Theoretical and Experimental Investigations of Ligand Exchange in Amidinate and Guanidinate Ligand Systems and the Atomic Layer Deposition of Aluminum Oxide

by

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in partial fulfillment of the requirements for the degree of
Master of Science

to

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Abstract

The mechanism for ligand exchange in amidinates and guanidates was investigated experimentally and theoretically. It was discovered that ligand exchange between guanidates and chlorides must proceed through a dimeric intermediate where the metal centre is bridged by two guanidate ligands. The mechanism of ligand exchange is driven by entropy and can be controlled stoichiometrically.

The exchange chemistry between six-coordinate amidinate and guanidate species, $[\text{RC}(\text{N}^i\text{Pr})_2]_3\text{M}$ (where $\text{R} = \text{NMe}_2, \text{Me}, \text{Et}$ and $\text{M} = \text{Al}, \text{Ga}$), and homoleptic three-coordinate aluminum and gallium compounds to form species of the type $[\text{RC}(\text{N}^i\text{Pr})_2]_{3-x}\text{MR}'_x$ (where $\text{R}' = \text{Me}, \text{Et}, \text{Cl}$ and $x = 1-3$) was studied. The thermal stability of these products was demonstrated by thermogravimetric analysis.

The atomic layer deposition (ALD) of aluminum oxide thin films was investigated using $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and water. Surface morphologies, thickness measurements and X-ray techniques were used to characterize these films. The aluminum source, $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$, was found to be an effective precursor in the ALD of aluminum oxide.

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List of Abbreviations

CSD – Chemical Solution Deposition
CVD – Chemical Vapour Deposition
ALD – Atomic Layer Deposition
CDI – Carbodiimide
ⁱPr CDI – 1,3-diisopropylcarbodiimide
^tBu CDI – 1,3-di-*tert*-butylcarbodiimide
DFT – Density Functional Theory
NMR – Nuclear Magnetic Resonance
HF – Hartree-Fock
MPPT – Møller-Plesset Perturbation Theory
TS – Transition State
TGA – Thermogravimetric Analysis
SEM – Scanning Electron Microscopy
AFM – Atomic Force Microscopy
EDX – Energy Dispersive X-ray Spectroscopy
WDS – Wavelength Dispersive Spectroscopy
RMS – Root Mean Square

List of Publications

Allison L. Brazeau, Gino A. DiLabio, Kevin A. Kreisel, Wesley Monillas, Glenn P. A. Yap and Seán T. Barry.* Theoretical and experimental investigations of ligand exchange in guanidinate ligand systems for group 13 metals, *Dalton Trans.* **2007**, 30, 3297.

Allison L. Brazeau; Zhaohui Wang; Chris N. Rowley and Seán T. Barry.* Synthesis and Thermolysis of Aluminum Amidinates: A Ligand-Exchange Route for New Mixed-Ligand Systems, *Inorg. Chem.* **2006**, 45, 2276.

Chapter 1: Introduction

1.1. Atomic Layer Deposition

Thin film deposition techniques have been a growing interest over the past few decades.¹⁻²⁴ There are a variety of methods available for thin film depositions, which can be divided into three general classes: chemical depositions, physical depositions and processes that use a combination of the previous two. Chemical depositions involve a chemical change occurring at a surface.¹ This can be accomplished in solution phase or in the vapour phase and are commonly referred to as chemical solution deposition (CSD) and chemical vapour deposition (CVD), respectively. Physical depositions rely on mechanical or thermodynamic processes to produce a thin film. These are typically achieved by using high energies, such as impact processes or thermal evaporation, to get the target material into the gas phase.¹ The material deposits when it encounters and condenses on the cooler substrate.¹ Some examples of physical deposition techniques are electron beam epitaxy,^{2,3} thermal evaporation,^{4,5} pulsed laser deposition^{6,7,8} and sputtering.^{9,10}

Atomic layer deposition (ALD) is a class of CVD that is capable of forming thin films exhibiting excellent conformality, uniformity, and precise thickness control over a three dimensional surface.¹¹ This technique is well known for its ability to deposit conformal layers of thin films over complicated surfaces. For example, it has been used to fill narrow trenches with high aspect ratios,^{12,13} and it has also been used to make inverse opals.¹⁴ Certain key characteristics of the vaporous precursor compound give ALD its characteristic self-limiting behaviour. Self-limiting behaviour occurs when the chemical reactions are limited by the number of reactive surface sites and no further reactions occur on the surface once these sites are occupied. Self-limiting behaviour allows for complete monolayer saturation and prevents continual growth of the thin film by inhibiting further surface reactions.

1.1.1. Method

Atomic layer deposition, unlike other CVD techniques, uses a cyclic reaction sequence to achieve a target film with controlled thickness. ALD is a four step process and proceeds as follows:

1. A volatile precursor compound containing the metal centre for the desired target film is entrained to a reaction chamber. This precursor chemisorbs on the substrate through a surface functional group (such as a hydroxyl group) yielding a new surface functional group and volatile byproducts.
2. The volatile side products and any excess precursor are removed from the reaction chamber either by purging with an inert gas, by evacuating the chamber, or by a combination of the two.
3. A second vaporous precursor, sometimes referred to as the reactant gas, is introduced to react with the chemisorbed precursor to form a monolayer of the target film. This results in volatile side products (e.g. free ligand) and new surface sites (e.g. hydroxyl groups or oxo-bridges).
4. The reaction chamber is again purged of the remaining volatile precursor and side products.

These four steps can be repeated to achieve a target film of desired thickness. Each cycle will deposit an additional monolayer and the thickness control is exhibited on the atomic level. The type of film deposited is dependent on the nature of both of the initial precursor and the reactant gas used. Typical target films include metal oxides, metal nitrides and reduced metals. Metal oxide films are most often grown using water as the oxygen source. Alternate oxygen sources for metal oxide films include hydrogen peroxide,¹⁵ ozone¹⁶ and metal alkoxides,¹⁷ which serve as both the metal and oxygen source. The most common metal nitride films are typically deposited using transition-metal containing precursors (most often halide species) and ammonia.¹¹ Metal films are deposited by ALD commonly using hydrogen or hydrogen plasma as reducing agents.¹¹ However, other reducing agents have successfully resulted in the deposition of metal films, for example tungsten metal can be deposited using WF_6 and Si_2H_6 .¹⁸ The ALD method is by no means limited to this short list of target films. There are many types of

films accessible using the ALD method including GaAs,¹⁹ In₂S₃,²⁰ CaF₂,²¹ and binary oxide films (ie. Zr_xTi_yO_z,²² SrTa₂O₆,²³ GdScO₃²⁴), to name a few.

Atomic layer deposition differs from CVD through the controlled decomposition of the initial precursor by the reactant gas. In CVD, thermal decomposition of the precursor occurs at the substrate to produce a target film. Due to this surface decomposition at the substrate CVD depositions occur by continual growth. In ALD, the two precursors are introduced in an alternating fashion, allowing controlled growth. These types of growth seen during a deposition process can be differentiated using a saturation curve (Figure 1.1). A saturation curve is a plot of the film growth rate as a function of the precursor concentration. The allowed pulse length, typically measured in seconds, measures the precursor concentration: the longer the pulse length the more precursor material is entrained to the reaction chamber and the higher the effective precursor concentration. If the process exhibits self-limiting behaviour (Figure 1.1a) then at a critical concentration of precursor the surface sites will become fully saturated by a monolayer of precursor and the resulting chemisorbed monolayer will prohibit any further reactions to occur on the surface. At such a concentration a plateau of the growth rate is expected because any further increase in precursor concentration will not affect the rate of growth: all surface sites are occupied and the precursor is designed not to react with itself. By generating a saturation curve, the optimal growth conditions can be found such that precursor waste and process times are kept to a minimum. In order for a process to be considered ALD, both precursors must exhibit self-limiting behaviour: saturation curves for both the initial precursor and reactant gas must be generated and illustrate a plateau of growth rate with respect to precursor concentration.

If the process has a CVD component, then one would expect continual growth (Figure 1.1b). Continual growth occurs if the saturation curve does not plateau at some growth rate for increasing precursor concentrations. Continual growth indicates that the film thickness and growth rate increase as precursor concentrations increase. This is indicative of CVD because the precursor is decomposing upon chemisorption to the substrate.

Figure 1.1: Saturation curves demonstrating (a) self-limiting behaviour for an ALD process and (b) continual growth for a CVD process.

There are two main types of chemical vapour phase reactors for film deposition: hot-walled reactors and cold-walled reactors. Within a hot-wall reactor (Figure 1.2a) the thermal reaction that occurs at the substrate surface is a consequence of the temperature of the reaction chamber, which is encased in a furnace. In this case the entire chamber is heated and deposition occurs everywhere, including the substrate, substrate holder and the walls of the reaction chamber. A hot-walled reactor is typically used under low pressures.²⁵ Cold-wall reactors (Figure 1.2b) are not encased in a furnace, but rather use resistive heating in order to heat only the substrate.²⁵ Graphite is frequently used as a susceptor in induction heating because it has high resistivity and a wide temperature range.²⁶ Radio-frequency induction is commonly employed to heat the susceptor.²⁶ In this way, the walls of the reactor are cold compared to the substrate and deposition only occurs on the surface of the substrate. Cold-wall reactors are usually operated at atmospheric pressure.²⁵

Figure 1.2: Schematic of a) hot-walled and b) cold-walled vapour deposition reactors.

1.1.2. Precursor Design

The sequential additional of vaporous precursors is a key concept to controlling target film thickness in ALD. However, the design of the precursor also plays a major role in achieving self-limiting ALD growth. There are six major characteristics involved in designing precursors:

1. **Volatility:** The precursor must have a high vapour pressure in order to be introduced into the reaction chamber in the gaseous phase. This can be achieved by coordinatively saturating the metal centre in order to prevent oligomerization and by keeping the molecular weight of the precursor to a minimum.
2. **Low melting point:** Preferably the precursor would be a distillable liquid or a low melting solid so that it has a reproducible vapour pressure. Thus, a constant concentration of precursor is introduced per ALD cycle to ensure complete and uniform monolayer formation. Introducing branching and asymmetry in order to discourage crystallization can achieve low melting complexes.
3. **Thermal stability:** Thermal stability is important in two aspects of the deposition process. First, the precursor must be thermally stable over long periods of time for the purpose of keeping a high vapour pressure within the bubbler for the

duration of the deposition. This ensures that the precursor introduced in the first pulse is the same as the precursor introduced in the last pulse. Typically, the bubbler is kept at a temperature just above the melting point or distillation temperature of the precursor. The duration of the deposition will vary depending on the desired film thickness. For example, a film thickness of 1000 Å can take approximately 15 hours to complete. Secondly, it is important that the precursor be thermally stable in order to obtain self-limiting film growth. Decomposition may result during the deposition of a film without a reactant gas, which is CVD-type growth. Since decomposition is thermally activated, its rate will increase exponentially with temperature. Reaction chamber temperatures are typically held as high as 300°C, so the precursors must be at least kinetically stable at these temperatures.

4. **Chemical reactivity:** The two independent precursors should react completely with each other to allow for shorter cycle times and fewer impurities in the resulting film. Also, the initial precursor should react with the surface functional groups and remain chemisorbed during purging periods to deposit a dense film. The bonds being formed during the deposition process must be stronger than those being broken within the precursor.
5. **Self-limiting:** The ligands should sterically protect the metal centre. This will prevent the vapour phase molecules from interacting with the chemisorbed monolayer, as well as prevent any gas phase reactions of the precursor with itself. Without self-limiting behaviour, more than one monolayer can deposit in each sequential pulse, which tends towards continual growth.
6. **Formation of stable by-products:** The side products produced from the reaction of the metal containing precursor with surface functional groups, as well as from the reaction of the reactant gas with the chemisorbed monolayer should be highly volatile. This ensures that the by-products are fully removed during the purging or evacuation of the reaction chamber. Otherwise they may adsorb onto the resulting films and cause impurities or inhibit film growth.

A technique used to satisfy some of the design characteristics of the ligand system is to vary the length of the alkyl chains on the ligands coordinated to the metal centre. Variations in these moieties can greatly affect the melting point and volatility of the resulting complexes.²⁷ Introducing asymmetry can also prompt lower melting points by making it more difficult for crystallization to occur. Since crystallization is optimized when a compound has a repeating unit in its structural motif, asymmetrical compounds have the ability to disrupt the repeating unit.²⁸

1.2. Amidinate and Guanidinate Ligands

The amidinate ligand (Figure 1.3) is a versatile ancillary ligand used to thermodynamically stabilize metal complexes. Amidinate ligands can act as two- or (more commonly) four-electron donors with metals in Groups 1 to 15.²⁹ Theoretically, the amidinate ligand can be predicted to have eight types of coordination (Figure 1.4) although not all coordination types are known in the literature.²⁹

Figure 1.3: An amidinate ligand

Figure 1.4: Theoretical bonding modes of the amidinate ligand.²⁹

The structures A and E have not yet been reported in the literature. Structure C is most commonly seen in Group 13 metals and is the type of coordination that will be discussed further. This type of coordination has a delocalized bond due to resonance effects in the ligand (Figure 1.5).

Figure 1.5: Resonance effects on amidinate ring causing a delocalized bond

An important factor in the planarity of the MNCN metallocycle is the degree of pyramidalization of the nitrogens in the amidinate ligand. The pyramidalization is determined by the sum of all bond angles around the nitrogen atom. The more this

number deviates from 360° , the more pyramidalized the nitrogen atom and the greater the deviation of the metallocycle geometry from planarity.²⁹

The amidinate ligand carries a net charge of -1 , thus for a $+3$ metal species, the metal amidinate complex can have one, two, or three amidinate rings, with the remaining valence occupied by other substituents. These different coordination geometries are denoted as mono-, bis- and trisamidinates. These species are four-, five- and six-coordinate complexes, respectively.

Amidines are versatile ligands that can be easily altered to achieve a desired amount of steric bulk, by altering the exocyclic and nitrogen substituents. The nature of the amidinate can vary significantly based on the exocyclic moiety and are named according to these substituents. Amidines with $R^3 = H$ are thus formamidinates. There are also: acetamidinates ($R^3 = Me$), ethylamidinates ($R^3 = Et$), chloroamidinates ($R^3 = Cl$) and guanidinates ($R^3 = amide$).

Guanidinate ligands differ from amidinate ligands by having an amido group in the exocyclic position on the sp^2 hybridized carbon. Having an amido moiety in the R^3 position allows for the delocalisation of the six π electrons across the guanidinate ligand. Due to the extended π system, the guanidinate ligand can have two bonding modes, $[(NR)_2C(NR_2)]^{-1}$ and $[(NR)_3C]^{-2}$ (Figure 1.6).³⁰ These different bonding modes are referred to as anionic and dianionic guanidinates, respectively.³⁰

Figure 1.6: Coordination of a) an anionic guanidinate ligand and b) a dianionic guanidinate ligand to a metal centre.

Amidates and guanidates are exceptional ligands in the synthesis of ALD precursors due to their versatility, ability to coordinately saturate the metal centre and the high volatility of the ligand. The potential to easily substitute the exocyclic substituents on the amidinate ring allows one to tune the volatility and melting points of the precursor. The coordination of the nitrogens to the metal centre aids in coordinately saturating the metal centre, thus discouraging dimerization. Protonation of the amidine or guanidine produces a volatile free ligand. This makes the ligand an attractive by-product in the ALD process because a volatile by-product is less likely to adsorb into the growing thin film and thus results in less contamination.

1.3. Synthesis

The synthesis of amidinate complexes is most commonly accomplished by three routes: salt metathesis,^{31,32,33} insertion of a carbodiimide^{34,35,36} and more recently by ligand exchange.^{37,38}

Lithium chloride salt metathesis is a high yield, facile route at room temperature. Lithium amidates are obtained by reacting alkyl or amido lithium reagents (e.g. MeLi, ^tBuLi, NMe₂Li) with dialkylcarbodiimide species (Figure 1.7). These can be isolated or reacted *in situ* in stoichiometric ratios to obtain the desired product.³² The resulting lithium reagents can be used to obtain four-, five- and six-coordinate group 13 amidates (Figure 1.8) by reaction with metal chlorides (MCl₃).³² The driving force of the salt metathesis reaction is the precipitation of the insoluble salt (LiCl) from solution, which pushes the reaction towards products, in accordance with LeChatelier's Principle.

Figure 1.7: Salt metathesis reaction for the synthesis of four-coordinate group 13 amidates.

Figure 1.8: Salt metathesis route to a) four-, b) five- and c) six-coordinate amidinates.

Insertion mechanisms for carbodiimides ($\text{R}'\text{N}=\text{C}=\text{NR}'$; R' = alkyl group) into a metal alkyl, chloride or amide bond have been studied extensively in the literature.³⁴⁻³⁸ The insertion reaction is high-yielding but can have complicated mechanisms depending on the metal bond being inserted into. The general reaction scheme is depicted in Figure 1.9, and (as in the salt metathesis route) has the capability to access four-, five- and six-coordinate amidinate complexes by reacting a metal species with a stoichiometric amount of carbodiimide (CDI).

Figure 1.9: Insertion reactions of carbodiimide into a metal alkyl bond to obtain a) monoamidinates, b) bisamidinates and c) trisamidinates.

The mechanism for the insertion of 1,3-diisopropylcarbodiimide (ⁱPr CDI) and 1,3-di-*tert*-butylcarbodiimide (^tBu CDI) into Al-CH₃ and Al-N(CH₃)₂ has previously been investigated using density functional theory (DFT) in our group.³⁶ The CDI was found to insert into the metal alkyl or amide group by first forming a dative bond between the lone pair of electrons of one of the nitrogens and the aluminum metal centre. An alkyl group then migrated from the metal centre to the sp hybridized carbon of the CDI resulting in an sp² hybridized carbon. The carbodiimide then rotated so that the second nitrogen coordinated to the metal centre, forming the four-membered ring (Figure 1.10).

Figure 1.10: Mechanism for carbodiimide insertion into an aluminum alkyl bond³⁶

Carbodiimide insertions into metal alkyl or amide bonds are well studied in the literature. However, the reverse reaction is also possible, where the CDI can deinsert to reform the metal alkyl or amide bond (Figure 1.11). The deinsertion process is primarily seen in the five- and six-coordinate complexes and occurs at elevated temperatures. This can be monitored by thermogravimetric analysis and “NMR boil-ups”. The NMR boil-up is an experiment conducted by heating the sample in deuterated solvent in an NMR tube and monitoring the reaction by ¹H NMR throughout the experiment. The deinsertion process is reversible, where the CDI deinserts at elevated temperatures, but once cooled to ambient temperatures the CDI can reinsert into the metal bond.³⁸ The tetrahedral species is thought to be the most stable and does not undergo CDI deinsertion because it would then produce a trigonal planar Lewis acid centre, which is less stable than the four-coordinate amidinate species if the trigonal planar species is unable to dimerize.

Figure 1.11: Deinsertion of carbodiimide from a trisamidinate to produce a bisamidinate and diisopropylcarbodiimide.³⁸

Investigations of single insertions of *i*Pr CDI and *t*Bu CDI into organoaluminum compounds, as well as the thermal rearrangements of the resulting amidinates has been investigated thoroughly by Chang *et al.*³⁵ When starting with heteroleptic aluminum species, this study examined the preference of migration onto the sp^2 hybridized carbon of *i*Pr and *t*Bu carbodiimides between amido, chloride and alkyl groups (Figure 1.12). It was concluded that when using *i*Pr CDI, the order of migration between moieties is $\text{NR}_2 > \text{Cl} > \text{R}$. The migration order using *t*Bu CDI was found to be $\text{Cl} > \text{R} > \text{NR}_2$. The bulkiness of the *tert*-butyl group did not allow for the migration of the bulky amido group to the sp^2 hybridized carbon, as no $[(t\text{BuN})_2\text{C}(\text{NR})]$ ligands were reported.³⁵ Our own study has shown that the selectivity between methyl and ethyl groups in the insertion of *i*Pr CDI is poor, giving a mixture of products (Figure 1.13).³⁸

Figure 1.12: Insertion preference of amido, chloro and alkyl moieties in aluminum heteroleptic species.

Figure 1.13: Lack of carbodiimide insertion preference between methyl and ethyl moieties at an aluminum centre.³⁸

The thermal rearrangement of the chloroamidinate $[(R'N)_2C(Cl)]$ complexes was also discovered in Chang's investigation.³⁵ Upon distillation it was found that chloroamidinates synthesized from $AlEt_2Cl$ $[(ClC(N^iPr)_2)_2AlEt_2]$ and $AlMe_2Cl$ $[(ClC(N^iPr)_2)_2AlMe_2]$ undergo a thermal rearrangement to give $[EtC(N^iPr)_2]_2AlClEt$ and $[MeC(N^iPr)_2]_2AlClMe$, respectively.³⁵ Obviously, such complexes are not suitable as precursors for ALD since they are not thermally stable and rearrange under reduced pressures and elevated temperatures, similar to the environment of the bubbler.

It can be rather complicated to obtain heteroleptic amidinate species by simple insertion mechanism reactions due to competitive migrations and insertion preferences

based on the type of CDI used. Ligand exchange can be used to avoid the competitive migration.

Ligand exchange was first reported in the literature for guanidinate ligand systems when an unexpected pathway linking mono-, bis- and trisguanidinate species was discovered.³⁷ It was found that upon initially mixing 1:1 and 1:2 ratios of $\text{Al}(\text{NMe}_2)_3$ and $i\text{Pr}$ CDI, the ^1H NMR of the early reaction mixture showed a mixture primarily consisting of the trisguanidinate species and $\text{Al}(\text{NMe}_2)_3$ with minimal amounts of the desired stoichiometric product. In the case of the 1:1 reaction mixture ^1H NMR also showed significant amounts of the bisguanidinate. However, given enough time to react each reaction will proceed completely to the stoichiometric product. The proposed mechanism for this was that the $i\text{Pr}$ CDI rapidly inserts into the aluminum amido bonds to form the trisguanidinate and then there is a slow exchange between the six-coordinate species and unreacted homoleptic aluminum amido species to get a redistribution of the guanidinate ligand among metal centres. It was proposed that this exchange occurs by the chelating guanidinate ligand transferring metal centres in exchange for the monodentate dimethylamido ligand and that this would occur by going through a doubly bridged intermediate whereby the two metal centres are bridged by one guanidinate ligand and one amido ligand (Figure 1.14).³⁷

Figure 1.14: Proposed ligand exchange mechanism from a five-coordinate guanidinate species to a four-coordinate guanidinate.³⁷

The mechanism of ligand exchange was further investigated using amidinates bearing methyl and ethyl groups in the exocyclic position in order to prove the proposed mechanism in Figure 1.14. The ethyl and methyl moieties were selected because CDI shows no preference between the two substituents in terms of insertion mechanisms, this was useful because the purpose of the study was to show that the mechanism for ligand exchange was indeed by a transfer of the entire chelating ligand and was not a consequence of the *i*Pr CDI deinserting and then reinserting (Figure 1.15). If this was indeed the mechanism then two homoleptic amidinate products would be expected, one bearing all methyl substituents and one with all ethyl substituents. Ligand exchange was used to synthesize heteroleptic aluminum amidinate complexes bearing methyl and ethyl substituents in the exocyclic position with ethyl and methyl groups, respectively, bonded to the metal (Figure 1.16).³⁸

Figure 1.15: Synthesis of aluminum monoamidates by CDI deinsertion and reinsertion.

Figure 1.16: Synthesis of heteroleptic aluminum amidates by ligand exchange.

It was found that the mechanism of ligand exchange is indeed by the transfer of the entire chelating ligand in exchange for a monodentate ligand. This was confirmed by ^1H NMR, where only one of each ethyl and methyl environments were present. In the literature, ligand exchange has been seen with NMe_2 , Et and Me in the exocyclic position and has been exchanged for monodentate ligands of the type Cl, Me, Et, NMe_2 , H.^{37,38} Thus, ligand exchange can be exploited for the use of making heteroleptic aluminum amidinate and guanidinate complexes, which would otherwise be difficult to obtain by simple insertion mechanisms.

1.4. Computational Methods

Computational methods have been used to determine the reaction mechanism for carbodiimide insertions into metal alkyl and metal amide bonds in the formation of amidinate and guanidinate complexes.³⁶ The mechanism for ligand exchange has so far only been proposed in the literature.³⁷ This thesis investigates the mechanism by which ligand exchange occurs for aluminum metal centres using computational methods. The B971³⁹ functional with Stuttgart effective core potentials called upon using the MWB^{40,41} keyword within the Gaussian-03 program suite⁴² was used in determining the ligand exchange mechanism. Additional single point energy calculations on the B971 optimized structures were performed using the G3(MP2) approach.⁴³

The B971 functional is a modification by Handy, Tozer and co-workers to Becke's B97⁴⁴ method. The B97 functional is a hybrid functional that includes Hartree-Fock (HF) exchange and DFT exchange-correlation. In this method Becke has expanded the exchange functional, the parallel spin correlation and the anti-parallel spin correlation functionals in a power series involving the density and its first derivative. It is a ten parameter functional optimized in a non-self consistent manner using only experimental data and includes a fraction of exact orbital exchange, calculated using HF theory. This was accomplished using local spin-density approximation (LSDA) densities. Optimal parameters were determined by fitting to 10 first-row atomic energies, 56 atomization energies, 42 atomic and molecular ionization potentials and 8 proton affinities.⁴⁴ The Handy and Tozer modification to this method was re-optimizing the parameters for use in self-consistent calculations by studying how this functional performs in a Kohn-Sham framework.³⁹ The re-parameterization was fit to energetic data only, due to the presence of nonmultiplicative exact orbital exchange. The quality of this method is assessed by comparison of d_E , the mean absolute error in energetic quantities (in kcal/mol) and d_G , the sum of the absolute gradient vectors (in a.u.). The mean absolute error in energetic quantities (equation [1.1]) is a sum of the difference between experimental quantities and computed Kohn-Sham quantities for total energies of the system, atomization energies and ionization potentials of the system.³⁹ The term d_G is a measure of how well geometry is predicted, where the smaller d_G is, the better the geometry prediction. The results are summarized in Table 1.1.³⁹

Equation [1.1] ³⁹:
$$d_E = \frac{1}{86} \left[\sum_{A_1}^{18} |E_0^{A_1} - E_{KS}^{A_1}| + \sum_M^{61} |AE_0^M - AE_{KS}^M| + \sum_{A_2}^7 |IP_0^{A_2} - IP_{KS}^{A_2}| \right]$$

Table 1.1: Comparison of d_E and d_G for a variety of methods³⁹

	B97	B971	HCTH	HCTH-A	MP2	BLYP	B3LYP
d_E (kcal/mol)	2.28	2.02	3.10	3.21	19.65	4.71	3.91
d_G (a.u.)	0.95	0.93	1.13	1.10	2.10	2.18	0.96

As one can see the B971 value of d_E is reduced by approximately 10% compared to B97 and has the least error in energetic quantities compared to the other methods, even B3LYP which is the most popular exchange and correlation functional used today. B971 also has the lowest d_G value, indicating that it has improved geometry predictions over both B97 and B3LYP.

The B971 functional was chosen not only for its improvements to the B97 and lower errors compared to B3LYP, but also because it can, to a certain extent reproduce, van der Waals interactions.⁴⁵ Johnson and DiLabio studied six density functionals (B3LYP, TPSS, HCTH407, PW91, PBE1PBE and B971) along with the ab initio MP2 method for their ability to predict binding energies and separations for different van der Waals dimers compared to a high level of theory. Van der Waals dimers involving dispersion, dipole-induced dipole, dipole-dipole and hydrogen bonded interactions were evaluated. The total mean absolute percent errors (MAPE) for counterpoise-corrected binding energies are summarized in Table 1.2.⁴⁵ The results of this study show that in terms of reproducing van der Waals interactions, the B971 functional is superior to the popular B3LYP method by 36%.

Table 1.2: Total mean absolute percent errors for DFT methods and MP2⁴⁵

	B3LYP	TPSS	HCTH407	PW91	PBE1PBE	B971	MP2
Total MAPE	65.8	51.2	46.5	41.2	42.9	29.9	18.4

Although B971 was found to reproduce van der Waals forces to a certain extent, the authors note that current DFT methods, in general, cannot accurately replicate these forces.

The van der Waals interactions were a concern when initially researching which calculation method to use because of the steric bulk associated with the guanidinate ligand system. Steric crowding was expected to play an important role in the reaction mechanism.

The pseudopotentials are called using the MWB keyword for calculations used to determine the reaction mechanism of ligand exchange. The M specifies that the reference system used to generate the pseudopotentials is for a neutral atom and WB denotes that the reference data use Wood-Boring quasi-relativistic level of theory.⁴¹ Pseudopotentials are used to model the potentials of core electrons. All non-valence electrons are replaced by effective potentials, since the core electrons are not directly participating in bonding interactions.^{40,41} A disadvantage to using pseudopotentials is that the representation of the core electrons is constant and thus there is no core polarization. This will only be a concern if there is a significant change in bonding environments, which may not be accurately represented. The advantage to using pseudopotentials is that it diminishes the total number of electrons and by doing so decreases computing time. In terms of modeling the ligand exchange reaction, the bonding environment surrounding the aluminum centre does change from pentavalent to tetravalent and therefore pseudopotentials could cause misrepresentation. Performing calculations on the same species using all-electron calculations and comparing the energies and bond lengths could investigate the significance of this consequence. However, a substantial benefit is gained by increasing the speed of the calculations due to the large size of the system, as well as the complexity associated with determining the reaction mechanism.

Additional basis functions are added using the keyword extrabasis. The extrabasis keyword is used to supply additional basis functions for elements not defined in a standard basis set.⁴¹ For the case of ligand exchange in aluminum amidinates extrabasis is used to supply single d-type polarization functions. The exponents used are from a 6-31G(d) basis set, and are as follows: Al 0.325, Cl 0.75, C and N 0.8. The 6-31G(d) basis set is a split-valence basis set that uses one contracted Gaussian comprised

of six primitive Gaussians in the core orbitals, and two contracted Gaussians for valence orbitals comprised of three tight primitive Gaussians and one diffuse primitive Gaussian. The (d) denotes that d-type polarization functions are added to all atoms. Polarization functions are used in order to polarize an atom's electronic density by using basis sets that contain functions of higher angular momentum than that of the occupied atomic orbitals, thereby adding additional flexibility. Thus, *d* functions are added to main group elements other than hydrogen and helium, in this case, aluminum, carbon, nitrogen and chlorine. The addition of *d* functions to carbon and nitrogen does not make them hypervalent, but rather improves the description of the molecular orbitals mainly composed of *s* and *p* orbitals.

The G3(MP2) approach is a composite method, which attempts to produce results by approximating full correlation treatment using very large basis sets in an economical fashion. It is generally used for calculating energies of molecules containing second and third row elements and is based on *ab initio* molecular orbital theory.⁴³ Second order Møller-Plesset perturbation theory (MPPT) [MP2/6-31G(d)] is used to optimize the geometry. Perturbation theory is an approach to taking correlation into effect, which is not represented in HF theory, by including a small perturbation value, *V*, to an exact solution of an unperturbed Hamiltonian, *H*₀. The MPPT uses *V* as the difference between electron/electron interactions of the true Hamiltonian, *H*, and the HF Hamiltonian. By doing this, double-counting of electron/electron interactions between the two Hamiltonians is avoided. Specifically, second order MPPT (MP2) recovers a majority of the correlation energy by accounting for doubly excited determinants. Zero point energies are obtained from an optimization and frequency calculation using HF theory with a 6-31G(d) basis set. This is then followed by a reoptimization using the MP2 method and a 6-31G(d) basis set. Single-point energy calculations are accomplished using quadratic configuration interaction [QCISD(T)].⁴³ QCISD(T) is a size-consistent non-variational method that introduces quadratic terms to the configuration interaction (CI) including both singly and doubly excited determinants (CISD). The (T) notation indicates that an estimate of the correlation energy from triply excited determinants is made. The CI method is a variation to the single Slater determinant of HF by making a linear combination of Slater determinants to account for correlation. HF and QCISD(T)

calculations use the 6-31G(d) basis set. Lastly, MP2 single point calculations are performed using the G3MP2large basis set.⁴³ The G3MP2large⁴⁶ basis set is a 6-311+G basis set that uses a frozen core approximation for core electrons, diffuse functions on hydrogen atoms, *2df* polarization functions on first row atoms (Li-Ne) and *3d2f* polarization functions on second row atoms (Na-Ar).⁴³ The frozen core approximation is a condition of the correlation treatment and is not used in geometry optimizations. It reduces the number of terms by not considering excitations of core electrons. The G3(MP2) energy is obtained using a series of corrections as seen in equation [1.2].⁴³

$$E_0[\text{G3(MP2)}] = \text{QCSID(T)/6-31G(d)} + \Delta E_{\text{MP2}} + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE}) \quad [1.2]$$

The ΔE_{MP2} term is the difference between the two MP2 calculations ($\Delta E_{\text{MP2}} = [E(\text{MP2/G3MP2large})] - [E(\text{MP2/6-31G(d)})]$). The spin-orbit correction $\Delta E(\text{SO})$ is taken from experiment where possible and from high level calculations otherwise, it is included for atomic species only. The higher level correction (HLC) is added to take into account all other remaining deficiencies in the energy calculations and therefore acts as a fudge factor.

