Synthesis, Structure and Thermochemistry of Selected Group 11 and 12 Metal Compounds

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Abstract

Novel monovalent gold complexes of amidinates and guanidines were synthesized in order to study their thermal chemistry for the purposes of application as CVD precursors. It was found that these compounds decomposed to metallic gold in the presence of light. This resulted in the solution phase deposition of gold metal films using gold (I) acetamidinate as the gold source. The films were characterized by SEM, EDS, and XRD.

Gold (I) dimethyl guanidinate proved to be the only sublimable compound. For this reason it was used as a single source precursor in the deposition of gold metal films by thermal CVD. This was obtained at lower operating temperatures than those previously reported in literature. The films were studied by SEM and EDS.

Monovalent silver guanidines were synthesized for the same purposes as the gold analogues. These were found to be too unstable to reach the vapour phase and made for poor CVD precursors. The crystal structure of silver (I) dimethyl guanidinate proved to be a trimeric complex.

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Table of Contents

Title Page.....	1
Acceptance Sheet.....	2
Abstract.....	3
Acknowledgements.....	4
Table of Contents.....	5
List of Tables.....	8
List of Figures.....	9
List of Abbreviations.....	12

1. Introduction

1.1. Chemical Vapour Deposition.....	13
1.1.1. Gold CVD.....	16
1.1.2. Silver CVD.....	18
1.2. Photodeposition.....	20
1.3. Ligands.....	21
1.3.1. Amidinates and Guanidines.....	21
1.3.2. Xanthates.....	26
1.3.3. Phosphines and Thiophenes.....	29
1.4. Group 11 Monovalent Stereochemistry.....	31

Results and Discussion

2. Gold(I) Complexes

2.1. Amidinates and Guanidines.....	33
2.1.1. Crystal Structures.....	49
2.1.2. Thermolysis.....	56
2.2. Xanthates (homoleptic).....	61
2.3. Xanthates (heteroleptic).....	63

2.4. Conclusions.....	64
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3. Silver (I) Complexes

3.1. Guanidines.....	65
3.1.1. Crystal Structures.....	72
3.1.2. Thermolysis.....	76
3.2. Conclusions.....	80

4. Zinc(II) Guanidinate Complexes

4.1. Heteroleptic guanidinate complexes.....	81
4.1.1. Crystal Structures.....	88
4.2. Conclusions.....	93

5. Gold Metal Photo Deposition

5.1. 4 day Exposure Period (a).....	95
5.2. 14 day Exposure Period (b).....	97
5.3. 7 day Novel substrate Deposition (c).....	100
5.4. Conclusions.....	102

6. Gold Metal Chemical Vapour Deposition

6.1. 85 °C Deposition Temperature.....	103
6.2. 120 °C Deposition Temperature.....	107
6.3. Conclusions.....	113

7. Experimental

7.1. General Synthetic Procedures.....	114
7.1.1. Xanthates.....	114
7.2. Group 11 Chlorides.....	115
7.3. Gold (I) Complexes.....	116
7.3.1. Guanidines & Amidines.....	117
7.3.2. Xanthates (homoleptic).....	118

7.3.3. Xanthates (heteroleptic).....	118
7.4. Silver (I) Complexes.....	118
7.4.1. Guanidines (homoleptic).....	118
7.5. Zinc (II) Complexes.....	120
7.6. Thermolysis Experiments.....	121
7.7. Photodeposition Experiments.....	121
7.8. CVD Experiments.....	123
7.8.1. Substrate Cleaning Procedure.....	124
7.8.2. CVD Deposition Procedure.....	124
8. Conclusions.....	125
9. References.....	126
10. Appendix: Crystallographic Data for Compounds 1, 2, 3, 10, 14, 16	
Compound 1.....	128
Compound 2.....	137
Compound 3.....	144
Compound 10.....	151
Compound 14.....	164
Compound 16.....	177

List of Tables

Table 1: Gold CVD precursors.....	17
Table 2: Silver CVD precursors.....	19
Table 3: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ (1)	50
Table 4: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2$ (2)	52
Table 5: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (3)	54
Table 6: Selected Bond Lengths and Angles for gold (I) amidinates/ guanidines.	56
Table 7: Selected Crystal Data of $\text{Ag}_3[(^i\text{PrN})\text{CN}(\text{Me})_2]_3$ (8).....	72
Table 8: Selected bond lengths and angles for $\text{Ag}_3[(^i\text{PrN})\text{CN}(\text{Me})_2]_3$ (8)	74
Table 9: Selected crystallographic data for 15	88
Table 10: Selected Bond Lengths and Angles for 15	90
Table 11: Selected Crystallographic data for 16	91
Table 12: Selected Bond Lengths and Angles for 16	93

List of Figures

Figure 1:	Schematic representation of basic CVD process (1)	15
Figure 2:	Diimides varying backbone functionality.....	21
Figure 3:	Theoretical bonding of S-alkylisoureas with soft metal centres	21
Figure 4:	Generalized structures for the diimides	22
Figure 5:	Synthesis routes for amidinate and guanidinate alkali salts	23
Figure 6:	Resonance stabilized coordination of metal centres in μ -1 and μ -2 chelation	24
Figure 7:	Monodentate bonding of amidinates and guanidinates	24
Figure 8:	Resonance structures of the guanidinate ligands.....	25
Figure 9:	N'-Isopropyl-N''-isopropylidene-N,N-dialkyl-guanidine ("oxidized guanidine").....	25
Figure 10:	Dithiolates, a) dithiocarbamates, b) alkyl dithiolates, c) xanthates.	26
Figure 11:	Resonance forms of chelating and bridging metal xanthates	27
Figure 12:	Possible bonding configurations through one sulphur moiety.	27
Figure 13:	Generalized synthesis of xanthate salts.....	28
Figure 14:	Generalized structures of a) thiophenes, b) phosphines.....	29
Figure 15:	a) Au(III) reduction by THT, b) Au(III) reduction by TPP, c) THT replacement by trialkylphosphine	30
Figure 16:	Hybridization of 5dz² , 6s and 6p orbitals (26).	31
Figure 17:	Complicated methylene proton signal for 2	37
Figure 18:	Au (I) n-Butyl amidinate	38
Figure 19:	Pathways toward monomeric gold guanidinates & amidinates.....	43
Figure 20:	¹ H NMR Spectra of Compound 7	45
Figure 21:	Methine proton of compound 7	46
Figure 22:	NMR spectra of 7 showing small TMS guanidine impurity.....	47
Figure 23:	Schematic of theoretical gold (I) guanidinate / amidinate monomer geometry	48
Figure 24:	Torsion angle in amidinates and guanidinates (resonance removed for clarity)	49
Figure 25:	SC-XRD of Au ₂ [(ⁱ PrN) ₂ CMe] ₂ (1).....	50
Figure 26:	SC-XRD of Au ₂ [(ⁱ PrN) ₂ CMe] ₂ (1)	50
Figure 27:	SC-XRD of Au ₂ [(ⁱ PrN) ₂ C ⁿ Bu] ₂ (2).....	52
Figure 28:	SC-XRD of Au ₂ [(ⁱ PrN) ₂ C ⁿ Bu] ₂ (2).....	52

Figure 30:	SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (3).....	54
Figure 29:	SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (3)	54
Figure 31:	SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (3).	55
Figure 32:	a) β -Hydride abstraction to produce one equivalent of oxidized guanidine and b) guanidine formation through a gold hydride intermediate	57
Figure 33:	CDI deinsertion to produce gold amide or alkyl gold complex.....	57
Figure 34:	Decomposition spectra of compound 3 after 2 hours at 120 °C	60
Figure 35:	TGA analysis of 8	62
Figure 36:	^1H NMR spectra of 10	67
Figure 37:	SC-XRD of $\text{Ag}_3[(^i\text{PrN})\text{CN}(\text{Me})_2]_3$ (8). Hydrogen	72
Figure 38:	SC-XRD of $\text{Ag}_3[(^i\text{PrN})\text{CN}(\text{Me})_2]_3$ (8)	73
Figure 39:	TGA of compound 10 at 5 °C/min ramp rate	77
Figure 40:	^1H NMR showing guanidine as the soluble decomposition product of 10	78
Figure 41:	Possible polymerization of oxidized guanidine, forming insoluble products.	79
Figure 42:	Possible solid phase decomposition pathways of 10	79
Figure 43:	^1H NMR of 14	82
Figure 44:	Unlabelled peaks showing new solid formation within liquid compound 14	83
Figure 45:	^1H NMR spectra of 15	84
Figure 46:	^1H NMR spectra of 16	86
Figure 47:	^1H NMR spectra showing possible alternate ethyl environments of compound 16	87
Figure 48:	SC-XRD of compound 15 . Hydrogen atoms were	88
Figure 49:	SC-XRD of compound 15 , looking down Cl-Zn bond.....	89
Figure 50:	SC-XRD compound 16	91
Figure 51:	SC-XRD compound 16	92
Figure 52:	SEM image of a) at (2.6 kV).....	96
Figure 53:	EDS of a).....	97
Figure 54:	SEM image of b)	98
Figure 55:	EDS of film b) deposited over 14 days.	99
Figure 56:	XRD of film c) indicating crystalline gold and glass slide substrate.	100
Figure 57:	SEM image of photodeposited gold on a fibre Bragg grating filament (2.6 kV).....	101
Figure 58:	Sublimed gold (I) dimethylguanidinate precursor on Si(100) wafer.....	104
Figure 59:	EDS data of rectangular region seen in Figure 58.....	104

Figure 60:	SEM image of structure from Figure 58, after three days of atmospheric exposure.....	105
Figure 61:	Nanoparticle formation	106
Figure 62:	SEM image of Gold CVD film (i).	108
Figure 63:	EDS spectra of (i), field seen in Figure 62	109
Figure 64:	SEM image of Gold CVD film (ii).	110
Figure 65:	EDS data of (ii) from Figure 64.....	110
Figure 66:	XRD of (ii)	111
Figure 67:	SEM cross sectional image of (ii)	112
Figure 68:	Schematic of photodeposition apparatus	122
Figure 69:	Schematic of Fibre Bragg Grating photodeposition apparatus	123
Figure 70:	Schematic of CVD deposition apparatus	123

List of Abbreviations

Acac – Acetylacetonate

ALD – Atomic Layer Deposition

CDI – diisopropyl Carbo Diimide

CVD – Chemical Vapour Deposition

DCM – Dichloromethane

DSC – Differential Scanning Calorimetry

DFT – Density Functional Theory

EDS – Energy Dispersive X-ray Spectroscopy

FBG – Fibre Bragg Grating

NMR – Nuclear Magnetic Resonance

SEM – Scanning Electron Microscopy

TBP – Tributyl phosphine

TGA – Thermogravimetric Analysis

THT – Tetra Hydro Thiophene

TMS – Trimethylsilane

TPP – Triphenyl Phosphine

XRD – X-Ray Diffractometry

1) Introduction

1.1. Chemical Vapour Deposition

Chemical Vapour Deposition (CVD) is a thin film growth technique used to deposit a variety of thin films. The materials being deposited can range from metals, semiconductors, insulators, superconductors and organic materials. This technique has been applied industrially for microelectronics, and optoelectronics. The resultant films can be polycrystalline, epitaxial or amorphous.

Each CVD process can be broken down into three categories and thus named using these conditions.

- i) **Film Source:** In the past, metal containing precursors tended to be the metal halides(1). Currently metals capped with organic ligands have been found to be more volatile, thus reducing the energy requirements (1). Operating pressures approach atmospheric with the use of organometallic precursors, decreasing system costs. Organometallic ligands also decrease in poisoning of the resultant metal film.
- ii) **Pressure:** Reduced pressure aids in volatilization of the precursor. This can be carried out under Ultra High Vacuum conditions (UHV-CVD), Low Pressure (LPCVD), or even atmospheric pressure (AP-CVD).
- iii) **Enhancement:** Different techniques have been used to increase CVD film growth rates, and film properties (morphology, impurities, conformality). For example a common CVD technique called Plasma Enhanced CVD (PECVD). In this method the precursor while in the gas phase is excited to an ion, radical or neutral excited species. This increases the reactivity of the precursor at the substrate. Photo excitation of the gaseous precursor, physisorbed or chemisorbed precursor on the substrate, or the substrate itself is often used to enhance CVD, and is generally called photo-CVD.

Desirable precursors should meet certain requirements.

- i) **Volatility:** They should have a significant vapour pressure to be carried via gas flow to the deposition substrate. This is achieved by keeping molecular weight low and limiting intermolecular interaction. Distillable liquids are ideal (due to their specific and reproducible vapour pressure); these can be achieved by frustrating crystallinity via asymmetric ligands and long branched alkyl chains (1).
- ii) **Reactivity:** While in the gas phase the precursor should not react with other precursor molecules. Coordinative saturation of the metal centre will prevent the possibility of oligomerization of the precursor molecules.
- iii) **Controlled Decomposition:** The precursor should decompose to the desired product at the substrate under a reasonable temperature. Decomposition products that are not associated with the target film should be chemically inert to the film as well as volatile so as to not introduce contamination in the target film.

CVD is sometimes used in conjunction with a reactive carrier gas. This initiates the decomposition of the precursor before contact with the substrate. Usually these reactive carrier gases are used to form semiconductor films in the case of metal nitrides, or oxides. This is not always the case as hydrogen can be used to form metallic films. A schematic based on that of C.R. Kleijn best describes this process(1). If no secondary reactive gas is used, reactivity occurs purely at the surface.

Figure 1: Schematic representation of basic CVD process (1)

The reactive surface sites of the substrate can vary as the substrates vary. Substrates tend to be metal oxides, typically alumina, titania, or silica. The surface oxygens can be occasionally terminated by hydrogen, forming surface hydroxyl sites. The most common substrate is silicon because of its application to microelectronics. Silicon has a native oxide layer at the surface; these can be oxygen atoms bridged between silicons or be hydroxyl sites. The hydroxyl density can be increased by using a variety of chemical and thermal methods that also clean the surface of impurities. These hydroxyl sites are the reactive sites at the surface. In metal film deposition the proton of the hydroxyl sites is lost in volatile reaction products, resulting in a single monolayer where the metal is chemically bound to the Si surface via oxygen. Continued growth proceeds from surface metal sites, without surface hydroxyl sites. Surface sites can also be silicon hydride sites, achieved by baking the surface under hydrogen, removing hydroxyl sites as H_2O .

1.1.1. Gold CVD

Current gold CVD methods utilize gold halides, as well as fluorinated organometallic precursors. Some drawbacks of these types of precursors are the existence destructive byproducts (HCl, HF) that can etch the film, substrate, as well as damaging vacuum systems. The etching of gold metal films is not really a concern in gold CVD as once the metal layer is formed, it is very resilient, requiring aqua regia to remove. Non-halogenated precursors contain Au-C bonds that result in carbon deposits within the film (2). These deposits can make for amorphous structure, poor conductivity and poor film uniformity (2).

Of the precursors in Table 1, i) and ii) are commercially available as CVD precursors.. The complex i) has a melting point of 81-82°C, and sublimes at 25°C with a pressure of 0.01 mmHg. The precursor is available from Strem chemicals for \$1,400.00 / 500 mg, or \$4,200 / 2 g. Haruta *et al.* sublimed the precursor at 33°C and a substrate temperature of 200°C to 500°C resulting in varied gold nanoparticle thin films. It was found that gold metal nanoparticles on metal oxide surfaces tend to be very active to oxidation by carbon monoxide at low temperatures (3).

Table 1: Gold CVD precursors

	Compound	Sublimation Temperature	Melting Point	Decomposition Temperature	Process Conditions
i		25°C @ 0.01 torr	81-82°C	24°C	Laser (4)
				200°C to 500°C	Thermal (3)
ii		25°C @ 0.01 torr	~5°C	24°C	Laser (4)
iii		20°C @ 0.04 torr	23-25°C	105°C	Laser (5)
iv		30-40°C @ 0.2 torr (6)	Unreported	200°C	Thermal (6), Solution/Thermal (6)
v		70°C @ 0.02 torr	70-71°C	70°C @ 0.02 torr	Monolayer growth on thiol functionalized surface (7)
vi		60°C @ 0.01 torr	Unreported	260°C	Thermal (7)

1.1.2. Silver CVD

The CVD of silver metal has received some attention recently. Typically, as film thickness decreases, conduction does as well. In the case of copper it was found that at low film thicknesses (<100 nm) resistivity increased dramatically (8). However, silver thin films tend not to follow this trend. The high conductivity of bulk silver can be maintained down to feature sizes lower than 100 nm (9). Thus, silver thin films are of interest as conductive films in microelectronics.

