s, 1H, NC(H)N); Elemental analysis calcd. (%) for C$_{29}$H$_{43}$AlCl$_2$N$_2$O (M = 533.58 g/mol): C 65.27, H 8.12, N 5.25. Calcd for C$_{27}$H$_{39}$AlCl$_2$N$_2$O (505.50 g/mol after loss ½ of thf

solvation) C 64.02, H 7.96, N 5.53. Found: C 64.55, H 7.90, N 5.36. IR (v/cm^{-1}, Nujol mull): 1667 (m), 1587 (w), 1341 (w), 1260 (w), 1234 (w), 1178 (w), 1096 (w), 917 (w), 803 (m), 727 (w), 694 (w).

[Al(DippForm)ClBr(thf)] (6)

A solution of Li(DippForm), prepared from DippFormH (0.36 g, 1.0 mmol) and *n*-BuLi (1.6 M solution in hexanes, 0.6 ml, 1.0 mmol) in THF (20 ml), was added dropwise through a cannula to a solution of AlBr$_3$ (0.135 g, 0.5 mmol) and AlCl$_3$ (0.065 g, 0.5 mmol) in THF (10 ml) at room temperature with stirring. The colourless reaction mixture was continued stirring for 16 h at ambient temperature. The solvent was evaporated under vacuum to the point of dryness and PhMe (20 ml) added. The mixture was then filtered to remove LiCl. The solvent was then concentrated to ca. 10ml, and slowly cooled to −30 °C, giving colourless crystals of (**6**).

Yield = 0.14 g (40%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.09 (br m, 4H, C*H$_2$*-thf), 1.31 (d, 24H, CH(C*H$_3$*)$_2$), 3.60 (br m, 4H, OC*H$_2$*-thf), 3.86 (sept, 4H, C*H*(CH$_3$)$_2$), 7.21-7.11 (br m 6H, *p*- and *m*-Ar*H*), 7.57 (s, 1H, NC(*H*)N). Elemental analysis calcd. (%) for C$_{29}$H$_{43}$AlBrClN$_2$O (*M* = 578.03 g/mol): C 60.25, H 7.49, N 4.84. Calcd for C$_{27}$H$_{39}$AlBrClN$_2$O (549.95 g/mol after loss ½ of thf solvation) C 58.86, H 7.31, N 5.08. Found: C 58.44, H 7.02, N 4.71. IR (v/cm^{-1}, Nujol mull): 1658 (s), 1640 (s), 1289 (w), 1105 (s), 921 (m), 803 (s), 770 (s), 665 (w), 556 (s), 406 (w).

[Al(XylFormH)Br$_3$] (7)

A solution of AlBr$_3$ (0.133 g, 0.5 mol) in PhMe (4 ml) was added dropwise to a solution of XylFormH (0.126 g, 0.5 mmol) in PhMe (4 ml), the reaction mixture was stirred overnight at room temperature. Filtration, concentration to ca. 3 ml, and keeping at −20 °C overnight resulted in formation of colourless crystals of **7**.

Yield = 0.23 g (88%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.55, 1.90, 2.20, 2.27 (s, 12H, C*H$_3$*), 5.63 (d, 1H, N*H*), 6.52-7.10 (m, 6H, Ar*H*), 7.80 (d, 1H, NC*H*N); Elemental analysis calcd. (%) for C$_{17}$H$_{20}$AlBr$_3$N$_2$ (*M* = 519.03 g/mol): C 39.34, H 3.96, N 5.39; found: C 39.28, H 5.01, N 5.42. IR (v/cm^{-1}, Nujol mull): 3247 (w), 1640 (m), 1586 (m), 1335 (w), 1259 (m), 1155 (m), 1092 (m), 1032 (m), 947 (m), 916 (w), 833 (m), 785 (m), 769 (m), 702 (w), 861 (m).

[Al(DippFormH)Br$_3$] (8)

A solution of AlBr$_3$ (0.197 g, 0.739 mmol) in PhMe (5 ml) was added dropwise to a solution of DippFormH (0.270 g, 0.740 mmol) in PhMe (5 ml), the reaction mixture was stirred overnight at room temperature. Filtration, concentration to ca. 5 ml, and keeping at −20 °C overnight resulted in formation of colourless crystals of **8**.

Yield = 0.42 g (91%). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 1.09 (d, 24H, CH(CH_3)$_2$), 3.11 (p, 4H, CH(CH$_3$)$_2$), 6.25 (t, 1H, NH), 6.94-7.10 (br m, 6H, ArH), 8.24 (d, 1H, NC(H)N). IR (v/cm^{-1}, Nujol mull): 3312 (w), 1681 (s), 1641 (s), 1585 (m), 1349 (m), 1326 (m), 1260 (m), 1178 (w), 1153 (w), 1096 (m), 1059 (m), 1042 (m), 1013 (m), 948 (m), 805 (s), 778 (m),755 (w), 721 (w), 676 (m).

[Al$_3$(XylForm)$_2$(μ_3-O)(OH)Cl$_4$]·0.5PhMe (9)

A solution of K(XylForm), prepared from XylFormH (0.75 g, 3.0 mmol) and KN(SiMe$_3$)$_2$ (0.5 M solution in PhMe, 6 ml, 3.0 mmol) in THF (30 ml), was added dropwise through a cannula to a solution of AlCl$_3$ (0.39 g, 3.0 mmol) in PhMe (30 ml) at room temperature with stirring. The reaction mixture was stirred for 18 h to yield a yellow solution with a white precipitate of KCl. Volatiles were removed under vacuum, and the residue was extracted by PhMe (20 ml) to ensure the complete forming of KCl. Filtration, concentration to ca. 10ml and keeping at −30 °C overnight giving light crystals of **9**.