The above methods and basis sets described have been used to complete all geometry optimizations and frequency calculations on stable stationary points along the reaction path for ligand exchange. All transition state (TS) structures are verified as such by vibrational analysis and, in some cases, by computing energies associated with the intrinsic reaction coordinate.

Chapter 2: Results and Discussion for Synthetic Ligand Exchange

Amidates and guanidates are popular ligands due to their ease of synthesis and modification, as well as their robust nature. There are many examples of these ligands with Group 1-15 metals,²⁹ and these compounds show a broad application: they are used in catalysis,⁴⁷ as precursors for chemical vapour deposition⁴⁸ and atomic layer deposition,²⁷ and gallium (I) guanidates have even been employed as σ -donor ligands in platinum and nickel complexes.⁴⁹

Ligand exchange provides a facile route to high yielding heteroleptic aluminum and gallium amidates and guanidates. It offers complete control over the exocyclic moiety by starting with the six-coordinate homoleptic parent amidine or guanidine and reacting it with a homoleptic metal alkyl or metal chloride complex, in order to control the metal bound substituents.

A collection of various homoleptic and heteroleptic amidate complexes has been synthesized by ligand exchange. Amidate and guanidate ligands have been exchanged for chloride moieties in aluminum and gallium centred complexes, as well as for alkyl groups in aluminum complexes. Comparisons between compounds **1-13** are made in terms of synthesis, yield, geometry, ¹H NMR and thermal stability. The potential for the use of these compounds as ALD precursors has also been evaluated.

2.1. Chloride Exchanges

Exchange reactions were attempted starting with various six-coordinate homoleptic parent amidates with different exocyclic moieties ($[\text{RC}(\text{N}^i\text{Pr})_2]_3\text{M}$ where $\text{R} = \text{Me, Et, NMe}_2$ and $\text{M} = \text{Al, Ga}$). These parent homoleptic amidates were reacted with a stoichiometric amount of the respective chloride species (AlCl_3 and GaCl_3) in order to obtain the bis- and monoamidate species.

2.1.1. The Dimers $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{Al}_2\text{Cl}_4$ and $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{Ga}_2\text{Cl}_4$

Ligand exchange has been shown to occur between $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$ and aluminum chloride.³⁷ The analogous gallium reaction was also attempted to investigate if gallium showed similar reactivity to aluminum:

where R = NMe₂, Me, Et and M = Al, Ga

The aluminum dichloride species has been synthesized by salt metathesis,⁵⁰ and it was also formed in high yield through reaction [2.1]. According to ¹H NMR, the reaction produced an intermediate dimer, identified as [Me₂NC(NⁱPr)₂]₂Al₂Cl₄ (**1**), which formed immediately on mixing [Me₂NC(NⁱPr)₂]₂AlCl and aluminum chloride.

When the dimer [Me₂NC(NⁱPr)₂]₂Al₂Cl₄ (**1**) was synthesized by ligand exchange (reaction [2.2]), it was isolated in a crude yield of 97% after 30 minutes of reaction time at room temperature.

The dimer was a long-lived intermediate, and decomposed over 48 hours at room temperature in solution to form the stoichiometric monomeric species. However, subjecting a solution (C₆D₆) of the dimer to 90°C for 18 hours accelerated the decomposition process. This was an irreversible process and the monomeric species was stable in solution over a period of a few months.

The ¹H NMR suggested that **1** had D₂ symmetry; it showed single resonances for the exocyclic dimethylamido moieties and the isopropyl methine protons. Two doublets of equal integration (1.43 ppm, 1.50 ppm) were assigned to the isopropyl methyl groups; the three C₂ axes relate all of the isopropyl groups (Figure 2.1), while the methyl groups within one isopropyl group are diastereotopic. This is a consequence of the twisted core of **1**, which does not allow for a plane of reflection within the molecule (Figure 2.2).

Figure 2.1: Three C_2 axes that relate the methine proton and the dimethyl amines (a and b are diastereotopic)

Figure 2.2: Reflection to equilibrate a and b

The dimeric structure of **1** was confirmed by a single crystal X-ray diffraction study to be a dimer where the guanidinate ligands bridge the two aluminum centres (Figure 2.3, Tables 2.1 and 2.2); compound **1** co-crystallized with one half of an equivalent of toluene.

Figure 2.3: A single crystal X-ray structure of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$ (**1**) with the thermal ellipsoids depicted at 30% probability, the co-crystallized solvent molecule, minor disordered contribution and hydrogen atoms were omitted for clarity. See the experimental for further details.

The eight-membered ring comprising the core of **1** formed a twisted boat, with the planes defined by each guanidinate ligand (N1, N2, and N3 for one ligand; N4, N5, and N6 for the other ligand) being 38° with respect to the plane defined by the aluminum centres and the quaternary carbon atoms of the ligand. This structure was similar to the dimers reported by Jordan and Young⁵¹ and earlier by Hausen.⁵² However, **1** was twisted symmetrically with respect to a C_2 axis perpendicular to the ring such that the nitrogen atoms of the dimer ring alternated above and below the Al1-C4-Al2-C13 plane (Figure 2.4).

Figure 2.4: Boat conformation of the twisted core of compound **1**. Thermal ellipsoids are shown with 30% probability. All atoms outside of the core have been removed for clarity.

This deformation allowed for a very slight pyramidalization of the nitrogen in the guanidinate ring with the sum of angles for N1 = 357.7° , N3 = 359.9° , N4 = 358.8° and N6 = 359.3° (Table 2.2). This could also be seen by the exocyclic N-C bond lengths being shorter than a single bond (N5-C13 was $1.349 \text{ \AA}$ and N2-C4 was $1.352 \text{ \AA}$), showing that the exocyclic dimethylamine moieties were participating in the extended π bonding of the guanidinate ring (Figure 2.5). Although the exocyclic amido groups were rotated out of the plane defined by the chelate rings (45° for the N4-C13-N6 ring and 40° for the N1-C4-N3 ring), there is a $\cos^2\theta$ relationship associated with overlap, and thus a significant overlap of the p orbital of the exocyclic group was expected.⁵³ Out-of-plane

rotations in the range of 23.5 – 41.0° are typical of dimethyl diisopropyl guanidinate ligands.³⁷

Figure 2.5: Guanidinate ligand resonance structures

Each aluminum centre had a distorted tetrahedral geometry, with the Cl-Al-Cl angle being close to ideal (110.6° for Cl1-Al1-Cl2 and 108.2° for Cl3-Al2-Cl4) and the N-Al-N bonds significantly widened (122.2° for N1-Al1-N6 and 124.2° for N3-Al2-N4). The exocyclic amide groups were planar (sp^2 hybridized), with the sum of angles around each nitrogen atom equaling 360° (Table 2.2). The three N-C bonds of the ligand bridgehead carbon are essentially equivalent, with bond lengths between 1.348 – 1.354 Å.

The similar dimer for gallium ($[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{Ga}_2\text{Cl}_4$, **2**) was isolated in the reaction of gallium trisguanidinate with gallium chloride (reaction [2.3]) in a crude yield of 86.7% after two hours of reaction time.

The ^1H NMR of the gallium dimer was analogous to that of the aluminum species, which suggested a similar dimeric structure. The major difference between these two dimers was that **2** appeared to be more stable than **1** in solution. Compound **1** decomposed to the monomeric species in solution over 48 hours at room temperature, while the gallium dimer was stable in solution for long periods of time and seemed to show no signs of decomposition to the monomeric species by ^1H NMR. A solution of **2** in deuterated benzene was heated to 85°C for 5 days and monitored daily by ^1H NMR. Over this period no peaks that could be identified as belonging to $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{GaCl}_2$ were observed. However, resonances corresponding to free 1,3-diisopropylcarbodiimide

(3.33 and 1.03 ppm) were observed after two days, which suggested that CDI deinsertion had occurred. The synthesis of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{GaCl}_2$ was also attempted by a salt metathesis route (reaction [2.4]), and also resulted in **2**:

Single crystal X-ray diffraction confirmed the analogous gallium dimeric species to compound **1** (Figure 2.6; Table 2.1 and Table 2.2). The exocyclic amido groups of **2** were rotated out of the plane of the guanidinate ligands by 42.1° for the N1-C1-N2 ring and by 40.6° for the N4-C10-N5 chelate ring. This suggested that these exocyclic dimethylamide groups were partially participating in the extended π system of the chelating rings. The shorter C-N bond lengths of the exocyclic moieties also showed that there were π interactions (C1-N3=1.335 Å, C10-N6=1.34 Å, compared to 1.47 Å for a single bond).

Figure 2.6: A single crystal X-ray structure of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{GaCl}_2]_2$ (**2**) with the thermal ellipsoids depicted at 30% probability. The hydrogen atoms were omitted for clarity.

The eight-membered ring of the core for **2** also had a twisted boat conformation, similar to compound **1** and was twisted out of the plane of the gallium metal centres and quaternary carbons by 45.2° .

Both gallium centres had a distorted tetrahedral geometry with Cl-Ga-Cl bond angles that were close to ideal ($\text{Cl1-Ga1-Cl2} = 107.9^\circ$ and $\text{Cl3-Ga2-Cl4} = 110.36^\circ$) and wider N-Ga-N angles ($\text{N1-Ga1-N4} = 123.57^\circ$ and $\text{N2-Ga2-N5} = 122.71^\circ$). This was offset by the smaller Cl-Ga-N angles ($\text{Cl1-Ga1-N1} = 101.04^\circ$; $\text{Cl2-Ga1-N4} = 100.67^\circ$; $\text{Cl3-Ga2-N5} = 103.84^\circ$ and $\text{Cl4-Ga2-N2} = 102.63^\circ$). The exocyclic amide groups had trigonal planar geometries with the sum of bond angles about N3 and N6 being 359.9° and 360.1° , respectively (Table 2.2).

Thermogravimetric analysis (TGA) of compounds **1** and **2** (Figure 2.7) showed thermal reactivity starting between 50°C and 100°C . The derivative curves for both the aluminum and gallium dimers showed three major thermal events. These occurred in the temperature ranges of $88\text{--}110^\circ\text{C}$, $110\text{--}175^\circ\text{C}$, and $175\text{--}260^\circ\text{C}$ for compound **1** and $65\text{--}120^\circ\text{C}$, $120\text{--}175^\circ\text{C}$ and $175\text{--}265^\circ\text{C}$ for compound **2**. Compound **1** had a small feature at 325°C , which was most likely due to the thermal decomposition of some non-volatilized material. The last feature in each TGA had a shape that was characteristic of volatilization and was thought to be due to volatilization of the final decomposed compound. The non-symmetrical shape of the third derivative feature is commonly associated with the volatilization of a compound, where the feature shows a slow onset and a rapid drop off when a maximum is achieved. This indicates that mass is being lost at an increasing rate as the temperature is increasing and when the entire compound has volatilized there is a rapid drop in the derivative mass curve, as the mass of volatile material is zero.

Figure 2.7: Thermogravimetric analysis (with derivative curve) for compounds **1** and **2**

Carbodiimide deinsertion was known to occur for the gallium dimer, thus it is possible that one of the weight loss features was due to the deinsertion and volatilization of the *i*-Pr CDI.³⁸ Although CDI deinsertion was not seen in **1** up to temperatures of 90°C it is possible that it occurs at higher temperatures or that reactivity is different between the solution and solid phase.

The Gibbs free energy of the aluminum and gallium dimers were investigated computationally, using the B971³⁹ method and Stuttgart effective core potentials called upon using the MWB.⁴⁰ It was found that the gallium dimer was more stable than the aluminum analogue by 7.97 kcal/mol. This is consistent with the result of **2** being more stable in solution than **1** at room temperature.

Table 2.1: Selected Crystal Data and Structure Refinement Parameters

Compound	1	2	4	6
Empirical formula	C _{21.50} H ₄₄ Al ₂ Cl ₄ N ₆	C ₂₅ H ₄₈ Cl ₄ Ga ₂ N ₆	C ₁₈ H ₃₈ AlClN ₄	C ₁₆ H ₃₄ ClGaN ₄
fw	582.39	713.93	372.95	387.64
T (K)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	Pbca	Pbca	C2/c	C2/c
a (Å)	13.383(5)	13.399(7)	18.821(3)	11.505(8)
b (Å)	14.935(6)	14.975(7)	8.0375(13)	12.788(8)
c (Å)	31.025(12)	31.039(16)	15.060(3)	14.102(9)
α (deg)	90	90	90	90
β (deg)	90	90	104.269(2)	108.130(9)
γ (deg)	90	90	90	90
V(Å ³)	6201(4)	6228(5)	2207.8(6)	1972(2)
Z	8	8	4	4
ρ (calcd) (Mg/m ³)	1.248	1.523	1.122	1.306
Abs coeff (mm ⁻¹)	0.46	2.100	0.22	1.534
R1, wR2 ^a	0.0781, 0.2098	0.0608, 0.1617	0.0338, 0.0931	0.0281, 0.0825

^a [I > 2 σ (I)]. R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; wR2 = $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$

Refinement method for compounds **1**, **2**, **4**, **6** was full-matrix least-squares on F2

Table 2.2: Selected Bond Lengths (Å) and Bond Angles (°) for compounds **1** and **2**

[Me ₂ NC(N ⁱ Pr) ₂ AlCl ₂] ₂ (1)		[Me ₂ NC(N ⁱ Pr) ₂ GaCl ₂] ₂ (2)	
Bond Lengths (Å)			
Al1-N1	1.851(4)	Ga1-N1	1.916(6)
Al1-N6	1.886(4)	Ga1-N4	1.919(5)
Al1-Cl1	2.156(2)	Ga1-Cl1	2.194(2)
Al1-Cl2	2.155(2)	Ga1-Cl2	2.2075(18)
N1-C4	1.363(7)	N1-C1	1.348(8)
N2-C4	1.351(6)	N2-C1	1.351(7)
N3-C4	1.347(6)	N3-C1	1.335(8)
Al2-N3	1.885(4)	Ga2-N5	1.902(5)
Al2-N4	1.879(5)	Ga2-N2	1.923(5)
Al2-Cl3	2.1624(19)	Ga2-Cl3	2.195(2)
Al2-Cl4	2.154(2)	Ga2-Cl4	2.197(2)
N4-C13	1.353(7)	N4-C10	1.358(8)
N5-C13	1.348(6)	N5-C10	1.338(8)
N6-C13	1.347(6)	N6-C10	1.340(7)
Bond Angles (°)			
Al1-N1-C4	114.9(3)	Ga1-N1-C1	116.9(4)
Al1-N6-C13	116.3(3)	Ga1-N4-C10	116.0(4)
N1-Al1-N6	22.18(18)	N1-Ga1-N4	123.6(2)
Cl1-Al1-Cl2	110.62(9)	Cl1-Ga1-Cl2	107.90(8)
N1-C4-N3	116.3(4)	N1-C1-N2	117.1(6)
Al2-N3-C4	115.2(3)	Ga2-N2-C1	116.3(4)
Al2-N4-C13	116.1(3)	Ga2-N5-C10	114.8(4)
N3-Al2-N4	124.19(17)	N2-Ga2-N5	122.7(2)
Cl4-Al2-Cl3	108.18(8)	Cl4-Ga2-Cl3	110.36(9)
N4-C13-N6	116.7(4)	N4-C10-N5	117.3(5)
Σ of Angles (°)			
N1	357.7	N1	359
N2	360	N2	359.4
N3	359.9	N3	359.9
N4	358.8	N4	359.2
N5	360	N5	359.2
N6	359.3	N6	360.1
C4	360	C1	360
C13	360	C10	360

2.1.2. Bischelates of Aluminum and Gallium

The bisamidinate compounds (**3** and **4**) were synthesized from their parent homoleptic amidinates ($[\text{RC}(\text{N}^i\text{Pr})_2]_3\text{Al}$, $\text{R} = \text{Me, Et}$) and aluminum chloride at room temperature, in a reaction similar to reaction [2.1]:

At room temperature, these reactions were slow, taking several days to reach completion. However, dimeric species similar to **1** were not detected in ^1H NMR studies of the reaction. Mechanistic calculations (see Chapter 3) show that the formation of the stable dimer relies significantly on π -stabilization of the exocyclic position; it is not surprising that the dimer is not stable when alkyl groups occupy this position. Compound **3** has been previously synthesized by salt metathesis and characterized by X-ray crystallography by Jordan et al.³²

The ^1H and ^{13}C NMR of compounds **3** and **4** supported a fluxional monomeric formulation. Both compounds showed only one resonance for their isopropyl methyl groups in both the ^1H and ^{13}C NMR, which suggested a solution structure that allows equilibration of these groups. This has previously been seen for group 13 bisguanidinates.³⁷ Further support for a monomeric structure came from a single crystal X-ray study of **4** (Figure 2.8, Tables 2.1 and 2.3).

Figure 2.8: A single crystal X-ray structure of $[\text{EtC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$ (**4**) with ellipsoids depicted at 30% probability. The hydrogen atoms were omitted for clarity.

Compound **4** crystallized in the $C2/c$ space group. It adopted a distorted trigonal bipyramidal structure, which has been seen for other bisguanidines³⁷ and bisamidines³⁸ of aluminum.

A geometric parameter, τ , has been defined as a measure of a five-coordinate structure as an index of trigonality.⁵⁴ For a five-coordinate structure (Figure 2.9), the geometry could be square pyramidal or trigonal bipyramidal, the parameter τ provides a measure of which geometry is dominant. In a square pyramidal system $\alpha = \beta = 180^\circ$ where α is the angle DME and β is the angle BMC with A being the axial ligand. However, in many square pyramidal systems M is shifted toward A and outside of the BCDE plane, such that $\alpha = \beta < 180^\circ$. For a perfectly trigonal bipyramidal system $\alpha = 120^\circ$ and $\beta = 180^\circ$. The parameter τ is defined as $\tau = (\beta - \alpha)/60$, where $0^\circ \leq \tau \leq 1^\circ$. A

square pyramidal C_{4v} geometry has a value of 0° and a trigonal bipyramidal D_{3h} geometry has a value of 1° .⁵⁴

Figure 2.9: Five coordinate structures of a) trigonal bipyramidal and b) square planar geometries.

Compound **4** had a $\alpha = 112.8^\circ$, $\beta = 168.7^\circ$ and $\tau = 0.93^\circ$, thus the geometry of **4** is distinguishably trigonal bipyramidal.

Given that this amidinate had an ethyl group on the sp^2 hybridized ring carbon, one might have expected the distortions in **4** to be intermediate compared to similar compounds synthesized by Jordan et al., with either methyl or *t*-butyl groups in this position.³² The authors determined that the steric bulk of the alkyl group on the sp^2 carbon forces the isopropyl groups closer to the metal centre.³² Indeed, compound **4** had an equatorial nitrogen angle (N2-Al-N2A) intermediate to the previously reported compounds with an angle of 112.8° (compared to $110.3 - 118.0^\circ$). The axial isopropyl groups in **4** were also forced as close to the metal center ($C4-N2-Al = 144.1^\circ$, compared to $136.4 - 147.6^\circ$ in the reference). However, the axial nitrogen angle (N1-Al-N1A) in **4** (168.7°) was less distorted (compared to $163.8 - 168.1^\circ$). The ethyl groups appeared to relieve some of the steric demand by adopting a position under the chelate ring with respect to the chloride position. This suggests that the chloride plays a role in distorting the equatorial plane of compound **4**. The Al-N1 axial, Al-N2 equatorial, and Al-Cl bond lengths in **4** (1.98, 1.92, and 2.19 Å respectively) were comparable to the bond lengths in the previously reported compounds (1.91 – 1.94 Å equatorial, 1.99 – 2.04 Å axial, 2.16 – 2.20 Å chloride).

The thermal stability of **3** and **4** was studied using TGA (Figure 2.10). Compound **3** appeared to be much more thermally stable than **4**. The derivative curve of **3** showed

one main feature with a shape indicative of volatilization. There was a small thermal event between room temperature and 88°C with a corresponding mass loss of 5.7%. This weight loss seemed too small to be a consequence of decomposition or CDI deinsertion, however it could be due to the loss of solvent that was trapped in the crystalline matrix of the material. The majority of the sample volatilized and a small weight percent of 2.3% remained. The width at half height is an indication of the rate of volatilization, where the thinner the peak is the shorter the time period in which volatilization occurs. The width at half height for **3** was 30.47°C. The analogous ethyl substituted complex (**4**) did not prove to be thermally stable. The derivative weight loss curve showed three predominate thermal events, which were broad features. The first feature began at approximately 50°C and continued to 150°C at which time the second feature started. The second feature had a weight loss of 47%, which was slightly larger than the weight percent of one ethylamidinate ligand (42%). The last feature was most likely due to thermal decomposition of the left over material, as this feature began at 225°C. A weight percent of 9.4% remained at the end of analysis, which is slightly larger than the weight percent of aluminum in the complex (7%). The left over material may have been a combination of aluminum metal and soot from the decomposed ligands.

Figure 2.10: The thermal stability of compounds **3** and **4** was demonstrated using thermogravimetric analysis.

In order to also test ligand exchange for gallium centres, a homoleptic gallium trisamidinate was required. In addition to the previously reported trisguanidinate $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Ga}$,³⁷ $[\text{MeC}(\text{N}^i\text{Pr})_2]_3\text{Ga}$ (**5**) was synthesized by a salt metathesis reaction with three equivalents of lithium acetamidinate (equation [2.6]).

This reaction proceeded smoothly at room temperature overnight. The ^1H NMR supported the homoleptic structure similar to the aluminum analogue, although the NMR spectrum (Figure 2.11) showed a broad feature at 1.27 ppm assigned to the isopropyl methyl signal. This was due to the fluxional exchange of the diastereoscopic methyl positions occurring on the NMR time-scale, and thus this was an “intermediate” between

two resolved doublets for the non-fluxional solution structure and one doublet for the fluxional structure.

Figure 2.11: ^1H NMR of compound **5**.

This intermediate of the Berry pseudo rotation was similar to the reported gallium trisguanidinate, which was studied by variable temperature NMR.³⁷ The variable temperature NMR demonstrated that as the sample was cooled the broad feature for the isopropyl moieties resolved into two doublets for the two inequivalent methyl groups (Figure 2.12). As the sample was heated the broad feature became one doublet, which was an indication that an exchange process that equilibrates the methyl groups was accessible.³⁷ The difference between the broad feature of **5** and the two resolved doublets of the analogous aluminum trisacetamidinate³⁶ was attributed to the larger metal centre of the gallium species.³⁷

Figure 2.12: Variable temperature ^1H NMR of $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_3\text{Ga}$.³⁷

Compound **5** showed surprisingly good thermal stability by TGA. The TGA's of the analogous aluminum trisacetamidinate³⁸ and similar gallium trisguanidinate⁵⁵ each showed three distinct features that were attributed to CDI deinsertion. The TGA of **5** however showed a single feature with a shape characteristic of volatilization (Figure 2.13). There was no significant weight loss before the onset of volatilization, which occurs relatively late at approximately 150°C. The rate of volatilization for **5** was comparable to lower coordinate complexes with a width at half height of 43.66°. A low residual mass of 7.1% was observed after heating the sample was heated to 400°C.

Figure 2.13: Thermogravimetric analysis of $[\text{MeC}(\text{N}^i\text{Pr})_2]_3\text{Ga}$.

Similarly to compounds **3** and **4**, the gallium compounds **6** and **7** could be easily synthesized from their parent homoleptic species: compound **5** and $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Ga}$, respectively. These underwent ligand exchange with gallium chloride:

These reactions proceeded much more quickly than their aluminum counterparts, giving moderate to excellent yields (54.4% for **6**, 86.8% for **7**) after reacting overnight. For compound **7**, the ^1H NMR showed a spectrum similar to the previously reported aluminum analogue, with the doublet at 1.39 ppm assigned to the methyl groups from all isopropyl moieties. This suggested that the guanidinate ligands are fluxional, with the axial and equatorial positions equilibrated, as explained above.

The yield of **6** did not improve over longer reaction times and ^1H NMR investigations suggested that some **5** remained in solution, in equilibrium with **6**. The ^1H

NMR of **6** was analogous to that of **3**, again showing only one resonance for the isopropyl methyl groups resulting from fluxionality in solution. This suggested that **6** was a monomer, which was confirmed by a single crystal X-ray study (Figure 2.14, Tables 2.1 and 2.3).

Figure 2.14: A single crystal X-ray structure of $[\text{MeC}(\text{N}^i\text{Pr})_2]_2\text{GaCl}$ (**6**) with ellipsoids depicted at 30% probability. The hydrogen atoms are omitted for clarity.

Compound **6** crystallized in the $C2/c$ space group. It adopted a distorted trigonal bipyramidal geometry, with a N2-Ga-N2A axial bond angle (β) of 162.7° and an equatorial bond angle (α) of 120.6° . The parameter τ had a value of 0.70, which indicated that the distortion of the trigonal bipyramidal geometry was greater than in the case of **4** and greater than the similar literature compound $[\text{PhC}(\text{NPh})_2]_2\text{GaMe}$.⁵⁶ This literature compound had an axial angle of 150.1° , an equatorial bond angle of 97.9° and

$\tau = 0.87^\circ$. While this more congested triphenyl example showed greater deviations from the ideal 120° equatorial bond angles (129.1° , 97.9° , and 132.9°) compared to compound **6**, the tau suggested that it was less distorted from ideal trigonal bipyramidal geometry. This was a consequence of both the axial and equatorial bond angles deviating from the ideal and resulting in a larger $\beta - \alpha$. The distortion in **6** was less severe than the similar literature example $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{GaNMe}_2$ with an axial bond angle of 157.2° , an equatorial bond angle of 120.4° and $\tau = 0.61^\circ$.³⁷ This reflected the lesser steric effect of the alkyl groups of the amidinate in **6**, compared to the dimethyl amide in the exocyclic position. Indeed, all of the equatorial angles were in the range of $119.7 - 120.6^\circ$, which agrees closely to the previously reported guanidinate (118.0° , 120.4° , and 121.6°).³⁷

All of the N-Ga bond lengths (N1-Ga = $1.953 \text{ \AA}$, N2-Ga = $2.129 \text{ \AA}$) were within the range defined by these two references ($1.979 - 2.165 \text{ \AA}$), and the Cl-Ga length ($2.20 \text{ \AA}$) was typical for Cl-Ga bonds.⁵⁷

Table 2.3: Selected Bond Lengths ($\text{\AA}$) and Bond Angles ($^\circ$) for **4** and **6**

[EtC(N ⁱ Pr) ₂] ₂ AlCl (4)		[MeC(N ⁱ Pr) ₂] ₂ GaCl (6)	
Bond Lengths (Å)			
Al-N1	1.9841(9)	Ga-N1	1.9531(16)
Al-N2	1.9225(10)	Ga-N2	2.1288(19)
Al-Cl	2.1933(7)	Ga-Cl	2.2025(16)
N1-C7	1.3205(14)	N1-C1	1.345(2)
N2-C7	1.3404(13)	N2-C1	1.315(2)
C7-C8	1.5057(15)	C1-C2	1.504(2)
Bond Angles (°)			
N1-Al-N2	67.94(4)	N1-Ga-N2	64.99(6)
N1-Al-Cl	95.68(3)	N1-Ga-Cl	119.72(4)
N2-Al-Cl	123.60(3)	N2-Ga-Cl	98.66(4)
N1-C7-N2	110.29(9)	N1-C1-N2	111.43(14)
Σ of Angles (°)			
N1	358.3	N1	357.2
N2	358.9	N2	357.4
C7	360	C1	360

Thermolysis studies of **6** and **7** were conducted by TGA (Figure 2.15). Both compounds showed a small weight loss between 95°C and 100°C that corresponded to a percent weight loss of 9.4% for **6** and 4.3% for **7**. In compound **6** this weight loss was consistent with losing the chloride moiety and in **7** the weight loss corresponded with the loss of a methyl group. The second feature in the derivative curve for **6** had a shape that suggested volatilization of the decomposed product. Further decomposition occurred between 235°C and 300°C, a final residual mass of 11.3% remained. The major feature in the derivative curve of **7** appeared to be comprised of two overlapping features, with a shoulder at approximately 200°C. The peak did not have a steep slope as in a volatilization, and thus this weight loss was thought to be due to decomposition. However, a low residual mass of 3.5% remained, suggesting that the decomposed products were volatile.

Figure 2.15: Thermolysis of **6** and **7** by TGA.

2.1.3. Monochelates of Aluminum

The ligand exchange route can be used to synthesize the monoamidinate aluminum dichloride compounds $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlCl}_2$ (**8**) and $[\text{EtC}(\text{N}^i\text{Pr})_2]\text{AlCl}_2$ (**9**) by reacting the parent homoleptic amidinate complex with two equivalents of AlCl_3 (reaction [2.8]).

Compounds **8** and **9** were isolated in good yield (85.9% and 80.0%, crude) after the reactions proceeded overnight at room temperature. The Jordan group has previously synthesized compound **8** using the salt metathesis route.³²

The ^1H NMR of compounds **8** and **9** showed single resonances for both the methyl and methine protons associated with the isopropyl moieties. This was an indication of the lack of steric bulk surrounding the metal centre. Compound **8** showed a singlet for the methyl substituent with a chemical shift of 1.08 ppm, which was consistent with the methyl group being located in an exocyclic position. The resonances for the ethyl-substituted amidinate (1.58 ppm, a quartet and 0.55 ppm, a triplet) were also indicative that the ethyl moiety was located in the exocyclic position. This further supported that ligand exchange is a consequence of the amidinate ligand transferring metal centres for a monodentate ligand and not due to a deinsertion/reinsertion of CDI. Chang et al. determined that chloride will insert preferentially to an alkyl group,³⁵ and these reactions showed no indication for the formation of a chloroamidinate. Similar to the bischelated amidinate species, there were no indications of a dimeric intermediate by ^1H NMR.

The TGA curves of compounds **8** and **9** showed single events during thermolysis (Figure 2.16). The derivative curve shape for both compounds was characteristic of a volatilization curve, as discussed earlier. Volatilization of compound **8** started at 62°C, while compound **9** started at 50.5°C. However, compound **8** volatilized slightly faster than **9**, this was seen by the derivative curve of **8** reaching its maximum sooner at 180.8°C with a width at half height of 33.98°C compared to **9** which reached its maximum at 186.9°C and had a width at half height of 38.50°C. These curves indicated

that both of these compounds would make acceptable precursors for ALD because they had relatively low onsets of volatilization and appeared to be thermally stable up to at least 200°C.

Figure 2.16: Thermogravimetric analysis curves for compounds 8 and 9.

2.1.4. Chloride Exchange Conclusions

The chloride exchanges were facile reactions at room temperature and many were high yielding with “overnight” reaction times. The aluminum (**1**) and gallium (**2**) dimeric species showed different reactivity from each other in the solution phase. However, the TGA of these compounds suggested similar reactivity, with respect to each other, in the solid phase, which was demonstrated by the same patterns in the derivative weight loss curves. The bisacetamidinate and bisethylamidinate aluminum complexes needed longer reaction times than the gallium bisacetamidinate and bisguanidinate complexes. The aluminum monoacetamidinate and monoethylamidinate showed no signs of a stable dimeric species; this highlighted that the additional π -stability supplied to the ring by

having an amido species in the exocyclic position was needed to obtain dimeric species of this nature.

The products of these chloride exchanges, while showing some promise as ALD precursors, were synthesized in order to investigate how chloride exchanges proceeded with varying exocyclic substituents and how chloride exchanges compared to alkyl exchanges. The chloride products are not desirable as ALD precursors due to the possibility of halide contamination into the growing thin films. Also, they can produce the detrimental by-product HCl, which can cause damage to the growing film or to the deposition apparatus itself.

2.2. Alkyl Exchanges of Aluminum

Ligand exchange can also occur between homoleptic parent amidinates or guanidinates and homoleptic trialkylaluminum compounds to form heteroleptic amidinate aluminum dialkyl complexes (reaction [2.9]).

where R = NMe₂, Me, Et and R' = Me, Et

The six-coordinate homoleptic parent species [MeC(NⁱPr)₂]₃Al,³⁶ [EtC(NⁱPr)₂]₃Al,³⁸ and [NMe₂C(NⁱPr)₂]₃Al³⁷ were synthesized following literature preparations.