Compounds that result in the best films are those of the silver (I) phosphine acetylacetonate (acac) family. In Table 2, a liquid precursor consisting of a datively bonded vinylsilane can be seen (i). The alkene silver complexes used for CVD are not advantageous as before volatilization they tend to lose alkene and form $\text{Ag}[\text{acac}]_n$ which is then subsequently volatilized (10). This behaviour has not been seen for Ag(I) precursors utilizing phosphine ligands, like that of (iii).

Table 2: Silver CVD precursors

	Compound	Sublimation Temperature	Melting Point	Decomposition Temperature	Process Conditions
i		Liquid – Introduced under Argon flow	Liquid	>180 °C	Thermal (10)
ii		275 °C @ 10 ⁻⁴ torr	Unreported	275 °C	Thermal (11)
iii		R=Me; 80-100 °C R=Et; 50-70 °C @ 5x10 ⁻² torr	R=Et; 45 °C	250-350 °C	Thermal (12)

1.2. Photodeposition

Much attention has been paid to different photodeposition techniques from solution phase recently (13, 14, 15). This has been primarily in the nanotechnology field. Photodeposition differs from that of chemical deposition techniques. Instead of utilizing a chemical reaction to initiate decomposition, the decomposition is initiated by absorption of photons.

Light has been used in the past to initiate decomposition of precursors to form uniformly distributed sizes of nanoparticles as well as quantum dots (14). Films have been deposited using photo techniques from solution to deposit organic (15), metallic (16), and ceramic films (13).

The decomposition to form metallic products results in the reduction of a metal containing precursor (14). The decomposition pathways are overall poorly understood (16).

1.3. Ligands

1.3.1. Amidinates and Guanidines

Carbodiimides are a class of compounds that contain a $RN=C=NR$ functionality. These compounds are named via the functionality of the central carbon. When the central carbon is functionalized these compounds share similar structure to that of ureas ($(NH_2)_2CO$) and are named as such. By having alcohols or thiols at the central carbon, O-alkylisoureas and S-alkylisoureas (respectively) can be formed. If an alkyl group is present at this carbon these can be called alkylisoureas, but a more common term is amidine. Similarly if an amine occupies this position it's called a guanidine and not an aminoisourea.

Figure 2: Diimides varying backbone functionality a) O-alkylisourea, b) S-alkylisourea, c) amidine, d) guanidine.

This document will primarily deal with the chemistry of the amidines and guanidines for silver and gold. The alcohol derivative is shown as a contrast with xanthic acids (see section 1.3.2.). Also the thiol derivative is shown as it was an early candidate for a ligand system in the gold(I) chemistry. It was believed that the ligand would show novel bonding to the gold centre making it a candidate for future work.

Figure 3: Theoretical bonding of S-alkylisoureas with soft metal centres

However these ligands decompose readily upon heating (17) making for a poor ligand for CVD/ALD applications and were thus taken out of consideration.

The amidinates and guanidates are dynamic ligands that allow for variations of the alkyl groups on the chelating nitrogens and in the backbone position. In the case of guanidates the amine in the backbone position can be primary or secondary. This proton resulting from a primary amine synthesis allows for the ligand to be dianionic, when both protons are abstracted (Figure 4). The ligands can be asymmetric. Asymmetric carbodiimides are those which contain different alkyl groups on chelating nitrogens. This thesis will deal with diisopropyl monoanionic amidinates and guanidates, alkyl groups on chelating nitrogens are isopropyl and in the case of guanidates equivalent backbone alkyl groups are used.

Figure 4: Generalized structures for the diimides a) amidine, b) monoanionic guanidine, c) dianionic guanidine.

The amidinate and guanidinate complexes make for excellent precursors due to their low molecular weight, high steric hindrance, and the existence of a nitrogen-metal bond that helps decrease carbon impurities in the product film. These compounds can be synthesized through a variety of pathways. This document pertains mostly to salt metathesis routes to products. Two general ligand syntheses are shown below.

Figure 5: Synthesis routes for amidinate and guanidinate alkali salts

The parent amidines and guanidines tend to be liquids; this is indicative of their potential to make volatile coordination complexes for CVD applications. They can also chelate the metal centre through both nitrogen groups in the case of the amidinates, or two out of the three in the case of the guanidinate. The chelation can be μ -1 or bridging μ -2 between two metal centres. The resonance stabilization of chelation increases the stability in the compound, hindering decomposition in the gas phase.

Figure 6: Resonance stabilized coordination of metal centres in μ -1 and μ -2 chelation

Both amidinate and guanidinate ligands can bond in a monodentate fashion through one nitrogen. This can be caused by steric hindrance around the metal centre. The metal centre may also have preference for a specific geometry.

Figure 7: Monodentate bonding of amidinates and guanidines

The decomposition pathways of metal amidinate and guanidinate complexes are not well understood, and thus will be a focus of this thesis. It is generally believed that metal guanidinate species decompose more readily than the amidinate analogues due to the weak N-C bond in the exocyclic position resulting in loss of amine and deinsertion of carbodiimide (18). This contrasts with amidinates

which have a C-C bond in the exocyclic position making the amidinates potentially more thermally stable as the metal nitrogen bonds are more likely to break than the C-C bonds.

Figure 8: Resonance structures of the guanidinate ligands

The benefit of the guanidinate ligand in precursor chemistry resides in its third resonance structure. The exocyclic amido moiety of the guanidinates participates in the π system of the chelate ring, allowing the amides to be slightly pyramidalized frustrating crystal packing giving greater volatility than similar amidinate analogues (19).

It is often stated that amidinates and guanidinates decompose to their analogous amidines and guanidines. However these postulated decomposition mechanisms do not adequately address the necessary proton source. Some groups discuss the possibility of transient water in their reaction as being the proton source (20). Recent findings in dimeric decompositions of guanidinates point toward a pathway where the formation of N'-Isopropyl-N''-isopropylidene-N,N-dialkyl-guanidine ("oxidized guanidine") supplies the proton to another ligand and producing the guanidine.

Figure 9: N'-Isopropyl-N''-isopropylidene-N,N-dialkyl-guanidine ("oxidized guanidine")

It is important to note that this decomposition pathway has only been studied in depth for the case of copper (I) guanidinate dimers. This decomposition can be applied easily to the gold (I) guanidinate dimers as they have similar structures.

1.3.2. Xanthates

Dithiolates are a class of compounds derived from carbon disulphide. Dithiolates can be further broken down into classes depending on functional group in the backbone position (similarly to guanidines and amidines). Dithiolates are sulphur derivatives of oxylates and are named as such by adding the prefix dithio to the pre-existing oxylate compound. If there is an alkyl group in the backbone position, the ligands are simply alkyl dithiolates. If a primary or secondary amine resides in the backbone position, the ligands are called dithiocarbamates. If an alkoxy moiety exists in the backbone position these are O-esters of dithiocarbonic acid (they are also the sulphurous derivatives of carbonate esters). These are commonly referred to as xanthates, where an alkoxy group occupies the exocyclic position. If a proton exists on one of the sulphur groups it is called a xanthic acid.

Figure 10: Dithiolates, a) dithiocarbamates, b) alkyl dithiolates, c) xanthates.

Xanthic acids are liquids, and thus could potentially form volatile CVD precursors when compounded with gold. They can also chelate the metal centre through both sulphur atoms, or to two metal centres in a bridging μ -type bonding. This resonance in chelation allows for greater stability in the compound, hindering decomposition in the gas phase.

Figure 11: Resonance forms of chelating and bridging metal xanthates

Xanthates can also ligate using only one of the available sulphur groups in a formal manner or in bridging μ -type bonding. Early in this work a third type of coordination was proposed, the possibility of weak coordination with the lone pairs on the oxygen group. However it is obvious that the metal centres used in this chemistry heavily favour sulphur coordination due to their inherent softness. Like guanidines, xanthates are monoanionic ligands that allow for resonance stabilization when in the chelation coordination mode.

Figure 12: Possible bonding configurations through one sulphur moiety.

Xanthates were chosen as ligands for Au (I) metal centres for a combination of reasons. Firstly they are easily synthesized and purified. Two different synthetic routes can be employed to produce

xanthate salts, one which can be applied to air sensitive syntheses and the other occurs in an aqueous environment (Figure 13).

Figure 13: Generalized synthesis of xanthate salts

This simple synthesis allows for easy variation in the alkyl group simply by varying the solvent which is also a reactant in the first reaction pathway. The ligand is inexpensive to synthesize, which is a priority in this research to offset the cost of gold-containing reactants. The ligand is also monoanionic allowing for a coordinatively saturated Au (I) xanthate.

By far the most important aspect in choosing a ligand is its decomposition products. In CVD/ALD applications, the ligand preferably decomposes cleanly to volatile by products that are unreactive towards the target film. Vreugdenhil *et al.* found via gas phase IR experiments that metal xanthates of Cu (I) decomposed to CS₂, COS, and CO₂ (21). Previous work done by Fackler *et al.* found that olefins of the alkyl group were also formed as Cu (I) xanthates decomposed (22). Similar decomposition studies have not been performed for gold (I) xanthates, but should yield similar results to that of Cu (I).

Even though gold is a noble metal there is some worry that Au₂S could be formed. Although there are no literature examples of this reactivity, it is known that silver xanthates form Ag₂S upon decomposition (23). However, these experiments were not performed at reduced pressure, and this

reactivity occurred with dimeric silver xanthates not heteroleptic compounds as discussed within this thesis. The possibility of gold sulphide formation will be discussed in subsequent chapters.

1.3.3. Phosphines and Thiophenes

Phosphines and thiophenes are common neutral ligands employed in main group and transition metal chemistries.

Figure 14: Generalized structures of a) thiophenes, b) phosphines, alkyl groups can be equivalent or inequivalent.

Group 11 metals in the +1 oxidation state prefer linear coordination modes to ligands. This is why dimeric structures are formed when using bidentate ligands. Rather than force the metal centre into a coordination mode that may cause instability in the product complex a dative bonding ligand might be used. A neutral dimeric complex might become monomeric if a strong enough dative bond is made to the metal centre, yet not so strong as to result in reduction of the metal centre. Thiophene has been shown to be a good stabilizing datively bonding ligand but has not yet been shown to form monomeric gold complexes (24). Phosphines prove to have similar reactivity to Au (III) as thiophenes.

Figure 15: a) Au(III) reduction by THT, b) Au(III) reduction by TPP, c) THT replacement by trialkylphosphine

That is the reduction of Au(III) to Au(I) complexes stabilized by a thiophene or phosphine yet without reduction to gold metal. The phosphines being stronger datively bonding ligands as they can replace thiophene in thiophene stabilized gold (I) complexes. The use of these in ligand environments with the above chelate ligands will be explored.

1.4. Group 11 first oxidation state stereochemistry

Much theoretical work has been done to explain the trend of coordination number in the coinage metals (25). Generally the first oxidation state of group 11 metals prefer a linear coordination, although other coordination numbers are possible. Au(I) complexes show the most affinity for two coordinate linear complexes, some trigonal planar complexes are possible such as $\text{AuCl}(\text{PPh}_3)_2$, also the tetrahedral complex of $[\text{Au}(\text{PMe}_3)_4]^+$ have been synthesized but lose phosphine ligands easily, reverting back to the diphosphine linear gold complex. Copper and silver also show a preference for two coordinate linear geometry, however not holding to that rule as stringently as gold. The trend of tendency for linear complexation of the coinage metals is $\text{Au(I)} > \text{Cu(I)} \gg \text{Ag(I)}$.

Based on Ligand Field Theory of bonding it may be favourable to hybridize the full nd_{z^2} orbital with the vacant 6s orbital. This hybridization leads to two orbitals, one with electronic density in the xy plane and the other. In a second order mixing scenario the ψ_2 (not the $5d_{z^2}$ directly) hybridizes with the 6p to form two linear hybridized orbitals that result in Au(I) linear complexes (26).

Figure 16: Hybridization of $5d_{z^2}$, 6s and 6p orbitals (26).

Since the valence shell is the $6s^1$ orbital it must be used in the hybridization, as opposed to mixing the $5d_{z^2}$ orbital directly with the $6p_z$ orbital which would result in a similar hybridized orbital.

Other theories utilize only s and p orbital mixing to describe the bonding orbitals of the coinage metals (27). This may be accurate for copper and silver but in the case of gold with an entire f-block of electrons it is less likely that the hybridization is as simple as s-p hybrids. Trigonal planar complexes can be adequately described using sp_xp_y hybridized orbitals but are of higher energy than that of the linear sp_x hybridized orbital. The energy gap between the two possible orbitals is least in the case of silver showing that it is more likely than the other coinage metals to make a trigonal planar coordination.

Results and Discussion

2. Gold(I) Complexes

2.1. Amidinates and Guanidines

Gold guanidines and amidines have been previously studied to a small extent as catalysts. Gold oligomers (such as dimers, trimers and tetramers) have been shown to have high catalytic activity for the room temperature oxidation of CO on TiO₂ surfaces. It's believed that the smaller the Au-Au distance, the higher the activity (28). These dimeric gold complexes have a high molecular weight, as the ligands contain bulky ring structures in the attempt to use steric bulk to force metal centres closer together (29). Since ring structures tend to π -stack in the solid phase causing high melting points, and high molecular weights decrease volatility in an idealized manner, the previously studied compounds are not likely CVD/ALD candidates, but are useful for comparison to our results. Surprisingly, no thermal studies of the Au (I) amidines or guanidines have previously been reported. Since low molecular weight guanidines and amidines had not been synthesized or studied thermally we decided to determine their potential as CVD precursors by studying their thermal properties via atmospheric TGA, DSC, and MP, as well as sublimation temperatures.

The Au(I) amidines and guanidines proved to be unstable at room temperature, decomposing to metallic gold as well as other insoluble products. The decomposition was faster while in solution of hexanes or pentane and resulted in a gold mirror deposited on vials and flasks accompanied by deep purple / black precipitate. It was found that the Au(I) amidinate and guanidinate complexes were unstable in polar solvents, prompting formation of Au(0) starting as a red solution, turning purple then black; likely indicating the formation and agglomeration of nanostructures. Due to this decomposition, the compounds were stable and soluble in only a handful of solvents: hexanes, pentane and benzene, with a short lifetime unless kept at freezer temperatures (-36 °C). While dissolved in these

solvents and shielded from light, decomposition occurred slower than when exposed to light. This shows a component of the decomposition is somehow photo assisted. Due the instability of this class of compounds, they were kept in the freezer at -36 °C where solutions of the Au(I) amidinates and guanidines had a lifetime of a few weeks, but as a solid could be kept indefinitely.

The synthesis of Au(I) amidinates and guanidines proved to be somewhat touchy. Firstly the reaction had to take place at low temperature (-36 °C). If the ligand salt was made *in situ* without being isolated as a solid before addition of AuCl(THT), then decomposition of the gold compound occurred, and greatly reduced yields. The reaction generally resulted in the highest yield when an isolated, solid lithium salt of the ligand was suspended in hexanes and subsequently cooled to -36 °C, followed by addition of solid AuCl(THT). Both AuCl(THT) and the ligand salt reactants were sparingly soluble in hexanes once isolated. This low solubility and low temperature likely limited the kinetics of side reactions that resulted in decomposition. The low solubility control of kinetics is in essence the same as using an extremely dilute reaction of soluble reactants. If the reaction took place at room temperature the reaction goes to the desired product, but decomposition occurred before the desired reaction can go to completion. Therefore the low temperature reduced the kinetics of reaction and maintained the stability of the reaction product until the reaction proceeded to completion.

Au₂[(ⁱPrN)₂CMe]₂ (1):

The Au(I) acetamidinate was initially synthesized in poor yield (~25%). These reactions were done overnight at -36 °C. Efforts were made to synthesize the sodium and potassium salts of the guanidines in an effort to increase yield, since it had been reported in literature that lithium salts resulted in Au(I) reduction side reactions to Au(0) leading to poor yields(30). The potassium and sodium salts were synthesized by first quenching the lithium acetamidinate salt with water, forming acetamidine. After drying the liquid amidine completely, sodium or potassium hydride was used in a

hydrogen elimination reaction that resulted in the production of either sodium or potassium amidinate salt, respectively. The combination of quenching by water, drying of the liquid amidine for reintroduction into the drybox and subsequent hydrogen elimination reaction made for an overall low yielding process for the ligand salt due to drying procedures. The synthesis of the sodium and potassium salts became more costly than possible benefits would yield, thus it was abandoned.

It was found that with continued use of the lithium salt the yield increased to acceptable levels (72%) with careful, concise syntheses, as well as the washing of product mixture with additional warm hexanes. The additional solvent wash dissolved product that was otherwise insoluble at freezer temperature or trapped by the formation of insoluble LiCl.