Yield = 0.49 g (65%). M.P. 196-198 °C (dec). ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ (ppm) = 0.41 (s, Al–OH), 2.24 (br m, 1.5H, CH_3-PhMe), 2.47 (br m, 12H, CH_3), 6.76 (m, 2H, p-ArH), 7.04 (m, 4H, m-ArH), 7.25 (m, 2.5H, ArH-PhMe), 8.19 (s, 1H, NCHN). IR (v/cm^{-1}, Nujol mull): 1936 (s), 1875 (vs), 1857 (s),1781 (s), 1637 (s), 1596 (s), 1537 (m), 1257 (s), 1205 (s), 1169 (s), 1093 (s), 1020 (s), 987 (vs), 936 (s), 917 (vs), 891 (s), 846 (s),782 (w), 720 (m), 602 (s), 584 (s), 557 (s), 424 (w).

5. *X-ray crystallography*

Single crystals covered with viscous hydrocarbon oil were mounted on a glass fibre. Data were obtained at -173 °C (100 K) on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia (compounds (**1**), (**2**), (**3**), (**4**), (**7**), (**8**), and (**9**)), or at 23 °C (296 K) on a Bruker APEX II CCD diffractometer (compounds (**5**) and (**6**)) equipped with graphite-monochromated MoK_a radiation (λ = 0.71073 Å). Data collection and integration on the MX1: Macromolecular Crystallography beamline was accomplished using Blu-Ice.[47] The structures were solved using SHELXS[48] and refined by full-matrix least-squares on all F^2 data using SHELX2014[48] in conjunction with the X-Seed graphical user interface.[49] All hydrogen atoms were placed in calculated positions using the riding model. Data collection and refinement details are collated below in Tables 1 and 2. The crystal structure data has been deposited with the CCDC, reference numbers 2056301-2056309 for compounds (**1**)-(**9**) and these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

7. *Conflicts of interest*

The authors declare no conflicts of interest

Table 1. Crystal data and refinement details for complexes **1-9**

Compound	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
formula	$C_{34}H_{38}AlClN_4$	$C_{41}H_{46}AlIN_4$	$C_{50}H_{70}AlClN_4$	$C_{50}H_{70}AlIN_4$	$C_{29}H_{43}AlCl_2N_2O$
Formula weight	565.14	748.73	789.53	880.98	533.58
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	P-1	$P2_1/n$	$P2_1/c$	P-1
a, Å	8.0280(16)	8.2260(16)	14.509(3)	14.156(3)	10.3175(4)
b, Å	8.5240(17)	15.064(3)	16.288(3)	16.573(3)	10.7120(4)
c, Å	44.624(9)	15.169(3)	21.112(4)	21.433(4)	14.7854(5)
α, deg	90	93.96(3)	90	90	91.983(2)
β, deg	92.20(3)	96.63(3)	109.86(3)	108.35(3)	98.268(2)
γ, deg	90	96.34(3)	90	90	103.631(2)
V, Å^3	3051.4(11)	1849.3(7)	4692.6(18)	4772.5(18)	1567.57(10)
Z	4	2	4	4	2
T, K	100(2)	100(2)	100(2)	100(2)	296(2)
no. of rflns collected	35848	22141	56762	39220	15311
no. of indep rflns	5120	5936	8217	8246	5297
R_{int}	0.0477	0.0338	0.0369	0.1102	0.0408
Final $R1$ values ($I > 2\sigma(I)$)	0.0588	0.0273	0.0491	0.0532	0.0821
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1535	0.0735	0.1226	0.1246	0.2646
Final $R1$ values (all data)	0.0656	0.0293	0.0527	0.0859	0.0990
Final $wR(F^2)$ values (all data)	0.1568	0.0748	0.1249	0.1393	0.2880
$GooF$ (on F^2)	1.198	1.064	1.118	1.030	1.052

Compound	(6)	(7)	(8)	(9)
formula	$C_{29}H_{43}AlBrClN_2O$	$C_{17}H_{20}AlBr_3N_2$	$C_{25}H_{36}AlBr_3N_2$	$C_{37.5}H_{43}Al_3Cl_4N_4O_2$
Formula weight	577.99	519.06	631.24	804.50
crystal system	triclinic	monoclinic	Monoclinic	triclinic
space group	P-1	$P2_1/n$	$P2_1/c$	P-1
a, Å	10.222(2)	7.7260(15)	10.278(2)	10.906(2)
b, Å	10.720(2)	14.013(3)	19.974(4)	12.427(3)
c, Å	14.529(3)	18.307(4)	14.178(3)	16.934(3)
α, deg	91.85(3)	90	90	87.83(3)
β, deg	98.80(3)	93.93(3)	108.59(3)	72.56(3)
γ, deg	104.04(3)	90	90	67.89(3)
V, Å^3	1522.3(6)	1977.3(7)	2758.7(11)	2021.2(9)
Z	2	4	4	2
T, K	296(2)	100(2)	100(2)	100(2)
no. of rflns collected	27931	15215	27489	17460
no. of indep rflns	7381	3240	4822	6653
R_{int}	0.0308	0.0572	0.0384	0.0926
Final $R1$ values ($I > 2\sigma(I)$)	0.0674	0.0348	0.0385	0.0846
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2289	0.0960	0.0993	0.2249
Final $R1$ values (all data)	0.0744	0.0358	0.0415	0.1312
Final $wR(F^2)$ values (all data)	0.2315	0.0970	0.1015	0.2590
$GooF$ (on F^2)	1.152	1.070	1.081	1.041

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