The ligand exchange reactions to obtain [MeC(NⁱPr)₂]AlEt₂ and [EtC(NⁱPr)₂]AlMe₂ are previously reported.³⁸ These reactions were accomplished to prove that ligand exchange could be used to easily obtain heteroleptic amidinate complexes without being concerned about CDI insertion preferences.³⁵ The synthesis, characterization and thermolysis of [MeC(NⁱPr)₂]AlMe₂ (**10**), [EtC(NⁱPr)₂]AlEt₂ (**11**), [NMe₂C(NⁱPr)₂]AlMe₂ (**12**), [NMe₂C(NⁱPr)₂]AlEt₂ (**13**) will be discussed herein.

The ligand exchange products [MeC(NⁱPr)₂]AlMe₂ (**10**) and [EtC(NⁱPr)₂]AlEt₂ (**11**) were synthesized merely to show that an acetamidinate ligand and an ethylamidinate ligand will exchange for a methyl and ethyl moiety, respectively. Both of these

compounds have formerly been synthesized by the CDI insertion mechanism in high yield.^{32,35}

Compounds **10** and **11** were obtained in high yield (97.1 and 92.2%, crude, respectively) from room temperature reactions, with reaction times of 3 hours for **10** and 24 hours for **11**. Compounds **10** and **11** were both distillable liquids with melting points lower than -30°C . The distillation temperatures for compounds **10** and **11** were 26°C and 50°C , respectively at a reduced pressure of 110 mTorr.

The ^1H NMR for **10** showed one doublet (0.95 ppm) for the methyl moieties and one septet (3.13 ppm) for the methine proton of the isopropyl group in a 6:1 ratio, as expected for a non-congested amidinate group. Two singlets were also present in the ^1H NMR at 1.29 and 0.31 ppm in a 1:2 ratio, which corresponded to the exocyclic methyl substituent and the methyl groups on the aluminum metal centre. Similarly, the ^1H NMR of compound **11** showed a single doublet (0.99 ppm) and septet (3.18 ppm) for the isopropyl moiety and two distinctive ethyl environments for the exocyclic (1.82 ppm, a quartet and 0.78 ppm, a triplet) and metal bound (1.37 ppm, a triplet and 0.30, a quartet) substituents.

The TGA of compound **10** (Figure 2.17) showed a single feature in the derivative weight loss curve with a shape indicative of volatilization. The volatilization of this compound began immediately, which was unsurprising considering it distills at room temperature. Thus, compound **10** was very volatile. The narrow width of the TGA derivative curve, which reaches maximum at 87.2°C and then drops off quickly and a width at half height of 25.95°C also indicated the highly volatile nature. Compound **11** also proved to be volatile and show good thermal stability as demonstrated by a single feature in the weight loss derivative curve and a 0% residual mass by TGA. The derivative curve for **11** was almost twice the width at half height as **10** with a value of 49.51°C . It was unsurprising that **11** was less volatile than **10** given the difference in distillation temperatures. The onset of volatilization for **11** was approximately 65°C , whereas **10** began volatilizing at 34°C , again proving the highly volatile nature of $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlMe}_2$.

Figure 2.17: Thermogravimetric analysis for compounds **10** and **11**.

The monoguanidinate dimethylaluminum, $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]\text{AlMe}_2$ (**12**), was also previously reported by the Jordan group using the salt metathesis method.⁵⁰ The advantage of synthesizing this compound by ligand exchange was that potential lithium and chloride contaminants were completely avoided, which could be detrimental to the electronic characteristics of a thin film. Also, the ligand exchange product appeared to need less purification. The ligand exchange product was isolated in a 93.6% crude yield as a low melting temperature solid, and did not require any further purification. Compound **12** was a solid at room temperature with a melting point in the range of 27-33°C. Jordan et al. reported the crude salt metathesis product as a sticky yellow solid, which required further purification.⁵⁰ Ligand exchange provides an alternate and cleaner route to obtaining compound **12**, compared to the salt metathesis route.

Compound **12** showed promise as an ALD precursor. It had several desirable characteristics including having a melting point just above room temperature, thermal stability, good volatility, lack of halides, and stable by-products. A precursor with a melting point just above room temperature is desirable because solids are easier to handle than liquids, but at thin film process temperatures it is preferential to have a liquid. A liquid is desirable because it supplies a constant vapour pressure, which ensures a constant concentration of precursor vapour in every pulse. Compound **12** was thermally stable over the temperature range of the TGA (Figure 2.18). The entire sample completely volatilizes by 175°C, with no signs of decomposition and 0% residual mass. The expected by-products of compound **12** are the volatile protonated guanidine ligand, (NⁱPr)NMe₂C(HNⁱPr), and methane. The free guanidine ligand also showed an early onset of volatilization at 26°C with no thermal decomposition and a 0% residual mass in its thermogravimetric curve (Figure 2.19). The TG curve of this ligand demonstrated that it would be easily removed from a reaction chamber in an ALD process.

Figure 2.18: Thermolysis of compounds **12** and **13** by TGA

Figure 2.19: Thermolysis of the protonated guanidine ligand by TGA

The reaction of $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_3\text{Al}$ with two equivalents of TEA to obtain $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{AlEt}_2$ (**13**) was a slow reaction at room temperature, which took 48 hours to reach completion. Compound **13** was a distillable liquid at 40°C, 90 mTorr, with a melting point below -30°C.

The ^1H NMR of compound **13** showed a single doublet (1.02 ppm) for the methyl groups of the isopropyl substituents, indicating that the product was less sterically congested than the parent homoleptic guanidinate species which had a pair of doublets for this group.³⁷ The single resonances for the ethyl (1.50 ppm, a triplet and 0.39 ppm, a quartet) and the amide (2.23 ppm, a singlet) moieties were consistent in chemical shift with the alkyl group being attached to the aluminum metal centre and the amido signal was similar to those of other monoguanidinato complexes.^{37,38}

Compound **13** also showed potential as an ALD precursor, for reasons similar to those described for compound **12**. The TGA of **13** (Figure 2.18) had a slightly higher residual mass of 5% compared to compound **12**. The onset of volatilization for both compounds was at approximately the same temperature (56°C), however the rate of

volatilization was slower for compound **13** ($0.0223\%/^{\circ}\text{C}^2$ compared to $0.0305\%/^{\circ}\text{C}^2$ for compound **12**). Another indication that the rate of volatilization was faster for compound **12** was the width of the peak at half height. Compound **12** had a width at half height of 42.2°C , while compound **13** was 49.33°C . Over the temperature range of volatilization (56°C - 300°C), compound **13** showed good thermal stability.

Interestingly, the five-coordinate bis-chelating amidinates and guanidines bearing one alkyl group on the metal centre were not obtained as easily by the exchange reaction as the analogous chloride species. The ligand exchange reaction of the parent amidinate with an alkyl species in a 2:1 stoichiometric ratio (reaction [2.10]) results in a mixture of mono- and tris-amidinate species.

where $\text{R} = \text{NMe}_2, \text{Me}, \text{Et}$ and $\text{R}' = \text{Me}, \text{Et}$

Bis-chelating amidinates and guanidines of the type $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{AlNMe}_2$ ³⁷ and $[\text{MeC}(\text{N}^i\text{Pr})_2]_2\text{AlMe}$ ³⁶ have been synthesized using insertion reactions. However, in an attempt to synthesize $[\text{MeC}(\text{N}^i\text{Pr})_2]_2\text{AlMe}$ by ligand exchange at both room temperature and elevated temperatures over a period of 5 days the ratio of the methine proton in tris to mono remained 1:0.22 as indicated by ^1H NMR. The same ratio was found in the reaction to make $[\text{EtC}(\text{N}^i\text{Pr})_2]_2\text{AlEt}$. The reactions to synthesize the heteroleptic species $[\text{MeC}(\text{N}^i\text{Pr})_2]_2\text{AlEt}$, $[\text{EtC}(\text{N}^i\text{Pr})_2]_2\text{AlMe}$, $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{AlMe}$ and $[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{AlEt}$ also resulted in a mixture of products, some of which contained the bis product but always as the minor product and it could not be isolated. The chlorine atom was suspected to add additional stability to the system, and the reason for this effect is an ongoing investigation in our laboratory.

2.2.1. Alkyl Exchange Conclusions

The monoamidinate and monoguanidinate aluminum dialkyl species appear to be more stable than the bisamidinate aluminum alkyl species. These monoamidinate dialkyl complexes were also easier to obtain than the analogous dichloride complexes. They were obtained in higher yields and required less reaction time.

The TGA of monoamidinate and monoguanidinate species (dialkyl and dichloride) showed that these compounds were thermally stable and did not undergo any type of decomposition over the temperature range of volatilization. The bis-chelating and dimeric species were not thermally stable and demonstrated thermal decomposition, presumably CDI deinsertion.

2.3. Conclusions

Through these experiments it was discovered that ligand exchange could be a valuable technique in synthesizing various amidinates and guanidines. It was found that the dimethylamide guanidinate would exchange aluminum centres for one or two chloride ligands or two alkyl (methyl and ethyl) ligands. The reactivity of the same ligand with a gallium metal centre resulted in similar products with the exception of exchanging for two chloride ligands. In this case the dimeric form was more stable and the monomeric species were inaccessible. The analogous aluminum dimer, while it was a stable intermediate along the pathway of ligand exchange, did eventually decompose to the monomeric complex. Dimeric species were only seen with the guanidinate and chloride ligands. The guanidinate provided extra stabilization with the ability to have an extended π system by the delocalisation of six π electrons across the ligand and the electron withdrawing chloride ligand also assisted in stabilizing the dimer. The acetamidinate and ethylamidinate ligands will both exchange aluminum centres for two chloride, methyl or ethyl substituents. Both ligands can also exchange metal centres for one chloride ligand. Acetamidinate ligands on gallium will also exchange for one or two chloride ligands. Trialkylgallium compounds are not readily available and so the exchanges of amidinate and guanidinate ligands on gallium for alkyl species were not feasible.

Chapter 3: Ligand Exchange Mechanism

3.1. Computational Methods

The reaction mechanism for a five-coordinate bisguanidinate aluminum, of the type $[\text{RC}(\text{N}^i\text{Pr})_2]_2\text{AlR}'$, to the four-coordinate species $[\text{RC}(\text{N}^i\text{Pr})_2]\text{AlR}'_2$, where $\text{R}=\text{NMe}_2$, Me, Et and $\text{R}'=\text{Cl}$, H, Me, Et, NMe_2 , by ligand exchange was investigated (Figure 3.1).

Figure 3.1: Ligand exchange from a five-coordinate to a four-coordinate species

The mechanisms for reactions [3.1] and [3.2] were studied using the methods and basis sets described earlier (Chapter 1; Section 1.4).

Single-point energy calculations were performed on B971 optimized geometries along the reaction paths of [3.1] and [3.2] using the composite G3(MP2) method. For the modeling of reaction [3.1], the G3(MP2) calculations were completed on frozen geometries previously optimized by B971 and in the case of reaction [3.2] the single point G3(MP2) calculations were performed on reduced models of frozen structures previously optimized by B971, where CH_3 and $\text{CH}(\text{CH}_3)_2$ substituents were replaced by hydrogen atoms. These G3(MP2) calculations were then used in an ONIOM-type⁵⁸ scheme with the B971 vibrational data to account for the steric effects associated with the

guanidinate ligand. These corrections were accomplished using equation [3.3] for reaction [3.1] and equation [3.4] for reaction [3.2].

$$\Delta H = E_{G3MP2(0\text{ K})} - E_{ZPE} + E_{B971(\text{enthalpy/free energy})} \quad [3.3]$$

$$\Delta H = (E_{G3MP2(0\text{ K})} - E_{ZPE}) + E_{B971(\text{full})} - E_{B971(\text{reduced})} + E_{B971(\text{enthalpy/free-energy (full)})} \quad [3.4]$$

where E_{ZPE} is the zero-point energy from the HF component of G3(MP2), E_{B971} is the electronic energy from the full system, $E_{B971(\text{reduced})}$ is the electronic energy from the hydrogen terminated geometries and $E_{B971(\text{enthalpy/free-energy})}$ is the thermal correction to enthalpy or free-energy obtained with the B971 vibration calculations of the full system.

The G3(MP2) calculations were completed so that a higher level of theory with large basis sets could be used for the energy calculations, while using the lower level B971 and MWB approach for the geometry optimizations. This is essentially the concept of ONIOM, where the system being studied is divided into multiple layers treated with different levels of theory and the results are combined to get the final predicted results. Geometry optimizations on large systems, such as [3.1] and [3.2], would require a lot of computing power and would be uneconomical.

3.2. Reduced System Mechanism

In order to gain insight into the ligand exchange reaction mechanism, a reduced model ([3.1]) was used as a starting point for more detailed calculations needed for the full system as outlined in reaction [3.2]. In the reduced model all dimethylamine, isopropyl groups and non-participating chlorine atoms were replaced with hydrogen atoms.

The free energies, calculated using [3.3], for the stationary points along the reaction coordinate of reaction [3.1], are shown in Figure 3.2. The initial reaction was the formation of an adduct, in which a dative bond formed between N6 of $[\text{HC}(\text{NH})_2]_2\text{AlCl}$ and Al2 of AlH_2Cl (Figure 3.3b). The calculations showed that the adduct formation occurs through a barrierless process and stabilized the system by 13.8 kcal/mol. The adduct formation caused the Al1-N6 bond to increase by 0.12 Å and

formed a bond between N6 and Al2 that was calculated to be 2.05 Å, which was 0.07 Å longer than a typical Al-N bond length seen in these systems. The geometry of N6 changed from being trigonal planar in $[\text{HC}(\text{NH})_2]_2\text{AlCl}$ to a distorted trigonal bipyramidal geometry in the adduct (Figure 3.3, a $\rightarrow$ b). The geometry of Al2 also changed from trigonal planar to a distorted tetrahedral geometry. Calculations showed that the adduct went through a low barrier process (Figure 3.3c, 2.55 kcal/mol) to adopt a bridging coordination, where the two aluminum centres were connected through both a bridging guanidinate and a chlorine atom (Figure 3.3d). The formation of this intermediate allowed the bridging guanidinate to become more planar, which was shown by the torsion angle of Al2-N6-C13-N4 changing from 109.7° in 3.3b to 4.81° in 3.3d. This hetero-bridged structure was calculated to be more stable than the adduct by 10.45 kcal/mol. Geometry scans on the initial adduct formation suggested that in order for Cl1 to transfer between aluminum metal centres the bridging guanidinate must be planar. The stable calculated hetero-bridged structure was formed by Cl1 migrating towards Al1. The Al1-Cl1 bond distance shortened from 3.97 Å in the adduct to 2.36 Å in the chloride bridged structure, while the Al2-Cl1 bond distance expanded from 2.19 Å to 2.31 Å.

Interestingly, the chloride transfer was not as simple as Cl1 migrating towards Al1, as first predicted. The action of Cl1 migrating towards Al1 was necessary to position the bridging guanidinate in the plane of Al1 and Al2. While this was an essential part of the overall mechanism of ligand exchange, it was not the route for the chloride transfer between metal centres. The chloride was transferred between metal centres because of a transition state where the chelating guanidinate ring on Al1 rotated about the Al1-C4 axis as N1 moved into a position to bond with Al2 (Figure 3.3e). The geometry about N1 changed from trigonal planar to a distorted tetrahedron. This was evident by the torsion angle of H4-N1-C4-H6 changing from 5.34° to 36.41°. The Al2-Cl1 bond was also partially broken, as seen by the bond length increasing by 0.26 Å. This process had a barrier height of 15.78 kcal/mol with respect to the chloride-bridged intermediate. The movement of N1 towards Al2 not only caused a rotation about the Al1-C4 axis, but also a rotation about the Al1-N4 axis. The rotation about Al1-N4 allowed for a concerted movement of Cl1 to a terminal position on Al1, and lead to an sp^3 hybridized guanidinate that bridged both aluminum centres through N1 (Figure 3.3f).

This nitrogen-bridged structure was calculated to be 3.80 kcal/mol more stable than the chloride-bridged structure with respect to the relative free energies.

The chelate ring opened as N3 migrated towards Al2 (Figure 3.3g), expanding Al1-Al2 from 3.23 Å to 3.45 Å. This allowed for the second guanidinate to adopt the same bridging geometry as the first guanidinate (Figure 3.3h). The process to obtain the double guanidinate-bridged dimer surmounted a barrier height of 9.37 kcal/mol and allowed for a calculated stabilization of 11.22 kcal/mol from structure g and 39.24 kcal/mol from the original reactants. The bridging rings have a torsion angle of 36.61° and -36.61° for Al1-N4-C13-N6 and Al1-N1-C4-N3, respectively. The ring geometry of the dimer had a pseudo-chair conformation (Figure 3.4), which has been seen in other dimers of this type.^{50,52} However, this core differs from that of compound **1**. The calculations of this modeled reduced ligand exchange predicted the products, [HC(NH)₂]AlCl₂ and [HC(NH)₂]AlH₂, to be 26.13 kcal/mol less stable than the double-guanidinate bridged dimer. This largely endothermic degradation was thought to be a consequence of using a reduced system and this issue was addressed in more detailed calculations.

A transition state between structure h and structure i was not identified. However, since this model was being used for more detailed calculations, and the energy of the products seemed misrepresented compared to experimental results, the lack of this transition state was not surprising.

Figure 3.2: Calculated free energies and enthalpies of stationary points along the reduced ligand exchange reaction. The labeled structures of each stationary point correspond to Figure 3.3.

Figure 3.3: The calculated stationary point structures along the reaction path of equation [3.1].

Figure 3.4: Pseudo chair conformation of structure g. Only chlorides and the atoms involved in the connectivity of the ring are shown.

The calculated relative free energies and enthalpies for the stationary points along the reaction pathway are shown as a comparison in Figure 3.2. Studying both energies suggested that the most stable stationary point was the double-guanidinate bridged dimer, which stabilized the reaction by 51.30 and 39.24 kcal/mol in terms of enthalpy and free energy, respectively, relative to the original reactants. The degradation of the dimer to the monomeric species was predicted to be an endoergic process resulting in products that were less stable than the dimer by 39.42 and 26.13 kcal/mol with respect to enthalpy and free energy. Comparing the free energy and enthalpy of the degradation, it can be seen that they differ by 13.29 kcal/mol but that with respect to the original reactants the energies of the products only differ by 1.23 kcal/mol.

The reduced system was modeled to get a general idea of how the reaction mechanism for ligand exchange might proceed. This model predicted some key features of this mechanism, hinting at the complexity of this reaction. For instance, the need for a planar bridging guanidinate before the chlorine atom was able to transfer metal centres was unexpected. Also, the fact that the chlorine atom transfers metal centres as a consequence of the formation of a doubly-bridged guanidinate dimer and not the reverse was an unanticipated result. The results of these calculations were used to great advantage in completing the full system calculations.

3.3. Full System Mechanism

More detailed calculations were performed for the chloride ligand exchange reaction using the model system described above as a starting point. These calculations were performed with all dimethyl amide, isopropyl and all chloride substituents included.

The free energies for the stationary points along the reaction coordinate of equation [3.2], calculated using equation [3.4], shown in Figure 3.5, are plotted in Figure 3.6. The energy involved in breaking the dimerized starting material Al_2Cl_6 is included in this full system. The AlCl_3 reactant was 10.8 kcal/mol less stable than the dimerized Al_2Cl_6 reactant. However, the calculations indicated that the formation of an adduct in which a dative bond was formed between one guanidinate nitrogen of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$ and the aluminum of AlCl_3 (Figure 3.5, a $\rightarrow$ b) stabilized the reactants by 12.8 kcal/mol, overcoming the energy necessary to break the Al_2Cl_6 dimer. Adduct formation occurred via a barrierless process and caused the guanidinate to effectively dechelate (i.e. $\text{R}(\text{N4-Al1})$ increased by 1.31 Å). The newly formed N4-Al2 bond had a calculated length of 1.94 Å, which was consistent with typical Al-N bond lengths in bisguanidinate systems.³⁷ The bonding geometry of Al2 changed from a trigonal planar geometry to a distorted tetrahedral geometry. The bridging guanidinate of the adduct (Figure 3.5b) had a torsion angle of 53.6° (Al2-N4-C13-N6). If the full system follows the same trend as the reduced system, then this angle will have to become more planar before the chloride will exchange.

The adduct converted to a lower-lying intermediate structure by an internal rotation about the Al1-N6 bond, which allowed Cl1 to adopt a bridging position (Figure 3.5c). The chloride bridging structure was calculated to be 5.6 kcal/mol more stable than the adduct. Geometry scans on the initial adduct structure suggested that the chelating guanidinate ring must be perpendicular to the plane of the bridging guanidinate ring in order for the chloride transfer to occur. This structure had an Al1-Cl1 distance of 2.59 Å, which was significantly larger than the typical Al-Cl bond length of 2.21 Å seen in these systems.³⁷ The motion of the chloride transferring metal centres, as was the case in [3.1], was a consequence of the chelating guanidinate becoming a bridging guanidinate. The dechelation was a consequence of N3 migrating towards Al2 and first forming a dative bond. The bonding environments within the chelating ring changed so that there was a

formal double bond between N1 and C4 and the exocyclic N2 was partially participating in an extended π system. The formation of a bridging guanidinate (Figure 3.5e) from a chelating guanidinate in the chlorine bridged structure required the formation of a transition state structure (Figure 3.5d) in which the Al2-Cl1 bridging bond was partially broken and the Al1-Cl1 bond was decreased by 0.19 Å. This process had a barrier of 19.5 kcal/mol with respect to the chloride-bridged intermediate (c). The Al1-N3 bond in structure d expanded from 1.95 Å to 2.01 Å, while Al2-N3 contracted from 4.20 Å to 2.39 Å, with respect to that in c. This left Al1 with a distorted square-based pyramidal geometry where Cl2 was in the apical position. The geometry of N3 changed from trigonal planar to a distorted tetrahedral, this changed the dihedral angle of N1-C4-N3-C6 from 7.15° to 45.5°. This change in torsion angle moved the isopropyl group to a position that allowed N3 to bond with Al2.

The chelate ring then opened up (Al1 – Al2 expanded from 3.00 Å to 3.52 Å) allowing the second guanidinate to adopt a bridging geometry and Cl1 to adopt a terminal position (Figure 3.5e). This guanidinate-bridged dimer allowed for a stabilization of 9.4 kcal/mol from the chlorine bridged dimer and was 16.9 kcal/mol lower in terms of relative free energies than the original reactants. Unlike the reduced dimer shown in Figure 3.3g, when calculations were performed on the dimer bearing all dimethylamide and isopropyl groups, the core structure adopted a boat conformation (Figure 3.7), similar to **1** (Chapter 2; Figure 2.4), as opposed to the chair conformation. This calculated structure was analogous to the same compound isolated experimentally (see Tables 3.1 and 3.2). It should be noted that bond angles of C1-N1-Al1, C4-N1-C1 and C10-N4-Al2 were significantly different between the XRD and DFT structures. This was a consequence of the two isopropyl groups (C10 and C1) being disordered each in two positions with refined site occupancies of roughly 60/40 for complex **1** in the XRD structure.

The dimer broke into the monomeric species by a lengthening of Al2-N4 from 1.91 Å to 2.65 Å (Figure 3.5f). The transition from the dimer to the monomer involved the lengthening of the Al2-N4 bond, which caused N4 to bond with Al1 (Al1-N4 contracted from 3.11 Å to 2.03 Å). A planar ring formed between Al1-N6-C13-N4 and Al2-N1-C4-N3 with torsion angles of 5.88° and 1.66°, respectively (Figure 3.5f). The

transition from structure e $\rightarrow$ f had pyramidilized nitrogen atoms (N4 and N1) that were still sharing electron density with Al2 and Al1, respectively. The atom N4 was pyramidilized by 51.6° and N1 by 62.25° . The isopropyl moiety on N1 was rotated 166.06° with respect to that on N3 to alleviate some of the steric bulkiness. Both aluminum centres had distorted trigonal bipyramidal geometries ($\tau = 0.56^\circ$ for Al1 and $\tau = 0.61^\circ$ for Al2) with the Cl atoms in axial positions. This process had a barrier height of 26.5 kcal/mol and allowed the final product (g) to be stabilized by 23.5 kcal/mol from the original reactants. The monomer had a stabilization of 6.64 kcal/mol compared to the dimer guanidinate-bridged species. The aluminum centre in the final product had a distorted tetrahedral geometry because of the 71.41° bite angle of the chelating guanidinate ligand. The exocyclic amide moiety was 30.41° out of plane with the ligand, which suggested that it was partially participating in the extended π system. Torsion angles in the range of $23.5 - 41.0^\circ$ are typical for these types of compounds.³⁷

Figure 3.5: The calculated stationary point structures along the reaction path of equation [3.2].

Figure 3.6: Calculated free energies of the stationary points along the ligand exchange reaction. The labeled structures corresponding to each enthalpy are shown in Figure 3.5.

Figure 3.7: Boat conformation of dimer core

The calculated enthalpies and free energies for the stationary points for the exchange reaction [3.2] are shown in Figure 3.8. Studying the enthalpies for the reaction mechanism suggested that the most stable stationary point was the dimer bridged by two guanidinate ligands. This calculated structure was stabilized by 25.52 kcal/mol compared to the original reactants and 10.48 kcal/mol lower in enthalpy than the chlorine bridged structure. The formation of the monomeric species from the dimeric structure was an

uphill process, with a barrier height of 25.86 kcal/mol and a stable calculated structure that was 11.82 kcal/mol endoergic than the doubly guanidinate-bridged dimer. The calculated relative free energies of the exchange reaction showed that the monomeric species allowed for a stabilization of 6.64 kcal/mol from the dimer and 23.5 kcal/mol from the original reactants. Therefore, by comparing the enthalpy and the free energy for the reaction coordinate of [3.2] it can be seen that the process was driven by entropy to some extent. The relative free energy plot was more representative of the experimental results. Experimentally, the dimer was formed upon mixing and was a long-lived species. However, over four days in solution at room temperature or in 18 hours at 90°C the dimer did decompose to the monomeric species, which was stable in solution.

Figure 3.8: Calculated free energies and enthalpies of stationary points along the ligand exchange reaction. The labeled structures of each stationary point correspond to Figure 3.5.

Table 3.1: Bond lengths for the crystal structure and calculated structure of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$

	Bond Lengths (Å)				
	XRD	DFT		XRD	DFT
Al1-N1	1.855(4)	1.908	N4-C13	1.353(7)	1.352
Al1-N6	1.880(4)	1.900	N4-C10	1.543(9)	1.510
Al1-Cl2	2.153(2)	2.178	N5-C13	1.350(6)	1.371
Al1-Cl1	2.155(2)	2.184	N5-C14	1.458(7)	1.461
Al2-N4	1.875(5)	1.914	N5-C15	1.461(8)	1.461
Al2-N3	1.886(4)	1.911	N6-C13	1.351(6)	1.350
Al2-Cl4	2.153(2)	2.183	N6-C16	1.487(6)	1.513
Al2-Cl3	2.164(19)	2.180	C1-C3	1.502(15)	1.530
N1-C4	1.360(7)	1.351	C1-C2	1.519(16)	1.536
N1-C1	1.550(19)	1.512	C7-C8	1.520(8)	1.536
N2-C4	1.351(6)	1.373	C7-C9	1.530(6)	1.531
N2-C6	1.452(8)	1.462	C10-C12	1.529(9)	1.530
N2-C5	1.456(7)	1.462	C10-C11	1.539(11)	1.535
N3-C4	1.349(6)	1.354	C16-C17	1.518(8)	1.533
N3-C7	1.498(6)	1.511	C16-C18	1.527(7)	1.538

Table 3.2: Bond angles for the crystal structure and calculated structure of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$

Bond Angles (°)					
	XRD	DFT		XRD	DFT
N1-Al1-N6	122.25(18)	122.75	C13-N5-C14	122.4(5)	122.46
N1-Al1-Cl2	109.00(16)	111.45	C13-N5-C15	122.0(5)	122.11
N6-Al1-Cl2	103.17(14)	102.42	C14-N5-C15	115.5(5)	115.24
N1-Al1-Cl1	104.52(14)	101.50	C13-N6-C16	122.7(4)	122.77
N6-Al1-Cl1	107.18(15)	107.26	C13-N6-Al1	116.7(3)	117.68
Cl2-Al1-Cl1	110.58(9)	111.46	C16-N6-Al1	120.0(3)	118.79
N4-Al2-N3	124.23(18)	123.20	C3-C1-C2	116(2)	111.00
N4-Al2-Cl4	101.77(14)	100.18	C3-C1-N1	103.8(11)	110.80
N3-Al2-Cl4	110.43(14)	110.35	C2-C1-N1	107(2)	113.89
N4-Al2-Cl3	109.98(14)	111.01	N3-C4-N2	122.2(5)	120.15
N3-Al2-Cl3	101.78(13)	101.22	N3-C4-N1	116.3(4)	119.41
Cl4-Al2-Cl3	108.05(8)	110.99	N2-C4-N1	121.5(5)	120.44
C4-N1-C1	103.0(8)	117.99	N3-C7-C8	113.5(4)	114.70
C4-N1-Al1	114.8(3)	116.57	N3-C7-C9	109.6(4)	110.36
C1-N1-Al1	139.8(8)	123.05	C8-C7-C9	110.0(5)	111.12
C4-N2-C6	122.6(5)	122.05	C12-C10-C11	108.8(9)	110.99
C4-N2-C5	122.6(5)	122.29	C12-C10-N4	108.1(6)	110.76
C6-N2-C5	114.8(5)	115.64	C11-C10-N4	110.0(7)	114.06
C4-N3-C7	118.2(4)	117.25	N5-C13-N6	121.9(5)	120.85
C4-N3-Al2	115.0(3)	116.75	N5-C13-N4	121.7(4)	120.89
C7-N3-Al2	125.7(3)	124.56	N6-C13-N4	116.3(4)	118.26
C13-N4-C10	110.1(5)	118.00	N6-C16-C17	114.1(4)	114.33
C13-N4-Al2	116.2(3)	116.35	N6-C16-C18	115.2(5)	115.13
C10-N4-Al2	132.4(5)	123.41	C17-C16-C18	111.3(4)	111.32

There were a few key differences between the ligand exchange reactions of [3.1] and [3.2]. The most important of these was the steric effect of the dimethyl amide, isopropyl substituents and the addition of the chlorine atoms on the energies along the reaction coordinate. The free energies and enthalpies of the reduced model, as well as the enthalpies of the complete model predicted that the most stable structure was the dimer bridged by both guanidinate rings. However, the free energies of the more detailed model predicted that the monomeric species was the most stable. This suggested that the dimethyl amide on the sp^2 carbon in the exocyclic position and the exocyclic isopropyl groups on the nitrogens significantly contributed to the entropy of the reaction, as seen in the disorder in the crystal structure of **1**.

The added steric bulk of the $N(CH_3)_2$ and $CH(CH_3)_2$ also changed the reaction mechanism between [3.1] and [3.2]. The reaction mechanism for [3.2] did not have a stable structure where the bridging ring was planar and a Cl was shared between the metal centres, (see Figure 3.3d). The torsion angle of the bridging ring (Al2-N4-C13-N6) in Figure 3.5c was 56.94° compared to 4.81° in Figure 3.3d. The Al1-Cl1 and Cl1-Al2 distances were 2.59 Å and 2.21 Å for [3.2] and 2.36 Å and 2.31 Å for [3.1]. In both mechanisms the chelating guanidinate ring must rotate about the Al1-N4 axis in order for the Cl to transfer. By performing this rotation the electron density found within the ring was rotated away from the chloride and allowed interaction between Cl1 and Al1. The calculations for the reduced mechanism required an intermediate step between the hetero-bridged and homo-bridged stationary points, where the two aluminum centres were bridged by a nitrogen atom (Figure 3.3f). This type of intermediate was not seen in the complete system: there are a couple of explanations for this. The first is that the added steric bulk of the isopropyl groups did not allow this calculated structure to be accessible, because the added substituents do not allow the ring to flip, rather, the N3 dechelates from Al1 then bonds to Al2. Another explanation for the difference between the two mechanisms could be the added stabilization that the dimethylamide substituent on the exocyclic position gives the guanidinate ring because it allows the π system to extend into the exocyclic position. This may have increased the stabilization of the ring when the nitrogen effectively dechelated, so that the ring did not need to flip to form the homo-bridged dimer in order to stabilize.