The ^1H NMR of **1** (see experimental) showed one doublet belonging to the methyl groups (δ 1.25 ppm) of the isopropyl moieties bound to the chelating nitrogens. There was also one septet belonging to the methine proton (δ 3.57 ppm), integrating with the methyl groups in a ratio of 2:12. The methyl groups are all equivalent due to free rotation about the methine-chelating nitrogen bond. Symmetry makes methyl protons on each chelating nitrogen equivalent. The single methine and methyl environments indicate a symmetric structure. A singlet was seen for the remaining methyl group bound to the backbone carbon (δ 1.62 ppm) its integration was three.

The ^{13}C NMR showed a weak peak at δ 168.49 ppm, this is the common shift range of the unsaturated bridgehead carbon. Generally on a 300MHz NMR, 500+ scans were required to resolve this signal. The methyl on the backbone carbon was found at δ 50.97 ppm due to its proximity to the NCN resonance, followed by the methine carbons of the isopropyl groups, giving one peak (δ 26.81 ppm), and the methyl carbons with one strong peak at δ 16.09 ppm.

The equivalent isopropyl peaks seen in the ^1H and ^{13}C NMR spectra is a common occurrence in the homoleptic monovalent gold and silver guanidines and amidinates. They are indicative of

symmetric structures, but does not clarify the extent of oligomerisation as these can also all be highly symmetric with equivalent ligand NMR spectra.

A solid phase experiment to determine the room temperature stability of solid phase gold (I) and silver (I) amidinate/guanidinate complexes was performed. Product was purified by recrystallization, dried and crushed into a powder. The samples were prepared in the drybox and left in vials exposed to ambient light and temperature. When discolouration was seen, this marked the stability of the complex. The longer the onset of discolouration the more stable the complex, this would determine whether a sublimation experiment could be performed, or whether the compound was too thermally unstable. It was found that the acetamidinate gold (I) compound would decompose in less than 12 hrs.

Au₂[(ⁱPrN)₂CⁿBu]₂ (2):

Compound **2** was always isolated in low yields despite the improved synthetic method discussed for **1**. The synthesis of **2** always resulted in decomposition, identified by the reaction solution going charcoal black and cloudy. This is possibly owing to the high solubility of the lithiated amidinate in hexanes. The long n-butyl backbone results in a high concentration of ligand in solution, causing the reaction to proceed too quickly, resulting in partial decomposition. This reaction was attempted under extremely dilute conditions with the same result.

After filtration of the aforementioned black precipitate, decomposition continued even when the supernatant was placed in the freezer. After 24 hours recrystallized product was found within the vial along with more of the black decomposition product, which was removed along with the solvent *via* pipette. The crystals were good enough for SC XRD analysis, and enough product was available for a ¹H and ¹³C NMR. The reaction had to be repeated to obtain enough product for thermogravimetric analysis.

The ^1H NMR had the typical methine proton septet at δ 3.74 ppm. An oddly shaped peak was seen at δ 2.26 ppm and it integrated to two protons. The peak looked like an overlap of one triplet and two doublets (Figure 17).

Figure 17: Complicated methylene proton signal for **2**

The integration and shift indicated that this was the methylene protons associated with the carbon directly bound to the bridgehead carbon (position 1, Figure 18). Theoretically these protons should have been a triplet, split by neighbouring methylene protons (position 2, Figure 18). However, the rotation around this position was hindered on the time frame of the NMR.

Figure 18: Au (I) n-Butyl amidinate

The NMR takes snapshots of the proton environments. At one time a population of molecules shows two inequivalent protons on the second methylene carbon position, causing a doublet of doublets formation. A population of the molecules also is in the position where the protons are equivalent causing a triplet formation. These two signals average out to the unique formation seen in Figure 17. The methylene peaks second from the bridgehead carbon (position 2, Figure 18) were similarly split into a multiplet and integrated to two protons (δ 1.44 ppm), which could be two overlapping quintets or similar to the previous example, two quartets and a quintet. A doublet at δ 1.33 ppm integrated to 12 protons corresponding to the isopropyl methyl groups. A sextet at δ 1.17 ppm corresponded to the methylene protons furthest from the bridgehead carbon and integrated to two protons. Finally the triplet corresponding to the methyl group at the end of the n-butyl moiety was seen at δ 0.80 ppm and integrated to 3 protons. The ^{13}C NMR was more straightforward with the bridgehead carbon at δ 171.55 ppm, a typical shift. The isopropyl methine was seen at δ 50.61 ppm similar to **1**. Two methylene peaks moving away from the bridgehead carbon (position 3, Figure 18) were seen at δ 30.73 ppm and δ 29.85 ppm respectively. The isopropyl methyl carbon was seen at δ 27.20 ppm, the final n-butyl methylene at δ 23.06 ppm, and the n-butyl methyl at δ 13.92 ppm, all were of typical NMR shifts. The solid phase ambient conditions experiment (the same as described for **1**) where a purified powdered sample of **2** was left at ambient light and temperature; resulted in similar longevity as compound **1**. The n-butyl acetamidinate was synthesized in the hopes of increasing volatility by increasing the degrees of freedom

of the ligand. The poor yield of the final product made this a poor choice for a precursor. Therefore a sublimation study was not performed.

Au₂[(ⁱPrN)₂CN(Me)₂]₂ (3):

Compound **3** was isolated in reasonable yields (71.8%), benefitting from the improved synthetic method discussed previously for **1**. Crystals were grown from hexanes that were of a quality acceptable for SC XRD.

The ¹H NMR was very straight forward. A single methine septet environment was seen at δ 3.80 ppm corresponding to the isopropyl groups and integrated as two protons. Six protons were seen in a singlet at δ 2.43 ppm, corresponding to the two methyl groups bound to the exocyclic amine. These were equivalent due to free rotation about the bridgehead carbon and exocyclic nitrogen. A doublet at δ 1.37 ppm belonged to the isopropyl methyl groups and integrated to twelve protons. The ¹³C NMR showed the bridgehead carbon at δ 170.65 ppm, methine carbons of the isopropyl groups at δ 50.32 ppm, methyl groups bound to the amine at δ 40.89 ppm and the isopropyl methyl carbons at δ 27.21 ppm. These were all standard shifts for these functionalities.

Compound **3** proved to be the only complex that was successfully sublimed. The compound was purified by recrystallization prior to sublimation. Some decomposition was seen in the pot of the sublimation apparatus as the compound was slowly heated. At approximately 60 °C, **3** slowly became off white-grey, then light purple, deep purple and finally black over time. The sublimed product on the cold finger remained white throughout the experiment. The decomposition seen in sublimation was slower than that seen in the melting point determination. This is due to a kinetic component to decomposition. When the compound was heated quickly as in the bench top melting point determination, the decomposition temperature was found to be higher. Yields during sublimation were thus increased dramatically once the sublimation temperature was found. A bench top solid phase experiment (the

same as that described for **1**) showed that this compound decomposed over a period of a day by showing a slight purple discolouration.

Au₂[(ⁱPrN)₂CN(Et)₂]₂ (4**):**

The diethyl Au (I) derivative was found to be in the lowest yield due to its instability relative to the other Au (I) guanidines. Similarly to **1**, the sodium and potassium salts of the diethyl guanidine were made from catalytically formed guanidine (**31**) for the purpose of applying the synthesis to the other Au (I) and Ag(I) guanidines. It was found that the losses incurred during ligand synthesis did not outweigh the losses of gold starting material and was thus abandoned. The synthesis was carried out similarly to that of **3**.

The ¹H NMR showed one septet belonging to two methine protons (δ 3.80 ppm). A quartet integrating to four protons was seen at a shift of δ 2.85 ppm, these corresponded to the methylene groups of the ethyl moieties bound to the exocyclic nitrogen. A doublet corresponding to the methyls of the isopropyl groups was seen at δ 1.39 ppm, integration showed twelve protons. Finally a triplet was seen (δ 0.83 ppm) corresponding to the methyls of the ethyl group bound to the exocyclic nitrogen, these integrated to six protons. The ¹³C NMR showed the resonance of the bridgehead carbon to be at a typical shift of δ 166.33 ppm. At δ 50.45 ppm the resonance for the methine carbon corresponding to the isopropyl groups was seen. The following peak was that of the methylene carbon bound to the exocyclic nitrogen (δ 44.19 ppm). A shift of δ 27.13 ppm showed the typical position of the isopropyl methyl carbon. At δ 13.30 ppm the methyl carbons of the exocyclic ethyl groups were seen.

The decomposition of the diethyl guanidine complex (72 °C) was found to occur at a lower temperature than all other gold (I) guanidines studied. Compound **4** also proved to be more sensitive to light and temperature during the isolation procedure of the experimental. The solid phase decomposition experiment under ambient conditions (the same as that described for **1**) resulted in

decomposition after 3 hours; the first of all compounds studied to decompose. It was determined that this was the least stable of the Au (I) guanidates and thus a sublimation experiment wasn't performed as we ruled it out as a precursor.

Au₂[(ⁱPrN)₂CN(ⁱPr)₂]₂ (5):

The tetraisopropyl guanidinate Au (I) complex proved to have great overall yield at 91.1%, greatly benefiting from an additional wash of hexanes.

The ¹H NMR was a little more complicated than that of the gold (I) guanidates seen previously. This is due to the existence of two inequivalent isopropyl groups. The isopropyl methine proton shift was seen at δ 3.96 ppm corresponded to the chelating nitrogen position. While the methine proton for the exocyclic nitrogen was seen at δ 3.26 ppm, both integrated to two protons each. Two sets of doublets were seen both integrating to twelve protons each. These corresponded to the methyls of the chelating position (δ 1.39 ppm) and the exocyclic position (δ 1.06 ppm). The ¹³C NMR showed the bridgehead carbon shift to be δ 167.15 ppm. The carbons for the methine peaks were seen at δ 50.06 ppm and δ 48.48 ppm corresponding to chelating and exocyclic positions respectively. Similarly the peaks for isopropyl methyls were seen at δ 27.23 ppm and δ 22.55 ppm again corresponding to chelating and exocyclic positions respectively.

The compound was found to have a longer lifetime in the ambient conditions experiment (as described for **1**) lasting more than a day, longer than all gold (I) amidates or guanidates, excluding compound **6**. Unfortunately **5** decomposed prior to sublimation, excluding it as a gold CVD precursor.

Au₂[(ⁱPrN)₂CN(TMS)₂]₂ (6):

Compound **6** was the only guanidinate in this work that was synthesized from a potassium salt as opposed to a lithium salt. This was for convenience only. The potassium bis trimethylsilylamide was purchased from Aldrich, for curiosities sake it was reacted with diisopropyl carbodiimide to form K[(ⁱPrN)₂CN(TMS)₂]. Nothing else in the experimental was changed from that of the other gold (I) guanidinates.

Compound **6** was found to be the most resilient to decomposition in the solid phase on the bench top. The white powder changed to slightly grey after a period of a week. Of the gold (I) guanidinates **6** had the highest decomposition temperature (92 °C). Unfortunately the compound contained Si, which acts as a poison for conducting films, thus this material was excluded as a potential precursor and a sublimation study was not done.

The yield was marginally higher for **6** than the other guanidinates. This was most likely due to its higher stability. Once the compound was formed in solution it would take longer to decompose thus all reactants could go towards products before decomposition began, increasing yield. It is unlikely that the potassium guanidinate had any effect as potassium salts had been tried previously in this chemistry and found to increase the yield very minimally.

The ¹H NMR spectra contained a septet at δ 4.21 ppm corresponding to the two methine protons of the isopropyl groups present on the chelating nitrogens. The isopropyl methyl doublet was seen at δ 1.39 ppm and integrated to twelve protons. At δ 0.17 ppm a singlet for the methyls of the trimethylsilyl moieties was seen and corresponded to eighteen protons. The ¹³C NMR showed four carbon environments. The bridgehead carbon had a typical shift at δ 165.04 ppm. The methine carbons on the isopropyl groups had a shift of δ 49.73, while the methyls had a shift of δ 27.46 ppm. The TMS carbons were located at δ 2.38 ppm.

Au[(ⁱPrN)₂CN(TMS)₂](TPP) (7):

Various attempts were made to synthesize monomeric gold (I) guanidines and amidines by utilizing a strong dative ligand to coordinate to gold. Phosphines were chosen since they are a classic example and are of low molecular weight. Two pathways to achieve monomeric complexes were attempted. One method is the coordination of the phosphine to the gold chloride before introduction of amidinate or guanidinate lithium salt. The second route would be adding two equivalents of phosphine to the pre-existing dimeric products.

Figure 19: Pathways toward monomeric gold guanidates & amidates

It was found that both pathways proceeded without decomposition to metallic gold, but the desired products of these reactions were short lived and eventually resulted in the formation of an insoluble species. Additionally, it was found that the reaction would only proceed at room temperature in benzene or toluene. No decomposition was seen in the form of black precipitate or gold mirror. After filtration of the LiCl , the solvent was removed under reduced pressure, during this time a white powder

formed. The white powder proved insoluble in organic solvents, while decomposing to gold metal in coordinative solvents. Attempts to crystallize the product directly from the reaction solution post filtration resulted in an insoluble white precipitate. Interestingly when the bis trimethylsilyl guanidinate was used it had a significant lifetime before becoming an insoluble product. It's believed that these compounds oligomerized as opposed to decomposed as gold metal was not formed.

The proton NMR of **7** proved to be quite complex. Firstly the NMR consisted of two compounds, the heteroleptic compound **7**, as well as the bis trimethylsilyl guanidine ligand. The guanidine ligand is a product of decomposition that occurred within the timeframe of preparing the NMR sample and collecting the spectrum. This was further demonstrated after the sample was ejected from the NMR and had a faint white cloudiness that was not there previously; this was the insoluble decomposition product starting to form.

The proton NMR spectra can be seen in Figure 20. The phenyl protons of the triphenyl phosphine were seen far downfield as to be expected of the electron withdrawing phenyl rings. There were two sets of peaks, one was centred at δ 7.51 ppm. These were the six protons closest to the phosphine centre. The other nine protons are centred about δ 6.96 ppm. These sets of peaks straddle the benzene NMR solvent peak at δ 7.15 ppm. The next environment centred at δ 5.56 ppm is somewhat complex (see Figure 21).

Figure 20: ^1H NMR Spectra of Compound 7

This is one of the methine protons. It exists as two overlapping septets, this is due to hindered rotation about the C-N bond. The hindered rotation is due to sterically bulky exocyclic bis TMS amide. This steric hindrance was not from the TPP moiety as a similar splitting pattern was seen in the guanidine where no TPP is present (see inset of Figure 22, overlapping septets at 4.09 ppm and 4.11 ppm). The methine proton shift is over 1ppm farther downfield than generally seen.

Figure 21: Methine proton of compound **7** showing two separate septets caused by hindered rotation of the isopropyl group.

Another methine proton is seen at δ 4.00 ppm corresponding to the other isopropyl group that is unhindered by the exocyclic TMS moiety and was seen as a classic septet. Two doublets were seen at δ 1.69 ppm and δ 1.49 ppm, these correspond to the two isopropyl methyl protons and both integrate to six protons each. It was unclear if the doublet which lies farther downfield corresponded to the same isopropyl group as the methine proton with a large downfield shift (δ 5.56 ppm) but this was most likely the case. Finally a large singlet at δ 0.39 ppm was seen to correspond to the 18 methyl protons of the exocyclic TMS position.

Figure 22: NMR spectra of 7 showing small TMS guanidine impurity, a product of slow decomposition

The existence of two separate methine and methyl environments on the chelating nitrogens suggests that the guanidinate is bonding to the gold centre through one nitrogen in a κ^1 fashion. This behaviour is not unexpected, since Au (I) prefers a two coordinate linear geometry. The question is: why does the bis trimethylsilyl guanidinate ligand have a resistance to oligomerization/polymerization, unlike all other guanidinate and amidinate ligands seen in this thesis that were attempted in these heteroleptic systems? The most straightforward answer is steric bulk: the size of the backbone position decreases the bite angle of the ligand. Au (I) preference for linear geometry forces the compound into a non chelating geometry (Figure 23 a)). In the case of a bulky exocyclic group like bis TMS amide, this could decrease the bite angle of the ligand. This in turn could force the nonchelating nitrogen into a weak

interaction with the metal centre (Figure 23 b)). Another possibility is that the guanidinate ligand rotates to a position in which the exocyclic position is partially protecting the metal centre (Figure 23 c)). In this position the larger exocyclic group offers greater protection to the metal centre, thus making the bis TMS amide the more stable of the guanidines due to its bulk (Figure 23 d)). However NMR data showed that the isopropyl group closest to the phenyl rings has hindered rotation caused by the bis TMS amide moiety. Thus this makes the geometry seen in Figure 23 b) most likely.

Figure 23: Schematic of theoretical gold (I) guanidinate / amidinate monomer geometry

2.1.1. Crystal Structures

There was concern that the amidinates and guanidates of gold (I) would form tetramers, as seen in literature for different solvent systems for Au(I) guanidates and Ag(I) guanidates(29, 32).

The torsion angle is a measure of the planarity of the metallocycle. For gold (I) amidinate and guanidinate dimeric structures, the torsion angle is measured using the chelating nitrogens in the structure in a 'Z' pattern, measuring the angle between the two ligand planes. If the nitrogens are all in the same plane the angle between ligand planes is 0° . The bite angle is defined as the angle between the chelating nitrogens and the bridgehead carbon.

Figure 24: Torsion angle in amidinates and guanidates (resonance removed for clarity)

The torsion angle can also predict the degree of participation in π resonance of the backbone amide moiety. In the case of copper (I) guanidinate dimers there was seen a decrease in planarity (or core twist) between the two ligands as the backbone amide participated in the resonance. A trend between melting point and core twist showed that with increasing backbone amide π participation increased core twist and decreased melting point(33). The degree that the backbone amide moiety is participating also corroborates the bond length of the nitrogen with the central or bridgehead carbon. The shorter the bond length the greater the π participation, increased core twist and ultimately greater volatility.

$\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ (1)
Table 3: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ (1)

Figure 25: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ (1). Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Empirical formula	$\text{C}_{16}\text{H}_{34}\text{Au}_2\text{N}_4$
fw	676.40
T (K)	120
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Monoclinic
Space group	C2/c
a (Å)	25.98
b (Å)	11.23
c (Å)	17.72
α (deg)	90.00
β (deg)	131.98
γ (deg)	90.00
V (Å ³)	4059
Z	8
ρ (calcd) (Mg/m ³)	2.214
Abs coeff (mm ⁻¹)	14.443
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0276 wR2 = 0.0507
^a R1 = $\sum F_o - F_c / \sum F_o $; wR2 = $(\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$

Figure 26: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ (1). Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Crystals of $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$ were grown from pentane in at -30°C and underwent single crystal X-ray analysis (Figure 25).

The central metallocycle that contained all the nitrogen, and gold centres was found to be perfectly planar with a torsion angle of 0° . The bridgehead carbons within the ring structure (C1/C1') were found to lie above and below the rings plane, offset by 8.7° from planarity, this also resulted in the methyl groups (C2/C2') to lie above and below the plane. The isopropyl groups on the chelating nitrogens showed a standard geometry in which the methyl group bonded to the methine carbon bent toward the metal centres while the proton on the methine carbon pointed away from the metal centres. The methine carbon of the isopropyl groups lay within the same plane as the nitrogen and gold centres. The nitrogen centres were found to have a sum of angles around them close to 360° , which indicated their planar geometry, signifying that a π resonance existed in the N-C-N moiety. Similar bond distances between the bridgehead carbon of the amidinate and the two chelating nitrogens also the existence of the resonance structure (see Table 6).

There is no reason to believe there is a Au-Au bond in these dimeric structures. As can be seen in Figure 25, the gold centres were bowed out away from each other, trying to limit interaction, they were held within a close proximity by the amidinate ligands. The gold centres deviated slightly from linear geometry (171.15°), which indicated a further lack of bonding interaction between the gold centres. The Au-Au distance was $2.653 \text{ \AA}$, shorter than the one other existing gold (I) amidinate dimeric species, $2.712 \text{ \AA}$ found by Fackler in his formamidinates (34). The bite angle is dependent on metal centres within multi metal centred systems. Larger bite angles are indicative of larger metal centres that have larger M-M distances. The bite angle of the amidinate ligand was found to be 122.37° , larger than those found in previously reported Cu (I) and Ag (I) amidinate complexes (20), and smaller than that found in the Au (I) formamidinate (127.8°)(34). The Au-N bond distances are similar to those seen in the monovalent Cu, Ag, and Au amidinate dimer examples (20, 34).

Table 4: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2 \text{ (2)}$

Figure 27: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2 \text{ (2)}$. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Empirical formula	$\text{C}_{22}\text{H}_{46}\text{Au}_2\text{N}_4 \text{ (2)}$
fw	760.56
T (K)	120
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Triclinic
Space group	P-1
a (Å)	7.851
b (Å)	8.88
c (Å)	10.21
α (deg)	104.22
β (deg)	102.47
γ (deg)	105.08
V (Å ³)	635
Z	1
ρ (calcd) (Mg/m ³)	1.987
Abs coeff (mm ⁻¹)	11.54
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0325 wR2 = 0.0681
^a $R1 = \sum F_o - F_c / \sum F_o $; $wR2 = (\sum w(F_o - F_c)^2 / \sum w F_o)^{1/2}$

Figure 28: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2 \text{ (2)}$, looking down the plane of the metallocycle. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

The $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2$ complex was found to have a general structure similar to that of the $\text{Au}_2[(^i\text{PrN})_2\text{CMe}]_2$. The metallocycle was again found to be planar with a torsion angle of 0° . The bridgehead carbons ($\text{C4}/\text{C4}^i$) were found to lie outside of the plane formed by the four nitrogens, lying 4.52° above and below the plane. The isopropyl groups bound to the chelating nitrogens showed standard geometry as the methine carbons laid within the same plane as the nitrogen and gold centres. The planarity of the nitrogen centres indicated the existence of π overlap between the nitrogens; similar bond distances to the metal centres and the bridgehead carbons were also seen. All Au-Au distances were similar in the amidinates and guanidates where $\text{Au}_2[(^i\text{PrN})_2\text{C}^n\text{Bu}]_2$ was the shortest (see Table 6). Shorter Au-Au amidinate bond distances are seen only in Au (II) dimeric complexes. These divalent gold compounds have halides directly bonded to the metal centres. By removing an electron and adding the electron withdrawing halide it's possible to create a smaller Au-Au distance (24, 29). Since the Au-Au distance in compound 2 is the shortest of the gold amidinates/guanidates it's fitting that the bite angle also be the smallest, as is seen (Table 6).

$\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (**3**)
Table 5: Selected Crystal Data of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (**3**)

Figure 29: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (**3**). Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Empirical formula	$\text{C}_{18}\text{H}_{40}\text{Au}_2\text{N}_6$
fw	734.49
T (K)	200
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Monoclinic
Space group	C2/c
a (Å)	19.48
b (Å)	11.35
c (Å)	12.08
α (deg)	90.00
β (deg)	113.21
γ (deg)	90.00
V (Å ³)	2454
Z	4
ρ (calcd) (Mg/m ³)	1.988
Abs coeff (mm ⁻¹)	11.96
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	
^a $R1 = \sum F_o - F_c / \sum F_o $; $wR2 = (\sum w(F_o - F_c)^2 / \sum w F_o)^{1/2}$

Figure 30: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (**3**), looking down the plane of the metalocycle. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

It was seen in copper (I) guanidates that the structure was heavily influenced by the existence of π resonance not only within the cyclic nitrogen system but also with the exocyclic nitrogen position. This caused high torsion angles within the metalocycle (**33**). This was not

seen in the gold (I) guanidinate. The $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ complex was found to have similar metallocyclic structure as the previously described Au (I) amidinates.

The methine carbons of the isopropyl groups bound to the chelating nitrogens lay above and below the central plane formed by the metal centres and the chelating nitrogens (see Figure 31). The sum of angles around the chelating nitrogen centres and surrounding bonds was 358.16° a slight deviation from planar while the sum of angles around the bridgehead carbon was 360.01° . This was indicative of an extended π system between the chelating and exocyclic nitrogens with the bridgehead carbon. The bond length of the bridgehead carbon with each of the nitrogens centres indicated by how much p orbital overlap there was with the exocyclic amide. The distance to chelating nitrogens was $1.337 \text{ \AA}$, while the distance to the exocyclic amide was $1.404 \text{ \AA}$. The similar bond length to the exocyclic position is indicative that the electron pair spent some time in the exocyclic position. This caused the chelating nitrogens to lose electron density in their sp^2 hybridized orbitals. This reduced their trigonal planar shape, and resulted in the methine protons to lie above and below the metallocycle plane.

Figure 31: SC-XRD of $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ (**3**), looking down the plane of the guanidinate ligand. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Table 6: Selected Bond Lengths and Angles for gold (I) amidinates/ guanidines.

Au ₂ [(ⁱ PrN) ₂ CN(Me) ₂] ₂		Au ₂ [(ⁱ PrN) ₂ CMe] ₂		Au ₂ [(ⁱ PrN) ₂ C ⁿ Bu] ₂	
Selected Bond Lengths (Å)					
Au1-N1	2.041(2)	Au1-N1	2.044(3)	Au1-N1	2.044(5)
Au1-N2	2.038(2)	Au1-N2	2.037(3)	Au1-N2	2.044(5)
Au1-Au1 ⁱ	2.6559(6)	Au1-Au1 ⁱ	2.6529(5)	Au1-Au1 ⁱ	2.6436(6)
N1-C4	1.337(3)	N1-C1	1.328(5)	N1-C4	1.339(7)
N2-C4	1.337(4)	N2-C1	1.346(5)	N2-C4	1.346(8)
N3-C4	1.404(3)				
Selected Bond Angles (°)					
N1-Au1-N2	170.64(10)	N1-Au1-N2	171.15(13)	N1-Au1-N2	171.63(19)
N1-C4-N2	123.8(2)	N1-C1-N2	122.6(4)	N1-C4-N2	121.8(5)
Sum of Angles (°)					
N1	358.2	N1	359.3	N1	359.8
N2	358.2	N2	359.8	N2	359.6
N3	359.9				
Torsion Angles (°)					
N1-N2-N1 ⁱ -N2 ⁱ	0	N1-N2-N2 ⁱ -N1 ⁱ	0	N1-N2-N2 ⁱ -N1 ⁱ	0

2.1.2. Thermolysis

It was found that the gold (I) amidinates and guanidines were relatively thermally unstable. In a melting point study all compounds were found to decompose, slowly turning purple then black before melting ranging from 72 °C for the diethyl guanidine complex and 96 °C for the n-butyl amidinate. All of the compounds were also found to decompose before sublimation at 20 mtorr except for the dimethyl guanidine which sublimates at ~80 °C. Since the dimethyl guanidine gold (I) complex could be volatilized and showed a low decomposition temperature (83 °C) it was applied to a simple CVD gold film deposition experiment (see Section 6.).

The decomposition of the gold (I) guanidines and amidinates were studied by NMR (see experimental section 7.6.). The decomposition of both guanidines and amidinates can proceed

through two different routes. Firstly the β -hydride abstraction route that can result in the formation of one equivalent of guanidine / amidine and one equivalent of oxidized guanidine / amidine (Figure 32).

Figure 32: a) β -Hydride abstraction to produce one equivalent of oxidized guanidine and b) guanidine formation through a gold hydride intermediate

The second major pathway is the deinsertion of CDI to produce a metal amide or metal alkyl intermediate that can then disproportionate to gold metal.

Figure 33: CDI deinsertion to produce gold amide or alkyl gold complex

Since there were two guanidates or amidates per molecule it became apparent that the CDI deinsertion pathway would have to occur twice, or the β -hydride abstraction would occur twice. Finally to make things more complicated an intermediate hydride could form the guanidine or amidine which can further decompose, depending on the temperature, to CDI and amine or alkane.

Decomposition studies for the gold (I) guanidates showed varying results depending on the alkyl groups on the backbone position. The tetraisopropyl guanidate was found by NMR to completely decompose at 120 °C after 2 hrs. The product peaks showed numerous isopropyl doublets all within δ 0.4 ppm range. CDI was seen as the major product in the decomposition spectra with a very distinct doublet shift of δ 1.04 ppm with corresponding septet at δ 3.33 ppm. A spectra of the parent guanidine showed the remaining doublet environments in the decomposition corresponded with the guanidine. However the tetraisopropylguanidine has five isopropyl environments as it exists as two isomers in solution. These peaks could be overlapping other isopropyl environments such as a diisopropyl amine, another possible decomposition product. A separate experiment under the same conditions containing only tetraisopropyl guanidine was performed to determine if the ligand itself would deinsert CDI producing diisopropyl amine. The resulting spectra showed parent guanidine, and again CDI as a major product. Diisopropyl amine was not seen. A spectrum of diisopropyl amine yielded confirmation that the doublet could exist beneath one of the isopropyl doublets of the parent guanidine. Luckily the methine proton of the amine had a characteristic septet shift of δ 2.78 ppm which can barely be seen. The low concentration of the diisopropyl amine was most likely due to amine volatility; once the cap on the NMR tube is opened to add solvent, the amine could escape. No oxidized tetraisopropyl guanidine was seen. This complex would have two singlets instead of an isopropyl environment, as well as having lost a methine proton environment. There is a possibility that the singlets could lie beneath the existing mass of doublets. But this is most likely not the case as the electron withdrawing ability of the newly formed

nitrogen carbon double bond most likely places the singlets farther downfield above δ 1.50 ppm, beyond the isopropyl doublet region.

The existence of tetraisopropyl guanidine as a major product in the NMR showed that a major decomposition pathway must have been β -hydride abstraction. The existence of CDI was confusing until it was realized that the guanidine itself would decompose to CDI and amine readily at the experimental conditions. The oxidized guanidine was not seen as a decomposition product, and the diisopropyl amine is seen in minimal quantities. The oxidized guanidine was presumed quite volatile as was the amine and could have escaped upon addition of NMR solvent. The other possibility was that they reacted with each other to produce an unknown complex or possibly insoluble oligomer or polymer.

The dimethyl guanidinate gold (I) complex decomposed via the β -hydride abstraction route as well. The NMR spectrum consists of free guanidine as the major product, but was absolutely devoid of CDI. In a separate experiment the dimethyl guanidine was found not to decompose under the same conditions. The lack of CDI gave insight into the decomposition of the previous tetraisopropyl guanidinate gold (I) complex. The deinsertion of CDI must have occurred after the formation of the guanidine, tetraisopropyl guanidine was less thermally stable than that of the dimethyl guanidine due to its steric bulk, thus resulted in amine and CDI at lower temperatures. The minor peaks of the decomposition spectra were of the most interest. A small isopropyl environment was seen as a doublet at δ 1.53 ppm that integrated as 6 protons, to two singlets one upfield at δ 1.43 ppm, and one downfield at δ 1.71 ppm, integrated to 3 protons each. Finally a third singlet at δ 2.67 ppm integrated to 6 protons. These peaks all revealed that the oxidized guanidine is formed as a decomposition product of the β -hydride abstraction. Unfortunately integration of the methine proton could not be determined as it overlapped with other environments, its shift was tentatively set at δ 3.34 ppm (see inset of Figure 34).

Figure 34: Decomposition spectra of compound 3 after 2 hours at 120°C

The dimethyl oxidized guanidinate was presumably much more volatile than its parent guanidine due to the lack of hydrogen bonding between molecules. This may have resulted in the loss of some product upon addition of NMR solvent; this was why the oxidized guanidine product was in a ratio of 1:6 with the other decomposition product dimethyl guanidine. Theoretically as per Figure 32, the ratio should be 1:1.

Unfortunately the dimethyl oxidized guanidine has not yet been successfully synthesized, to show comparative spectra to the single decomposition product. This product was hypothesized as a result of theoretical DFT work done by a colleague studying the decomposition of copper (I) guanidinate dimers.

2.2. Xanthates (homoleptic)

$\text{Au}_2[\text{S}_2\text{CO}^n\text{Bu}]_2$ (8):

The dimeric structure of Au (I) n-butyl xanthate has been synthesized previously by Fackler et al(35). However the thermolysis of this species and other analogues has not been studied nor has their applicability as CVD precursors studied. The n-butyl xanthate was synthesized to compare with Facklers results.

The synthesis of the compound was straight forward and was done on the bench top. Any alcohol could be used as the solvent; water was used as it was more convenient than methanol and ethanol. Also if methanol or ethanol is used, the solubility of the potassium xanthate salt is reduced, thus would require overnight synthesis as opposed to a couple hours in water. Contrary to gold (I) guanidinate or amidinate synthesis the product gold (I) xanthate is insoluble in the solvent and the potassium chloride is soluble. The yield was found to be quantitative. Unfortunately purification by recrystallization was impossible. The gold (I) homoleptic xanthates were found to be insoluble in most solvents, except for dimethylsulphoxide (DMSO). This made NMR analysis possible, but did not help with purification by recrystallization as the solvation was too strong.

Figure 35: TGA analysis of 8

The TGA data was very compelling. It showed a slow onset of volatility initiating around 75 °C. This slow onset could mean evaporation, whereas a quick onset would have meant rapid decomposition. The % weight loss was found to equal that of the n-butyl xanthate ligand. The derivative curve shows one feature which is indicative of a clean decomposition, a requirement of CVD and ALD. When the sample pan was removed it was coated in gold metal. All of these findings lead us to believe that this could make a viable CVD precursor. However once a sublimation experiment was performed it was evident that the compound decomposed prior to sublimation. The homoleptic Au (I) xanthates were then abandoned as plausible precursors for CVD.