The mechanism of ligand exchange for reaction [3.2] was investigated using computational methods. This mechanism was inspired by the isolated aluminum dimer, $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{Al}_2\text{Cl}_4$ (**1**) (Chapter 2, Section 2.1.1) and the mechanism previously proposed by our group.³⁷ The dimer was a surprising addition to the mechanism, but as calculations and experiments proved, it played an important role and was a stable, long-lived intermediate in the reaction path of ligand exchange. The process of ligand exchange between guanidates and chlorines is driven by entropy.

Chapter 4: Atomic Layer Deposition of Aluminum Oxide Thin Films

Aluminum oxide (Al_2O_3) thin films were first deposited using the ALD method thirty years ago for the purpose of TFEL displays, using AlCl_3 and H_2O as the precursors.⁵⁹ Over the decades further applications of Al_2O_3 have been discovered, such as corrosion resistant coatings,⁶⁰ optical coatings^{61,62} and as a high dielectric material for gate oxides.^{63,67}

Much of the investigation of ALD in the area of microelectronics has been in the direction of depositing insulating materials with high dielectric constants (k), for example, Al_2O_3 ($k = 9.34$),⁶⁴ ZrO_2 ($k = 12.5$)⁶⁴ and HfO_2 ($k = 23$).⁶⁵ These high- k dielectrics are being studied to replace the wide spread use of the relatively low dielectric material silicon dioxide ($k = 4.42$)⁶⁴ as gate oxides in metal-oxide semiconductor field-effect transistors (MOSFET). Higher- k dielectrics are desirable to reduce high tunneling currents when devices are downscaled and require thinner gate dielectrics.²⁴

Alkyl aluminum or aluminum chloride precursors are commonly employed as precursors in the ALD of Al_2O_3 thin films. A major disadvantage of trialkylaluminum precursors, such as trimethylaluminum (TMA), is that they require special handling conditions due to their pyrophoricity. Aluminum chloride has two major disadvantages. It can allow the incorporation of halide contamination into the growing film, and its HCl byproduct can be detrimental not only to the film, but also to the deposition apparatus itself.

Aluminum amidinates are good substitutes to these precursors in the ALD of Al_2O_3 for several reasons. For example, they have tunable properties, they are not pyrophoric but are highly chemically reactive with water, they have volatile byproducts and they are thermally stable.

4.1. Experiments

The Al_2O_3 films were grown on mechanical grade N-doped Si(111) substrates with a resistance of 1-10 Ω and a native SiO_2 layer. The deposition apparatus was a hot-walled ALD reactor (Angstrom Engineering Inc.) The reactor had an automated valve array comprised of five pneumatic valves, illustrated in Figure 4.1 as a schematic

diagram. The valve array was heated to 105°C to avoid the condensation of precursors before reaching the deposition chamber. The deposition chamber was a stainless steel tube with a diameter of one inch encased in a furnace, which led to vacuum pump. Bubblers 1 and 2 were heated independently and were connected to the reactor by manual valves. The base pressure of the ALD reactor was less than 1×10^{-3} Torr and the typical operating pressure was in the range of 0.8-3.0 Torr.

Figure 4.1: Schematic diagram of the ALD reactor.

The aluminum containing precursor was the literature compound $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ ³⁸ and H_2O was used as the oxygen source. Nitrogen (UHP 5.0 from Praxair) was used as a carrier and purging gas. The water was evaporated from an external bubbler held at room temperature. The aluminum precursor was heated in an external bubbler in the temperature range of 28-60°C. The pulsing sequence for one ALD cycle was:

1. 5.0 s N_2 , evacuate for 10.0 s
2. 5.0 s fill $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ bubbler with N_2
3. 0.5-6.0 s $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$
4. 5.0 s N_2 , evacuate for 10.0 s
5. 5.0 s fill H_2O bubbler with N_2
6. 0.25-5.0 s H_2O

Steps two and five in the pulsing sequence filled the bubblers and lines (by which the precursors were introduced to the furnace) with nitrogen gas. This was done in order to increase the pressure within the bubbler, so that when the valve to the furnace was opened maximum mass transport of the precursor molecules in the carrier gas was

achieved. The number of cycles of Al_2O_3 film growth varied between 100-500 cycles, but typically 250 cycles were used. The growth temperatures were in the range of 125-300°C, but most commonly were 175°C and 200°C.

Silicon (111) substrates were cleaned and prepared for the ALD experiments. The three inch Si wafers were fractured into strips with a width of ~1.5 cm using a diamond tipped glass cutter to score the substrates, which were then snapped by hand along the scoreline. Substrates were cleaned of surface organics and silicon dust by sonication in an acetone bath for 30 minutes. The wafers were then rinsed with deionized water, dried and subjected to UV/ O_3 for one minute. This was followed by a 10% hydrofluoric acid (HF) dip for 30 seconds to remove the native silicon oxide layer and whatever contaminants lay on top of it, and the substrates were then rinsed with deionized water and dried by blotting with a Kimwipe. The UV/ O_3 and HF treatment were repeated a second time and a final UV/ O_3 (to regenerate clean, native oxide) finished the cleaning process. The substrate was then loaded onto a substrate holder and placed in the furnace, as close to the injection point as possible and the system was placed under vacuum. The furnace was heated to 300°C for one hour, at which time water was passed over the substrate for 30 min to homogenize the surface with respect to hydroxyl density. This was accomplished by opening the valve to the water bubbler for that time period. The substrate was then kept under vacuum at 300°C in order to control the number of hydroxyl surface sites between 2-3 OH^-/nm^2 on the surface.⁶⁶

The Al_2O_3 film thicknesses were determined by ellipsometry (PLASMOS). Surface morphology was studied by a scanning electron microscope (SEM) (Jeol 840) and atomic force microscopy (AFM) (Nanosurf easyScan 2). Energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive spectroscopy (WDS) concomitant with the SEM (Cameca Camebox) were used to confirm the presence of aluminum and oxygen.

4.2. Furnace Temperature Optimization

Furnace optimization was performed to determine the temperature at which the Al_2O_3 film growth rate was the fastest without having a component of CVD-type growth (see Chapter 1, Section 1.1.1). The aluminum precursor-containing bubbler was held at

50°C and the water was kept at room temperature. All pneumatic valves had pulse times of five seconds, to ensure complete saturation. The furnace temperature was varied from 125-300°C in 25°C increments and 250 cycles were completed at each temperature setting. Thickness measurements were taken by ellipsometry for each temperature and the growth rate was calculated by dividing the thickness of the Al₂O₃ film by the number of cycles. The growth rate was plotted as a function of the furnace temperature (Figure 4.2) and the curve had an exponential-type shape, with the exception of plateau between 225° and 250°. In the temperature range of 125-175°C the growth rate was linear with $R^2=1$. The growth rate began to grow exponentially between 200-300°C, where CVD-type growth was seen: the precursor was thermally decomposing at the surface causing continual growth as indicated by the large growth rates (3.43-8.44 Å/cycle). A common misconception in ALD is that an “ALD window” must be found for a process to be deemed ALD. An ALD window is when a plateau is seen in the growth rate with increasing temperatures. A process may be considered ALD without an ALD window as long as self-limiting growth is seen from each of the precursors. A small ALD window was seen over a 25°C temperature range between 225°C and 250°C, however a lower furnace temperature of 175°C was chosen because it gave a reasonable growth rate of 2.71Å/cycle and the precursor at this temperature demonstrated ALD type growth.

Figure 4.2: The growth rate of Al_2O_3 films from $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and H_2O as a function of growth temperature.

4.3. Saturation Curves

A true indication as to whether film growth is ALD or CVD is the shape of the saturation curve. A saturation curve demonstrates that the growth rate plateaus at a certain pulse length, indicating self-limiting behaviour (see Chapter 1, Section 1.1.1). Both precursors ($[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and H_2O) should demonstrate self-limiting behaviour in an ALD process.

4.3.1. Aluminum Precursor Saturation Curve

A preliminary test of precursor **1** ($[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$) was completed to see if the precursor demonstrated self-limiting growth, before any other optimizations. The thin films were deposited at a furnace temperature of 200°C where the precursor was known to be thermally stable by TGA and with a bubbler (precursor **1**) just above room temperature at 28°C . The valve for the precursor was varied between 2.0 – 7.0 seconds and all other valves were set to a pulse length of 5.0 seconds. The deposition of these

films occurred over 500 ALD cycles. Aluminum oxide films with a thickness range of 820 – 1420 Å were deposited over the various pulse lengths. The saturation curve is shown in Figure 4.3 and demonstrates self-limiting growth at a growth rate of 2.75 Å/cycle. A pulse length of 5.5 seconds was necessary at the low bubbler temperature of 28°C to get a fully saturated surface and for the growth rate to plateau. This saturation curve was a good indication that $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ would be a good ALD precursor for the deposition of Al_2O_3 thin films

Figure 4.3: Saturation curve for precursor **1** at 200°C and with a bubbler temperature of 28°C.

The saturation curve for precursor **1** (Figure 4.4) was also collected with a bubbler temperature of 50°C to ensure the maximum concentration of precursor per pulse. The furnace temperature was 175°C, where growth was known to occur by an ALD mechanism, and a water pulse of five seconds was used to ensure there was full saturation from the second precursor.

The pulse length of precursor **1** was varied from 0.5 – 6.0 seconds. The maximum growth rate of 2.7 Å/cycle was achieved with a minimum pulse length of four seconds. Pulse lengths longer than this also resulted in the same growth rate within

experimental error. This indicated that at a minimum pulse of four seconds the substrate surface was fully saturated in a self-limiting monolayer of the aluminum precursor, demonstrating ALD growth.

The growth rates for the different temperature processes were similar and within experimental error. However, the maximum growth rate was accomplished sooner with a higher bubbler temperature. This was unsurprising, given that at higher temperatures the precursor would have a higher vapour pressure and thus a higher concentration of precursor was introduced per cycle.

The growth rate seen with this aluminum amidinate precursor was significantly larger than growth rates seen with other precursors. Growth rates of 0.7, 1.1 and 1.4 Å/cycle have previously been reported for the aluminum precursors $\text{Al}(\text{CH}_3)_2\text{Cl}$,⁶⁷ $\text{Al}(\text{CH}_3)_3$ ⁶⁸ and $\text{Al}(\text{NEt}_2)_3$,⁶⁹ respectively. The Al-O bond distance in amorphous Al_2O_3 films is 1.8-1.9 Å.⁷⁰ One cycle through the ALD pulse sequence results in two Al-O bonds, thus the reason for the higher growth rate could be that a more complete monolayer is being deposited per cycle in this process compared to the literature processes. This is an indication that the precursor has a better sticking coefficient than the literature examples. Also, the fact that a relatively low deposition temperature was used could mean that there were a higher number of hydroxyl sites on the alumina surface after the N_2 purge, which means there were a high number of reactive surface sites for the subsequent pulse of precursor **1**.⁶⁷

Figure 4.4: Growth rate of Al_2O_3 thin films as a function of the pulse time of precursor 1.

4.3.2. Water Saturation Curve

The water (precursor 2) saturation curve was acquired by varying the pulse length for the water bubbler between 0.25-5.0 seconds (Figure 4.5). The aluminum precursor had a pulse time of four seconds and all other valves had a pulse length of five seconds. The furnace temperature and precursor 1 bubbler temperature were set to the optimal temperatures of 175°C and 50°C , respectively. Precursor 2 was kept at room temperature.

The large vapour pressure of water, even at room temperature, allowed for a significant growth rate of 1.75 Å/cycle at a pulse length of only 0.25 seconds. A pulse time of one second was sufficient to obtain a maximum growth rate of approximately 2.3 Å/cycle . The growth rate plateaued when pulse times longer than one second were used; this indicated the self-limiting behaviour of precursor 2. This growth rate was slightly less than that seen for precursor 1 (2.7 Å/cycle), which is considered to be reasonable given the unsophisticated nature of our deposition apparatus. If conditions are not the exact same from day to day it is unsurprising that the growth rates will vary slightly.

Figure 4.5: Growth rate of Al_2O_3 thin films as a function of the pulse length of water

4.4. Film Thickness as a Function of Deposition Cycles

The optimum parameters for the temperatures and pulse sequence were used to determine if the deposited Al_2O_3 films exhibited linear growth with respect to the number of ALD cycles used. The number of cycles was varied between 100-250 cycles and the thickness of the resulting Al_2O_3 films were measured by ellipsometry. The film thickness was plotted as a function of the number of cycles (Figure 4.6) and the Al_2O_3 films were found to have a linear growth with an R^2 value of 0.9817. The growth rates varied between 2.28-2.75 Å/cycle with varied number of cycles. Ideally, the growth rate would remain constant while varying the number of ALD cycles, but the difference of 0.47 Å/cycle was acceptable considering that the standard deviation of the thickness across the samples ranged from 0.17 to 0.58 Å.

Figure 4.6: Linear film growth of Al_2O_3 with a varying number of cycles.

4.5. Surface Composition

The composition of the Al_2O_3 films were determined by EDX, which confirmed the presence of aluminum, oxygen and silicon (Figure 4.7 and Figure 4.8). This technique works by an electron or photon beam ejecting an electron from the inner shell of an atom. This leaves a “hole” which is filled with an electron from an outer (higher energy) shell; the excess energy is released as a characteristic X-ray. The spectral lines of the X-ray are specific to an element and so can be used to characterize composition. The energies for aluminum, oxygen and silicon are 1.560 keV, 0.532 keV and 1.839 keV, respectively.⁶⁴

Figure 4.7: Energy dispersive X-ray spectrum for an Al_2O_3 film deposited at 175°C .

Figure 4.8: Energy dispersive x-ray spectrum for an Al_2O_3 film deposited at 200°C .

The EDX spectrum for the aluminum oxide film deposited at 200°C was lacking a signal for oxygen because the SEM on which it was performed was not equipped to detect lighter elements with lower energies.

Wavelength dispersive spectroscopy was also used to confirm the presence of aluminum in the Al_2O_3 film grown at 200°C (Figure 4.9). The WDS was used to determine the energy spectrum of the x-rays from the EDX. The emitted x-rays are

diffracted from a known single crystal, in this case, thallium acid phthalate (TAP), which gives each element a characteristic “ $2\sin\theta$ ” value based on Bragg’s law.

Figure 4.9: Wavelength dispersive spectrum for aluminum in an Al_2O_3 film deposited at 200°C .

Oxygen could not be detected by this method because the electron microprobe is not equipped with a crystal of appropriate d-spacing to detect lighter elements.

The presence of aluminum was confirmed by both EDX and WDS, and the presence of oxygen was also verified by EDX.

4.6. Surface Morphology

The scanning electron microscopy (SEM) images show the surface morphology of Al_2O_3 films (Figure 4.10). This particular film was grown over 500 cycles at 200°C and had a measured thickness of 104.6 nm by ellipsometry, which corresponded to the thickness measurement of approximately 100 nm by SEM (the bar in each image is one micron). The SEM images show a flat, conformal surface morphology.

Figure 4.10: SEM images showing the surface morphology from a) side view and b) 45° to the side view for an Al_2O_3 film grown at 200°C over 500 cycles.

The surface was also studied by atomic force microscopy (AFM) for Al_2O_3 films grown at 200°C for 500 cycles (Figure 4.11) and at 175°C for 250 cycles (Figure 4.12). The AFM scan lengths were $2.0\ \mu\text{m}$ and were acquired using contact mode. The Al_2O_3 film grown at 200°C had a root mean square (RMS) area roughness of $15.96\ \text{\AA}$. This film was rougher than the film grown at 175°C , which had a RMS area roughness of $4.21\ \text{\AA}$. A possible reason for the significant difference in the RMS area roughness is that the film grown at the higher temperature was a non-optimized process; the film from this “preliminary” run was used to prove that the precursor ($[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$) was suitable as an ALD precursor. The bubbler temperature for precursor **1** in these preliminary runs was held just above room temperature at 28°C . Perhaps this temperature was not producing a high enough vapour pressure to get complete monolayers. Another possibility is that it may have been the substrate itself. The film depositions were performed on mechanical grade silicon, so the substrate may have been rough to start with. At both temperatures the AFM topography scale spans less than 10 nm, indicating flat and conformal Al_2O_3 films.

Figure 4.11: Atomic force microscope images of an Al_2O_3 film grown at 200°C over 500 cycles showing a) a derived line fit and b) a three-dimensional derived fit.

Figure 4.12: Atomic force microscope images of an Al_2O_3 film grown at 175°C over 250 cycles showing a) a derived line fit and b) a three-dimensional derived fit.

4.7. Interference Colours

Aluminum oxide is a colourless film, but because of interference patterns Al_2O_3 films can be brightly coloured. The colour of these films will vary depending on the thickness and follow the trend: bronze; purple; blue; green (Figure 4.13), in order of increasing thickness. Note that the green appears as yellow due to the direct tungsten-bulb lighting of the optical microscope used to collect this image.

Figure 4.13: Optical microscope images of Al_2O_3 thin films varying in colour due to the film thickness. Thickness ranges for each colour were measured by ellipsometry.

The interference colours were due to light interacting to produce constructive and destructive interference. The light was reflected from the surface of the thin film as well as from the back surface of the film (Figure 4.14). The reflected light waves reinforce or cancel each other to produce the visible colour of these otherwise colourless films, depending both on the films thickness and index of refraction.

Figure 4.14: A wave of light reflected from the top of the surface and from the back of the surface to cause interference colours.

The interference colours were also seen on the backside of the silicon substrate, which was a good indication that ALD growth was occurring. The ALD process is conformal and allows deposition to occur in small crevices, including on the backside of the substrate by precursors getting into the space between the substrate and substrate holder. The interference colours were seen as a ring around the outer edge of the substrate and had a colour pattern of blue, purple, bronze from the outer edge towards the centre (Figure 4.15).

Figure 4.15: Backside interference colours of an Al_2O_3 film. The speckling is due to the unpolished silicon surface.

This fade of colour can be explained as the precursor depleting as it moves from the outer edge towards the centre, resulting in thicker films around the outside and thinner films further away from the edge (Figure 4.16).

Figure 4.16: Depletion of precursor on backside of Si substrate.

4.8. Conclusions

Aluminum oxide thin films were grown using $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and H_2O as precursors. The optimal deposition parameters for these precursors were investigated for furnace temperature and pulse lengths for the $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and H_2O valves. It was found that the optimal deposition temperature was 175°C and pulse lengths of 4.0 s and 1.0 s were sufficient for saturation of the substrate with $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and H_2O , respectively. The saturation curves for both precursors demonstrated self-limiting behaviour with a growth rate plateau of $2.7 \text{ \AA}/\text{cycle}$ for $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{AlEt}_2$ and $2.3 \text{ \AA}/\text{cycle}$ for H_2O . These films were confirmed to have aluminum and oxygen present and exhibited flat and conformal surface morphologies.

The predicted mechanism of film growth is that the ethyl “anchoring” ligands react with the surface hydroxyl sites and release ethane as a byproduct, and the acetamidinate ligand acts as an “umbrella” which protects the metal centre and prevents the reaction of precursor **1** with chemisorbed species. The purging pulse and evacuation remove any additional precursor **1** and ethane. The water pulse protonates the acetamidinate ligand, freeing it from the metal centre as a volatile species and hydroxyl species bridge and terminate the aluminum atoms. Purging and evacuating the deposition chamber remove the volatile free ligand and additional water. This mechanism is summarized in equation [4.1] and depicted in Figure 4.17.

where * denotes a surface species

Figure 4.17: Proposed mechanism for ALD of Al_2O_3 .

Chapter 5: Experimental Section

5.1. General Synthetic Procedures

All manipulations were performed in a nitrogen-filled glovebox. The chemicals: aluminum trichloride, gallium trichloride, deuterated benzene, 1,3-diisopropylcarbodiimide, triethylaluminum, lithium dimethylamide, and trimethylaluminum were purchased from Aldrich Chemical Co. and used as received. All solvents used were reagent grade and purified using an MBraun Purification System. The synthesis of $[\text{MeC}(\text{N}^i\text{Pr})_2]_3\text{Al}$,³⁶ $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$,³⁷ $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3\text{Ga}$,³⁷ $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{Li}$,³² and $[\text{EtC}(\text{N}^i\text{Pr})_2]_3\text{Al}$ ³⁸ followed literature procedures.

The ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were collected on a Bruker 300 MHz spectrometer using the residual protons of the deuterated solvent for reference. Abbreviations used in assigning peaks are as follows: s = singlet, d = doublet, t = triplet, quart = quartet, sept = septet, Guelph Chemical Laboratories performed combustion analysis. Mass spectra were obtained using either the electron impact or the chemical impact method on a VG ZAB-2HF triple-focusing spectrometer.

Thermogravimetric analyses were performed in a nitrogen-filled glovebox at a ramp rate of 10°/minute.

5.2. Chloride Exchanges

5.2.1. Dimers

$[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{Al}_2\text{Cl}_4$ (1)

In a 50 mL round-bottom flask $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$ (0.814 g, 2.02 mmol) was dissolved in a 10 mL 1:1 hexane:ether mixture. Aluminum chloride (0.274 g, 2.05 mmol) was saturated with hexane (2 mL) and dissolved with diethyl ether. The AlCl_3 solution was added dropwise to the hexane/ether solution of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{AlCl}$. This produced an opaque white solution with a colourless waxy solid on the bottom. This solution was left to stir for 30 minutes at room temperature. The volatiles were removed under reduced pressure, yielding a microcrystalline colourless solid (0.961 g, 1.79 mmol, 88.7 %). Colourless, X-ray quality crystals (0.211 g, 19.5 %) were isolated from a toluene layered with hexane solution at -30°C . Mp: $89-95^\circ\text{C}$. ^1H NMR: δ 3.69 (sept, 4H, $\text{CH}(\text{CH}_3)_2$),

2.39 (s, 12H, N(CH₃)₂), 1.50 (d, 12H, CH(CH₃)₂), 1.43 (d, 12H, CH(CH₃)₂). ¹³C NMR: δ 171.25 (NC(N(CH₃)₂)N), 51.16 (CH(CH₃)₂), 41.07 (N(CH₃)₂), 23.88 (CH(CH₃)₂), 21.96 (CH(CH₃)₂). Anal. Calcd for Al₂Cl₄C₁₈H₄₀N₆: Calc.: C, 40.31; H, 7.52; N, 15.67. Found: C, 39.93; H, 7.81; N, 15.27.

[Me₂NC(NⁱPr)₂]₂Ga₂Cl₄ (2)

[Me₂NC(NⁱPr)₂]₃Ga (1.004 g, 1.73 mmol) was dissolved in 10 mL of hexane. GaCl₃ (0.616 g, 3.50 mmol) was saturated with 3 mL of hexane and dissolved with 2 mL of diethyl ether. The GaCl₃ solution was added slowly with rapid stirring to the [Me₂NC(NⁱPr)₂]₃Ga hexane solution. Upon addition the solution turned cloudy, but cleared within 20 minutes. The reaction mixture was left to stir for 2 hours at ambient temperature, at which time the volatiles were removed in vacuo. A white powder resulted (1.40 g, 2.25 mmol, 86.7%). Mp: 123-127°C. ¹H NMR: δ 3.69 (sept, 4H, CH(CH₃)₂), 2.38 (s, 12H, N(CH₃)₂), 1.49 (d, 12H, CH(CH₃)₂), 1.44 (d, 12H, CH(CH₃)₂). ¹³C NMR: δ 170.12 (NC(N(CH₃)₂)N), 51.82 (CH(CH₃)₂), 41.02 (N(CH₃)₂), 23.82 (CH(CH₃)₂), 21.87 (CH(CH₃)₂). Anal. Calcd for Ga₂Cl₄C₁₈H₄₀N₆: C, 34.77; H, 6.48; N, 13.52. Found: C, 34.76; H, 6.84; N, 12.96.

5.2.2. Bischelates of Aluminum and Gallium

[MeC(NⁱPr)₂]₂AlCl (3)

[MeC(NⁱPr)₂]₃Al (2.702 g, 6.0 mmol) was dissolved in 15 mL of hexane. AlCl₃ (0.394 g, 2.95 mmol) was saturated in 2 mL of hexane and dissolved in 4 mL of ether. The aluminum chloride solution was added slowly with rapid stirring to the [MeC(NⁱPr)₂]₃Al solution. Upon addition the reaction mixture was originally cloudy but turned translucent within ten minutes. This was left to stir at room temperature for four days. The volatiles were removed under reduced pressure and yielded a slightly yellow solid (2.328 g, 6.75 mmol, 76%). Mp: 75-77°C. ¹H NMR: δ 3.375 (sept, 4H, CH(CH₃)₂), 1.455 (s, 6H, (NC(CH₃)N), 1.231 (d, 24H, CH(CH₃)₂). ¹³C NMR: δ 173.29 (NC(CH₃)N), 45.61 (CH(CH₃)₂), 24.24 (CH(CH₃)₂), 11.12 (NC(CH₃)N). Mass spectra *m/e* (relative abundance): 344 (26.8) M⁺. Anal. Calcd for AlClC₁₆H₃₄N₄: C, 55.72; H, 9.94; N, 16.24. Found: C, 55.49; H, 10.18; N, 15.98.

[EtC(NⁱPr)₂]₂AlCl (4)

In a 50 mL flask [EtC(NⁱPr)₂]₃Al (0.976 g, 2.0 mmol) was dissolved in 10 mL of hexane. Aluminum chloride (0.138 g, 1.0 mmol) was saturated with 2 mL of hexane and dissolved with 1 mL of diethyl ether. The AlCl₃ solution was added dropwise to the [EtC(NⁱPr)₂]₃Al hexane solution and the solution changed from a light transparent yellow to a light opaque yellow solution. This was left to stir for 3 days at room temperature at which time the solution was a yellow colour with a yellow waxy substance on the sides of the round-bottom flask. The volatiles were removed under reduced pressure and a waxy yellow solid remained (0.828 g, 2.2 mmol, 71.6%). A supersaturated hexane solution was kept at -30°C for 2 days to yield colourless, X-ray quality crystals (55%). Mp: 77-80°C. ¹H NMR: δ 3.41 (sept, 4H, CH(CH₃)₂), 1.96 (quart, 4H, (NC(CH₂CH₃)N), 1.28 (d, 24H, CH(CH₃)₂), 0.83 (t, 6H, (NC(CH₂CH₃)N). ¹³C NMR: δ 177.14 (NC(CH₂CH₃)N), 45.39 (CH(CH₃)₂), 24.59 (CH(CH₃)₂), 18.27 (NC(CH₂CH₃)N), 11.06 (NC(CH₂CH₃)N). Mass spectra *m/e* (relative abundance): 372 (21.4) M⁺. Anal. Calcd for AlClC₁₈H₃₈N₄: C, 57.97; H, 10.27; N, 15.02. Found: C, 57.60; H, 10.67; N, 14.78.

[MeC(NⁱPr)₂]₃Ga (5)

[MeC(NⁱPr)₂]₂Li (0.91 g, 6.14 mmol) was suspended in 15 mL of hexane. Gallium chloride (0.363 g, 2.06 mmol) was suspended in 2 mL of hexane and dissolved in 2 mL of diethyl ether. The gallium chloride solution was added slowly to the [MeC(NⁱPr)₂]₂Li suspension with rapid stirring. The opaque, white suspension was left to stir overnight at room temperature. Lithium chloride was removed by filtration and the filtrate was dried under vacuum. A light yellow microcrystalline solid (0.0.908 g, 1.84 mmol, 89.3%) resulted. The product was dissolved in toluene and left at -30°C for 5 days, resulting in clear, colourless crystals (47.8%). Mp >320°C. ¹H NMR: δ 3.58 (sept, 6H, CH(CH₃)₂), 1.57 (s, 9H, (NC(CH₃)N), 1.27 (br, 36H, CH(CH₃)₂). ¹³C NMR: δ 164.95 (NC(CH₃)N), 47.22 (CH(CH₃)₂), 26.10 (CH(CH₃)₂), 24.33 (CH(CH₃)₂), 11.69 (NC(CH₃)N). Mass spectra *m/e* (relative abundance): 492 (0.1) M⁺. Anal. Calcd for GaC₂₄H₅₁N₆: C, 58.42; H, 10.42; N, 17.03. Found: C, 58.13; H, 10.85; N, 16.62.

[MeC(NⁱPr)₂]₂GaCl (6)

[MeC(NⁱPr)₂]₃Ga (0.65g, 1.22mmol) was dissolved in 15 mL of hexane. GaCl₃ (0.114g, 0.65mmol) was saturated with 2 mL of hexane and dissolved with 2 mL of diethyl ether. The GaCl₃ solution was added dropwise to the [MeC(NⁱPr)₂]₃Ga solution with rapid stirring, resulting in a colourless cloudy solution that cleared after 10 minutes. The solution was left to stir at room temperature overnight. The volatiles were evacuated at reduced pressure and a fine white powder resulted (0.42g, 1.08 mmol, 54.8%). The product was then redissolved in 4 mL of toluene and left at -30°C for two weeks, resulting in clear colourless crystals (0.411g, 1.06mmol, 53.6%). Mp: 102-109°C. ¹H NMR: δ 3.43 (sept, 4H, CH(CH₃)₂), 1.39 (s, 6H, (NC(CH₃)N), 1.25 (d, 24H, CH(CH₃)₂). ¹³C NMR: δ 169.13 (NC(CH₃)N), 46.73 (CH(CH₃)₂), 24.63 (CH(CH₃)₂), 11.20 (NC(CH₃)N). Mass spectra *m/e* (relative abundance): 387 (16.2) M⁺. Anal. Calcd for GaClC₁₆H₃₄N₄: C, 49.57; H, 8.84; N, 14.45. Found: C, 48.89; H, 9.23; N, 14.17.

[Me₂NC(NⁱPr)₂]₂GaCl (7)

[Me₂NC(NⁱPr)₂]₃Ga (1.27 g, 2.19 mmol) was dissolved in 8 mL of hexane. GaCl₃ (0.214 g, 1.22 mmol) was saturated with 2 mL of hexane and dissolved with 2 mL of diethyl ether. The GaCl₃ solution was added dropwise to the [Me₂NC(NⁱPr)₂]₃Ga solution with rapid stirring, resulting in a white opaque solution with a white precipitate sticking to the sides of the flask. The solution was left to stir at room temperature overnight. The volatiles were evacuated at reduced pressure and a fine white powder resulted (1.32 g, 2.96 mmol, 81.2 %). Mp: 98-107°C. ¹H NMR: δ 3.55 (sept, 4H, CH(CH₃)₂), 2.41 (s, 12H, (NC(N(CH₃)₂)N), 1.39 (d, 24H, CH(CH₃)₂). ¹³C NMR: δ 168.94 (NC(N(CH₃)₂)N), 46.76 (CH(CH₃)₂), 39.45 (NC(N(CH₃)₂)N), 24.39 (CH(CH₃)₂). Mass spectra *m/e* (relative abundance): 446 (1.4) M⁺. Anal. Calcd for GaClC₁₈H₄₀N₆: C, 48.50; H, 9.05; N, 18.85. Found: C, 48.56; H, 9.37; N, 18.80.

5.2.3. Monochelates of Aluminum

[MeC(NⁱPr)₂]₃AlCl₂ (8)

In a 50 mL flask [MeC(NⁱPr)₂]₃Al (0.635 g, 1.4 mmol) was dissolved in 10 mL of hexane. Aluminum chloride (0.374 g, 2.8 mmol) was saturated with 2 mL of hexane and dissolved in 2 mL of diethyl ether. The aluminum chloride solution was added slowly with rapid stirring to the [MeC(NⁱPr)₂]₃Al solution. The solution was clear with immiscible yellow beads of solution. This was left to stir at room temperature for 24 hours. The volatiles were removed under reduced pressure and an off-white solid resulted (0.859 g, 3.6 mmol, 85.9%). Pure sample was isolated as a microcrystalline white solid (0.540 g, 2.26 mmol, 54.0%) from pentane kept at -30°C for 24 hours. Mp: 60-63°C. ¹H NMR: δ 2.92 (sept, 2H, CH(CH₃)₂), 1.08 (s, 3H, (NC(CH₃)N), 0.91 (d, 12H, CH(CH₃)₂). ¹³C NMR: δ 177.16 (NC(CH₃)N), 45.19 (CH(CH₃)₂), 24.46 (CH(CH₃)₂), 10.1 (NC(CH₃)N). Anal. Calcd for AlC₈H₁₇N₂: C, 40.18; H, 7.17; N, 11.72. Found: C, 39.95; H, 7.52; N, 11.52.

[EtC(NⁱPr)₂]₃AlCl₂ (9)

[EtC(NⁱPr)₂]₃Al (0.649 g, 1.32 mmol) was dissolved in 8 mL of hexane. Aluminum chloride (0.351 g, 2.63 mmol) was saturated with 3 mL of hexane and dissolved with 3 mL of diethyl ether. The aluminum chloride solution was added slowly with stirring to the [EtC(NⁱPr)₂]₃Al solution. The solution initially became cloudy, but cleared within 10 minutes. The reaction mixture was left to stir at room temperature for 24 hours after which the volatiles were removed at reduced pressure. An off-white solid remained (0.80 g, 3.16 mmol, 80%). The crude product was redissolved in hexane and filtered to remove a filmy residue. The filtrate was kept at -30°C for 3 days and a white powder was obtained (0.382 g, 1.5 mmol, 38.2%). Mp: 56-64°C. ¹H NMR: δ 2.98 (sept, 2H, CH(CH₃)₂), 1.58 (quart, 2H, (NC(CH₂CH₃)N), 0.95 (d, 12H, CH(CH₃)₂), 0.55 (t, 3H, (NC(CH₂CH₃)N). ¹³C NMR: δ 180.84 (NC(CH₂CH₃)N), 45.18 (CH(CH₃)₂), 24.99 (CH(CH₃)₂), 18.48 (NC(CH₂CH₃)N), 10.97 (NC(CH₂CH₃)N). Mass spectra *m/e* (relative abundance): 252 (1.5) M⁺.

5.3. Alkyl Exchanges of Aluminum

[MeC(NⁱPr)₂]₃AlMe₂ (10)

[MeC(NⁱPr)₂]₃Al (2.273 g, 5.04 mmol) was dissolved in 7 mL of hexane.

Trimethylaluminum (2 M in hexane, 5.0 mL, 10.0 mmol) was added dropwise with rapid stirring to the [MeC(NⁱPr)₂]₃Al solution. The solution went slightly cloudy but was clear within 15 minutes. The reaction mixture was left to stir at room temperature for 3 hours. The volatiles were removed in vacuo and a yellow iridescent liquid remained (2.912 g, 14.48 mmol, 97.1%). The liquid was kept at -30°C for a week and remained a liquid. The liquid was distilled at 26°C, 110 mTorr, to yield a colourless viscous liquid (9.80 mmol, 67.3%). ¹H NMR: δ 3.13 (sept, 2H, CH(CH₃)₂), 1.29 (s, 3H, (NC(CH₃)N), 0.95 (d, 12H, CH(CH₃)₂), 0.31 (s, 6H, (Al(CH₃)₂)). ¹³C NMR: δ 171.86 (NC(CH₃)N), 45.04 (CH(CH₃)₂), 25.17 (CH(CH₃)₂), 10.29 (NC(CH₃)N), -9.22 (Al(CH₃)₂). Mass spectra *m/e* (relative abundance): 198 (1.0) M⁺.

[EtC(NⁱPr)₂]₃AlEt₂ (11)

[EtC(NⁱPr)₂]₃Al (0.683 g, 1.39 mmol) was dissolved in 8 mL of hexane.

Triethylaluminum (2.8 mL, 1 M in hexane, 2.8 mmol) was added dropwise to the [EtC(NⁱPr)₂]₃Al solution with rapid stirring. The reaction mixture was left to stir at ambient temperature for 24 hours. The volatiles were removed under reduced pressure and a yellow liquid remained (0.922 g, 4.13 mmol, 92.2%). ¹H NMR: δ 3.18 (sept, 2H, CH(CH₃)₂), 1.82 (quart, 2H, NC(CH₂CH₃)N), 1.37 (t, 6H, CH₂CH₃), 0.99 (d, 12H, CH(CH₃)₂), 0.78 (t, 3H, NC(CH₂CH₃)N), 0.30 (quart, 4H, CH₂CH₃). ¹³C NMR: δ 176.34 (NC(CH₂CH₃)N), 44.61 (CH(CH₃)₂), 25.62 (CH(CH₃)₂), 18.07 (NC(CH₂CH₃)N), 11.88 (NC(CH₂CH₃)N), 9.60 (CH₂CH₃), 0.33 (CH₂CH₃). Mass spectra *m/e* (relative abundance): 239 (1.2) M⁺.

[Me₂NC(NⁱPr)₂]₃AlMe₂ (12)

In a 50 mL round-bottom flask [Me₂NC(NⁱPr)₂]₃Al (0.783 g, 1.46 mmol) was dissolved in 10 mL of hexane. Trimethylaluminum (2 M in hexane, 1.5 mL, 3.0 mmol) was added to the hexane solution of [Me₂NC(NⁱPr)₂]₃Al dropwise with rapid stirring. The colourless solution stirred at room temperature for 4 hours. The volatiles were removed *in vacuo*

from the slightly cloudy colourless solution. A colourless low melting solid was isolated (0.933g, 4.1 mmol, 93.6%) Mp: 27-33°C. ^1H NMR: δ 3.27 (sept, 2H, $\text{CH}(\text{CH}_3)_2$), 2.23 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.03 (d, 12H, $\text{CH}(\text{CH}_3)_2$), -0.21 (s, 6H, CH_3). ^{13}C NMR: δ 167.2 ($\text{NC}(\text{N}(\text{CH}_3)_2)\text{N}$), 45.07 ($\text{CH}(\text{CH}_3)_2$), 38.44 ($\text{N}(\text{CH}_3)_2$), 24.39 ($\text{CH}(\text{CH}_3)_2$), -8.18 (CH_3).

[Me₂NC(NⁱPr)₂]AlEt₂ (13)

In a 50 mL round-bottom flask [Me₂NC(NⁱPr)₂]₃Al (0.702 g, 1.31 mmol) was dissolved in 10 mL of hexane. Triethylaluminum (1 M in hexane, 3.6 mL, 3.6 mmol) was added to the hexane solution of [Me₂NC(NⁱPr)₂]₃Al dropwise with rapid stirring. The colourless solution stirred at room temperature for 48 hours. The volatiles were removed *in vacuo* from the slightly yellow solution, leaving a slightly yellow viscous liquid. This liquid was distilled at 40°C, 90 mTorr to yield a colourless viscous liquid (2.25 mmol, 61.3%). The product was kept at -30°C for 2 weeks and remained a liquid. ^1H NMR: δ 3.25 (sept, 2H, $\text{CH}(\text{CH}_3)_2$), 2.23 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.50 (t, 6H, CH_2CH_3), 1.02 (d, 12H, $\text{CH}(\text{CH}_3)_2$), 0.39 (quart, 4H, CH_2CH_3). ^{13}C NMR: δ 167.41 ($\text{NC}(\text{N}(\text{CH}_3)_2)\text{N}$), 44.77 ($\text{CH}(\text{CH}_3)_2$), 38.53 ($\text{N}(\text{CH}_3)_2$), 24.55 ($\text{CH}(\text{CH}_3)_2$), 10.18 (CH_2CH_3), 1.34 (CH_2CH_3). Mass spectra *m/e* (relative abundance): 254 (3.6) M^+ .

5.4. Structural Determination for Compounds 1, 2, 4 and 6

A suitable data crystal was mounted with viscous oil on a fibre loop and cooled to the data collection temperature. Unit cell parameters were determined using 60 data frames from three different sections of the Ewald sphere. Systematic absences in the diffraction data were consistent for *Cc* and *C2/c* in complexes **4** and **6**, and, uniquely, for *Pbca* in complex **1** and **2**. SADABS multi-scan absorption corrections were applied. The structures were solved using direct methods and refined with full matrix least squares procedures on F^2 data. Two isopropyl groups were located disordered each in two positions with refined site occupancies of roughly 60/40 for complex **1**. A half-occupied molecule of co-crystallized toluene solvent was found severely disordered in the asymmetric unit in complex **1** and was treated as diffused contributions using the Squeeze filter in the Platon program.⁷¹ All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized

contributions. Structure factors are contained in the SHELXTL program library (Sheldrick, G., Bruker-AXS, Inc., Madison WI, 2001).

Conclusions

The mechanism for ligand exchange in amidinates and guanidines was investigated experimentally and theoretically. It was discovered that ligand exchange between guanidines and chlorides must proceed through a dimeric intermediate where the metal centre is bridged by two guanidine ligands. The mechanism of ligand exchange is partially driven by entropy and can be controlled stoichiometrically.

The exchange chemistry between parent homoleptic six-coordinate amidinate and guanidine species, $[RC(N^iPr)_2]_3M$ (where $R = NMe_2, Me, Et$ and $M = Al, Ga$), and homoleptic three-coordinate aluminum and gallium compounds (trimethylaluminum, triethylaluminum, aluminum chloride and gallium chloride) to form species of the type $[RC(N^iPr)_2]_{3-x}MR'_x$ (where $R' = Me, Et, Cl$ and $x = 1-3$) was studied. The thermal stability of these products was demonstrated by thermogravimetric analysis. The monoamidinate species ($[RC(N^iPr)_2]MR'_2$) are the most thermally stable of the complexes studied. The TGA of these compounds showed little to no decomposition at elevated temperatures and demonstrated the volatile nature of these complexes.

The atomic layer deposition of aluminum oxide thin films was investigated using $[MeC(N^iPr)_2]AlEt_2$ and water. Surface morphologies were studied by scanning electron microscopy and atomic force microscopy, which showed the ability to grow conformal and flat films by ALD using these precursors. Thickness measurements were determined by ellipsometry. Energy dispersive X-ray and wavelength dispersive X-ray spectroscopy were used to confirm the presence of aluminum and oxygen. The aluminum source, $[MeC(N^iPr)_2]AlEt_2$, was found to be an effective precursor in the ALD of aluminum oxide. The growth rates of these thin films varied between 2.3-2.7 Å/cycle and with a root mean square surface roughness as low as 4.21 Å.

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Appendix 1: Crystallographic Data for Compounds 1, 2, 4, 6**Compound 1**

data_seab005s

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'C21.50 H44 Al2 Cl4 N6'
_chemical_formula_weight    582.39

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'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Al' 'Al' 0.0645 0.0514
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl' 0.1484 0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M  Pbca

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'-x+1/2, -y, z+1/2'
'-x, y+1/2, -z+1/2'
'x+1/2, -y+1/2, -z'
'-x, -y, -z'

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'x-1/2, y, -z-1/2'
 'x, -y-1/2, z-1/2'
 '-x-1/2, y-1/2, z'

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 _cell_length_b 14.935(6)
 _cell_length_c 31.025(9)
 _cell_angle_alpha 90.00
 _cell_angle_beta 90.00
 _cell_angle_gamma 90.00
 _cell_volume 6201(4)
 _cell_formula_units_Z 8
 _cell_measurement_temperature 120(2)
 _cell_measurement_reflns_used 982
 _cell_measurement_theta_min 2.63
 _cell_measurement_theta_max 27.70

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 _exptl_crystal_size_mid 0.39
 _exptl_crystal_size_min 0.08
 _exptl_crystal_density_meas ?
 _exptl_crystal_density_diffn 1.248
 _exptl_crystal_density_method 'not measured'
 _exptl_crystal_F_000 2472
 _exptl_absorpt_coefficient_mu 0.460
 _exptl_absorpt_correction_type multi-scan
 _exptl_absorpt_correction_T_min 0.8304
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 _exptl_absorpt_process_details 'SADABS, Sheldrick (2003)'

_exptl_special_details

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Data collection is performed with four batch runs at
 $\varphi = 0.00^\circ$ (600 frames), at $\varphi = 90.00^\circ$
 (600 frames), at $\varphi = 180^\circ$ (600 frames) and
 at $\varphi = 270^\circ$ (600 frames).

Frame width = 0.30 $^\circ$ in φ . Data is
 merged, corrected for decay, and treated with
 multi-scan absorption corrections.

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 _diffn_radiation_wavelength 0.71073
 _diffn_radiation_type MoK α

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_diffrn_radiation_monochromator graphite
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_diffrn_detector_area_resol_mean 836.6
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_diffrn_reflns_limit_k_min      -16
_diffrn_reflns_limit_k_max      16
_diffrn_reflns_limit_l_min      -33
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_diffrn_reflns_theta_min        2.01
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_computing_cell_refinement      'SHELXTL, Sheldrick (2001)'
_computing_data_reduction       'SHELXTL, Sheldrick (2001)'
_computing_structure_solution   'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics   'SHELXTL, Sheldrick (2001)'
_computing_publication_material 'SHELXTL, Sheldrick (2001)'

_refine_special_details
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Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on  $F^2$ , conventional R-factors R are based
on F, with F set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on  $F^2$  are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;
# SQUEEZE RESULTS (APPEND TO CIF)
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_platon_squeeze_void_average_z
_platon_squeeze_void_volume
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  2  0.000  0.500  0.500  224.2  53.8
  3  0.180  0.403  0.346   7.3  -0.6
  4  0.180  0.097  0.846   7.4  -0.6
  5  0.500  0.000  0.500  224.2  54.1
  6  0.500  0.500  1.000  224.2  53.8
  7  0.319  0.903  0.346   7.3  -0.7
  8  0.319  0.597  0.846   7.4  -0.6
  9  0.680  0.403  0.154   7.4  -0.6
 10  0.680  0.097  0.654   7.5  -0.6
 11  0.819  0.903  0.154   7.4  -0.6
 12  0.819  0.597  0.654   7.4  -0.6
_platon_squeeze_details
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PLATON Reference : Spek, A.L. (2003), J.Appl.Cryst. 36, 7-13
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_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.1198P)^2^+16.7306P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens  geom
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_refine_ls_extinction_method    none
_refine_ls_extinction_coef      ?
_refine_ls_number_reflns        4047
_refine_ls_number_parameters    299
_refine_ls_number_restraints    338
_refine_ls_R_factor_all         0.0832
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loop_
  _atom_site_label

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_atom_site_fract_z
_atom_site_U_iso_or_equiv
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_atom_site_occupancy
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Al2 Al 0.09630(9) 0.51619(11) 0.11830(4) 0.0436(4) Uani 1 1 d U A .
Cl1 Cl -0.25066(10) 0.59309(11) 0.15904(6) 0.0832(6) Uani 1 1 d U . .
Cl2 Cl -0.08059(14) 0.74434(11) 0.20746(5) 0.0823(5) Uani 1 1 d U . .
Cl3 Cl 0.20725(9) 0.43930(11) 0.15302(4) 0.0667(5) Uani 1 1 d U . .
Cl4 Cl 0.13050(10) 0.50807(11) 0.05060(4) 0.0610(4) Uani 1 1 d U . .
N1 N -0.0390(3) 0.5305(3) 0.19421(13) 0.0474(9) Uani 1 1 d U . .
N2 N -0.0846(3) 0.3775(3) 0.19219(14) 0.0567(11) Uani 1 1 d U . .
N3 N -0.0217(3) 0.4523(2) 0.13073(12) 0.0388(9) Uani 1 1 d U . .
N4 N 0.1139(3) 0.6387(3) 0.12919(12) 0.0487(10) Uani 1 1 d U . .
N5 N 0.0754(4) 0.7718(3) 0.09166(15) 0.0623(12) Uani 1 1 d U . .
N6 N -0.0499(3) 0.6697(2) 0.11293(12) 0.0425(9) Uani 1 1 d U . .
C1 C -0.0061(12) 0.5005(13) 0.2399(6) 0.0487(18) Uani 0.341(7) 1 d PDU A 1
H1A H -0.0015 0.4338 0.2413 0.058 Uiso 0.341(7) 1 calc PR A 1
C1' C -0.0021(6) 0.5452(6) 0.2408(3) 0.0487(18) Uani 0.659(7) 1 d PDU A 2
H1'A H 0.0423 0.5990 0.2397 0.058 Uiso 0.659(7) 1 calc PR A 2
C2 C -0.085(3) 0.534(2) 0.2709(12) 0.067(3) Uani 0.341(7) 1 d PDU A 1
H2A H -0.0652 0.5206 0.3006 0.100 Uiso 0.341(7) 1 calc PR A 1
H2B H -0.1491 0.5042 0.2647 0.100 Uiso 0.341(7) 1 calc PR A 1
H2C H -0.0934 0.5989 0.2675 0.100 Uiso 0.341(7) 1 calc PR A 1
C2' C -0.0796(13) 0.5649(8) 0.2748(5) 0.067(3) Uani 0.659(7) 1 d PDU A 2
H2'A H -0.1210 0.6154 0.2655 0.100 Uiso 0.659(7) 1 calc PR A 2
H2'B H -0.0462 0.5801 0.3019 0.100 Uiso 0.659(7) 1 calc PR A 2
H2'C H -0.1218 0.5120 0.2790 0.100 Uiso 0.659(7) 1 calc PR A 2
C3 C 0.0959(11) 0.5413(10) 0.2450(5) 0.0516(16) Uani 0.341(7) 1 d PDU A 1
H3A H 0.1431 0.5110 0.2258 0.077 Uiso 0.341(7) 1 calc PR A 1
H3B H 0.1180 0.5346 0.2749 0.077 Uiso 0.341(7) 1 calc PR A 1
H3C H 0.0929 0.6051 0.2376 0.077 Uiso 0.341(7) 1 calc PR A 1
C3' C 0.0633(6) 0.4686(5) 0.2549(2) 0.0516(16) Uani 0.659(7) 1 d PDU A 2
H3'A H 0.1199 0.4627 0.2351 0.077 Uiso 0.659(7) 1 calc PR A 2
H3'B H 0.0244 0.4130 0.2548 0.077 Uiso 0.659(7) 1 calc PR A 2
H3'C H 0.0883 0.4801 0.2841 0.077 Uiso 0.659(7) 1 calc PR A 2
C4 C -0.0484(3) 0.4516(3) 0.17267(16) 0.0445(11) Uani 1 1 d U A .
C5 C -0.1672(4) 0.3804(5) 0.2227(2) 0.0769(18) Uani 1 1 d U A .

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H5A H -0.1415 0.3727 0.2520 0.115 Uiso 1 1 calc R . .
 H5B H -0.2144 0.3321 0.2161 0.115 Uiso 1 1 calc R . .
 H5C H -0.2014 0.4382 0.2204 0.115 Uiso 1 1 calc R . .
 C6 C -0.0445(5) 0.2887(4) 0.1841(2) 0.0813(19) Uani 1 1 d U A .
 H6A H 0.0200 0.2939 0.1694 0.122 Uiso 1 1 calc R . .
 H6B H -0.0911 0.2550 0.1659 0.122 Uiso 1 1 calc R . .
 H6C H -0.0355 0.2572 0.2115 0.122 Uiso 1 1 calc R . .
 C7 C -0.0750(4) 0.3902(3) 0.10053(16) 0.0488(12) Uani 1 1 d U A .
 H7A H -0.1258 0.3563 0.1176 0.059 Uiso 1 1 calc R . .
 C8 C -0.0064(5) 0.3224(4) 0.0790(2) 0.0709(17) Uani 1 1 d U . .
 H8A H 0.0325 0.2910 0.1011 0.106 Uiso 1 1 calc R A .
 H8B H 0.0391 0.3535 0.0593 0.106 Uiso 1 1 calc R . .
 H8C H -0.0466 0.2791 0.0628 0.106 Uiso 1 1 calc R . .
 C9 C -0.1304(4) 0.4446(3) 0.06629(17) 0.0523(13) Uani 1 1 d U . .
 H9A H -0.1724 0.4897 0.0804 0.078 Uiso 1 1 calc R A .
 H9B H -0.1726 0.4046 0.0491 0.078 Uiso 1 1 calc R . .
 H9C H -0.0819 0.4744 0.0475 0.078 Uiso 1 1 calc R . .
 C10 C 0.2019(6) 0.6927(8) 0.1481(2) 0.045(2) Uani 0.653(12) 1 d PDU A 1
 H10A H 0.1945 0.7575 0.1406 0.054 Uiso 0.653(12) 1 calc PR A 1
 C10' C 0.2156(12) 0.6444(13) 0.1506(5) 0.045(2) Uani 0.347(12) 1 d PDU A 2
 H10B H 0.2178 0.5964 0.1730 0.054 Uiso 0.347(12) 1 calc PR A 2
 C11 C 0.3015(9) 0.6566(11) 0.1305(5) 0.055(3) Uani 0.653(12) 1 d PDU A 1
 H11A H 0.3568 0.6918 0.1424 0.083 Uiso 0.653(12) 1 calc PR A 1
 H11B H 0.3019 0.6612 0.0990 0.083 Uiso 0.653(12) 1 calc PR A 1
 H11C H 0.3093 0.5938 0.1389 0.083 Uiso 0.653(12) 1 calc PR A 1
 C11' C 0.3062(18) 0.630(2) 0.1210(10) 0.055(3) Uani 0.347(12) 1 d PDU A 2
 H11D H 0.2856 0.5953 0.0956 0.083 Uiso 0.347(12) 1 calc PR A 2
 H11E H 0.3579 0.5966 0.1367 0.083 Uiso 0.347(12) 1 calc PR A 2
 H11F H 0.3328 0.6878 0.1119 0.083 Uiso 0.347(12) 1 calc PR A 2
 C12 C 0.2006(6) 0.6811(5) 0.1971(2) 0.0461(16) Uani 0.677(8) 1 d PDU A 1
 H12A H 0.2687 0.6870 0.2083 0.069 Uiso 0.677(8) 1 calc PR A 1
 H12B H 0.1744 0.6217 0.2043 0.069 Uiso 0.677(8) 1 calc PR A 1
 H12C H 0.1579 0.7271 0.2100 0.069 Uiso 0.677(8) 1 calc PR A 1
 C12' C 0.2121(12) 0.7329(10) 0.1743(5) 0.0461(16) Uani 0.323(8) 1 d PDU A 2
 H12D H 0.1424 0.7492 0.1800 0.069 Uiso 0.323(8) 1 calc PR A 2
 H12E H 0.2436 0.7794 0.1566 0.069 Uiso 0.323(8) 1 calc PR A 2
 H12F H 0.2481 0.7274 0.2017 0.069 Uiso 0.323(8) 1 calc PR A 2
 C13 C 0.0470(4) 0.6946(3) 0.11065(15) 0.0473(11) Uani 1 1 d U A .
 C14 C 0.1627(4) 0.7776(5) 0.0637(2) 0.0765(18) Uani 1 1 d U A .
 H14A H 0.1859 0.7172 0.0566 0.115 Uiso 1 1 calc R . .
 H14B H 0.2161 0.8103 0.0785 0.115 Uiso 1 1 calc R . .
 H14C H 0.1448 0.8093 0.0371 0.115 Uiso 1 1 calc R . .
 C15 C 0.0229(6) 0.8561(4) 0.0993(3) 0.087(2) Uani 1 1 d U A .
 H15A H -0.0319 0.8461 0.1197 0.130 Uiso 1 1 calc R . .
 H15B H -0.0043 0.8785 0.0720 0.130 Uiso 1 1 calc R . .
 H15C H 0.0695 0.9002 0.1112 0.130 Uiso 1 1 calc R . .

C16 C -0.1225(4) 0.6872(3) 0.07760(18) 0.0518(12) Uani 1 1 d U A .
 H16 H -0.1655 0.6325 0.0765 0.062 Uiso 1 1 calc R . .
 C17 C -0.0753(4) 0.6935(3) 0.03322(17) 0.0555(13) Uani 1 1 d U . .
 H17A H -0.1273 0.6880 0.0111 0.083 Uiso 1 1 calc R A .
 H17B H -0.0264 0.6452 0.0297 0.083 Uiso 1 1 calc R . .
 H17C H -0.0417 0.7515 0.0302 0.083 Uiso 1 1 calc R . .
 C18 C -0.1947(4) 0.7645(4) 0.0856(2) 0.0711(17) Uani 1 1 d U . .
 H18A H -0.2141 0.7653 0.1161 0.107 Uiso 1 1 calc R A .
 H18B H -0.2543 0.7567 0.0677 0.107 Uiso 1 1 calc R . .
 H18C H -0.1620 0.8212 0.0782 0.107 Uiso 1 1 calc R . .

loop_

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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
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 Al2 0.0244(7) 0.0701(10) 0.0363(8) 0.0042(7) -0.0004(5) 0.0026(6)
 Cl1 0.0330(7) 0.0852(11) 0.1313(14) 0.0486(10) 0.0202(8) 0.0077(7)
 Cl2 0.1076(13) 0.0671(10) 0.0721(10) -0.0088(8) 0.0344(9) 0.0147(9)
 Cl3 0.0327(7) 0.1095(12) 0.0579(8) 0.0024(7) -0.0084(6) 0.0214(7)
 Cl4 0.0473(8) 0.0946(11) 0.0412(7) -0.0055(6) 0.0060(5) -0.0053(7)
 N1 0.031(2) 0.068(3) 0.043(2) 0.0102(19) 0.0084(16) -0.0014(18)
 N2 0.045(2) 0.062(3) 0.064(3) 0.036(2) -0.004(2) 0.003(2)
 N3 0.0288(18) 0.044(2) 0.044(2) 0.0124(16) -0.0026(16) 0.0051(16)
 N4 0.0324(19) 0.081(3) 0.0325(19) 0.0007(19) 0.0020(16) -0.0199(19)
 N5 0.071(3) 0.057(3) 0.059(3) 0.005(2) 0.005(2) -0.034(2)
 N6 0.039(2) 0.037(2) 0.051(2) 0.0054(17) 0.0036(17) -0.0071(16)
 C1 0.062(4) 0.041(5) 0.042(3) 0.006(4) 0.021(3) -0.011(4)
 C1' 0.062(4) 0.041(5) 0.042(3) 0.006(4) 0.021(3) -0.011(4)
 C2 0.096(5) 0.050(10) 0.054(4) -0.002(6) 0.037(4) -0.008(6)
 C2' 0.096(5) 0.050(10) 0.054(4) -0.002(6) 0.037(4) -0.008(6)
 C3 0.062(4) 0.051(4) 0.042(4) 0.003(3) -0.010(3) -0.008(3)
 C3' 0.062(4) 0.051(4) 0.042(4) 0.003(3) -0.010(3) -0.008(3)
 C4 0.022(2) 0.056(3) 0.055(3) 0.020(2) -0.008(2) 0.005(2)
 C5 0.050(3) 0.095(4) 0.086(4) 0.045(4) 0.002(3) -0.017(3)
 C6 0.100(5) 0.068(4) 0.076(4) 0.044(3) -0.017(3) 0.019(3)
 C7 0.052(3) 0.038(3) 0.056(3) 0.014(2) -0.014(2) -0.001(2)
 C8 0.096(5) 0.047(3) 0.069(4) 0.005(3) -0.018(3) 0.014(3)
 C9 0.052(3) 0.044(3) 0.061(3) 0.018(2) -0.020(2) -0.010(2)
 C10 0.044(3) 0.053(6) 0.038(3) -0.003(4) 0.000(2) -0.015(4)
 C10' 0.044(3) 0.053(6) 0.038(3) -0.003(4) 0.000(2) -0.015(4)
 C11 0.034(3) 0.094(11) 0.037(7) -0.011(5) -0.002(3) -0.028(4)

C11' 0.034(3) 0.094(11) 0.037(7) -0.011(5) -0.002(3) -0.028(4)
 C12 0.058(4) 0.043(4) 0.037(3) -0.004(3) -0.001(3) -0.021(3)
 C12' 0.058(4) 0.043(4) 0.037(3) -0.004(3) -0.001(3) -0.021(3)
 C13 0.047(3) 0.055(3) 0.040(3) -0.007(2) 0.006(2) -0.021(2)
 C14 0.064(4) 0.102(5) 0.064(4) 0.018(3) -0.001(3) -0.041(3)
 C15 0.106(5) 0.049(3) 0.105(5) -0.003(3) 0.007(4) -0.036(3)
 C16 0.043(3) 0.039(3) 0.074(3) 0.010(2) -0.004(2) -0.009(2)
 C17 0.057(3) 0.045(3) 0.065(3) 0.011(2) -0.018(2) -0.005(2)
 C18 0.063(4) 0.047(3) 0.104(5) 0.021(3) 0.005(3) 0.012(3)

_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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Al1 N6 1.880(4) . ?

Al1 C12 2.153(2) . ?

Al1 C11 2.155(2) . ?

Al2 N4 1.875(5) . ?

Al2 N3 1.886(4) . ?

Al2 C14 2.153(2) . ?

Al2 C13 2.1643(19) . ?

N1 C4 1.360(7) . ?

N1 C1' 1.542(10) . ?

N1 C1 1.550(19) . ?

N2 C4 1.351(6) . ?

N2 C6 1.452(8) . ?

N2 C5 1.456(7) . ?

N3 C4 1.349(6) . ?

N3 C7 1.498(6) . ?

N4 C13 1.353(7) . ?

N4 C10' 1.516(17) . ?

N4 C10 1.543(9) . ?

N5 C13 1.350(6) . ?

N5 C14 1.458(7) . ?
 N5 C15 1.461(8) . ?
 N6 C13 1.351(6) . ?
 N6 C16 1.487(6) . ?
 C1 C3 1.502(15) . ?
 C1 C2 1.519(16) . ?
 C1' C3' 1.507(10) . ?
 C1' C2' 1.508(10) . ?
 C7 C8 1.520(8) . ?
 C7 C9 1.530(6) . ?
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 C10 C11 1.539(11) . ?
 C10' C12' 1.513(15) . ?
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 N6 A11 C11 107.18(15) . . ?
 C12 A11 C11 110.58(9) . . ?
 N4 A12 N3 124.23(18) . . ?
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 N3 A12 C14 110.43(14) . . ?
 N4 A12 C13 109.98(14) . . ?
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 C4 N1 C1 103.0(8) . . ?
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 C1' N1 A11 116.7(4) . . ?
 C1 N1 A11 139.8(8) . . ?
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 C6 N2 C5 114.8(5) . . ?

C4 N3 C7 118.2(4) .. ?
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 C7 N3 A12 125.7(3) .. ?
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 C13 N4 A12 116.2(3) .. ?
 C10' N4 A12 104.3(8) .. ?
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 C3' C1' N1 110.5(7) .. ?
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 Al1 N1 C1 C2 40.2(18) ?
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Al1 N1 C1' C2' 66.1(8) ?
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 C1' N1 C4 N3 -140.4(5) ?
 C1 N1 C4 N3 -144.2(7) ?
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 C1' N1 C4 N2 40.9(7) ?
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 C13 N4 C10 C11 -126.2(9) ?
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 Al2 N4 C10 C11 40.4(10) ?
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 C16 N6 C13 N4 -144.5(4) ?
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 C10' N4 C13 N5 27.6(12) ?
 C10 N4 C13 N5 32.0(6) ?
 Al2 N4 C13 N5 -137.0(4) ?
 C10' N4 C13 N6 -151.2(10) ?
 C10 N4 C13 N6 -146.8(5) ?
 Al2 N4 C13 N6 44.2(5) ?
 C13 N6 C16 C17 27.1(6) ?

Al1 N6 C16 C17 -163.1(3) ?
C13 N6 C16 C18 -103.5(5) ?
Al1 N6 C16 C18 66.3(5) ?

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_refine_diff_density_rms 0.084

Compound 2

data_seab018s

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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H'  0.0000  0.0000
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'N' 'N'  0.0061  0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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'Ga' 'Ga'  0.2307  1.6083
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M  Pbca

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'-x, -y, -z'
'x-1/2, y, -z-1/2'
'x, -y-1/2, z-1/2'
'-x-1/2, y-1/2, z'

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_cell_formula_units_Z  8
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_exptl_crystal_F_000        2960
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_exptl_absorpt_correction_type multi-scan
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Data collection is performed with four batch runs at
\>f = 0.00 \% (600 frames), at \>f = 90.00 \%
(600 frames), at \>f = 180 \% (600 frames) and
at \>f = 270 \% (600 frames).
Frame width = 0.30 \& in \>w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
_computing_publication_material SHELXTL

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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

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;
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_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2)+(0.1000P)^2^] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary    direct
_atom_sites_solution_secondary  difmap

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_refine_ls_extinction_method none
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_refine_ls_number_parameters 287
_refine_ls_number_restraints 3
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_refine_ls_R_factor_gt 0.0608
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_refine_ls_goodness_of_fit_ref 1.025
_refine_ls_restrained_S_all 1.025
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loop_

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_atom_site_symmetry_multiplicity
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Ga2 Ga -0.09695(5) 0.12809(5) 0.33325(2) 0.0580(3) Uani 1 1 d . A .
Cl1 Cl 0.13361(13) 0.00761(13) 0.45116(5) 0.0680(5) Uani 1 1 d . . .
Cl2 Cl 0.20995(12) -0.06450(13) 0.34700(6) 0.0685(5) Uani 1 1 d . . .
Cl3 Cl -0.25468(13) 0.09204(15) 0.34106(7) 0.0895(7) Uani 1 1 d . . .
Cl4 Cl -0.08251(17) 0.24653(13) 0.29196(6) 0.0861(6) Uani 1 1 d . . .
N1 N 0.1139(4) 0.1398(4) 0.37155(15) 0.0526(14) Uani 1 1 d . . .
N2 N -0.0500(3) 0.1708(3) 0.38805(15) 0.0480(12) Uani 1 1 d . . .
N3 N 0.0755(4) 0.2706(4) 0.40927(18) 0.0706(17) Uani 1 1 d . . .
N4 N -0.0217(3) -0.0504(3) 0.36856(16) 0.0474(12) Uani 1 1 d . . .
N5 N -0.0404(4) 0.0273(4) 0.30507(16) 0.0540(14) Uani 1 1 d D . .
N6 N -0.0839(4) -0.1246(4) 0.30798(18) 0.0637(16) Uani 1 1 d . . .
C1 C 0.0469(5) 0.1952(5) 0.38992(19) 0.0551(17) Uani 1 1 d . . .
C2 C 0.2054(5) 0.1779(7) 0.3516(2) 0.095(3) Uani 1 1 d . . .
H2A H 0.2016 0.2413 0.3615 0.114 Uiso 1 1 calc R . .
C3 C 0.3031(5) 0.1471(6) 0.3733(2) 0.082(2) Uani 1 1 d . . .