2.3. Xanthates (heteroleptic)

Au[S₂CO^tBu](TPP)₂ (9):

Compound **9** was air stable thus synthesis was carried out on the bench top. AuCl(TPP) was dissolved in benzene while the ligand was added as a solution dropwise. The reaction yielded two immiscible liquids. KCl was dissolved in the aqueous phase while **9** was dissolved in the benzene. Attempts to grow SC XRD quality crystals resulted in failure.

The product was found to be pure by NMR once isolated. The proton NMR showed a multiplet at δ 7.41 ppm and corresponded to the twelve proton environments on the phenyl rings closest to the phosphine. At δ 6.94 ppm the other eighteen phenyl proton environments were seen as a multiplet. The methyl proton environments were seen at δ 1.66 ppm and corresponded to the *t*-butyl group of the xanthate ligand. The integration was nine protons.

¹³C spectrum gave the typical triphenyl phosphine carbon splitting pattern showing six separate environments. These were seen at δ 134.50 ppm, δ 134.29 ppm, δ 130.46 ppm, δ 130.44 ppm, δ 129.06 ppm, δ 128.92 ppm. The methyl carbon of the xanthate moiety yielded a peak at δ 28.20 ppm. The carbon bound between the sulphur groups of the xanthate was not seen as previously discussed.

Compound **9** was found to melt at 120 °C before decomposing. This prompted a sublimation experiment that resulted in melting at 120 °C followed by decomposition at 135 °C prior to sublimation.

2.4. Conclusions

2.4.1. Amidinates and Guanidines

The synthesis of all compounds was found to be good yield (>71%) excluding that of compounds **2** and **7**. The amidinates and guanidines were found to be unstable in the presence of light, decomposing to metallic gold. Decomposition rates were increased when the compounds were dissolved in solution. The production of guanidine upon decomposition was found to be indicative of a β hydride abstraction decomposition mechanism. The tetraisopropyl guanidine was found to decompose under the experimental conditions of 120 °C. **3** was the only compound found to be sublimable. The crystal structures of compounds **1**, **2**, and **3** showed these compounds to be dimeric, it was assumed that the compounds without crystals would have also been dimeric, excluding **7**.

2.4.2. Xanthates (homoleptic)

The work of Fackler *et al.* was recreated (35), in order to study the possibility of homoleptic xanthates as CVD precursors. It was found that these compounds decompose cleanly to metallic gold in a TGA experiment. However attempts to sublime (a requirement of vapour deposition techniques) **8** resulted in decomposition prior to sublimation.

2.4.3. Xanthates (heteroleptic)

With the introduction of ligand bearing sulphur in conjunction with two datively bonding phosphine ligands a compound stable under ambient conditions was prepared. **9** also proved stable enough to form a liquid at 120 °C but decomposed prior to sublimation at 135 °C. For the purposes of CVD or ALD this novel compound was seen as promising. Gold (I) xanthates utilizing low molecular weight phosphines have been shown to be distillable liquids, but never applied to the CVD or ALD field.

3. Silver (I) Complexes

3.1. Guanidines

Silver (I) guanidine chemistry has not been very well studied. The only published data on the subject that could be found pertains to a hexanuclear bimetallic Ag(I), Au(II) guanidine complex in which the gold centres bear the ligand and silvers bridge the gold centres(36). Ag(I) amidinate complexes have been synthesized by Gordon et al(20). These proved to be a mixture of dimeric and trimeric structures. The trimer differs from other homoleptic amidinate or guanidine complexes of the +1 oxidation state group 13 metals, as these tend toward dimeric or tetrameric oligomers (24, 29, 32-34, 37, 38). Our driving force for studying the guanidines of Ag(I) was that the third resonance structure where the exocyclic group adopts an N=C bond (see introduction) could force the silver centres to adhere to a dimeric conformation. It has been shown that the dimers of group 13 metals are volatile enough to prove useful in the formation of metal thin films via CVD (33).

The synthesis of the silver guanidines was done in hexanes at room temperature. Like the gold (I) guanidines, it was found that these compounds were sensitive to light and thus had to be wrapped in foil during synthesis. Unlike their gold counterparts the silver guanidines did not form from the addition of AgCl to a suspension of the previously isolated guanidine lithium salt. An *in situ* synthesis of the ligand at lower temperatures (-36 °C) also did not result in the formation of silver guanidine without significant decomposition. Only upon addition of AgCl to a room temperature solution of ligand generated *in situ* could silver guanidine be formed. It is likely that, upon drying, the ligand salt forms an insoluble oligomer that does not break upon re-suspension in hexanes (39). The reaction of silver chloride with the lithiate ligand in this case is less favourable than breaking the oligomer. Another possibility may be that, without a coordinating solvent, the alkali salts of the guanidines and amidines oligomerize into insoluble units larger than dimers. This conclusion is supported by the fact that all single crystal XRD of alkali guanidine and amidinate dimers have a solvent of crystallization in

the unit cell, all of which are polar (39, 40). The silver (I) guanidates were also found to be pure by ^1H NMR without recrystallization. This was beneficial as the compounds did not have considerable lifetimes in solution during attempts to recrystallize them. These compounds were considerably less stable than their gold counterparts and couldn't be stored in the solid phase for more than a couple weeks. Decomposition was then seen as grey discolouration of the white solid.

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_3$ (10):

Compound **10** was synthesized in hexanes by first forming the lithium salt in hexanes and rather than isolating the ligand product, AgCl was added. The reaction was done in the absence of light, as was the isolation process (see Section 7.4.). Crude yields were high (85%) and the crude product was very pure by NMR, recrystallization resulted in considerably reduced yields (45%). This was due to further handling of the unstable product to achieve slow crystal formation for high purity and for SC XRD quality crystals.

It was important to isolate crude product and perform a ^1H NMR analysis to determine if a mixture of dimer or trimer existed in solution, while crystallization may preferentially crystallize out one of the isomers. The crude NMR can be seen in Figure 36. One product was seen, and was very pure excluding the residual ether (from BuLi) and hexanes, the reaction solvent.

Figure 36: ^1H NMR spectra of **3b**.

Interestingly, the methine proton septet (δ 5.58 ppm) that corresponds to the chelating isopropyl positions was seen to be broadened (Figure 36), this was present in the recrystallized NMR as well (Figure 36 inset). This could have been indicative of almost equivalent methine protons overlapping. This broadening could be indicative of a more complex structure, most likely a trimeric species. The peak broadening wasn't seen in the methyl doublet (δ 1.35 ppm), corresponding to the twelve protons also on the isopropyl group. The exocyclic methyl protons bound to the amide were seen to have a shift of δ 2.63 ppm, and corresponded to six protons.

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{Et})_2]_3$ (11**):**

The silver (I) diethyl guanidinate proved to be in poor yield (36.4%). This was due to the unstable nature of compound **11**. Synthesis was carried out by the same synthesis that the other silver (I) guanidinate were. However it was found when removing the solvent under vacuum that the result was a mixture of guanidine (liquid) and compound **11**, making a viscous liquid. The silver complex could be isolated by recrystallization: a minimum of hexanes was used to dissolve the liquid then allowed to cool to $-36\text{ }^\circ\text{C}$. The resulting solid was shown to be pure by NMR. Interestingly, it decomposed in the NMR solvent over the period of extended carbon scan durations owing to its instability. Similarly the diethylguanidinate complex of gold (I) (compound **4**) was found to be the least thermally stable.

The ^1H NMR showed the typical isopropyl methine septet at δ 3.65 ppm, corresponding to two protons. The broadening of this peak was seen but was not as pronounced as in **10**. A quartet integrating to four protons was seen at δ 3.01 ppm. These protons were from the methylene groups bound directly to the nitrogen in the exocyclic position. Twelve protons were found to correspond to a doublet found at δ 1.36 ppm. These were the methyl protons of the isopropyl groups bound to the chelating nitrogen positions. The final peak seen was at δ 0.95 ppm, a triplet of six protons corresponding to the methyl groups of the ethyl moieties bound to the exocyclic nitrogen.

The ^{13}C NMR spectrum shows five environments. The bridgehead carbon is seen at δ 168.40 ppm, similar to that seen for the other Ag (I) guanidinate. The next signal was seen at δ 48.62 ppm corresponded to that of the methine carbons bound to the chelating nitrogen positions. At δ 43.91 ppm the methylene carbons of the exocyclic positions were seen. The isopropyl methyls showed a signal at δ 27.85 ppm while the methyl carbons on the ethyl moieties of the exocyclic position showed a signal at δ 13.44 ppm.

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(^i\text{Pr})_2]_3$ (12):

The tetraisopropyl guanidinate silver (I) complex experimental differs from that of the other guanidines (see Section 7.4.1.). The reaction was carried out at freezer temperature ($-36\text{ }^\circ\text{C}$) whereas the other compounds were able to be synthesized at room temperature. This was due to the increased solubility of the lithiated tetraisopropyl guanidinate in hexanes. At the concentrations used in the synthesis the ligand was completely dissolved at room temperature, upon addition of AgCl the reaction proceeded too quickly and instantly turned black. By cooling the ligand solution to $-36\text{ }^\circ\text{C}$ the concentration of the lithiated ligand salt was decreased in solution. Upon addition of the AgCl the reaction proceeded slower with less concentration of ligand, thus being less exothermic. Once the synthesis was performed in the freezer the yields were found to be similar to those of the other silver (I) guanidines (70%).

The ^1H NMR spectra showed two methine protons at δ 3.85 ppm and two at δ 3.46 ppm as septets. These protons corresponded to methine groups of the chelating isopropyl positions and exocyclic positions respectively. The septet at δ 3.85 ppm showed similar broadening that was seen for **10** in the inset of Figure 36. This broadening could be indicative of a more complex structure, most likely a trimeric species similar to that found for compound **10**. The broadening would be due to more than one partially overlapping septets. Two doublets were seen, also corresponding to both chelating and exocyclic methyl positions (δ 1.34 ppm, δ 1.21 ppm). The peaks both integrated to twelve protons each.

The ^{13}C NMR showed a typical bridgehead carbon shift of δ 167.28 ppm. There were two separate carbon environments seen at δ 49.13 ppm, and δ 47.98 ppm. These corresponded to the methine isopropyl carbons in the chelating and exocyclic positions respectively. The methyl carbons of the chelating isopropyl group showed a shift of δ 27.60 ppm, with the exocyclic methyl carbon environment at δ 23.44 ppm.

Ag₃[(ⁱPrN)₂CN(TMS)₂]₃ (13):

Similarly to that of **6**, compound **13** was synthesized using the potassium guanidinate salt. The synthesis differed from the gold (I) TMS derivative in the same way as the other silver guanidinates. The ligand was made *in situ* by addition of CDI to a suspension of potassium bis trimethylsilyl amide. The guanidinate was not isolated, prior to metal halide introduction. The addition of potassium instead of lithium did not seem to hurt the yield (69.9% crude) or rate of reactivity of the reaction when compared to the other Ag (I) guanidinates. The final compound was able to be recrystallized and yielded a purified yield of 41.6%.

The recrystallized product yielded a ¹H NMR consisting of a methine environment at δ 3.76 ppm, corresponding to the isopropyl environments bound to chelating nitrogens. Integration was seen as two protons. The doublet for the methyl protons on the isopropyl groups was seen at δ 1.11 ppm, and showed an integration of twelve protons. The methyl protons bound to the silicon of the exocyclic trimethylsilylamide moiety was seen at δ 0.29 ppm, and corresponded to eighteen protons. The ¹³C NMR gave a bridgehead carbon shift of δ 157.92 ppm. The isopropyl methine carbon environments yielded a shift of 46.66 ppm, with the isopropyl methyls at δ 28.00 ppm. The TMS methyl carbons had a shift of δ 3.00 ppm.

The single crystal x-ray structure of silver (I) dimethyl guanidinate combined with NMR data leads us to believe that all the silver (I) guanidinates studied form trimeric complexes. Gordon et al(20) found that the amidinates of silver (I) formed a 1:1 mixture of dimer to trimer (as shown by NMR) but also forms a 1:2 dimer/trimer equilibrium in the solid phase seen by SCXRD. The acetamidinate silver (I) was also found to sublime at 80 °C and 40 mtorr. It's likely that the silver amidinate sublimed as a monomeric or dimeric species, then formed 1:2 trimer/dimer equilibrium in the solid phase and a 1:1

equilibrium in NMR solvent. It was also found that the acetamidinate silver (I) melted at 95 °C without decomposition.

The silver (I) dimethyl guanidinate complex was found to have only one product set of environments via NMR spectra. The SC XRD spectra showed that the compound exists as a trimer in the solid phase and not as a mixture of dimer to trimer. Gordon found two separate sets of environments in NMR spectra, one being the dimer and one the trimer. In the solid phase he found an increase in trimer concentration. The fact that we see one set of peaks in the NMR and one structure in the solid phase could mean that the trimer exists in the liquid and solid phase. It could also mean that the compound is dimeric in solution and converts completely to a trimeric structure in the solid phase, although this explanation is needlessly complicated.

Amidinate / Guanidinate Heteroleptic Complexes

An issue with bidentate ligands and monovalent metal centres is that they can form dimeric, trimeric, or complexes with a higher number of metal centres. As the units in the oligomer (and thus, the molecular weight) increases, the volatility of these complexes decreases, making poor precursors for CVD. In the effort of creating volatile CVD precursors, trialkyl phosphines have been used in conjunction with amidinates and guanidinates to promote monomer formation. Silver (I) metal centres are the best candidates of the group 11 monovalent metals for adduction, as they are the most likely to form tricoordinate species (26).

Using tributyl phosphine as the dative bonding ligand with silver (I) chloride yields a liquid silver halide that is stable at room temperature and ambient conditions (41). The halide was added to a solution of hexanes and pre-isolated guanidinate or amidinate lithium salt. It was found that after short reaction times (3-6 hours.), followed by filtration of the LiCl, and removal of the solvent under reduced pressure yielded a viscous liquid. This liquid was extremely sensitive to oxygen and water. The liquid

decomposed in a matter of minutes even within the drybox if left uncapped. In the freezer, this species had a lifetime of a day but never actually froze. Unfortunately the NMR spectra were extremely hard to discern. This is due to overlapping environments of the n-butyl phosphine ligand obscuring or overlapping with the xanthate alkyl environment. We were able to determine that the chloro silver phosphine, as well as guanidine (a decomposition product) was present in the NMR. Attempts to distill were unsuccessful due to the compound's reactive nature. If the reaction is done over an extended period, the result is the homoleptic silver (I) guanidines. When attempts were made to crystallize the product as a softer method of isolation, the homoleptic silver compound recrystallized leaving n-butyl phosphine in the mother liquor.

3.1.1. Crystal Structures

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_3$ (**8**)

Figure 37: SC-XRD of $\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_3$ (**8**). Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

Table 7: Selected Crystal Data of $\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_3$ (**8**)

Empirical formula	$\text{C}_{27}\text{H}_{60}\text{Ag}_3\text{N}_9$
fw	834.45
T (K)	200
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Triclinic
Space group	P-1
a (Å)	10.36
b (Å)	11.86
c (Å)	15.30
α (deg)	98.86
β (deg)	91.26
γ (deg)	105.5
V (Å ³)	1786
Z	2
ρ (calcd) (Mg/m ³)	1.552
Abs coeff (mm ⁻¹)	1.658
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0505 wR2 = 0.0741
^a $R1 = \sum F_o - F_c / \sum F_o $; $wR2 = (\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$	

It was found that **8** existed as a trimer in the solid phase. The structure of **8** was best described by imagining a plane formed by the three silver metal centres (Figure 37). Carbon C22 is the only other atom that lies within this plane (within approx. 6°). If one imagines each ligand forming a plane via two chelating nitrogens and the bridgehead carbon, the ligand containing C22 crosses that of the metal centres at an angle of 67.5° . Of the two other ligand planes, one lay above the silver plane, the other laid below it (see Figure 38).

Figure 38: SC-XRD of $\text{Ag}_3[\text{[}^i\text{PrN)CN(Me)}_2\text{]}_3$ (**8**). Hydrogen atoms were omitted for clarity, as were isopropyl groups. Thermal ellipses are shown at 30%.

The three silver centres were each seen to be in a semi-linear, two coordinate geometry. The bond angles of the metal centres deviated from linearity as much as 16.92° , whereas the gold (I) dimeric structures deviated from linearity by 9.36° at their maximum. The bond angles of Ag1 and Ag3 were similar while Ag2 was larger by almost 6° . The metallocycle was not planar as was the case with the gold (I) amidinates and guanidates studied. This was due to monovalent silver's lessened tendency towards linear geometries, as well as the guanidates increased flexibility to allow the chelate nitrogens to pyramidalize, compared to the amidinates. The bite angles of the ligands were decreased compared to the gold structures even though the silver metal centres were larger. This was due to the non planar

metallocycle conformation, and the distance between metal centres is increased by moving out of the plane of the ligand, instead of bowing outward within the plane as the case was with gold.

Table 8: Selected bond lengths and angles for $\text{Ag}_3[(^i\text{PrN})\text{CN}(\text{Me})_2]_3$ (**8**)

Selected Bond Lengths (Å)			
Ag1-N1	2.098(3)	Ag2-N4	2.091(3)
Ag1-N8	2.094(3)	Ag3-N5	2.102(2)
Ag2-N2	2.084(3)	Ag3-N7	2.117(2)
Ag1-Ag2	2.9545(5)	Ag3-Ag1	3.2173(5)
Ag2-Ag3	2.9896(5)		
N1-C4	1.338(4)	N6-C13	1.393(4)
N2-C4	1.336(4)	N7-C22	1.316(4)
N3-C4	1.402(4)	N8-C22	1.353(4)
N4-C13	1.329(4)	N9-C22	1.385(4)
N5-C13	1.338(4)		
Selected Bond Angles (°)			
N1-Ag1-N8	164.41(10)	N1-C4-N2	120.4(3)
N2-Ag2-N4	168.87(10)	N4-C13-N5	120.3(3)
N5-Ag3-N7	163.08(10)	N7-C22-N8	118.8(3)
Sum of Angles (°)			
N1	359.2	N6	359.6
N2	359.8	N7	359.9
N3	359.8	N8	359.8
N4	359.9	N9	360.0
N5	359.3		
Torsion Angles (°)			
Ag2-N4-N5-Ag3	44.9	Ag3-N7-N8-Ag1	62.7
Ag1-N1-N2-Ag2	41.8		

A few questions arose from Gordon's work with silver (I) amidinates (20), as well as the work presented here with silver (I) guanidates. Firstly why of the group 11 monovalent metals does silver differ so dramatically, while copper and gold are so similar? Secondly, why was it possible to form silver dimers of amidinates but not guanidates?

As shown in Section 1.3.4, silver (I) had the least tendency toward two coordinate linear structures of group 11.

It can be seen in Table 8 that the metal centres are two coordinate and semi linear coordination. However the close proximity of other silver metal centres could be indicative of some sp_xp_y hybrid orbital character forming a distorted trigonal planar geometry around each metal centre. It has been shown that silver (I) has a stronger affinity for trigonal planar geometry than the other coinage metals (26). This is reasonable, considering that silver has the highest ionic radius of the group 11 compounds.

The amidinate ligand in silver (I) amidinate dimers allow for π stabilization to exist between the chelating nitrogens only. This causes purely trigonal planar geometry around the sp^2 hybridized chelating nitrogens, making for a rigid ligand that has a limited bite angle range. Guanidinate on the other hand have an exocyclic amide group that can participate marginally in the π resonance of the chelating nitrogens. This allows for "flex" within the ligand as the nitrogens are not rigidly bound to trigonal planar geometry. The guanidinate allows for the trimer to exist while being flexible enough to minimize steric interactions between ligands.

3.1.2. Thermolysis

A sublimation study found that none of the guanidines could be successfully sublimed prior to decomposition. The decomposition result was deposition of a silver mirror on the sublimation apparatus sidewalls in the heating zone with no deposition seen on the cold finger. This occurred even when the sublimation apparatus was shielded from light.

Thermogravimetric analysis (TGA) of **10** (Figure 39) found that there was a weight loss of one equivalent of ligand while one equivalent of silver metal was left in the pan, which was obvious on inspection of the pan after the experiments were completed. This is consistent with the stoichiometry of these compounds, although the source of protons to produce free ligand is unknown. The TGA was further broken down to show that there was a weight loss of approximately two ligands (when considering trimeric **10**) corresponding to 40% of the weight loss. At this point a second feature was seen, corresponding to a less volatile decomposition product, possibly the dimethyl guanidine.

Figure 39: TGA of compound **10** at 5 °C/min ramp rate

An NMR study to determine the decomposition products of thermolysis of silver dimethylguanidinate (**10**) was undertaken. A screw cap NMR tube was charged with the compound and then heated to 120 °C for 4 hrs. The tube was chilled in liquid nitrogen and NMR solvent added to determine the decomposition products. The ^1H NMR spectrum of the decomposition was surprisingly clean and consisted of one major product, dimethyl guanidine.

Figure 40: ^1H NMR showing guanidine as the soluble decomposition product of **10**

The presence of the guanidine suggests a β -hydride abstraction mechanism (Figure 40) as the proton source. However, the necessary equivalent of oxidized dimethyl guanidine was not seen. This could be a situation like that of the gold (I) dimethyl guanidinate decomposition (section 2.1.2.) where the ratio of guanidine to oxidized guanidine is not as predicted (1:1) due to losses of volatile products when adding NMR solvent to the tube. The loss of two ligands at temperatures lower than that of the boiling point of the guanidine further solidified this theory.

It was shown in the gold (I) dimethyl guanidinate (section 2.1.2.) that under the conditions of the NMR decomposition experiment; the guanidine does not decompose to amine and CDI. Looking at Figure 40, it can be seen that there are a couple broadened doublets. This is indicative of partially soluble products, possibly a polymer. It has been discussed previously in the gold (I) guanidinate decomposition

that the pathway of β -hydride abstraction results in the production of an oxidized guanidine (see Figure 32).

Figure 41: Possible polymerization of oxidized guanidine, forming insoluble products.

The oxidized guanidine is relatively reactive as it contains two unsaturated carbon sites that can react with another oxidized guanidine in a polymerization reaction forming chains of oxidized guanidine. The reactive unsaturated carbon sites of the oxidized guanidine can react intermolecular manner to form a metal organic insoluble macromolecule. The oxidized guanidine can also react with a metal hydride forming the insoluble product seen.

Figure 42: Possible solid phase decomposition pathways of **10**

The TGA of **10** indicates a 2:1 oxidized guanidine to guanidine ratio through decomposition. This pathway would differ in products only by the expulsion of hydrogen gas (see Figure 42).

3.2. Conclusions

The silver (I) guanidines were found to decompose in light and over time to a greater extent than the analogous gold compounds. The silver (I) dimethylguanidine (**8**) was found to form a trimeric species, not dimeric species as the analogous copper (**33**) and gold compounds. It was believed that the other Ag (I) guanidines also form trimers. TGA study of the silver (I) dimethylguanidine showed a weight loss corresponding to loss of ligand while leaving silver in the pan, beginning at 95 °C. Sublimation attempts of the same compound resulted in decomposition prior to sublimation even in the absence of light. Since this class of compounds seems to decompose before becoming a gas; the silver (I) guanidines could not be applicable as CVD precursors. There is however the possibility for solution phase photo deposition that can be explored further since these compounds are photo unstable. Solution phase decomposition studies showed guanidine formation as well as an insoluble side product while forming a silver mirror. The decomposition pathway seems identical to that seen in the gas phase.

4. Zinc (II) Guanidinate Complexes

We managed to isolate a number of different zinc compounds serendipitously through the use of zinc metal in the reduction of Ti (IV) to Ti (III). In some cases these compounds were isolated and recrystallized to yield SCXRD quality crystals. This work began by attempting to recreate the serendipitous synthesis of **15** under controlled conditions to better understand the complex chemistry of Zn (II).

4.1. Zn (II) Triisopropyl Guanidinate Complexes

$\text{Zn}[(^i\text{PrN})_2\text{CN}(^i\text{Pr})]_2$ (**14**):

Compound **14** was synthesized by either salt metathesis or alkane elimination; alkane elimination having the greatest yield. The compound was found to be a clear liquid with a viscosity similar to honey. The liquid was pure by NMR without the need for distillation (see Figure 43).

The ^1H NMR spectra showed a multiplet of two overlapping methine environments that integrated for one proton at δ 3.76 ppm, this corresponded to the exocyclic isopropyl methine. The amine proton participated in the unusual splitting pattern. The methine proton was split into a septet by the six neighbouring methyl protons, this septet was then split again by the amine proton into a doublet of septets. A septet for another methine proton of an isopropyl environment was seen at δ 3.62 ppm. This corresponded to the isopropyl environments bound to the chelating positions. The methine proton peaks can be seen in the inset of Figure 43. A broad doublet was seen next to the methine environments, generally the amine proton was not seen due to its broadness, but the splitting (by the exocyclic methine proton) and integration indicated that this was the amine proton on the exocyclic position. The methyl protons of the chelating isopropyl positions showed a shift of δ 1.37 ppm. This environment was a doublet that

corresponded to twelve protons. The exocyclic methyl protons were seen at δ 1.08 ppm also as a doublet and corresponded to six protons.

Figure 43: ^1H NMR of 14

Given that this product formed from salt metathesis (from zinc dichloride) and by alkane elimination (from diethyl zinc), the homoleptic formulation in Figure 43 is the most likely structure of this compound. This was supported by the proton NMR, as well as the ^{13}C NMR.

The ^{13}C NMR showed the bridgehead carbon peak at δ 164.35 ppm, there were two methine carbon peaks at δ 45.77 ppm, and δ 45.33 ppm corresponding to the chelating and exocyclic isopropyl groups respectively. Similarly the methyl carbon environments were seen at δ 26.31 ppm and δ 23.78 ppm, corresponding to chelating and exocyclic positions.

Over a period of a few weeks the isolated liquid product formed crystallites. This was likely due to the slow formation of a larger oligomer, possibly a dimeric species that was no longer a liquid at room temperature. This new compound showed a distinctively different NMR and can be seen “growing in” a spectrum of the original liquid compound (see Figure 44).

Figure 44: Unlabelled peaks showing new solid formation within liquid compound 14.

All attempts to synthesize this compound directly by heating or using a more coordinating solvent such as diethyl ether failed. Attempts to recrystallize the compound failed as it powdered out of solution.

$\text{Zn}_2\text{Cl}[(^i\text{PrN})_2\text{CNH}(^i\text{Pr})]_3$ (15):

This compound was isolated serendipitously. The complex was thus made by a rationale synthesis from a reaction of 3:2 molar ratio of lithiated monoanionic triisopropyl guanidinate and $\text{ZnCl}_2\cdot\text{THF}$ respectively. The product was recrystallized and SC XRD obtained. The crystal structure was exactly the same as that which was achieved serendipitously (see Figure 48). The crystal structure was necessary to understand the structure, as the ^1H NMR proved to be quite complex and difficult to interpret.

Figure 45: ^1H NMR spectra of 15

The ^1H NMR seen in Figure 45 was collected from the same batch as the crystal structure in Figure 48. Four separate methine environments can be seen. The first septet seen at δ 4.06 ppm integrated to three protons, due to its integration compared to that of the other methine protons, this is most likely a methine proton existing on an exocyclic amine position. The next methine peak corresponded to six protons; twice that of the previous methine proton;

most likely being the isopropyl groups of the chelating positions on the same ligand. Interestingly the next two methine environments correspond exactly to those found for compound **14**. The corresponding methyl peaks can also be seen. This leads us to believe that in solution the compound exists as two complexes, the bis complex already characterized as well as a chloride-containing compound. The chloride containing compound was most likely partially soluble and caused broadening of its signals, this caused the integration to be overestimated. This is why the proton NMR was very difficult to interpret.

Zn₄Et₄[(ⁱPrN)₂CN(ⁱPr)]₂ (16**):**

When a 1:1 molar ratio of triisopropyl guanidine was reacted with diethyl zinc, the recrystallized product was that of the spectrum seen in Figure 46. The spectra lead us to believe this compound consisted of one ethyl group and one guanidinate per metal centre. However the SC XRD structure (Figure 50) showed a ratio of one guanidinate per two ethyl groups. This forced us to re-examine the NMR, in an effort to explain how the other ethyl moiety was represented in the spectrum.

Figure 46: ^1H NMR spectra of **16**

It was not clear where the other ethyl moiety lay. It is possible that sterics cause some unexpected splitting patterns that mask the remaining five protons. The most likely answer is seen in Figure 47. The signals **g** and **h** are those of previously unassigned peaks that closely match the integration requirements, and theoretical shift of the structure found by SC XRD. Sterics could cause the triplet to be seen as a doublet (**g**), as well the misshapen quartet (**h**) is most likely the unassigned methyl protons. This, like compound **16** would benefit from a variable temperature NMR.

Figure 47: ^1H NMR spectra showing possible alternate ethyl environments of compound 16.

4.2. Crystal Structures

Table 9: Selected crystallographic data for 15

Figure 48: SC-XRD of compound 15. Hydrogen atoms were omitted for clarity, excluding those bound to nitrogen, the thermal ellipses are shown at 30%.

Empirical formula	$\text{C}_{30}\text{H}_{66}\text{Zn}_2\text{N}_9\text{Cl}$
fw	719.14
T (K)	120(2)
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Monoclinic
Space group	P 1 23/c 1
a (Å)	10.725
b (Å)	34.697
c (Å)	10.581
α (deg)	90.00
β (deg)	104.21
γ (deg)	90.00
V (Å ³)	3817
Z	4
ρ (calcd) (Mg/m ³)	1.251
Abs coeff (mm ⁻¹)	1.358
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0614 wR2 = 0.1135
^a R1 = $\sum F_o - F_c / \sum F_o $; wR2 = $(\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$	

The crystal structure of 16 can be seen in

Figure 48. The structure was a “lantern” dimer. The two metal centres are bridged by three triisopropyl guanidinate ligands that bonded in a κ^1 fashion to each of the zinc centre. The distance between the zinc centres was 2.709 Å, larger than the 2.34 Å found in a Zn-Zn bond (42). Zn2 was found to be tetracoordinate with a chloride bound to one face. Zn2 was seen to be very close to tetrahedral with bond angles ranging from $\sim 107^\circ$ - 112° . In contrast, Zn1 was found to be tricoordinate. The sum of angles around Zn1 was 359.83° , very near planar, thus a trigonal planar bonding geometry to the guanidinate ligands. The large Zn-Zn distance was believed to be caused by the existence of the electron withdrawing chloride that minimized the

interaction between zinc centres. This resulted in a large guanidinate bite angle not expected of first row transition metals.

Figure 49: SC-XRD of compound **15**, looking down Cl-Zn bond. Hydrogen atoms were omitted for clarity excluding those bound to nitrogen; thermal ellipses are shown at 30%.

The bond distance between the exocyclic nitrogen and the bridgehead carbon of all the guanidines was found to be considerably less than the bond lengths of the bridgehead carbon to the chelating nitrogen positions. This indicates that the π resonance has a greater contribution from the exocyclic position. Each of the nine nitrogens in the structure were found to be sp^2 hybridized as they all deviated by no more than 0.5° from planarity, the bridgehead carbons also showed the same character.

Table 10: Selected Bond Lengths and Angles for 15

Selected Bond Lengths (Å)							
Zn1-Zn2		2.709		Zn2-Cl1		2.288	
Zn1-N4		1.928		Zn2-N1		2.040	
Zn1-N2		1.932		Zn2-N5		2.038	
Zn1-N8		1.931		Zn2-N7		2.055	
C3-N7	1.337	C4-N4	1.337	C10-N1	1.338		
C3-N8	1.333	C4-N5	1.347	C10-N2	1.335		
C3-N9	1.394	C4-N6	1.383	C10-N3	1.385		
Selected Bond Angles (°)							
Zn1-Zn2-Cl1		179.29		N1-Zn2-N5		110.22	
N2-Zn1-N4		119.43		N5-Zn2-N7		112.63	
N4-Zn1-N8		120.45		N7-Zn2-N1		110.36	
N8-Zn1-N2		119.95		N7-C3-N8		119.41	
N4-C4-N5		118.95		N1-C10-N2		119.22	
Sum of Angles (°)							
Zn1	359.83		N4	359.37		N9	360.00
Zn2	384.01		N5	360.43		C3	359.99
N1	359.81		N6	360.00		C4	359.98
N2	359.50		N7	359.88		C10	360.00
N3	360.00		N8	359.63

Table 11: Selected Crystallographic data for **16** Figure 50: SC-XRD compound **16**. Hydrogen atoms were omitted for clarity; thermal ellipses are shown at 30%.