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H3A H 0.3602 0.1667 0.3560 0.122 Uiso 1 1 calc R . .
 H3B H 0.3035 0.0819 0.3755 0.122 Uiso 1 1 calc R . .
 H3C H 0.3077 0.1733 0.4022 0.122 Uiso 1 1 calc R . .
 C4 C 0.2032(7) 0.1885(7) 0.3075(3) 0.138(5) Uani 1 1 d . . .
 H4A H 0.1351 0.2030 0.2984 0.206 Uiso 1 1 calc R . .
 H4B H 0.2246 0.1329 0.2936 0.206 Uiso 1 1 calc R . .
 H4C H 0.2483 0.2370 0.2992 0.206 Uiso 1 1 calc R . .
 C5 C 0.0238(7) 0.3559(5) 0.4017(3) 0.091(3) Uani 1 1 d . . .
 H5A H -0.0292 0.3472 0.3803 0.137 Uiso 1 1 calc R . .
 H5B H 0.0716 0.4001 0.3909 0.137 Uiso 1 1 calc R . .
 H5C H -0.0054 0.3772 0.4287 0.137 Uiso 1 1 calc R . .
 C6 C 0.1623(6) 0.2767(6) 0.4371(2) 0.085(3) Uani 1 1 d . . .
 H6A H 0.1880 0.2167 0.4430 0.128 Uiso 1 1 calc R . .
 H6B H 0.1434 0.3055 0.4643 0.128 Uiso 1 1 calc R . .
 H6C H 0.2142 0.3122 0.4229 0.128 Uiso 1 1 calc R . .
 C7 C -0.1240(5) 0.1872(4) 0.4225(2) 0.0603(18) Uani 1 1 d . . .
 H7A H -0.1666 0.1324 0.4233 0.072 Uiso 1 1 calc R . .
 C8 C -0.0779(5) 0.1940(4) 0.4678(2) 0.0639(18) Uani 1 1 d . . .
 H8A H -0.0283 0.1466 0.4716 0.096 Uiso 1 1 calc R . .
 H8B H -0.1305 0.1875 0.4896 0.096 Uiso 1 1 calc R . .
 H8C H -0.0456 0.2524 0.4712 0.096 Uiso 1 1 calc R . .
 C9 C -0.1951(5) 0.2633(5) 0.4141(2) 0.079(2) Uani 1 1 d . . .
 H9A H -0.2103 0.2661 0.3832 0.119 Uiso 1 1 calc R . .
 H9B H -0.1643 0.3196 0.4232 0.119 Uiso 1 1 calc R . .
 H9C H -0.2569 0.2536 0.4303 0.119 Uiso 1 1 calc R . .
 C10 C -0.0496(4) -0.0498(5) 0.3265(2) 0.0506(16) Uani 1 1 d . A .
 C11 C -0.0732(5) -0.1118(4) 0.3996(2) 0.0537(16) Uani 1 1 d . . .
 H11A H -0.1241 -0.1466 0.3831 0.064 Uiso 1 1 calc R . .
 C12 C -0.1279(5) -0.0566(4) 0.4334(2) 0.0577(17) Uani 1 1 d . . .
 H12A H -0.1719 -0.0136 0.4191 0.086 Uiso 1 1 calc R . .
 H12B H -0.0792 -0.0245 0.4512 0.086 Uiso 1 1 calc R . .
 H12C H -0.1677 -0.0963 0.4518 0.086 Uiso 1 1 calc R . .
 C13 C -0.0040(6) -0.1777(4) 0.4214(2) 0.074(2) Uani 1 1 d . . .
 H13A H 0.0292 -0.2144 0.3995 0.111 Uiso 1 1 calc R . .
 H13B H -0.0427 -0.2163 0.4407 0.111 Uiso 1 1 calc R . .
 H13C H 0.0463 -0.1452 0.4381 0.111 Uiso 1 1 calc R . .
 C14 C -0.0046(6) 0.0323(7) 0.2595(2) 0.094(3) Uani 0.670(9) 1 d PD A 1
 H14A H 0.0372 0.0877 0.2597 0.113 Uiso 0.670(9) 1 calc PR A 1
 C15 C 0.0613(8) -0.0310(6) 0.2442(3) 0.057(2) Uani 0.670(9) 1 d PD A 1
 H15A H 0.1183 -0.0356 0.2639 0.086 Uiso 0.670(9) 1 calc PR A 1
 H15B H 0.0848 -0.0135 0.2155 0.086 Uiso 0.670(9) 1 calc PR A 1
 H15C H 0.0276 -0.0890 0.2424 0.086 Uiso 0.670(9) 1 calc PR A 1
 C16 C -0.0858(7) 0.0555(7) 0.2263(3) 0.101(3) Uani 0.670(9) 1 d PD A 1
 H16A H -0.0544 0.0727 0.1990 0.152 Uiso 0.670(9) 1 calc PR A 1
 H16B H -0.1263 0.1052 0.2371 0.152 Uiso 0.670(9) 1 calc PR A 1
 H16C H -0.1286 0.0033 0.2216 0.152 Uiso 0.670(9) 1 calc PR A 1

C14' C -0.0046(6) 0.0323(7) 0.2595(2) 0.094(3) Uani 0.330(9) 1 d PD A 2
 H14B H -0.0058 -0.0335 0.2541 0.113 Uiso 0.330(9) 1 calc PR A 2
 C15' C 0.0940(12) 0.0421(13) 0.2537(6) 0.057(2) Uani 0.330(9) 1 d PD A 2
 H15D H 0.1295 0.0205 0.2792 0.086 Uiso 0.330(9) 1 calc PR A 2
 H15E H 0.1095 0.1054 0.2492 0.086 Uiso 0.330(9) 1 calc PR A 2
 H15F H 0.1151 0.0077 0.2284 0.086 Uiso 0.330(9) 1 calc PR A 2
 C16' C -0.0858(7) 0.0555(7) 0.2263(3) 0.101(3) Uani 0.330(9) 1 d PD A 2
 H16D H -0.0544 0.0726 0.1990 0.152 Uiso 0.670(9) 1 calc PR A 2
 H16E H -0.1262 0.1053 0.2371 0.152 Uiso 0.670(9) 1 calc PR A 2
 H16F H -0.1287 0.0033 0.2217 0.152 Uiso 0.670(9) 1 calc PR A 2
 C17 C -0.0430(6) -0.2125(5) 0.3151(3) 0.089(3) Uani 1 1 d . A .
 H17A H 0.0219 -0.2072 0.3295 0.133 Uiso 1 1 calc R . .
 H17B H -0.0344 -0.2429 0.2874 0.133 Uiso 1 1 calc R . .
 H17C H -0.0886 -0.2471 0.3333 0.133 Uiso 1 1 calc R . .
 C18 C -0.1689(5) -0.1225(6) 0.2769(2) 0.087(3) Uani 1 1 d . A .
 H18A H -0.2010 -0.0637 0.2779 0.130 Uiso 1 1 calc R . .
 H18B H -0.2176 -0.1686 0.2847 0.130 Uiso 1 1 calc R . .
 H18C H -0.1439 -0.1337 0.2477 0.130 Uiso 1 1 calc R . .

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 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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 Ga2 0.0456(4) 0.0614(5) 0.0669(5) -0.0062(4) -0.0175(3) 0.0024(3)
 Cl1 0.0537(10) 0.1055(14) 0.0448(9) 0.0063(9) -0.0056(7) -0.0078(9)
 Cl2 0.0369(8) 0.1020(14) 0.0667(10) 0.0001(9) 0.0108(7) 0.0175(9)
 Cl3 0.0395(10) 0.0982(14) 0.1307(18) -0.0428(13) -0.0174(10) 0.0071(9)
 Cl4 0.1129(17) 0.0725(13) 0.0729(12) 0.0073(10) -0.0293(11) 0.0172(12)
 N1 0.039(3) 0.076(4) 0.042(3) 0.000(3) 0.003(2) -0.020(3)
 N2 0.035(3) 0.053(3) 0.055(3) -0.001(2) -0.001(2) -0.003(2)
 N3 0.075(4) 0.067(4) 0.069(4) -0.008(3) -0.007(3) -0.029(3)
 N4 0.037(3) 0.049(3) 0.055(3) -0.011(2) 0.003(2) 0.005(2)
 N5 0.038(3) 0.081(4) 0.043(3) -0.013(3) -0.006(2) -0.004(3)
 N6 0.049(3) 0.071(4) 0.071(4) -0.041(3) 0.001(3) 0.004(3)
 C1 0.058(4) 0.065(4) 0.042(3) 0.013(3) -0.009(3) -0.019(4)
 C2 0.048(4) 0.195(9) 0.041(4) 0.009(5) 0.000(3) -0.043(5)
 C3 0.036(4) 0.138(7) 0.071(5) -0.015(5) 0.009(3) -0.031(4)
 C4 0.074(6) 0.198(11) 0.141(9) 0.120(9) 0.008(6) 0.013(7)
 C5 0.105(7) 0.060(5) 0.109(6) 0.001(5) 0.006(5) -0.023(5)
 C6 0.079(5) 0.119(7) 0.057(4) -0.028(4) 0.005(4) -0.038(5)
 C7 0.047(4) 0.046(4) 0.088(5) -0.012(4) 0.007(3) -0.002(3)

C8 0.064(4) 0.049(4) 0.078(5) -0.007(4) 0.022(4) -0.002(3)
 C9 0.073(5) 0.060(5) 0.106(6) -0.017(4) -0.009(4) 0.016(4)
 C10 0.026(3) 0.064(4) 0.061(4) -0.028(4) 0.005(3) 0.003(3)
 C11 0.065(4) 0.041(4) 0.055(4) -0.016(3) 0.010(3) -0.002(3)
 C12 0.055(4) 0.053(4) 0.065(4) -0.022(3) 0.019(3) -0.011(3)
 C13 0.095(6) 0.050(4) 0.078(5) 0.000(4) 0.018(4) 0.016(4)
 C14 0.064(5) 0.174(9) 0.044(4) -0.002(5) -0.020(4) -0.008(6)
 C15 0.075(6) 0.044(5) 0.052(5) 0.000(4) 0.012(4) -0.002(5)
 C16 0.120(7) 0.123(7) 0.061(5) -0.007(5) -0.044(5) 0.008(6)
 C14' 0.064(5) 0.174(9) 0.044(4) -0.002(5) -0.020(4) -0.008(6)
 C15' 0.075(6) 0.044(5) 0.052(5) 0.000(4) 0.012(4) -0.002(5)
 C16' 0.120(7) 0.123(7) 0.061(5) -0.007(5) -0.044(5) 0.008(6)
 C17 0.104(7) 0.073(5) 0.090(6) -0.040(5) 0.019(5) 0.013(5)
 C18 0.055(5) 0.119(7) 0.087(6) -0.041(5) -0.008(4) -0.012(4)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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 Ga1 C11 2.194(2) . ?
 Ga1 C12 2.2075(18) . ?
 Ga2 N5 1.902(5) . ?
 Ga2 N2 1.923(5) . ?
 Ga2 C13 2.195(2) . ?
 Ga2 C14 2.197(2) . ?
 N1 C1 1.348(8) . ?
 N1 C2 1.488(8) . ?
 N2 C1 1.351(7) . ?
 N2 C7 1.479(8) . ?
 N3 C1 1.335(8) . ?
 N3 C6 1.453(9) . ?
 N3 C5 1.472(10) . ?

N4 C10 1.358(8) . ?
 N4 C11 1.498(8) . ?
 N5 C10 1.338(8) . ?
 N5 C14 1.497(9) . ?
 N6 C10 1.340(7) . ?
 N6 C17 1.443(9) . ?
 N6 C18 1.493(8) . ?
 C2 C4 1.377(10) . ?
 C2 C3 1.543(10) . ?
 C7 C9 1.508(9) . ?
 C7 C8 1.539(9) . ?
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 C14 C15 1.380(11) . ?
 C14 C16 1.537(10) . ?

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 N4 Ga1 C11 112.03(16) . . ?
 N1 Ga1 C12 111.17(16) . . ?
 N4 Ga1 C12 100.65(15) . . ?
 C11 Ga1 C12 107.90(8) . . ?
 N5 Ga2 N2 122.7(2) . . ?
 N5 Ga2 C13 103.85(16) . . ?
 N2 Ga2 C13 107.39(15) . . ?
 N5 Ga2 C14 109.72(19) . . ?
 N2 Ga2 C14 102.62(16) . . ?
 C13 Ga2 C14 110.36(9) . . ?
 C1 N1 C2 119.3(6) . . ?
 C1 N1 Ga1 116.9(4) . . ?
 C2 N1 Ga1 122.8(5) . . ?
 C1 N2 C7 124.6(5) . . ?
 C1 N2 Ga2 116.3(4) . . ?
 C7 N2 Ga2 118.5(4) . . ?
 C1 N3 C6 123.4(7) . . ?
 C1 N3 C5 121.8(6) . . ?
 C6 N3 C5 114.7(6) . . ?
 C10 N4 C11 119.7(5) . . ?

C10 N4 Ga1 116.0(4) . . ?
 C11 N4 Ga1 123.5(4) . . ?
 C10 N5 C14 122.9(6) . . ?
 C10 N5 Ga2 114.8(4) . . ?
 C14 N5 Ga2 121.5(5) . . ?
 C10 N6 C17 124.5(6) . . ?
 C10 N6 C18 121.4(6) . . ?
 C17 N6 C18 114.2(6) . . ?
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 N3 C1 N2 121.6(7) . . ?
 N1 C1 N2 117.1(6) . . ?
 C4 C2 N1 116.1(6) . . ?
 C4 C2 C3 119.1(7) . . ?
 N1 C2 C3 113.8(6) . . ?
 N2 C7 C9 115.0(6) . . ?
 N2 C7 C8 113.8(5) . . ?
 C9 C7 C8 111.2(5) . . ?
 N5 C10 N6 122.7(6) . . ?
 N5 C10 N4 117.3(5) . . ?
 N6 C10 N4 120.0(7) . . ?
 N4 C11 C13 113.9(5) . . ?
 N4 C11 C12 109.4(5) . . ?
 C13 C11 C12 109.8(6) . . ?
 C15 C14 N5 119.6(8) . . ?
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 C12 Ga1 N1 C1 177.3(4) ?
 N4 Ga1 N1 C2 -134.3(4) ?
 C11 Ga1 N1 C2 99.7(4) ?
 C12 Ga1 N1 C2 -14.6(5) ?
 N5 Ga2 N2 C1 59.0(5) ?
 C13 Ga2 N2 C1 179.0(4) ?

Cl4 Ga2 N2 C1 -64.7(5) ?
 N5 Ga2 N2 C7 -129.8(4) ?
 Cl3 Ga2 N2 C7 -9.9(4) ?
 Cl4 Ga2 N2 C7 106.5(4) ?
 N1 Ga1 N4 C10 59.0(5) ?
 Cl1 Ga1 N4 C10 -179.9(4) ?
 Cl2 Ga1 N4 C10 -65.5(4) ?
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 Cl1 Ga1 N4 C11 -10.2(4) ?
 Cl2 Ga1 N4 C11 104.2(4) ?
 N2 Ga2 N5 C10 62.8(5) ?
 Cl3 Ga2 N5 C10 -58.8(4) ?
 Cl4 Ga2 N5 C10 -176.8(4) ?
 N2 Ga2 N5 C14 -127.1(5) ?
 Cl3 Ga2 N5 C14 111.2(5) ?
 Cl4 Ga2 N5 C14 -6.7(5) ?
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 C5 N3 C1 N1 134.1(7) ?
 C6 N3 C1 N2 137.5(7) ?
 C5 N3 C1 N2 -46.2(9) ?
 C2 N1 C1 N3 -32.7(8) ?
 Ga1 N1 C1 N3 135.9(5) ?
 C2 N1 C1 N2 147.6(5) ?
 Ga1 N1 C1 N2 -43.9(7) ?
 C7 N2 C1 N3 -35.4(9) ?
 Ga2 N2 C1 N3 135.1(5) ?
 C7 N2 C1 N1 144.3(6) ?
 Ga2 N2 C1 N1 -45.1(7) ?
 C1 N1 C2 C4 -98.8(10) ?
 Ga1 N1 C2 C4 93.4(10) ?
 C1 N1 C2 C3 117.3(8) ?
 Ga1 N1 C2 C3 -50.5(8) ?
 C1 N2 C7 C9 103.3(7) ?
 Ga2 N2 C7 C9 -67.1(6) ?
 C1 N2 C7 C8 -26.7(8) ?
 Ga2 N2 C7 C8 162.9(4) ?
 C14 N5 C10 N6 -39.4(8) ?
 Ga2 N5 C10 N6 130.6(5) ?
 C14 N5 C10 N4 140.1(6) ?
 Ga2 N5 C10 N4 -49.9(6) ?
 C17 N6 C10 N5 138.9(7) ?
 C18 N6 C10 N5 -40.0(9) ?
 C17 N6 C10 N4 -40.6(9) ?
 C18 N6 C10 N4 140.6(6) ?
 C11 N4 C10 N5 149.2(5) ?
 Ga1 N4 C10 N5 -40.7(6) ?

C11 N4 C10 N6 -31.3(8) ?
 Ga1 N4 C10 N6 138.9(5) ?
 C10 N4 C11 C13 120.4(6) ?
 Ga1 N4 C11 C13 -48.9(6) ?
 C10 N4 C11 C12 -116.2(6) ?
 Ga1 N4 C11 C12 74.4(6) ?
 C10 N5 C14 C15 -29.9(11) ?
 Ga2 N5 C14 C15 160.8(7) ?
 C10 N5 C14 C16 107.9(8) ?
 Ga2 N5 C14 C16 -61.3(9) ?

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 _diffn_reflns_theta_full 25.00
 _diffn_measured_fraction_theta_full 1.000
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 _refine_diff_density_rms 0.084

SQUEEZE RESULTS (APPEND TO CIF)

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_platon_squeeze_void_count_electrons						
1	0.000	0.000	0.000	279.8	23.7	
2	0.000	0.500	0.500	279.8	23.8	
3	0.167	0.902	0.156	9.5	-0.2	
4	0.167	0.598	0.656	9.9	-0.2	
5	0.500	0.500	0.000	279.8	24.3	
6	0.500	0.000	0.500	279.8	23.9	
7	0.333	0.402	0.156	9.4	-0.2	
8	0.333	0.098	0.656	9.7	-0.2	
9	0.667	0.902	0.344	9.3	-0.2	
10	0.667	0.598	0.844	9.6	-0.3	
11	0.832	0.402	0.344	9.1	-0.2	
12	0.832	0.098	0.844	9.4	-0.2	

_platon_squeeze_details

;

Reference : Spek, A.L. (2003), J.Appl.Cryst. 36, 7-13

Void space analysis is consistent with 1 molecule of
cocrystallized toluene per asymmetric unit.

;

Compound 4

data_seab009

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;
?
;
_chemical_name_common      ?
_chemical_melting_point    ?
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'C18 H38 Al Cl N4'
_chemical_formula_weight    372.95

loop_
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_atom_type_description
_atom_type_scatter_dispersion_real
_atom_type_scatter_dispersion_imag
_atom_type_scatter_source
'C' 'C'  0.0033  0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H'  0.0000  0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N'  0.0061  0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Al' 'Al'  0.0645  0.0514
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl'  0.1484  0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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loop_
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'x+1/2, y+1/2, z'
'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x, -y, z-1/2'
'-x+1/2, -y+1/2, -z'
'x+1/2, -y+1/2, z-1/2'

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_cell_length_c      15.060(3)
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_cell_angle_gamma    90.00
_cell_volume         2207.8(6)
_cell_formula_units_Z  4
_cell_measurement_temperature 120(2)
_cell_measurement_reflns_used  985
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_exptl_crystal_F_000        816
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_exptl_absorpt_correction_T_max 0.9074
_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

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Data collection is performed with four batch runs at
\(\varphi = 0.00^\circ\) (600 frames), at \(\varphi = 90.00^\circ\)
(600 frames), at \(\varphi = 180^\circ\) (600 frames) and
at \(\varphi = 270^\circ\) (600 frames).
Frame width = 0.30 mm in \(\omega\). Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_radiation_wavelength 0.71073
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_diffn_radiation_monochromator graphite
_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'

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_diffn_reflns_number           8812
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_diffn_reflns_limit_l_max      19
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_reflns_number_gt              2261
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_computing_structure_solution   'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics   'SHELXTL (Sheldrick, 2001)'
_computing_publication_material SHELXTL

_refine_special_details
;
Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on  $F^2$ , conventional R-factors R are based
on F, with F set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on  $F^2$  are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[ $s^2(F_o^2)+(0.0602P)^2+0.8074P$ ] where  $P=(F_o^2+2F_c^2)/3$ '
_atom_sites_solution_primary    direct

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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
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_refine_ls_extinction_method none
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loop_

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_atom_site_symmetry_multiplicity
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_atom_site_refinement_flags
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Al Al 1.0000 0.54828(5) 0.2500 0.01932(13) Uani 1 2 d S . .
Cl Cl 1.0000 0.27540(5) 0.2500 0.03267(14) Uani 1 2 d S . .
N1 N 0.89503(5) 0.57270(11) 0.18569(6) 0.0221(2) Uani 1 1 d . . .
N2 N 0.98679(5) 0.68066(11) 0.14081(6) 0.0222(2) Uani 1 1 d . . .
C1 C 0.82101(6) 0.50650(14) 0.17740(8) 0.0256(2) Uani 1 1 d . . .
H1A H 0.7845 0.5940 0.1498 0.031 Uiso 1 1 calc R . .
C2 C 0.80693(6) 0.35210(15) 0.11648(8) 0.0304(3) Uani 1 1 d . . .
H2A H 0.8130 0.3802 0.0554 0.046 Uiso 1 1 calc R . .
H2B H 0.7569 0.3123 0.1114 0.046 Uiso 1 1 calc R . .
H2C H 0.8419 0.2647 0.1435 0.046 Uiso 1 1 calc R . .
C3 C 0.81162(7) 0.46379(19) 0.27234(10) 0.0411(3) Uani 1 1 d . . .
H3A H 0.8160 0.5653 0.3093 0.062 Uiso 1 1 calc R . .
H3B H 0.8496 0.3844 0.3020 0.062 Uiso 1 1 calc R . .
H3C H 0.7632 0.4141 0.2668 0.062 Uiso 1 1 calc R . .
C4 C 1.02347(6) 0.79544(14) 0.09073(8) 0.0251(2) Uani 1 1 d . . .

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H4A H 0.9860 0.8762 0.0570 0.030 Uiso 1 1 calc R . .
 C5 C 1.05458(8) 0.70300(17) 0.02062(9) 0.0370(3) Uani 1 1 d . . .
 H5A H 1.0146 0.6487 -0.0241 0.055 Uiso 1 1 calc R . .
 H5B H 1.0896 0.6188 0.0518 0.055 Uiso 1 1 calc R . .
 H5C H 1.0796 0.7820 -0.0109 0.055 Uiso 1 1 calc R . .
 C6 C 1.08256(7) 0.89364(15) 0.15772(9) 0.0326(3) Uani 1 1 d . . .
 H6A H 1.0603 0.9549 0.2003 0.049 Uiso 1 1 calc R . .
 H6B H 1.1057 0.9723 0.1237 0.049 Uiso 1 1 calc R . .
 H6C H 1.1197 0.8168 0.1922 0.049 Uiso 1 1 calc R . .
 C7 C 0.91377(6) 0.66329(13) 0.12192(7) 0.0221(2) Uani 1 1 d . . .
 C8 C 0.86126(6) 0.74540(15) 0.04226(8) 0.0276(2) Uani 1 1 d . . .
 H8A H 0.8173 0.6747 0.0212 0.033 Uiso 1 1 calc R . .
 H8B H 0.8849 0.7583 -0.0092 0.033 Uiso 1 1 calc R . .
 C9 C 0.83862(7) 0.91621(15) 0.07089(9) 0.0333(3) Uani 1 1 d . . .
 H9A H 0.8090 0.9740 0.0171 0.050 Uiso 1 1 calc R . .
 H9B H 0.8826 0.9820 0.0975 0.050 Uiso 1 1 calc R . .
 H9C H 0.8098 0.9021 0.1164 0.050 Uiso 1 1 calc R . .

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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12

Al 0.0214(2) 0.0188(2) 0.0195(2) 0.000 0.00817(16) 0.000
 Cl 0.0362(2) 0.0189(2) 0.0403(3) 0.000 0.00462(17) 0.000
 N1 0.0210(4) 0.0225(5) 0.0241(5) 0.0004(3) 0.0081(3) -0.0021(3)
 N2 0.0224(4) 0.0229(4) 0.0231(4) 0.0027(3) 0.0090(3) -0.0005(3)
 C1 0.0221(5) 0.0262(6) 0.0309(6) -0.0020(4) 0.0108(4) -0.0037(4)
 C2 0.0276(5) 0.0283(6) 0.0362(6) -0.0047(5) 0.0096(5) -0.0055(4)
 C3 0.0402(7) 0.0522(8) 0.0374(7) -0.0074(6) 0.0222(6) -0.0190(6)
 C4 0.0272(5) 0.0234(5) 0.0277(6) 0.0056(4) 0.0124(4) -0.0006(4)
 C5 0.0479(7) 0.0371(7) 0.0339(7) -0.0003(5) 0.0251(6) -0.0058(5)
 C6 0.0349(6) 0.0263(6) 0.0400(7) -0.0008(5) 0.0156(5) -0.0072(5)
 C7 0.0248(5) 0.0202(5) 0.0225(5) -0.0021(4) 0.0081(4) -0.0003(4)
 C8 0.0255(5) 0.0295(6) 0.0269(6) 0.0036(4) 0.0045(4) -0.0009(4)
 C9 0.0304(6) 0.0289(6) 0.0406(7) 0.0083(5) 0.0086(5) 0.0052(4)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

;

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Al N2 1.9225(10) 2_755 ?
Al N2 1.9226(10) . ?
Al N1 1.9841(9) . ?
Al N1 1.9841(9) 2_755 ?
Al Cl 2.1933(7) . ?
Al C7 2.3802(11) 2_755 ?
Al C7 2.3803(11) . ?
N1 C7 1.3205(14) . ?
N1 C1 1.4674(13) . ?
N2 C7 1.3404(13) . ?
N2 C4 1.4673(13) . ?
C1 C3 1.5225(17) . ?
C1 C2 1.5271(16) . ?
C4 C5 1.5213(16) . ?
C4 C6 1.5246(16) . ?
C7 C8 1.5057(15) . ?
C8 C9 1.5305(17) . ?
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  _geom_angle_atom_site_label_2
  _geom_angle_atom_site_label_3
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  _geom_angle_site_symmetry_1
  _geom_angle_site_symmetry_3
  _geom_angle_publ_flag
N2 Al N2 112.79(6) 2_755 . ?
N2 Al N1 105.43(4) 2_755 . ?
N2 Al N1 67.94(4) . . ?
N2 Al N1 67.95(4) 2_755 2_755 ?
N2 Al N1 105.43(4) . 2_755 ?
N1 Al N1 168.65(6) . 2_755 ?
N2 Al Cl 123.60(3) 2_755 . ?
N2 Al Cl 123.60(3) . . ?
N1 Al Cl 95.68(3) . . ?
N1 Al Cl 95.68(3) 2_755 . ?
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N2 Al C7 34.25(4) 2_755 2_755 ?
 N2 Al C7 113.37(4) . 2_755 ?
 N1 Al C7 139.04(4) . 2_755 ?
 N1 Al C7 33.70(4) 2_755 2_755 ?
 Cl Al C7 112.85(3) . 2_755 ?
 N2 Al C7 113.37(4) 2_755 . ?
 N2 Al C7 34.25(4) . . ?
 N1 Al C7 33.69(4) . . ?
 N1 Al C7 139.04(4) 2_755 . ?
 Cl Al C7 112.85(3) . . ?
 C7 Al C7 134.29(5) 2_755 . ?
 C7 N1 C1 123.79(9) . . ?
 C7 N1 Al 89.84(6) . . ?
 C1 N1 Al 144.67(8) . . ?
 C7 N2 C4 122.96(9) . . ?
 C7 N2 Al 91.92(6) . . ?
 C4 N2 Al 144.05(7) . . ?
 N1 C1 C3 109.23(9) . . ?
 N1 C1 C2 111.49(9) . . ?
 C3 C1 C2 109.74(10) . . ?
 N2 C4 C5 111.10(9) . . ?
 N2 C4 C6 110.13(9) . . ?
 C5 C4 C6 111.67(10) . . ?
 N1 C7 N2 110.29(9) . . ?
 N1 C7 C8 125.49(9) . . ?
 N2 C7 C8 124.11(10) . . ?
 N1 C7 Al 56.46(6) . . ?
 N2 C7 Al 53.83(5) . . ?
 C8 C7 Al 176.78(8) . . ?
 C7 C8 C9 110.02(10) . . ?

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 _geom_torsion_atom_site_label_3
 _geom_torsion_atom_site_label_4
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 _geom_torsion_site_symmetry_1
 _geom_torsion_site_symmetry_2
 _geom_torsion_site_symmetry_3
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 N2 Al N1 C7 0.37(6) ?
 N1 Al N1 C7 56.32(6) 2_755 . . . ?
 Cl Al N1 C7 -123.67(6) ?

C7 Al N1 C7 101.10(10) 2_755 ... ?
 N2 Al N1 C1 -87.56(13) 2_755 ... ?
 N2 Al N1 C1 163.67(14) ... ?
 N1 Al N1 C1 -140.39(13) 2_755 ... ?
 Cl Al N1 C1 39.62(13) ... ?
 C7 Al N1 C1 -95.60(14) 2_755 ... ?
 C7 Al N1 C1 163.29(16) ... ?
 N2 Al N2 C7 -98.48(6) 2_755 ... ?
 N1 Al N2 C7 -0.37(6) ... ?
 N1 Al N2 C7 -170.63(6) 2_755 ... ?
 Cl Al N2 C7 81.52(6) ... ?
 C7 Al N2 C7 -135.81(7) 2_755 ... ?
 N2 Al N2 C4 68.32(12) 2_755 ... ?
 N1 Al N2 C4 166.43(14) ... ?
 N1 Al N2 C4 -3.83(14) 2_755 ... ?
 Cl Al N2 C4 -111.69(12) ... ?
 C7 Al N2 C4 30.98(14) 2_755 ... ?
 C7 Al N2 C4 166.79(17) ... ?
 C7 N1 C1 C3 -160.07(11) ... ?
 Al N1 C1 C3 40.16(17) ... ?
 C7 N1 C1 C2 78.47(13) ... ?
 Al N1 C1 C2 -81.29(15) ... ?
 C7 N2 C4 C5 -101.49(12) ... ?
 Al N2 C4 C5 94.30(15) ... ?
 C7 N2 C4 C6 134.25(11) ... ?
 Al N2 C4 C6 -29.96(17) ... ?
 C1 N1 C7 N2 -168.99(9) ... ?
 Al N1 C7 N2 -0.53(9) ... ?
 C1 N1 C7 C8 14.65(17) ... ?
 Al N1 C7 C8 -176.89(10) ... ?
 C1 N1 C7 Al -168.46(11) ... ?
 C4 N2 C7 N1 -170.25(10) ... ?
 Al N2 C7 N1 0.55(9) ... ?
 C4 N2 C7 C8 6.17(16) ... ?
 Al N2 C7 C8 176.97(10) ... ?
 C4 N2 C7 Al -170.80(12) ... ?
 N2 Al C7 N1 -82.77(7) 2_755 ... ?
 N2 Al C7 N1 -179.38(10) ... ?
 N1 Al C7 N1 -165.53(7) 2_755 ... ?
 Cl Al C7 N1 63.99(6) ... ?
 C7 Al C7 N1 -116.01(6) 2_755 ... ?
 N2 Al C7 N2 96.61(8) 2_755 ... ?
 N1 Al C7 N2 179.38(10) ... ?
 N1 Al C7 N2 13.86(9) 2_755 ... ?
 Cl Al C7 N2 -116.63(6) ... ?
 C7 Al C7 N2 63.37(6) 2_755 ... ?