Empirical formula	$\text{C}_{28}\text{H}_{60}\text{Zn}_4\text{N}_6$
fw	738.22
T (K)	120(2)
λ (Å)	0.71073 (Mo K_α)
Cryst syst	Monoclinic
Space group	P 1 21/c 1
a (Å)	10.276
b (Å)	9.897
c (Å)	17.350
α (deg)	90.00
β (deg)	95.34
γ (deg)	90.00
V (Å ³)	1757
Z	2
ρ (calcd) (Mg/m ³)	1.403
Abs coeff (mm ⁻¹)	2.723
Refinement method	full-matrix least-squares on F ²
R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0412 wR2 = 0.0838
^a R1 = $\sum F_o - F_c / \sum F_o $; wR2 = $(\sum w(F_o - F_c)^2 / \sum w F_o ^2)^{1/2}$	

The crystal structure of compound **16** consisted

of four zinc centres each of which was bound to a single ethyl group. Each zinc centre was tricoordinate. Two of the zinc centres participated in a central eight member metallocycle (Zn2 and Zn2ⁱ). The metallocyclic zinc centres acted as bridges between the two equivalent units within the unit cell bridging to N1 and N1ⁱ respectively. The metallocycle formed a distorted chair conformation (see Figure 51). The zinc centres Zn2 and Zn2ⁱ, along with N1 and N1ⁱ, formed a planar centre with a torsion angle of 0° (see Table 12). The remaining centres (Zn2, N3, N1, C1) participating in the ring formed two semi planar structures (see Table 12). The other two zinc centres (Zn1 and Zn1ⁱ) were bound within chelating pockets of the each of the guanidinate moieties bonded in a κ^2 coordination.

Figure 51: SC-XRD compound **16**. Hydrogen atoms were omitted for clarity; thermal ellipses are shown at 30%.

Bond lengths around N1 were considerably shortened as it formed a tetracoordinated geometry linking the two equivalent units. The tetrahedral coordination indicates that N1 was sp^3 hybridized. The planarity of the other nitrogen centres (N3 and N2) indicates that they are sp^2 . The bite angle of the guanidinate chelating Zn1 and Zn1ⁱ was found to be considerably smaller than other bite angles given in this thesis. This is due to chelation of one metal centre (M-M repulsion forces aren't an issue) as well as there is a smaller ionic radii of zinc.

Table 12: Selected Bond Lengths and Angles for **16**

Selected Bond Lengths (Å)			
Zn1-N1	2.124	Zn2-N1	2.056
Zn1-N2	1.959	Zn2-N3	1.980
Zn1-C13	1.951	Zn2-C5	1.985
N1-C1	1.420	N3-C1	1.340
N2-C1	1.340		
Selected Bond Angles (°)			
N1-C1-N2	108.64	N1-Zn2-N3	111.68
Sum of Angles (°)			
N1	418.02	Zn1	359.90
N2	358.26	Zn2	359.30
N3	359.99	C1	359.99
Torsion Angles (°)			
Zn2-N1 ⁱ -N1-Zn2 ⁱ		0	
Zn2-N3 ⁱ -N1 ⁱ -C1 ⁱ		18.64	
Zn2-N3-N1-C1		18.64	

4.2. Conclusions

A liquid bis triisopropyl guanidinate zinc complex was created (**14**). It was found over an extended period of time (weeks) to oligomerize into a solid product. The NMR spectrum of the new compound was obtained, growth of SC XRD quality crystals for structural analysis failed. The “lantern” dimeric compound **15** was successfully recreated using a 2:3 ratio of THF stabilized zinc (II) chloride and triisopropyl lithium guanidinate. It was found to form compound **14** in solution phase NMR. A tetrameric compound was also synthesized (**16**) and a SC XRD structure obtained. The structure showed each guanidine bonding to two zinc centres.

5. Gold Metal Photo Deposition

Early in the synthesis of the gold (I) amidinates it became evident that the compounds were unstable at room temperature. In solution as the compounds decomposed they resulted in the deposition of a gold mirror on sample vials and flasks. It was found that in the absence of light, a solution of hexanes and completely solvated gold (I) acetamidinate dimer would decompose at a much slower rate. The light exposed sample decomposed in a matter of hours while the vial shielded from light would begin to decompose after a few days; a dramatically different time scale.

Since the eventual goal of the gold (I) amidinate research was to develop a process of depositing gold metal films, the photodeposition of gold (I) acetamidinate was studied further. The hope of these experiments was to develop a method of controlling the film thickness as an alternative to CVD.

The acetamidinate gold (I) complex was chosen as it was in the highest yield, thus limiting financial losses in synthesis. Gold (I) n-butylamidinate has greater solubility in organic solvents than that of the acetamidinate. This increased solubility of the ligand made for poor yields of the gold (I) n-butylamidinate (see Section 7.3.1.).

Film depositions were conducted in pentane (higher purity than hexanes) in the drybox as the precursor was air sensitive. The precursor was purified by recrystallization prior to use. The concentration of the gold (I) acetamidinate dimer was kept constant throughout all experiments by obtaining a supersaturated solution at room temperature in pentane. The product was allowed to recrystallize in the freezer where it could be stored for long periods of time. When conducting an experiment, a volume of mother liquor was pipetted from the vial to a deposition vial. The mother liquor would remain at the same concentration provided that the freezer remained at the same temperature throughout experimentation. Also when new precursor was synthesized it would be easy to obtain the exact same concentration as previously used.

The experiments were simple in their design. Vials were charged with the supersaturated solution from the freezer, left for varied amounts of time (4, 14 days) in ambient light then the films deposited were studied via SEM, EDS, and XRD.

5.1. 4 day Exposure Period (a)

A short exposure experiment was conducted in order to determine a lower limit of deposition. The period of the experiment was determined via visual inspection. When colour could be seen within the photodeposition apparatus the experiment was halted. This period was found to be four days. After which time the deposition substrate was studied via SEM, EDS, and XRD.

Scanning electron microscopy of films consisting of short deposition times were difficult to obtain due to the insulating nature of glass, which limits the drain of the electrons causing a charging effect at the substrate surface (Figure 52). This requires lowering the potential making for images of poor contrast to minimize the charging effect around the images. A general procedure when imaging a material that insulates is to coat it in gold utilizing a physical vapour technique. This would give false EDS measurements and thus was not done. Deposition on silicon wafers would have been optimal however they are opaque, thus limiting photodeposition. The SEM image seen in Figure 52 was of the edge of the slide. This SEM shows some small crystallite growth along the edges of the glass slide, most likely on defect sites created when the glass slide was cut. These small crystallites running along the edge seem like they have grown out of the surface, showing that decomposition of the precursor molecules could have been originating at the surface. Other larger crystallites were seen to be sitting on the surface (as opposed to growing out of it) as if placed there. This may have shown a different decomposition pathway, one that does not include surface decomposition.

Figure 52: SEM image of a) at (2.6 kV)

The deposition done for 4 days was halted upon initial visual evidence of deposition. This resulted in a glass slide that had a uniform cloudy purple tinge to it. The film was determined to be gold metal as was seen by EDS (see Figure 53).

The EDS spectra showed the existence of gold metal (Figure 53). The signal was found to be very weak due to the short exposure time resulting in minimal deposition. This peak can be seen in the inset of Figure 53. The other peaks seen are associated with the glass substrate that contained traces of calcium, sodium, and potassium. The strongest peak belonged to that of silicon.

Figure 53: EDS of a)

Due to the short deposition time resulting in minimal gold sample deposited, XRD micrograph did not yield any gold crystalline phases and instead showed only the broad $\text{SiO}_2(101)$ crystalline face.

5.2. 14 day Exposure Period (b)

A long exposure experiment was conducted in order to determine an upper limit of deposition as well as to obtain insights into surface structure and a growth mechanism. The period of two weeks was set arbitrarily. After this period the glass slide was found to be opaque and have the golden lustre of gold metal. The film was via SEM, EDS, and XRD.

Figure 54: SEM image of b)

The film was found to have complete coverage over the glass slide (Figure 54). This was beneficial as a larger potential was used due to a lack of charging effects. The film was found to consist of large particulates ($>1\ \mu\text{m}$). The particles were arranged in a random manner. The structure did not seem to indicate uniform growth originating at the surface as there did not seem to be a regularity to the structure as would indicate surface decomposition and growth. Rather the SEM seemed to indicate that the decomposition of the precursor did not occur at the surface but rather in the solution where agglomerates formed then adhered themselves to the surface.

An EDS analysis of the film showed that the film did indeed consist of gold (see Figure 55). The EDS was compared to that of a gold standard and found to correspond nicely. The only peaks that were found to differ was that of the substrate Si and a small peak that could have

been labelled as either Mg or Li. Since lithiated ligands were used in the synthesis of the precursor molecules this was determined to be the most likely impurity.

Figure 55: EDS of film b) deposited over 14 days.

A XRD study of the film showed that the deposited gold film was crystalline. All the typical Au crystalline faces could be seen.

Figure 56: XRD of film c) indicating crystalline gold and glass slide substrate.

5.2. 7 day Novel substrate Deposition (c)

An interesting side experiment was conducted in trying to tune the decomposition to occur at the surface of the substrate as opposed to decomposition within solution. It occurred to us that if the light source (the decomposition initiator) could be confined within the substrate, that this might promote decomposition at the substrate surface as opposed to within the solution. The logic behind this was that the light path would not have to travel through the precursor solution possibly initiating solution phase decomposition as was seen in a) and b) experiments before coming in contact with the substrate.

Therefore an optically clear substrate that could confine light within it was required. We decided to use a fibre Bragg grating filament to act as a substrate as well as the light source.

Fibre Bragg grating filaments differ from normal fibre optics in that light can escape out the sidewalls of the fibre optic as well as the end of the filament whereas in the case of normal fibre optics the light would only escape out the end. However most of the light still escapes out of the end of the fibre Bragg grating making it the most likely point on the fibre for gold deposition. A description of the experiment can be seen in section 7.7.

The SEM images of the fibre Bragg grating filament after deposition (Figure 57) showed what looked to small crystalline deposits along the sidewall of the filament. It could not be determined conclusively if this was gold deposited by surface decomposition pathway or from an in solution decomposition. A SEM image of the end of the filament was taken (Figure 57 inset) and showed what looked like crystalline growth originating at the surface. The deposits were found to differ dramatically from the large agglomerations seen in Figure 54 and thus must deposit via a different pathway.

Figure 57: SEM image of photodeposited gold on a fibre Bragg grating filament (2.6 kV)

5.4. Conclusions

The gold films proved to be weakly adhered to the glass surface. The deposited gold films failed the scotch tape test, and could be removed by acetone, but not dilute acid, water or alkanes. This weak interaction indicates that a photo excited acetamidinate gold (I) precursor molecule is not decomposing at a hydroxyl site and resulting in a chemically bound gold site. More likely a photo excited precursor molecule is physisorbed at the surface and undergoes decomposition and acts as a site for further decomposition to occur on. Since the hydroxyl density in untreated glass vials is relatively low; increasing them using different chemical methods may result in stronger film adhesion to the glass.

Decomposition was not limited to the vial walls. Upon removal of the pentane solution post deposition it was evident that some microparticulate gold was being formed. These particles ranged from red to purple to black in colour, indicating a range of sizes from nanoparticle to microparticle while still being suspended in solution. It's postulated that this solution phase decomposition was most likely that which created the film seen in Figure 54. This film was most likely the result of gold particulates that became too large to remain suspended in solution and deposited electrostatically on the substrate surface.

A fibre Bragg grating fibre optic was used in an attempt to confine the decomposition to the substrate surface by having the substrate double as the light source.

6. Gold Metal Chemical Vapour Deposition

Compound **3** was shown to have a small window between sublimation and decomposition. For this reason Heating Zone #1 (see Figure 70 in Experimental Section) was always kept at 85 ± 2 °C. The temperature of the deposition zone (Heating Zone #2) was varied to determine the limits of the gold CVD process. Gold CVD experiments were performed on Si(100) wafers only.

6.1. 85 °C Deposition Temperature

It was found that with the sublimation and decomposition of the gold (I) dimethyl guanidinate occurring at almost identical temperatures (83 °C, and 85 °C respectively) that the entire deposition reactor could be heated to 85 °C and result gold CVD. Long exposure times were used to ensure kinetic decomposition of the precursor once physically adsorbed to the substrate surface.

Experiments done with an exposure time of 8hrs showed that 85 °C was not a sufficient temperature to completely decompose the precursor at the surface. Some sublimation component was seen that did not result in complete precursor decomposition, but rather grew crystal islands (Figure 58) of precursor within a field of gold nanocrystals (Figure 61).

Figure 58: Sublimed gold (I) dimethylguanidinate precursor on Si(100) wafer. Rectangular area represents an area of prolonged electron exposure.

The first indication that these islands were not gold metal was that they appeared as though they were charging. Charging occurs when the electrons do not escape from the surface, a characteristic of non conducting films or even substrates (seen in Section 5). The EDS confirmed that there was a high level of carbon and nitrogen within the islands (see Figure 59).

Figure 59: EDS data of rectangular region seen in Figure 58.

A comparison was made between the theoretical weight percentages of compound 3, the precursor that was used in the CVD experiments with the found value from the EDS taken of the island seen in Figure 58. The results showed a very good correlation. The experiment seemed to overestimate the quantity of gold centres and underestimate the amount of nitrogen and carbon centres. This is most likely due to partial decomposition within the condensed precursor. This could be caused simply by exposure to atmosphere prior to SEM analysis or simply thermal decomposition as was the goal of the experiment. The electron beam of the microscope also helped to decompose the compound as can be seen in Figure 58. The dark square area was a portion of sample that had been imaged for extended periods. The electron beam would have etched away organic ligands leaving the gold centres behind.

Figure 60: SEM image of structure from Figure 58, after three days of atmospheric exposure.

The structure was then imaged three days later after being allowed to sit at ambient conditions exposed to air. The results were a partially decomposed structure, which consisted of

large cracks and fissures. Interestingly the most well preserved area was that which was exposed to the SEM electrons for an extended period. This was attributed to a higher density of gold centres in the area, as the electron beam had already removed a percentage of ligand from the surface. Effectively decomposing the area before it could undergo decomposition under ambient conditions.

Figure 61: Nanoparticle formation

These islands were found to be a rare occurrence. The remainder of the slide consisted of gold nanoparticles (see Figure 61). EDS showed gold metal with little impurities. This showed that the decomposition is occurring at the surface but not completely. A higher temperature is required for complete decomposition. The islands found also showed that there is physical adsorption happening at the surface. It concentration of condensed precursor in only these islands showed a high mobility of physically adsorbed precursor on the surface.

6.2. 120 °C Deposition Temperature

This deposition temperature was chosen as thermolysis experiments (see Section 2.1.2.) showed the complete decomposition of compound **3** under these conditions. Substrates were cleaned as per the procedure found in section 7.8.1.

6.2.1. Exposure experiments

The exposure time was varied in order to obtain variable thicknesses of gold films. The overall goal of these experiments was to obtain a film thickness vs exposure time plot. This would yield a growth rate for this process that could result in a predictable process.

Film 1 (i):

The first experiment conducted was that for a 2hr exposure time, the Si(100) wafers exhibited a gold lustre with a mirror-like quality when visually inspected. The films were then inspected via SEM and EDS.

Figure 62: SEM image of Gold CVD film (i).

The SEM images showed a field of white conduction on a black field. The white areas are gold metal which is of higher conduction than that of the silicon surface, seen as the black spaces between particles. The films were found to consist of a conformal thickness throughout. (i) was found to resemble the film deposited at 85 °C; in that they were composed of nanoparticles. The film was more extensive than that shown at lower temperatures (see Figure 61).

Figure 63: EDS spectra of (i), field seen in Figure 62

The EDS found that the film was composed of gold metal, the substrate was the major signal in the spectra due to the thinness of the film. The lack of carbon seen in the film is inconclusive as there may not have been enough sample to register a carbon signal.

A cross sectional SEM did not yield images of the film. This is indicative of a film less than 10nm thick, the limit of the SEM used.

Film 2 (ii):

In order to achieve a film thick enough to obtain a cross sectional thickness measurement, the exposure time was increased to 6 hrs. The film had a gold lustre but was considerably less reflective than that of (i). The lack of reflectivity was indicative of the thickness of the gold film, the reflective nature of the Si(100) was not be seen as the film obscured it.

Figure 64: SEM image of Gold CVD film (ii).

The film was found to consist of small prism shaped crystallites stacked on top of each other, the high crystalline growth is indicative of a slow rate of deposition. The crystallites were more tightly packed than that seen for (i) indicative of complete coverage. The substrate could not be seen between the crystallites.

Figure 65: EDS data of (ii) from Figure 64

An EDS (Figure 65) of the field seen in Figure 64 showed a significant increase in gold content when compared to (i). The Au peaks in the spectrum were seen to obscure the peaks for

the Si surface. The atomic and weight percentages confirm that gold is the major surface material. Carbon values were not significant in this film, indicating that our precursor is decomposing cleanly once coming into contact at the surface.