N2 Al C7 C8 45.5(14) 2_755 ... ?
N2 Al C7 C8 -51.1(14) ?
N1 Al C7 C8 128.3(14) ?
N1 Al C7 C8 -37.2(14) 2_755 ... ?
Cl Al C7 C8 -167.7(14) ?
C7 Al C7 C8 12.3(14) 2_755 ... ?
N1 C7 C8 C9 86.12(13) ?
N2 C7 C8 C9 -89.76(13) ?
Al C7 C8 C9 -40.4(14) ?

_diffn_measured_fraction_theta_max 0.926
_diffn_reflns_theta_full 25.00
_diffn_measured_fraction_theta_full 0.998
_refine_diff_density_max 0.341
_refine_diff_density_min -0.118
_refine_diff_density_rms 0.048

Compound 6

data_seab011

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_audit_creation_method      SHELXL-97
_chemical_name_systematic
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?
;
_chemical_name_common      ?
_chemical_melting_point    ?
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_atom_type_scatter_source
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl' 0.1484 0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Ga' 'Ga' 0.2307 1.6083
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting      Monoclinic
_symmetry_space_group_name_H-M Cc

```

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loop_
_symmetry_equiv_pos_as_xyz
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'-x, y, -z+1/2'
'x+1/2, y+1/2, z'
'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x, -y, z-1/2'
'-x+1/2, -y+1/2, -z'
'x+1/2, -y+1/2, z-1/2'

```

```

_cell_length_a      11.505(8)
_cell_length_b      12.788(8)
_cell_length_c      14.102(9)
_cell_angle_alpha    90.00
_cell_angle_beta     108.130(9)
_cell_angle_gamma    90.00
_cell_volume         1972(2)
_cell_formula_units_Z 4
_cell_measurement_temperature 120(2)
_cell_measurement_reflns_used 938
_cell_measurement_theta_min 2.45
_cell_measurement_theta_max 28.01

_exptl_crystal_description block
_exptl_crystal_colour colorless
_exptl_crystal_size_max 0.68
_exptl_crystal_size_mid 0.60
_exptl_crystal_size_min 0.55
_exptl_crystal_density_meas ?
_exptl_crystal_density_diffn 1.306
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000 824
_exptl_absorpt_coefficient_mu 1.534
_exptl_absorpt_correction_type multi-scan
_exptl_absorpt_correction_T_min 0.4241
_exptl_absorpt_correction_T_max 0.4880
_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

_exptl_special_details
;
Data collection is performed with four batch runs at
\<math>\varphi</math> = 0.00 \% (600 frames), at \<math>\varphi</math> = 90.00 \%
(600 frames), at \<math>\varphi</math> = 180 \% (600 frames) and
at \<math>\varphi</math> = 270 \% (600 frames).
Frame width = 0.30 \& in \<math>w</math>. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_radiation_wavelength 0.71073
_diffn_radiation_type MoK\<math>\alpha</math>
_diffn_radiation_source 'fine-focus sealed tube'
_diffn_radiation_monochromator graphite
_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'

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_diffn_detector_area_resol_mean 836.6
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_diffn_standards_decay_%       1
_diffn_reflns_number           7012
_diffn_reflns_av_R_equivalents  0.0461
_diffn_reflns_av_sigmaI/netI    0.0415
_diffn_reflns_limit_h_min      -14
_diffn_reflns_limit_h_max      14
_diffn_reflns_limit_k_min      -16
_diffn_reflns_limit_k_max      16
_diffn_reflns_limit_l_min      -18
_diffn_reflns_limit_l_max      18
_diffn_reflns_theta_min        2.45
_diffn_reflns_theta_max        28.17
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_reflns_number_gt              2046
_reflns_threshold_expression    >2sigma(I)

_computing_data_collection      'SMART (Bruker, 2002)'
_computing_cell_refinement      'SAINT (Bruker, 2002)'
_computing_data_reduction       SAINT
_computing_structure_solution    'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics    'SHELXTL (Sheldrick, 2001)'
_computing_publication_material SHELXTL

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_refine_special_details
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;
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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

```
;
```

```

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[s^2*(Fo^2)+(0.0550P)^2] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary    direct

```



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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment constr
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_number_reflns 2206
_refine_ls_number_parameters 101
_refine_ls_number_restraints 0
_refine_ls_R_factor_all 0.0305
_refine_ls_R_factor_gt 0.0281
_refine_ls_wR_factor_ref 0.0843
_refine_ls_wR_factor_gt 0.0827
_refine_ls_goodness_of_fit_ref 1.046
_refine_ls_restrained_S_all 1.046
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loop_

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_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
Ga Ga 0.5000 0.240534(18) 0.7500 0.01914(11) Uani 1 2 d S . .
Cl Cl 0.5000 0.41276(4) 0.7500 0.02868(16) Uani 1 2 d S . .
N1 N 0.35102(12) 0.16481(10) 0.67866(10) 0.0218(3) Uani 1 1 d . . .
N2 N 0.47405(12) 0.21547(12) 0.59553(10) 0.0209(3) Uani 1 1 d . . .
C1 C 0.37288(14) 0.16473(12) 0.59033(12) 0.0209(3) Uani 1 1 d . . .
C2 C 0.29002(15) 0.11248(14) 0.49859(11) 0.0258(3) Uani 1 1 d . . .
H2A H 0.3005 0.1453 0.4390 0.039 Uiso 1 1 calc R . .
H2B H 0.2048 0.1200 0.4975 0.039 Uiso 1 1 calc R . .
H2C H 0.3108 0.0381 0.4995 0.039 Uiso 1 1 calc R . .
C3 C 0.26209(14) 0.09697(12) 0.70338(11) 0.0228(3) Uani 1 1 d . . .
H3A H 0.2005 0.0737 0.6397 0.027 Uiso 1 1 calc R . .
C4 C 0.32538(16) 0.00001(15) 0.75988(14) 0.0331(4) Uani 1 1 d . . .
H4A H 0.3670 -0.0376 0.7192 0.050 Uiso 1 1 calc R . .
H4B H 0.2643 -0.0458 0.7736 0.050 Uiso 1 1 calc R . .
H4C H 0.3854 0.0214 0.8230 0.050 Uiso 1 1 calc R . .

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C5 C 0.19605(16) 0.15855(15) 0.76314(14) 0.0315(4) Uani 1 1 d . . .
 H5A H 0.1565 0.2198 0.7247 0.047 Uiso 1 1 calc R . .
 H5B H 0.2550 0.1815 0.8261 0.047 Uiso 1 1 calc R . .
 H5C H 0.1340 0.1141 0.7772 0.047 Uiso 1 1 calc R . .
 C6 C 0.50262(17) 0.24978(12) 0.50564(14) 0.0250(4) Uani 1 1 d . . .
 H6A H 0.4236 0.2650 0.4526 0.030 Uiso 1 1 calc R . .
 C7 C 0.57616(17) 0.35056(16) 0.52784(15) 0.0346(4) Uani 1 1 d . . .
 H7A H 0.5314 0.4030 0.5535 0.052 Uiso 1 1 calc R . .
 H7B H 0.5890 0.3766 0.4665 0.052 Uiso 1 1 calc R . .
 H7C H 0.6555 0.3371 0.5779 0.052 Uiso 1 1 calc R . .
 C8 C 0.56996(17) 0.16605(15) 0.46547(14) 0.0334(4) Uani 1 1 d . . .
 H8A H 0.5208 0.1020 0.4514 0.050 Uiso 1 1 calc R . .
 H8B H 0.6491 0.1513 0.5153 0.050 Uiso 1 1 calc R . .
 H8C H 0.5831 0.1912 0.4040 0.050 Uiso 1 1 calc R . .

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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12

Ga 0.01834(15) 0.02099(17) 0.01710(16) 0.000 0.00406(11) 0.000
 Cl 0.0337(3) 0.0205(3) 0.0340(3) 0.000 0.0137(2) 0.000
 N1 0.0220(6) 0.0249(7) 0.0164(6) 0.0000(5) 0.0031(5) -0.0035(5)
 N2 0.0227(6) 0.0242(7) 0.0156(6) 0.0025(5) 0.0058(5) 0.0031(5)
 C1 0.0230(7) 0.0199(8) 0.0185(8) 0.0023(6) 0.0044(6) 0.0061(6)
 C2 0.0261(7) 0.0293(9) 0.0194(8) -0.0030(6) 0.0033(6) 0.0019(7)
 C3 0.0221(7) 0.0263(8) 0.0186(7) 0.0005(6) 0.0045(6) -0.0037(6)
 C4 0.0329(8) 0.0299(9) 0.0362(10) 0.0100(8) 0.0102(7) -0.0007(7)
 C5 0.0283(8) 0.0380(10) 0.0294(9) -0.0009(7) 0.0107(7) -0.0037(7)
 C6 0.0243(8) 0.0341(10) 0.0182(8) 0.0059(6) 0.0089(7) 0.0061(6)
 C7 0.0411(10) 0.0348(10) 0.0337(10) 0.0082(8) 0.0201(8) 0.0013(8)
 C8 0.0343(9) 0.0433(12) 0.0264(9) -0.0027(7) 0.0147(8) 0.0037(7)
 N1b 0.0220(6) 0.0249(7) 0.0164(6) 0.0000(5) 0.0031(5) -0.0035(5)
 N2b 0.0227(6) 0.0242(7) 0.0156(6) 0.0025(5) 0.0058(5) 0.0031(5)
 C1b 0.0230(7) 0.0199(8) 0.0185(8) 0.0023(6) 0.0044(6) 0.0061(6)
 C2b 0.0261(7) 0.0293(9) 0.0194(8) -0.0030(6) 0.0033(6) 0.0019(7)
 C3b 0.0221(7) 0.0263(8) 0.0186(7) 0.0005(6) 0.0045(6) -0.0037(6)
 C4b 0.0329(8) 0.0299(9) 0.0362(10) 0.0100(8) 0.0102(7) -0.0007(7)
 C5b 0.0283(8) 0.0380(10) 0.0294(9) -0.0009(7) 0.0107(7) -0.0037(7)
 C6b 0.0243(8) 0.0341(10) 0.0182(8) 0.0059(6) 0.0089(7) 0.0061(6)
 C7b 0.0411(10) 0.0348(10) 0.0337(10) 0.0082(8) 0.0201(8) 0.0013(8)
 C8b 0.0343(9) 0.0433(12) 0.0264(9) -0.0027(7) 0.0147(8) 0.0037(7)

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Ga N2 2.1289(19) 2_656 ?
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Ga C1 2.2025(16) . ?
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Ga C1 2.4696(19) . ?
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Ga C1 2.4697(19) 2_656 ?
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N1 C1 1.345(2) . ?
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N1 C3 1.464(2) . ?
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N2 C1 1.315(2) . ?
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N2 C6 1.472(2) . ?
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C1 C2 1.504(2) . ?
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C3 C5 1.519(3) . ?
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C3 C4 1.530(2) . ?
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C6 C7 1.520(3) . ?
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N1 Ga N2 105.88(6) 2_656 . ?
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N1 Ga N2 105.87(6) . 2_656 ?
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N1 Ga N2 64.99(6) 2_656 2_656 ?
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N2 Ga N2 162.68(8) . 2_656 ?
 N1 Ga C1 119.72(4) . . ?
 N1 Ga C1 119.72(4) 2_656 . ?
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 Cl Ga C1 113.11(4) . . ?
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 Cl Ga C1 113.11(4) . 2_656 ?
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 C1 N1 C3 124.47(13) . . ?
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 N1 C1 Ga 51.96(9) . . ?
 C2 C1 Ga 174.74(12) . . ?
 N1 C3 C5 109.41(14) . . ?
 N1 C3 C4 110.46(13) . . ?
 C5 C3 C4 111.75(15) . . ?
 N2 C6 C7 109.55(15) . . ?
 N2 C6 C8 112.62(14) . . ?
 C7 C6 C8 110.86(16) . . ?

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 Cl Ga N1 C3 -112.76(15) ... ?
 C1 Ga N1 C3 160.2(2) ... ?
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 N2 Ga N2 C1 59.74(9) 2_656 ... ?
 Cl Ga N2 C1 -120.26(9) ... ?
 C1 Ga N2 C1 101.88(14) 2_656 ... ?
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 Cl Ga N2 C6 38.0(2) ... ?
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 C3 N1 C1 N2 -166.05(14) ... ?
 Ga N1 C1 N2 -2.18(13) ... ?
 C3 N1 C1 C2 14.0(2) ... ?
 Ga N1 C1 C2 177.86(13) ... ?
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 N1 Ga C1 N2 177.64(14) ... ?
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 Cl Ga C1 N2 68.20(10) ... ?
 C1 Ga C1 N2 -111.81(10) 2_656 ... ?
 N1 Ga C1 N1 105.52(12) 2_656 ... ?
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 Cl Ga C1 N1 -109.44(9) ... ?
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 N1 Ga C1 C2 -19.9(12) ... ?
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 N2 Ga C1 C2 162.4(13) ... ?
 N2 Ga C1 C2 4.5(13) 2_656 ... ?

Cl Ga C1 C2 -129.4(12) ?
C1 Ga C1 C2 50.6(12) 2_656 . . . ?
C1 N1 C3 C5 -140.05(15) ?
Ga N1 C3 C5 64.2(2) ?
C1 N1 C3 C4 96.53(18) ?
Ga N1 C3 C4 -59.3(2) ?
C1 N2 C6 C7 148.21(16) ?
Ga N2 C6 C7 -5.9(3) ?
C1 N2 C6 C8 -87.9(2) ?
Ga N2 C6 C8 117.95(19) ?

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Appendix 2: Optimized Geometries of Calculated Structures

Reduced System

Bisguanidinate ($[HC(NH)_2]_2AlCl$)

Al,0,-0.0593257067,-0.0244266916,0.051381539
 Cl,0,1.5119989078,0.6253877335,-1.3138290945
 N,0,-1.3935463484,1.4319533553,0.1651890702
 H,0,-1.6043706971,2.3766372698,0.4550858624
 N,0,-1.682547617,-0.3705653557,-1.0254092352
 H,0,-2.1351574188,-0.933912204,-1.7315957901
 C,0,-2.1616897957,0.8185147807,-0.7144786873
 H,0,-3.0737628065,1.2455390681,-1.1395834508
 N,0,0.7019014682,-0.0348429039,1.8773078889
 H,0,1.08283357,0.4979248708,2.6467058372
 N,0,0.4128874062,-1.8374414086,0.6866568782
 H,0,0.5521040121,-2.8122680687,0.4602596826
 C,0,0.9156957172,-1.334163932,1.7975989193
 H,0,1.4507062035,-1.9177963144,2.5513288518

AlClH₂

Al,0,0.,0.,-1.0824073785
 Cl,0,0.,0.,1.0388431906
 H,0,1.4078518487,0.,-1.7945191599
 H,0,-1.4078518487,0.,-1.7945191599

Adduct ($ClAl[HC(NH)_2]_2AlClH_2$)

Al,0,1.0684249272,0.1162636739,0.0614468534
 Cl,0,2.8311878217,-0.9022687111,-0.6542371658
 N,0,-0.364361932,-1.355530395,-0.3729329731
 H,0,-0.1731669003,-2.1629397974,-0.9738172577
 N,0,0.345811023,-0.8318253088,1.649161533
 H,0,0.364892032,-0.8801965382,2.6627889877
 C,0,-0.3361773087,-1.6826805421,0.9715015387
 H,0,-0.8490750862,-2.5496201052,1.3906716459
 N,0,0.3375482352,1.5997554761,-0.8913648012
 H,0,-0.339504906,1.8945344805,-1.5809674729
 N,0,1.6416529794,1.8354150717,0.8419048016
 H,0,2.2474001982,2.3567438107,1.4603333285
 C,0,0.9401625191,2.4603091197,-0.0833469717
 H,0,0.8632479017,3.5446883927,-0.1788955472
 Cl,0,-2.8337443768,0.5543167206,0.6253745072
 Al,0,-2.1883243302,-0.7101357943,-1.0407153374
 H,0,-3.0143136749,-2.0737623622,-1.1100357636
 H,0,-1.8457892913,0.1055981498,-2.3652297588

TSI

Al,0,-1.1042276621,0.4827519433,0.0489688857
 Cl,0,-1.9328515845,2.1996680604,-0.91563593
 N,0,1.3271647022,1.0498579557,-0.4270059212
 H,0,1.8941515897,1.7317106222,-0.9355496361
 N,0,0.0819343071,0.9828794741,1.4390723322
 H,0,-0.0166774592,1.1042832497,2.4412088612
 C,0,1.1711164454,1.4062395881,0.855773183
 H,0,1.8879190884,2.0403001266,1.383350815
 N,0,-1.0748493504,-1.2003651512,-0.812987656
 H,0,-0.5492821312,-1.805604827,-1.4287139595
 N,0,-2.4508916361,-0.6957637503,0.8099395513
 H,0,-3.2402614968,-0.8584646694,1.4184491767
 C,0,-2.0405913377,-1.6403138446,-0.0216476876
 H,0,-2.4423537062,-2.6538147736,-0.053080404
 Cl,0,2.0717163628,-1.8977430028,0.9004187837
 Al,0,2.2544850237,-0.6936666994,-0.9203411094
 H,0,3.7386883374,-0.1634003508,-1.1694864087
 H,0,1.4471120411,-1.3376576881,-2.1375291657

Heterodimer bridged through Cl (ClAl[HC(NH)₂]₂AlClH₂)

Al,0,-0.8367169945,0.1402911804,0.1152576703
 Cl,0,-2.3095964807,1.6503376628,-0.4348725295
 N,0,2.6521974541,0.699092811,0.5233085246
 H,0,3.601626087,1.0465162514,0.6286539354
 N,0,0.4456755308,1.4670936166,0.7659914116
 H,0,-0.0421729269,2.3166254336,1.0415743737
 C,0,1.7478132793,1.607506097,0.8541304033
 H,0,2.1223609403,2.5627431077,1.2265422968
 N,0,-1.9794667877,-1.4963227411,-0.1719587065
 H,0,-2.6387691615,-2.0033643759,-0.7464495456
 N,0,-0.9349414964,-0.9838936155,1.6657351234
 H,0,-0.5474054451,-1.1798799772,2.5776849279
 C,0,-1.7329411922,-1.862629728,1.0574411346
 H,0,-2.125346673,-2.7622043719,1.5362706841
 Cl,0,0.6245043241,-0.5573241981,-1.5982807154
 Al,0,2.4686694927,-1.0218970636,-0.2813710432
 H,0,1.9710315228,-2.1260998037,0.7464813552
 H,0,3.7163744135,-1.2457373934,-1.2386427161

TS2

Al,0,0.83392244,-0.0020035694,0.0498826615
 Cl,0,2.9009193484,-0.5360814654,0.1924247203
 N,0,-2.1736666229,0.489644675,1.0712114696
 H,0,-3.0981705558,0.6700271091,1.4569054046
 N,0,0.059636852,0.4440866419,1.726766636
 H,0,0.6604378841,0.5921906545,2.5322097835
 C,0,-1.2240475097,0.6256948158,1.9715481931
 H,0,-1.5124781861,0.9179245652,2.9821586525
 N,0,-0.1702823454,0.5176410326,-1.5097053133
 H,0,-0.2679841189,0.0887740532,-2.4279182152
 N,0,0.9843295341,2.0844358524,-0.4973968374
 H,0,1.2551597822,3.0463089247,-0.3182534606
 C,0,0.2164681621,1.8341649479,-1.4962918587
 H,0,-0.1170180178,2.5544363139,-2.245461765
 Cl,0,-0.374656382,-1.9673011344,-0.1712726301
 Al,0,-2.2674241404,-0.3082932089,-0.6940212808
 H,0,-2.8362112607,0.7761653291,-1.7346475876
 H,0,-3.2493296896,-1.5642806304,-0.6184459833

Heterodimer bridged through N (Cl₂Al[HC(NH)₂]₂AlH₂)

Al,0,0.8911249401,-0.0344971154,0.0371452233
 Cl,0,2.1268127255,1.5065706675,0.8659485269
 N,0,-2.066312515,-1.375896018,0.7331330398
 H,0,-2.9548963184,-1.7207083021,1.086454324
 N,0,0.1245488412,-0.9963380616,1.457495372
 H,0,0.7058961582,-1.1182426153,2.2824924988
 C,0,-1.1150533767,-1.4279493465,1.6347978531
 H,0,-1.35583881,-1.8565964177,2.607825642
 N,0,-0.6104407555,0.694819017,-0.961424198
 H,0,-0.2881313287,0.8237365377,-1.9254452645
 N,0,-1.5364964211,1.9866065674,0.7420286938
 H,0,-1.8318840527,2.9305523239,0.9882776986
 C,0,-1.0870441564,1.9413228867,-0.4334722324
 H,0,-1.0159768242,2.7839908458,-1.1261797404
 Cl,0,1.9360250573,-1.2825641415,-1.3502988333
 Al,0,-2.0819768666,-0.6746516757,-1.0604324786
 H,0,-3.4703569838,0.0697445964,-1.2813094426
 H,0,-1.5424879515,-1.7462354024,-2.1020102675

TS3

Al,0,0.9881179653,-0.1020190432,0.0812251142
 Cl,0,1.835845644,1.5877227097,1.1191635027
 N,0,-2.0923267261,-1.191244356,0.8824551663
 H,0,-2.9759364545,-1.4952990558,1.2831336896
 N,0,0.1969711097,-1.2079182471,1.3755010604
 H,0,0.832668022,-1.5751732667,2.0794440653
 C,0,-1.0688974844,-1.5164885098,1.6295968676
 H,0,-1.2597540662,-2.0824474416,2.5423577609
 N,0,-0.3891031199,0.5606632136,-1.0729995868
 H,0,-0.0228274933,0.4915866374,-2.0282516977
 N,0,-2.1145590986,1.782373362,-0.3620568287
 H,0,-2.5592567111,2.6641331288,-0.1127291623
 C,0,-0.9274664209,1.8373244163,-0.8008029494
 H,0,-0.3399301842,2.7427016545,-0.9616658682
 Cl,0,2.3896678461,-1.18940556,-1.1087993555
 Al,0,-2.3003051735,-0.4599121219,-0.903638518
 H,0,-3.8810656869,-0.2163817031,-1.0236535193
 H,0,-1.7978847748,-1.527539598,-1.9965137086

Homodimer bridged by two guanidines ($Cl_2Al[HC(NH)_2]_2AlH_2$)

Al,0,1.0109645144,-0.0000062398,-0.0549728983
 Cl,0,0.9928515596,-0.0002374548,2.0959341724
 N,0,-1.936279603,-1.6221989192,0.182827314
 H,0,-2.6186168115,-2.2454151945,0.6083338473
 N,0,0.2471542047,-1.6310532275,-0.6207170256
 H,0,0.9398605355,-2.2744223633,-0.9985539042
 C,0,-0.8433538719,-2.2466594023,-0.1895073105
 H,0,-0.8250248817,-3.3375826127,-0.146909481
 N,0,0.2484087275,1.6307469636,-0.6218107286
 H,0,0.9412024047,2.2734808351,-1.0005366488
 N,0,-1.9349328267,1.624109779,0.1820921605
 H,0,-2.617244652,2.2482100964,0.60632077
 C,0,-0.841819305,2.2474601621,-0.1908625702
 H,0,-0.8225470691,3.3384141578,-0.1492374046
 Cl,0,2.9628418513,-0.0016765351,-0.9609176496
 Al,0,-2.7012181422,0.0007970363,-0.5388393636
 H,0,-4.1978349066,0.0022884097,0.0187842362
 H,0,-2.3326998994,0.0012474154,-2.0884456571

Monomer ([HC(NH)₂]AlCl₂)

Al,0,0.0640425821,-0.0000035496,0.035967836
 Cl,0,1.9268715345,0.0000624649,-0.9869264007
 N,0,-1.3116582093,1.0950881232,-0.7345158168
 H,0,-1.6780960757,2.0128213337,-0.9399841875
 N,0,-1.3116895752,-1.0949430789,-0.734676095
 H,0,-1.6782440814,-2.0126356554,-0.9401179026
 C,0,-1.960558542,0.0001084506,-1.0982880794
 H,0,-2.911860311,0.0001610627,-1.6322080032
 Cl,0,0.1650362681,-0.0001781477,2.1586205233

Monomer ([HC(NH)₂]AlH₂)

Al,0,-0.00005508,0.5580736629,0.9816718948
 H,0,-0.0001567061,2.1510292363,0.9835681796
 N,0,1.097020926,-0.2436675077,-0.4301722997
 H,0,2.0038024204,-0.4656267418,-0.8145410865
 N,0,-1.0969726819,-0.2438006495,-0.4302198466
 H,0,-2.003711053,-0.4658008287,-0.8146668284
 C,0,0.0000601582,-0.6094450372,-1.0707899786
 H,0,0.0001135683,-1.1509860824,-2.0205088768
 H,0,-0.0000308914,-0.2546258774,2.3518988752

Full System*Bisguanidinate ([NMe₂C(NⁱPr)₂]AlCl)*

Al,0.0223297938,-0.0678049216,0.5758926177
 Cl,0.1523851375,-0.1955106661,2.7798876828
 N,-1.8825696011,0.6896819968,0.4118507061
 N,-1.1762092442,-1.2603841053,-0.3705665002
 C,-2.226341577,-0.420876634,-0.2394317316
 N,-3.4958133424,-0.7059462352,-0.7129162788
 C,-4.298885782,0.2864372272,-1.4115131878
 H,-3.7070564593,1.1861900647,-1.5756474844
 H,-5.2056050496,0.5528389603,-0.8530008108
 H,-4.6026491575,-0.1120992224,-2.3881191948
 C,-4.1154884911,-2.0090900387,-0.5214305127
 H,-5.0861718496,-1.8803559543,-0.0259637122
 H,-3.4824783119,-2.6223050486,0.1173503413
 H,-4.2818880988,-2.5329159348,-1.4718002604
 C,-1.1267170906,-2.2942192512,-1.4152414309
 H,-2.067817994,-2.2595607567,-1.9714593623
 C,-0.9768339286,-3.6923947195,-0.8022871754
 H,-0.9785664099,-4.4582491118,-1.586072473
 H,-1.7893170546,-3.9112450531,-0.1030117807
 H,-0.0365384109,-3.7649282232,-0.2509703309

C,0.0067232647,-2.0207629128,-2.4141837038
 H,0.0280395575,-2.7983074014,-3.1864313029
 H,0.9695691516,-2.0067699385,-1.8965740974
 H,-0.1372036619,-1.0525574226,-2.9041176656
 C,-2.8989759984,1.4981295138,1.1105527483
 H,-3.8845988194,1.0972909119,0.8604163357
 C,-2.7663300017,1.4163494994,2.6379261833
 H,-3.5930766883,1.9685573828,3.1011151451
 H,-1.8230055538,1.8493282162,2.9769238873
 H,-2.7974431825,0.3795182514,2.9798610656
 C,-2.8552125522,2.9641598576,0.6620796485
 H,-3.6833115947,3.5226525664,1.1123710439
 H,-2.9257498838,3.0592505049,-0.4266726324
 H,-1.9210927891,3.4321740858,0.9865180536
 N,1.8815060952,-0.7954522111,0.1782308203
 N,1.1359591644,1.2153858386,-0.3669259941
 C,2.1910520673,0.3725796826,-0.3885342379
 N,3.408290644,0.712580559,-0.947234634
 C,4.2600985363,-0.2765760089,-1.5885663555
 H,5.0597046366,-0.6411673021,-0.9292964309
 H,3.6545929268,-1.1190743348,-1.9221657431
 H,4.7242001343,0.18466106,-2.4674939625
 C,4.0518584135,1.9862256839,-0.6392491475
 H,3.4049581711,2.5773254199,0.0058587441
 H,4.9957754367,1.8049218661,-0.1086083072
 H,4.2709690245,2.5553986523,-1.5503761855
 C,1.009090228,2.339866007,-1.3055553268
 H,1.9204870322,2.3857612125,-1.9081505541
 C,-0.165626466,2.1264935261,-2.2707239053
 H,-0.009215954,1.2252736631,-2.8718804345
 H,-1.0972157655,2.0129710119,-1.7102508131
 H,-0.2621672894,2.9812065221,-2.9501075907
 C,0.861295877,3.6647150919,-0.5476306401
 H,1.7127609564,3.83848386,0.1175945009
 H,0.7904554156,4.5051465594,-1.2471817236
 H,-0.0422268582,3.6497843757,0.0655472479
 C,2.9009678976,-1.6324060376,0.8452052761
 H,3.635719146,-1.9693585274,0.1070337393
 C,3.6573386551,-0.8745620877,1.9507043173
 H,2.9610020868,-0.5448509682,2.7247811374
 H,4.4104542401,-1.5279716617,2.4067131185
 H,4.1728493114,0.0050785338,1.5495229477
 C,2.2387257591,-2.8901965484,1.4116355781
 H,2.9866743322,-3.5017908958,1.9274629042
 H,1.4526378061,-2.626754132,2.1228754497
 H,1.804133937,-3.492698491,0.6091073403

Al₂Cl₆

Al,0,-1.5364722344,-0.481248263,0.0161544371
 Al,0,1.5365615201,0.4813353418,-0.0161987077
 Cl,0,-0.4871740572,1.5554982431,0.0006919659
 Cl,0,0.4871878095,-1.5554292384,-0.0007733664
 Cl,0,-2.4920025037,-0.781356722,1.855547427
 Cl,0,-2.5277378523,-0.7909026487,-1.8026171169
 Cl,0,2.5275407931,0.7907878883,1.8027832606
 Cl,0,2.4921175331,0.781335888,-1.8555983162

AlCl₃

Al,0,0.,0.,0.
 Cl,0,2.0886062717,0.,0.0000000751
 Cl,0,-1.0443032009,0.,1.8087860523
 Cl,0,-1.0443030708,0.,-1.8087861274

Adduct (ClAl[NMe₂C(ⁱPr)₂]₂AlCl₃)

Al,0,-0.9960475554,0.6250571116,0.7315138754
 Cl,0,-1.1180660538,1.2422756322,2.818970779
 N,0,-2.5985179689,0.8692323774,-0.2881317832
 N,0,-1.9292247592,-1.044665436,0.630606267
 C,0,-2.8981884279,-0.436603953,-0.0604282333
 N,0,-4.0631074929,-1.0280035819,-0.4956715757
 C,0,-4.4935070299,-0.884811215,-1.8842902949
 H,0,-3.7504859168,-0.3151701917,-2.4412049031
 H,0,-5.4666054654,-0.3837593814,-1.959239802
 H,0,-4.5786310815,-1.8772915073,-2.3427844825
 C,0,-4.9340966141,-1.8107073685,0.3737355783
 H,0,-5.9479769448,-1.393031221,0.3340737308
 H,0,-4.5856162681,-1.7534470852,1.4047104104
 H,0,-4.9864992412,-2.8630726934,0.0687985866
 C,0,-1.9053042856,-2.4816908075,0.9579694133
 H,0,-2.8300503297,-2.92192486,0.5833956169
 C,0,-1.8645396965,-2.6588188657,2.4805128732
 H,0,-1.8890258693,-3.7222442245,2.7404916027
 H,0,-2.7122803568,-2.1607138494,2.9622901275
 H,0,-0.9491890737,-2.2273440962,2.8976787843
 C,0,-0.7578927245,-3.2102074897,0.2643951904
 H,0,-0.7547091043,-4.2660847452,0.557383628
 H,0,0.203938153,-2.7835883789,0.5496027191
 H,0,-0.8458532856,-3.1489873049,-0.8208609148
 C,0,-3.6878002466,1.8476825082,-0.5096805251
 H,0,-4.5954010725,1.2721371391,-0.7020038481
 C,0,-3.9677193669,2.6771267127,0.752647236
 H,0,-4.819977971,3.3441688715,0.5809789426
 H,0,-3.1127874923,3.2938329428,1.043079947

H,0,-4.2036445681,2.0244428779,1.5984645838
 C,0,-3.4387017994,2.7220786007,-1.7426635615
 H,0,-4.3177716764,3.3444257799,-1.9420620528
 H,0,-3.2456201628,2.1048836039,-2.6256556248
 H,0,-2.583830945,3.3894565476,-1.607910262
 N,0,2.1647876035,-0.4347053427,0.420937423
 N,0,0.6631494964,1.3612056459,0.1653771591
 C,0,1.8587072843,0.8727743748,0.588198792
 N,0,2.7585494742,1.7265338223,1.1695237199
 C,0,4.1886183007,1.7029820638,0.8575167935
 H,0,4.7874860665,1.3317253996,1.6967170186
 H,0,4.3640456506,1.0919634498,-0.0242688255
 H,0,4.5049590812,2.7274898582,0.632873775
 C,0,2.3528054701,2.7674672527,2.1132742024
 H,0,1.3248883642,2.6025189658,2.4284484612
 H,0,3.0004301897,2.703977005,2.9945306056
 H,0,2.4548444974,3.770970513,1.6834695635
 C,0,0.6840477681,2.7267627664,-0.4876940166
 H,0,1.7056304558,3.0961202498,-0.388746076
 C,0,0.3874484678,2.5986921973,-1.9857631256
 H,0,1.1430311462,1.9876428887,-2.4826368086
 H,0,-0.5869320141,2.1382695945,-2.1627328702
 H,0,0.3920447024,3.5951443144,-2.4435113188
 C,0,-0.2502459688,3.7340752701,0.1876633338
 H,0,-0.0439606629,3.8547860141,1.2525581664
 H,0,-0.1417523648,4.7101286925,-0.2970792167
 H,0,-1.2966766092,3.4404289062,0.0817527906
 C,0,3.0512574511,-1.0687949297,1.4730848517
 H,0,3.2701942926,-0.2746046944,2.1877731938
 C,0,2.2802542461,-2.1509982534,2.2336672346
 H,0,2.0562948139,-3.0057384273,1.5911884607
 H,0,2.8913329734,-2.5103683133,3.0695289441
 H,0,1.3465099614,-1.7535374737,2.6442296048
 C,0,4.385665011,-1.6280150588,0.9543354013
 H,0,5.0263477163,-1.8541556157,1.8141551261
 H,0,4.2428478715,-2.5518200434,0.3927693092
 H,0,4.918028726,-0.9245474138,0.3114178609
 Cl,0,3.463389728,0.0211230841,-2.5036057059
 Al,0,2.0044111437,-1.1334266832,-1.3777018194
 Cl,0,0.0539379174,-0.8776266671,-2.2980495342
 Cl,0,2.4589381531,-3.2437381015,-1.433703575

Heterdimer bridged by Cl (ClAl[NMe₂C(NⁱPr)₂]₂AlCl₃)

Al,0,-0.7988644763,0.3301336637,-0.8939577748
 Cl,0,-1.745668383,1.0234058768,-2.7391597205
 N,0,1.5365248068,-0.1554035461,0.9677467075
 N,0,0.8424079243,1.3703543734,-0.6575240823
 N,0,-2.0307224519,-1.0858525874,-0.3680406734
 N,0,-1.922671926,0.8767433566,0.6350584152
 C,0,-2.6403348811,-0.254952175,0.4790775742
 Cl,0,0.7395446378,-1.4701124978,-1.9472845096
 Al,0,2.1435751172,-1.489946942,-0.2353358965
 C,0,-2.4818267427,-2.4647608026,-0.6311270641
 H,0,-3.4352454021,-2.5961670749,-0.1159881754
 C,0,-1.5314598913,-3.5130489045,-0.0420942249
 H,0,-0.5610811915,-3.5119880409,-0.5376663268
 H,0,-1.3741505158,-3.3377706205,1.0270050343
 H,0,-1.9688335696,-4.5111710194,-0.1615640117
 C,0,-2.7157637164,-2.6832661041,-2.1305662027
 H,0,-3.1199295649,-3.686655718,-2.3048398644
 H,0,-3.4189781869,-1.9472521133,-2.5327166667
 H,0,-1.7811569754,-2.5911231671,-2.6892807666
 C,0,-2.5120135344,2.1016637288,1.1995476013
 H,0,-3.5557131156,1.8933000107,1.4516790222
 C,0,-2.5259661137,3.2433997896,0.1778389169
 H,0,-3.0578079559,2.9498413228,-0.7305327466
 H,0,-3.0179843838,4.1252325866,0.6036545551
 H,0,-1.5100827953,3.528729781,-0.1082108669
 C,0,-1.784114421,2.5150115584,2.4855513984
 H,0,-1.8423331282,1.7317606891,3.2478405272
 H,0,-0.7241730874,2.7016560713,2.2852694673
 H,0,-2.2177348884,3.4303924123,2.903295164
 N,0,-3.8630749323,-0.5029214578,1.0797365597
 C,0,-5.0428495469,-0.8509206361,0.2942736086
 H,0,-5.4520826911,-1.827008942,0.5827352557
 H,0,-5.8224150581,-0.093207502,0.4486966549
 H,0,-4.7928950868,-0.8680801143,-0.7661391692
 C,0,-4.0790793903,-0.3098630342,2.5063323775
 H,0,-4.7904584955,0.5005385158,2.7140912781
 H,0,-4.4778830049,-1.2335095753,2.9441414239
 H,0,-3.1335997896,-0.0836813365,2.9981269309
 Cl,0,2.151741298,-3.4832211674,0.5593933216
 Cl,0,4.1090775117,-0.9126695412,-0.9180620914
 C,0,1.5371690781,1.1179191301,0.4616477593
 N,0,2.2551964647,2.0972314975,1.0946763618
 C,0,3.5720392388,1.8505623543,1.6852121725
 H,0,3.9608459231,0.8971950873,1.3377061221
 H,0,4.2522447791,2.639086194,1.3465457558

H,0,3.5388503755,1.866438912,2.7802578032
 C,0,1.8173821029,3.4880121374,1.164594439
 H,0,1.9062489134,3.8299599009,2.2015170569
 H,0,2.4265365733,4.1430737751,0.5313684677
 H,0,0.7771952943,3.5644074476,0.8599592627
 C,0,1.4918023622,-0.3315198038,2.4657729611
 C,0,1.4450147767,2.3386251575,-1.6575022633
 H,0,2.3654462929,2.7002350699,-1.1951891094
 C,0,2.7015008615,-1.0625655568,3.069249346
 H,0,2.6932485976,-2.1237602836,2.8150429056
 H,0,3.6567327461,-0.6452762135,2.7450100586
 H,0,2.6535797229,-0.9829277068,4.1610804437
 C,0,1.8583022604,1.6146245391,-2.9473437911
 H,0,0.9947054564,1.2122209542,-3.4798315088
 H,0,2.3566574003,2.3364614407,-3.6046611611
 H,0,2.5590064529,0.8035463422,-2.7429839424
 C,0,0.5657961369,3.5501646568,-1.9875894074
 H,0,-0.3643441082,3.246730617,-2.4686899488
 H,0,0.3250109834,4.1509141333,-1.1072505745
 H,0,1.1112660132,4.1953034683,-2.6849933713
 C,0,0.1949281298,-1.0489968056,2.853787077
 H,0,0.172013343,-2.0605858147,2.437856678
 H,0,0.127639913,-1.1302058897,3.9450632595
 H,0,-0.670637013,-0.4945046189,2.4855222883
 H,0,1.4544573448,0.677981411,2.8832648301

TSI

Al,0,-0.3403528177,1.0794482013,-0.8445337695
 Cl,0,-0.993603815,2.7190120274,-2.1154022537
 N,0,1.203672185,-0.8175631191,0.7742156005
 N,0,1.522601953,1.2393735443,-0.2968875518
 N,0,-1.6036210429,-0.4343190107,-0.4710119693
 N,0,-1.3075076046,1.3617477086,0.8254911251
 C,0,-2.0143160611,0.255411161,0.6846037401
 Cl,0,0.4278086898,-0.4911900942,-2.5015168996
 Al,0,0.3259976454,-1.8388671944,-0.6042218903
 C,0,-2.7905976569,-0.918791288,-1.3053456418
 H,0,-3.342580262,-1.6087576821,-0.6682797172
 C,0,-2.4530435042,-1.7117056819,-2.5755033457
 H,0,-2.0528366605,-1.0791187242,-3.3679247807
 H,0,-1.7671769897,-2.5426776513,-2.4035891949
 H,0,-3.3907970635,-2.1518606916,-2.9337033815
 C,0,-3.7091969814,0.2480345685,-1.690757542
 H,0,-4.6092824963,-0.1432994078,-2.1762141339
 H,0,-4.0262492338,0.8389608316,-0.8258693026
 H,0,-3.206451363,0.9202193348,-2.3905365647

C,0,-1.3394396983,2.3121406624,1.9484360448
 H,0,-1.9465945153,1.8934968409,2.7533836018
 C,0,-1.9438360894,3.6471475038,1.4846290985
 H,0,-2.944751308,3.5228275428,1.0608162723
 H,0,-2.0062204329,4.3460828319,2.3248895585
 H,0,-1.3188279071,4.0936870088,0.7060570673
 C,0,0.0635248083,2.5488762293,2.5143579712
 H,0,0.5278526259,1.6156327049,2.8426463253
 H,0,0.7037509553,3.008112837,1.75914324
 H,0,0.0024648778,3.2257132046,3.3728232759
 N,0,-3.0587381227,-0.1415117735,1.4677738863
 C,0,-4.0072364638,0.7956509482,2.0702781354
 H,0,-5.0188493572,0.430267487,1.8631413932
 H,0,-3.8864124404,0.8658601406,3.1568880781
 H,0,-3.9096486584,1.7837186131,1.6277914459
 C,0,-3.3845514463,-1.5457526953,1.7259990405
 H,0,-3.3651728187,-1.720066268,2.8081965815
 H,0,-4.3896869959,-1.782710726,1.3572184411
 H,0,-2.6596079005,-2.2046284054,1.2577382377
 Cl,0,-0.9694383717,-3.4990511536,0.0471677071
 Cl,0,2.0059609332,-3.0844990022,-1.3558379522
 C,0,1.9774545025,0.271337398,0.5072485647
 N,0,3.237783593,0.3552634409,1.078170951
 C,0,4.2093761827,-0.7253240754,0.9025431868
 H,0,3.8074130552,-1.4630303862,0.2069454847
 H,0,5.1257887131,-0.300010578,0.4703775279
 H,0,4.4623646444,-1.2071495476,1.8552940637
 C,0,3.7139496915,1.5186120604,1.8124937707
 H,0,3.9936661611,1.2173622134,2.8298629656
 H,0,4.5970201394,1.9624774895,1.3369817897
 H,0,2.9312238485,2.2743423339,1.8798050005
 C,0,1.3930043642,-1.4624005373,2.135276071
 C,0,2.5086426613,2.1717114956,-0.9473209938
 H,0,3.4855467692,1.9218365704,-0.5395320412
 C,0,1.9245108919,-2.9040676387,2.1181960267
 H,0,1.1499721579,-3.6166964002,1.828732753
 H,0,2.7704137379,-3.0441334229,1.4465549924
 H,0,2.2484855519,-3.1622636883,3.1352823442
 C,0,2.6205641369,1.9713863764,-2.465307352
 H,0,1.6969316838,2.2350844304,-2.9834928652
 H,0,3.4148375707,2.629597627,-2.8368410735
 H,0,2.8799708357,0.9406334286,-2.7156435166
 C,0,2.2124294724,3.6402870738,-0.617358606
 H,0,1.2380135641,3.9429935804,-1.006493589
 H,0,2.2359591147,3.8372359168,0.4592074799
 H,0,2.9712419113,4.2763210171,-1.086065976

C,0,0.0867134639,-1.4029072581,2.9352008038
H,0,-0.6831199141,-2.025852756,2.4750015564
H,0,0.2600988712,-1.7853177779,3.9478982715
H,0,-0.2870532152,-0.3799474325,3.0155834851
H,0,2.1255031958,-0.8439290938,2.6544901253

Homodimer bridged by two guanidinate ligands ($\text{Cl}_2\text{Al}[\text{NMe}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{AlCl}_2$)

Al,0,0.825689739,0.8936756435,-1.2936987132
Al,0,-0.861133486,-0.7170050354,1.3389677171
Cl,0,0.3884643386,0.7516717321,-3.4288341003
Cl,0,2.5626987652,2.1533367244,-0.9178265197
Cl,0,-1.9852380399,0.4682222453,2.7831621749
Cl,0,-0.9606316251,-2.8427612018,1.8254911901
N,0,-0.7734608339,1.6945508348,-0.6305122107
N,0,-3.0777802369,1.4649914484,-1.107511719
N,0,-1.8277368558,-0.3576410645,-0.2696020317
N,0,1.0198095204,-0.4160761579,1.5204616281
N,0,2.962753379,-1.6149199394,0.8896854528
N,0,1.4305092491,-0.815973372,-0.7270642693
C,0,-0.9365029963,3.1873493212,-0.4547148275
C,0,-0.3723282813,4.0157871483,-1.6179784208
C,0,-0.3468617567,3.6447258884,0.8805234736
C,0,-1.8897303569,0.9350052559,-0.6674511568
C,0,-3.1755727365,2.2477360642,-2.3385712137
C,0,-4.3330562611,1.2591096794,-0.3873482464
C,0,-2.7611519395,-1.3347374198,-0.944836966
C,0,-3.7540103321,-2.0307221455,-0.0013126623
C,0,-1.9639635455,-2.3573928818,-1.7584682543
C,0,1.6709297559,0.0243683203,2.8100731212
C,0,1.1302822066,-0.6863775447,4.0589720617
C,0,1.5906925903,1.5440031215,2.9664866426
C,0,1.8086135867,-0.9521294149,0.5619387262
C,0,3.0268984082,-2.5862528273,1.979347374
C,0,4.2392052964,-1.3178955837,0.2437695705
C,0,1.6753138263,-1.8842953049,-1.769328628
C,0,1.719410311,-3.3115656185,-1.2122634377
C,0,2.8587448284,-1.6159890076,-2.7141501374
H,0,-2.0107497286,3.3626693927,-0.4005677954
H,0,-0.6629791942,5.0626196056,-1.4760269186
H,0,0.7181685759,3.9773992925,-1.6486486747
H,0,-0.7492828699,3.687183524,-2.5885989015
H,0,-0.5596516835,4.7111407034,1.0187295974
H,0,0.73624097,3.5120829369,0.9053756715
H,0,-0.7955122955,3.095608716,1.7113965247
H,0,-3.976632264,1.824844941,-2.9556371351
H,0,-3.4097470023,3.3007055326,-2.1425115343

H,0,-2.2434416328,2.1776869621,-2.8954762002
H,0,-4.8209614904,2.2318346542,-0.2591711795
H,0,-4.1281337852,0.8475044812,0.5989744458
H,0,-5.0186263896,0.5968336145,-0.9290651283
H,0,-3.3355759281,-0.7436438329,-1.6585979347
H,0,-4.2481727505,-1.3284263644,0.6736656636
H,0,-4.5258000717,-2.5217973636,-0.6047176241
H,0,-3.2676387595,-2.7946504359,0.6051636314
H,0,-1.3140094048,-2.9566912278,-1.1162343176
H,0,-1.3599774683,-1.8579304166,-2.521128164
H,0,-2.6562306844,-3.0389132909,-2.2657878218
H,0,2.7273815146,-0.2232159899,2.7072653354
H,0,1.7591200253,-0.4174109685,4.9149637246
H,0,0.1093153029,-0.3755632292,4.2888110978
H,0,1.1374385846,-1.7735611618,3.9594107057
H,0,2.1565929437,1.8426597304,3.8565782179
H,0,2.0256608521,2.045877337,2.0991033031
H,0,0.5597314121,1.8783790842,3.0955185081
H,0,2.0211609216,-2.8373140751,2.3098389005
H,0,3.6143206112,-2.2187429408,2.8291362753
H,0,3.5026722902,-3.4985090018,1.6018118966
H,0,4.1162442673,-0.5057465239,-0.4695467284
H,0,4.9550399033,-0.9995761548,1.0117825843
H,0,4.6488507551,-2.1996270812,-0.2611764583
H,0,0.7787563986,-1.8166279039,-2.3848424069
H,0,0.9169045497,-3.492183389,-0.4914135377
H,0,2.6736604047,-3.5460205393,-0.7339529222
H,0,1.5894375266,-4.0096344312,-2.0461710929
H,0,2.9034701964,-0.5700215806,-3.0239124778
H,0,2.7253009385,-2.2193429883,-3.6187114547
H,0,3.8182995322,-1.8934635711,-2.2743234552

TS2

AI,0.7301419155,1.2401559401,0.0826260106
 AI,-0.7701790845,-1.3785500599,-0.0171859894
 CI,1.0071619155,3.1655589401,1.0733710106
 CI,-0.2377770845,1.7236219401,-1.8814849894
 CI,0.4032489155,-2.0334130599,-1.7135159894
 CI,-1.1583810845,-3.1514150599,1.1500560106
 NI,2.4809739155,0.7599459401,-0.6589979894
 NI,3.5344439155,-1.2913320599,0.0269090106
 NI,1.4940639155,-0.4169770599,0.9718550106
 NI,-2.4112180845,-0.6626690599,-0.7720199894
 NI,-3.2178830845,1.4906479401,-0.0680809894
 NI,-1.1815760845,0.4409119401,0.7441020106
 CI,3.2761869155,1.1052719401,-1.8622559894
 CI,3.1696959155,2.6104789401,-2.1273689894
 CI,2.8832299155,0.2698199401,-3.0870769894
 CI,2.5618859155,-0.3363720599,0.0698800106
 CI,4.9232459155,-1.0184870599,-0.3400349894
 CI,3.2558019155,-2.6845860599,0.3837790106
 CI,1.9824399155,-0.6649650599,2.3926930106
 CI,1.2303009155,-1.7565230599,3.1567290106
 CI,2.0885409155,0.6266229401,3.2150230106
 CI,-3.3186600845,-0.9763370599,-1.8985769894
 CI,-4.1652130845,-2.1996560599,-1.5330639894
 CI,-2.5364580845,-1.1968190599,-3.1996629894
 CI,-2.3324530845,0.4633639401,-0.1014119894
 CI,-4.6502640845,1.3164059401,-0.3082899894
 CI,-2.7852880845,2.8954099401,-0.0379759894
 CI,-1.5162290845,0.5343659401,2.2412980106
 CI,-2.6929800845,-0.3654550599,2.6532900106
 CI,-1.7623490845,1.9387779401,2.8042500106
 HI,4.3258109155,0.9077229401,-1.6429919894
 HI,3.8568929155,2.8851709401,-2.9352259894
 HI,2.1580869155,2.8926119401,-2.4235689894
 HI,3.4376829155,3.1810419401,-1.2332339894
 HI,3.5065009155,0.5581189401,-3.9418319894
 HI,1.8354219155,0.4332709401,-3.3456539894
 HI,3.0220689155,-0.7996100599,-2.9019069894
 HI,5.5527979155,-1.7344830599,0.1947990106
 HI,5.1107189155,-1.1327250599,-1.4136139894
 HI,5.2136699155,-0.0164540599,-0.0227799894
 HI,3.5532049155,-3.3312920599,-0.4483249894
 HI,2.1923049155,-2.8203440599,0.5500180106
 HI,3.8126929155,-2.9824440599,1.2799600106
 HI,3.0073329155,-1.0283510599,2.2884400106
 HI,1.1928919155,-2.6927130599,2.5984150106

H,1.7496059155,-1.9438430599,4.1037590106
 H,0.2005739155,-1.4824550599,3.4001830106
 H,1.1157009155,1.0901669401,3.4040170106
 H,2.7125569155,1.3696459401,2.7124350106
 H,2.5414209155,0.3996199401,4.1875790106
 H,-3.9732200845,-0.1217870599,-2.0654539894
 H,-4.8424760845,-2.4510780599,-2.3556519894
 H,-3.5212240845,-3.0635230599,-1.3405749894
 H,-4.7633550845,-2.0212280599,-0.6326679894
 H,-3.2485160845,-1.2478580599,-4.0310239894
 H,-1.8403150845,-0.3748480599,-3.3805069894
 H,-1.9684060845,-2.1286390599,-3.1743319894
 H,-4.9389270845,0.2769409401,-0.1599419894
 H,-4.9492350845,1.6447649401,-1.3103199894
 H,-5.1862930845,1.9285959401,0.4240250106
 H,-1.7430290845,2.9790739401,0.2491490106
 H,-2.9008840845,3.3284909401,-1.0369249894
 H,-3.4055030845,3.4500819401,0.6712260106
 H,-0.6102100845,0.1522109401,2.7036240106
 H,-3.6275650845,-0.0144320599,2.2008350106
 H,-2.8184610845,-0.2997740599,3.7394180106
 H,-2.5488500845,-1.4132830599,2.3971570106
 H,-1.0086700845,2.6579129401,2.4920630106
 H,-1.7305160845,1.8699419401,3.8978840106
 H,-2.7543260845,2.3093119401,2.5338740106

Monomer ([NMe₂C(NⁱPr)₂]₂AlCl₂)

Al,0,1.2850511633,-0.0428877135,0.0225993735
 Cl,0,2.7118814661,0.4226172295,-1.5020421946
 Cl,0,2.2033638546,-0.6339589648,1.8684180517
 N,0,-0.2454251299,-1.0458117746,-0.4763510848
 N,0,-0.2453636643,1.0749712201,0.1712240519
 C,0,-1.0166616333,0.0346921716,-0.2077479378
 N,0,-2.3774582624,0.0715459054,-0.3082292288
 C,0,-0.5963658799,2.499923468,0.0569985741
 H,0,-1.650551551,2.5782633521,-0.2237700718
 C,0,0.2289666419,3.1697957034,-1.0491722533
 H,0,0.0788459422,2.6673141721,-2.0091757101
 H,0,-0.0638022492,4.2200253427,-1.1555821013
 H,0,1.297763355,3.1352594376,-0.8160442357
 C,0,-0.3844702668,3.1937651001,1.4065035671
 H,0,-0.6389103607,4.2567134611,1.3408155998
 H,0,-0.997401917,2.7381320176,2.1910004628
 H,0,0.6635385366,3.1111909093,1.7138564091
 C,0,-3.2082930573,0.8143578146,0.6377337648
 H,0,-2.5901029033,1.221353518,1.4358045617

H,0,-3.7535952127,1.6286966673,0.1476843945
 H,0,-3.938559806,0.129595847,1.0843484525
 C,0,-3.0982098241,-0.7466896405,-1.2784408005
 H,0,-3.9055269536,-0.1436784223,-1.7059323547
 H,0,-2.4273347186,-1.039649451,-2.0847566705
 H,0,-3.5387850207,-1.6426614387,-0.8235570791
 C,0,-0.6481673061,-2.4583375159,-0.3322349313
 H,0,-1.4385925312,-2.6876102781,-1.0539714815
 C,0,-1.1683678082,-2.7696084734,1.0783248422
 H,0,-0.3906978672,-2.5713612856,1.8227829884
 H,0,-2.0432750173,-2.1583957372,1.325877065
 H,0,-1.460122048,-3.8227859658,1.1545762127
 C,0,0.5608641703,-3.3266284624,-0.6872229893
 H,0,1.3758911763,-3.1693404658,0.0286483002
 H,0,0.2892735883,-4.3865001471,-0.6606589614
 H,0,0.9290691606,-3.0867702071,-1.6890843903

Full System Reduced

Bisguanidinate ($[\text{NH}_2\text{C}(\text{NH})_2]_2\text{AlCl}$)

Al,0.0000217563,0.0002515775,0.2027307313
 Cl,-0.0012422437,0.0001805775,2.4233427313
 N,1.8179007563,-0.8384334225,-0.0573032687
 N,1.2189207563,1.1752365775,-0.7571682687
 C,2.2171827563,0.2725075775,-0.6828082687
 N,3.4781367563,0.4831085775,-1.2060932687
 N,-1.8175272437,0.8389085775,-0.0589062687
 N,-1.2178952437,-1.1749654225,-0.7575762687
 C,-2.2164912437,-0.2725784225,-0.6836402687
 N,-3.4775492437,-0.4843914225,-1.2061362687
 H,-1.1924697637,-1.9080827925,-1.4372029787
 H,-2.4501233237,1.4150246275,0.4586963813
 H,2.4505106263,-1.4139474125,0.4609518713
 H,1.1939372763,1.9083395075,-1.4368269487
 H,-3.9721942637,-1.3425893325,-1.0689405987
 H,-4.0080651837,0.2560345575,-1.6188373687
 H,4.0074284463,-0.2578125025,-1.6194771787
 H,3.9737566563,1.3408738375,-1.0697126087

Adduct ($\text{ClAl}[\text{NH}_2\text{C}(\text{NH})_2]_2\text{AlCl}_3$)

Al,-1.5309433446,0.8147567935,0.9169100075
 Cl,-1.7828493446,1.6612147935,2.9102430075
 N,-3.1248423446,0.7257387935,-0.1408099925
 N,-2.2438833446,-0.9603662065,1.0150450075
 C,-3.2636543446,-0.5701082065,0.2443800075

N,-4.3334723446,-1.3543032065,-0.1254219925
 N,1.7449486554,0.1381677935,0.7713360075
 N,0.0364306554,1.6825367935,0.2799960075
 C,1.2727276554,1.4063047935,0.7718970075
 N,2.0429426554,2.4326327935,1.2514600075
 Cl,3.0501596554,0.3963007935,-2.1743209925
 Al,1.7196696554,-0.7894152065,-0.9280719925
 Cl,-0.2233523446,-0.8994022065,-1.8921189925
 Cl,2.4372166554,-2.8151862065,-0.7170689925
 H,-2.1108770046,-1.8907511465,1.3566488275
 H,-3.9335900246,1.2637170035,-0.3785212425
 H,-0.0522893046,2.5195458235,-0.2599527325
 H,2.3601812954,-0.1142533465,1.5181776075
 H,3.0192227954,2.5157792735,1.0515506475
 H,1.6618299854,3.1763921835,1.8006185475
 H,-4.8734714046,-1.8862204765,0.5268548075
 H,-4.6137243446,-1.4114387465,-1.0836465725

Heterdimer bridged by Cl (ClAl[NH₂C(NH)₂]₂AlCl₃)

Al,-1.2607880779,0.7737933162,-0.4518294891
 Cl,-2.2046060779,1.4681823162,-2.2981404891
 N,1.0721649221,0.2833783162,1.4116505109
 N,0.3831649221,1.8097353162,-0.2152334891
 N,-2.4968030779,-0.6384246838,0.0744655109
 N,-2.3840150779,1.3246593162,1.0760855109
 C,-3.1046590779,0.1947963162,0.9205665109
 Cl,0.2733479221,-1.0314566838,-1.5028214891
 Al,1.6763009221,-1.0537576838,0.2099795109
 N,-4.3284250779,-0.0493756838,1.5206895109
 Cl,1.6785759221,-3.0464196838,1.0062805109
 Cl,3.6437709221,-0.4823616838,-0.4720264891
 C,1.0765709221,1.5562953162,0.9045505109
 N,1.7968809221,2.5341513162,1.5372375109
 H,1.4995170021,3.4877595062,1.5842068309
 H,2.6955872921,2.3635494462,1.9412447609
 H,1.0416203121,0.1675311862,2.4044478109
 H,0.7825823021,2.4465037862,-0.8747724691
 H,-2.7823830479,2.1582667062,1.4587102409
 H,-4.4770310679,0.0844197162,2.5004930909
 H,-5.1371327479,-0.2860516038,0.9821949309
 H,-2.8051785079,-1.5729115338,-0.1034078091

TS1 (ClAl[NH₂C(NH)₂]₂AlCl₃)

Al,-0.3905426801,1.5139048285,-0.3240524165
 Cl,-1.0437936801,3.1534688285,-1.5949204165
 N,1.1534823199,-0.3831061715,1.2946975835
 N,1.4724123199,1.6738308285,0.2235935835
 N,-1.6538106801,0.0001378285,0.0494695835
 N,-1.3576976801,1.7962048285,1.3459725835
 C,-2.0645056801,0.6898678285,1.2050855835
 Cl,0.3776193199,-0.0567331715,-1.9810354165
 Al,0.2758083199,-1.4044101715,-0.0837404165
 N,-3.1089276801,0.2929448285,1.9882555835
 Cl,-1.0196276801,-3.0645941715,0.5676495835
 Cl,1.9557713199,-2.6500421715,-0.8353564165
 C,1.9272653199,0.7057938285,1.0277305835
 N,3.1875943199,0.7897198285,1.5986525835
 H,1.2782117499,-0.8079169515,2.1913459935
 H,3.8513726399,0.0514776285,1.4786659435
 H,3.5146769899,1.5888346185,2.1030655935
 H,2.1276516699,2.2933830385,-0.2086291065
 H,-1.3793981901,2.4420776385,2.1091091435
 H,-2.4298048101,-0.3165889715,-0.4959818365
 H,-3.7571661201,0.9334365085,2.4000289835
 H,-3.3314032801,-0.6659161315,2.1645799235

Homodimer bridged by two guanidinate ligands (Cl₂Al[NH₂C(NH)₂]₂AlCl₂)

Al,-0.1484843092,1.7519560276,-0.0634741565
 Al,0.1408416908,-1.7488749724,0.1127848435
 Cl,-1.0900543092,2.9240190276,-1.6477241565
 Cl,0.7169426908,3.0345250276,1.4699148435
 Cl,-0.9167083092,-2.8399249724,1.6765208435
 Cl,1.2983926908,-3.1082879724,-1.1432091565
 N,-1.6331743092,0.7624370276,0.6110988435
 N,-3.5110013092,-0.2987229724,-0.3573121565
 N,-1.3174773092,-1.0099369724,-0.8762721565
 N,1.5510266908,-0.6868899724,0.8510328435
 N,3.5246546908,0.2913460276,-0.0195891565
 N,1.3858646908,0.9197110276,-0.8137561565
 C,-2.1512533092,-0.1809979724,-0.2049001565
 C,2.1591476908,0.1750420276,0.0051038435
 H,-4.0998468992,0.4912691476,-0.5281141465
 H,-3.9741535292,-1.1843326124,-0.3228796765
 H,-1.6211915792,-1.3392284324,-1.7703218065
 H,-2.1878996992,1.0703725676,1.3840512635
 H,3.9835632508,1.1785762276,0.0275861635
 H,2.0129818008,-0.9056591324,1.7105312635
 H,1.6622550608,1.1670296676,-1.7424336365

H,4.1312903608,-0.5035835224,-0.0106352665

TS2

Al,0.6845892689,1.2613661557,0.2144375912
 Al,-0.8157317311,-1.3573398443,0.1146255912
 Cl,0.9616092689,3.1867691557,1.2051825912
 Cl,-0.2833297311,1.7448321557,-1.7496734088
 Cl,0.3576962689,-2.0122028443,-1.5817044088
 Cl,-1.2039337311,-3.1302048443,1.2818675912
 N,2.4354212689,0.7811561557,-0.5271864088
 N,3.4888912689,-1.2701218443,0.1587205912
 N,1.4485112689,-0.3957668443,1.1036665912
 N,-2.4567707311,-0.6414588443,-0.6402084088
 N,-3.2634357311,1.5118581557,0.0637305912
 N,-1.2271287311,0.4621221557,0.8759135912
 C,2.5163332689,-0.3151618443,0.2016915912
 C,-2.3780057311,0.4845741557,0.0303995912
 H,-3.0698275611,-0.8533691443,-1.4012966788
 H,-4.2426424811,1.3927425457,-0.1004814988
 H,-2.9691875311,2.4673677957,0.0842078112
 H,-1.4448621811,0.5229256257,1.8500260512
 H,1.7692294789,-0.5586214243,2.0367358312
 H,3.2986888189,-2.2211641343,0.4023218712
 H,2.9716215789,1.0140043457,-1.3385253988
 H,4.4387310789,-1.0835156543,-0.0922424788

Monomer ([NH₂C(NH)₂]AlCl₂)

Al,-0.397929086,-0.1431706421,0.0162808799
 Cl,-1.556574086,-1.0682406421,-1.5260741201
 Cl,-1.487361086,0.0887723579,1.8490528799
 N,0.698176914,1.3281473579,-0.4642791201
 N,1.422376914,-0.6640836421,0.1865828799
 C,1.791660914,0.5797143579,-0.1839541201
 N,3.082600914,1.0154413579,-0.2666501201
 H,3.360831604,1.7141104479,-0.9257777101
 H,3.783184234,0.7329253879,0.3886114499
 H,0.622419024,2.3202783079,-0.3645950501
 H,1.981492504,-1.4899566321,0.1136201999