Figure 66: XRD of ii)

The XRD of ii) was found to be highly crystalline with the (111) face in preference. Compared to the photodeposited gold XRD (Figure 56) the CVD deposited film was found to be of higher crystallinity.

Figure 67: SEM cross sectional image of (ii)

The wafer was broken to achieve a cross sectional thickness measurement. The SEM images of the cross section can be seen in Figure 67. The bright area on the left side of the figure indicates the gold film while the black area on the right is the substrate. It was found that the film varied in thickness from 600-1150 nm. This variance is higher than expected for a process that showed high conformality over thinner films (see previous two examples). The darkened areas in Figure 65 where the areas meet the surface could be indicative of the film lifting from the surface. This is the more likely case.

6.6. Conclusions

Gold metal films were grown on glass from solution by the photoreduction of a Au (I) acetamidinate precursor. These films were found to be highly crystalline by XRD but lacked conformality. These films stood up to the tape test.

Gold metal nanoparticles were grown by thermal CVD on Si(100) wafers at 85 °C from Au (I) dimethyl guanidinate as a single source precursor. This was found to be by far the lowest thermal CVD deposition reported. Gold films were found to form at temperatures of 120 °C by changing only the temperature of the process yet still at lower temperatures than that found in literature. These films failed the tape test indicating decomposition at the surface without chemically reacting with surface hydroxyl sites.

7. Experimental

7.1. General Synthetic Procedures

General Considerations. All manipulations were performed in an MBraun Unilab inert atmosphere drybox, unless otherwise stated. Drybox solvents were degassed and dried on an MBraun solvent purification system. These were stored over activated 4A sieves. The chemicals: 1,3-diisopropyl carbodiimide, diethyl amine, diisopropyl amine, butyl lithium (2.5 M in hexanes), methyl lithium (1.6 M in diethyl ether), silver(I) chloride, lithium dimethyl amide, carbon disulphide, sodium t-butoxide and potassium bistrimethylsilylamide were purchased from Aldrich Chemical Co. and used as received. The gold(I) starting material AuCl·THT was synthesised by literature methods(43) as was AuCl·TPP, these syntheses were adapted for AgCl·TPP and AgCl·TBP. AuCl was an isolated decomposition product of failed sublimation of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$. The compounds $\text{Li}[(^i\text{PrN})_2\text{CN}(^i\text{Pr})_2]$, $\text{Li}[(^i\text{PrN})_2\text{CNH}(^i\text{Pr})]$, $\text{Li}[(^i\text{PrN})_2\text{CN}(\text{Et})_2]$, $\text{Li}[(^i\text{PrN})_2\text{CN}(\text{Me})_2]$, $\text{Li}[(^i\text{PrN})_2\text{CMe}]$, $\text{Li}[(^i\text{PrN})\text{C}^n\text{Bu}]$, and $\text{K}[(^i\text{PrN})_2\text{CN}(\text{SiMe}_3)_2]$ were prepared by literature methods(44, 45).

7.1.1. Xanthates

Xanthate ligands followed literature methods as described for $\text{K}[\text{S}_2\text{CO}^n\text{Bu}]$ (35), followed by the isolation and drying of the ligand salt in order to determine ^1H and ^{13}C NMR spectra. Synthesis of $\text{Na}[\text{S}_2\text{CO}^t\text{Bu}]$ was prepared by alternate methods due to the potassium salt derivative's hygroscopic nature.

$\text{Na}[\text{S}_2\text{CO}^t\text{Bu}]$: In a 250mL flask on schlenk lines, (5g, 8.91×10^{-2} mol) sodium t-butoxide was suspended in hexanes. (6.78g, 5.38mL, 8.91×10^{-2} mol) of CS_2 was added to the solution dropwise at a rate of 2 drops/s. The reaction was allowed to progress for 1hr. The white powdered sodium xanthate salt precipitate was then filtered and washed with 30mL of ethanol followed by 30mL of ether; dried under vacuum. (8.91×10^{-2} mol, 15.7g, 100%) ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 1.55 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 28.39 (3C, $\text{C}(\text{CH}_3)_3$).

$\text{K}[\text{S}_2\text{CO}^n\text{Bu}]$: In a 250mL flask on schlenk lines, (5g, 8.91×10^{-2} mol) crushed, dried KOH was dissolved in 100mL of n-butanol. (6.78g, 5.38mL, 8.91×10^{-2} mol) of CS_2 was added to the reaction mixture dropwise at a rate of 2 drops/s. The reaction was allowed to progress for 1hr. The white powdered potassium xanthate salt precipitate was then filtered and washed with 30mL of ethanol followed by 30mL of ether; dried under vacuum. (8.91×10^{-2} mol, 15.7g, 100%). ^1H NMR

(300 MHz, $(\text{CD}_3)_2\text{SO}$): 4.18 (t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.56 (pen, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 1.32 (sex, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 0.89 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 70.14 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 30.61 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 18.88 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 13.71 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$).

7.2. Group 11 Chlorides

AuCl(TPP): In a 200 mL flask 100 mL anhydrous acetone, (8.13 g, 2.54×10^{-2} mol) AuCl(THT) was suspended. (6.65 g, 2.54×10^{-2} mol) triphenylphosphine was added. The reaction was allowed to stir for 3hrs. Under reduced pressure THT was removed. The solution was placed in the freezer to recrystallize. The product was collected as white crystals (11.46 g, 2.32×10^{-2} mol, 91.3 %). ^1H NMR (300 MHz, C_6D_6): 7.14, (m, 12H, PPh_3) 6.90 (m, 18H, PPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): 134.35, 134.16, 131.28, 131.25, 129.21, 129.06 (PPh_3)

AuCl(TPP)₂: In a 100 mL flask, 50 mL of reaction grade acetone was added. Crude AuCl (0.33 g, 1.42 mmol) was suspended in the acetone. TPP (0.37 g, 1.42 mmol) was added in excess. The reaction was allowed to proceed overnight. Unreacted Au was filtered off, and the volume of the reaction solution reduced to 25 mL under reduced pressure. The flask was then placed at -36 °C for recrystallization (0.49 g, 0.65 mmol, 45.7 %). ^1H NMR (300 MHz, C_6D_6): 7.21, (m, 12H, PPh_3) 6.93 (m, 18H, PPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): 134.35, 134.16, 131.28, 131.25, 129.21, 129.06 (PPh_3)

AuCl(TBP): On the benchtop in 50 mL acetone, (2.04 g, 6.36 mmol) AuCl(THT) was suspended. (1.38 g, 1.68 mL, 6.36 mol) tributylphosphine was added. The reaction was allowed to stir for 3hrs. Under reduced pressure THT and solvent was removed. The product was collected as a yellow oil (2.71 g, 6.24 mmol, 98.1 %). ^1H NMR (300 MHz, C_6D_6): 1.19 (m, 18H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.77 (t, 9H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): 27.36 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 25.64 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 25.18 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.34 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.14 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.80 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

AgCl(TPP): See Ref. (23)

AgCl(TBP) : See Ref. (23)

7.3. Gold (I) Complexes

7.3.1. Guanidines & Amidines

Au₂[(ⁱPrN)₂CMe]₂ (1): In a 100 mL round bottomed flask, AuCl·THT (0.57 g, 1.78 mmol) suspended in 50 mL of hexanes. The slurry was cooled to -36 °C. Solid Li[(ⁱPrN)₂CCH₃] (0.27 g, 1.78 mmol) was added to the solution and allowed to react at -36 °C overnight. The reaction was then warmed to room temperature and immediately filtered, and the LiCl was washed with an additional 50 mL of hexanes. The solution was concentrated under reduced atmosphere and returned to the freezer for 24 hours. A white precipitate of **1** formed (0.43 g, 1.28 mmol, 71.8 %). m.p. 79 °C (dec). Anal. Calcd for C₁₆H₃₄Au₂N₄: C, 28.41; H, 5.07; N, 8.28. ¹H NMR (300 MHz, C₆D₆): 3.57 (sept, 4H, (CH₃)₂CHN), 1.62 (s, 6H, (NCCH₃)N), 1.25 (d, 24H, (CH₃CHN) ¹³C{¹H} NMR (300 MHz, C₆D₆): 168.49 (NCN), 50.97 (CH₃CHN), 26.81 ((CH₃)₂CHN), 16.09 (CH₃CNCH(CH₃)₂)

Au₂[(ⁱPrN)₂CⁿBu]₂ (2): Compound **2** was prepared in a analogous manner as compound **1** substituting: AuCl·THT (1.01 g, 3.15 mmol) Li[(ⁱPrN)₂CⁿBu] (0.60 g, 3.15 mmol); **2** was isolated by recrystallisation (0.30 g, 0.79 mmol, 25.0 %). m.p. 96 °C (dec). Anal. Calcd for C₂₂H₂₆Au₂N₄: C, 34.74; H, 6.10; N, 7.37. ¹H NMR (300 MHz, C₆D₆): 3.74 (sept, 4H, (CH₃)₂CHN), 2.26 (t, 4H, (CH₃CH₂CH₂CH₂), 1.44 (q, 4H (CH₃CH₂CH₂CH₂), 1.33 (d, 24H, (CH₃CHN), 1.17 (sex, 4H, (CH₃CH₂CH₂CH₂); 0.80 (t, 6H, (CH₃CH₂CH₂CH₂)) ¹³C{¹H} NMR (300 MHz, C₆D₆): 171.55 (NCN), 50.61 (CH₃CHN), 30.73 (CCH₂CH₂CH₂CH₃), 29.85 (CCH₂CH₂CH₂CH₃) 27.20 ((CH₃)₂CHN), 23.06 (CCH₂CH₂CH₂CH₃), 13.92 (CCH₂CH₂CH₂CH₃)

Au₂[(ⁱPrN)₂CN(Me)]₂ (3): Compound **3** was prepared in a analogous manner as compound **1** substituting: AuCl·THT (0.99 g, 3.09 mmol), Li[(ⁱPrN)₂CN(Me)] (0.548 g, 3.09 mmol). Compound **10** was isolated by recrystallization (0.99 g, 2.70 mmol, 87.4 %). m.p. 83 °C (dec). Anal. Calcd for C₁₈H₄₀Au₂N₆: C, 29.43; H, 5.49; N, 11.44. ¹H NMR (300 MHz, C₆D₆): 3.80 (sept, 4H, (CH₃)₂CHN), 2.43 (s, 12H, (CH₃)₂N), 1.37 (d, 24H (CH₃)₂CHN); ¹³C{¹H} NMR (300 MHz, C₆D₆): 170.65 (NCN), 50.32 ((CH₃)₂CHN), 40.89 ((CH₃)₂N), 27.21 ((CH₃)₂CHN).

Au₂[(ⁱPrN)₂CN(Et)]₂ (4): Compound **4** was prepared in a analogous manner as compound **1** substituting: AuCl·THT (0.71 g, 2.23 mmol), Li[(ⁱPrN)₂CN(Et)] (0.46 g, 2.23 mmol). Compound **9** was isolated by reduced pressure (0.71g, 1.80 mmol, 80.6 %) crude yield. m.p. 72 °C (dec). Anal. Calcd for C₂₂H₄₈Au₂N₆: C, 33.42; H, 6.12; N, 10.63. ¹H NMR (300 MHz, C₆D₆): 3.80 (sept, 4H, (CH₃)₂CHN), 2.85 (q, 8H, (CH₃CH₂)₂N), 1.39 (d, 24H (CH₃)₂CHN), 0.83 (t, 12H, (CH₃CH₂)₂N); ¹³C{¹H}

NMR (300 MHz, C_6D_6): 166.33 (NCN), 50.45 ($(CH_3)_2CHN$), 44.19 ($(CH_3CH_2)_2N$), 27.13 ($(CH_3)_2CHN$), 13.30 ($(CH_3CH_2)_2N$).

$Au_2[(^iPrN)_2CN(^iPr)_2]_2$ (5): Compound 5 was prepared in a analogous manner as compound 1 substituting: AuCl·THT (0.85 g, 2.64 mmol), $Li[(^iPrN)_2CN(^iPr)_2]$ (0.62 g, 2.64 mmol) Compound 10 was isolated by recrystallization (1.02 g, 2.41 mmol, 91.1 %). m.p. 87 °C (dec). Anal. Calcd for $C_{26}H_{56}Au_2N_6$: C, 36.88; H, 6.67; N, 9.93. 1H NMR (300 MHz, C_6D_6): 3.96 (sept, 4H, $(CH_3)_2CHN$), 3.26 (sept, 4H, $(CH_3)_2CHNCH(CH_3)_2$), 1.39 (d, 24H, $(CH_3)_2CHN$), 1.06 (d, 24H, $(CH_3)_2CHNCH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): 167.15 (NCN), 50.06 ($(CH_3)_2CHN$), 48.48 ($(CH_3)_2CHNCH(CH_3)_2$), 27.23 ($(CH_3)_2CHN$), 22.55 ($(CH_3)_2CHNCH(CH_3)_2$).

$Au_2[(^iPrN)_2CN(TMS)_2]_2$ (6): In a 100 mL round bottomed flask, AuCl·THT (0.542, 1.69 mmol) was suspended in 50 mL of hexanes. $K[(^iPrN)_2CN(SiMe_3)_2]$ (0.551g, 1.69mmol) was added to the solution and allowed to react for 3 h, then immediately filtered. The remaining solution was concentrated under reduced atmosphere and placed in the freezer at -35 °C for 24 hours. A white precipitate of 13 was isolated (0.824g, 1.69mmol, 100.0%). m.p. 92 °C (dec). Anal. Calcd for $C_{26}H_{64}Au_2N_6Si_4$: C, 32.29; H, 6.67; N, 8.69. 1H NMR (300 MHz, C_6D_6): 4.21 (sept, 4H, $(CH_3)_2CHN$), 1.39 (d, 24H, $(CH_3)_2CHN$), 0.17 (s, 36H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): 165.04 (NCN), 49.73 ($(CH_3)_2CHN$), 27.46 ($(CH_3)_2CHN$), 2.38 ($Si(CH_3)_3$).

$Au[(^iPrN)_2CN(TMS)_2](TPP)$ (7): In a 100 mL round bottomed flask, AuCl·TPP (0.166 g, 0.33 mmol) was suspended in 50 mL of hexanes. $K[(^iPrN)_2CN(SiMe_3)_2]$ (0.109 g, 0.33 mmol) was added slowly over a period of 15min. The reaction was allowed to proceed overnight. KCl was filtered and the hexanes removed under reduced pressure to yield a white powdered product. (0.104 g, 0.14 mmol, 42 %). m.p. 68 °C; 1H NMR (300 MHz, C_6D_6): 7.51 (m, 6H, $P(Ph)_3$), 6.96 (m, 9H, $P(Ph)_3$), 5.56 (sept, 1H, $NCHCH_3$), 4.00 (sept, 1H, $NCHCH_3$), 1.69 (d, 6H, $NCHCH_3$), 1.49 (d, 6H, $NCHCH_3$), 0.39 (s, 18H, $N(Si(CH_3)_3)_2$); $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): 195.29 (NCN) 134.41, 134.23, 131.36, 131.32, 129.14, 128.99 (PPh_3), 49.04, 48.25 ($NCH(CH_3)_2$), 27.29, 26.85 ($NCH(CH_3)_2$), 3.31 ($N(Si(CH_3)_3)_2$).

7.3.2. Xanthates (homoleptic)

$Au_2[S_2CO^nBu]_2$ (8): See Ref. (35)

7.3.3. Xanthates (heteroleptic)

Au[S₂COⁱBu](TPP)₂ (9): On the bench top a 100 mL flask was charged with 50 mL of benzene. AuCl(TPP)₂ (0.24, 0.28 mmol) was dissolved in the benzene. A 10mL solution of K[S₂COⁱBu] (0.05g, 0.28 mmol) was added and the solution allowed to stir over night. KCl was removed by removing the aqueous phase; 9 was isolated by removal of benzene under reduced pressure (0.27 mmol, 0.23g, 98%) Mp: 120 °C, dec.: 135 °C. ¹H NMR (300 MHz, C₆D₆): 7.41 (m, 12H, PPh₃), 6.94 (m, 18H, PPh₃), 1.66 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (300 MHz, C₆D₆): 134.50, 134.29, 130.46, 130.44, 129.06, 128.92 (PPh₃), 28.20 (C(CH₃)₃).

7.4. Silver (I) Complexes

7.4.1. Guanidines (homoleptic)

Ag₃[(ⁱPrN)₂CN(Me)₂]₃ (10): In a 50 mL flask, lithium dimethylamide (0.189 g, 3.70 mmol) was suspended in 30 mL of hexanes. Diisopropylcarbodiimide (0.467 g, 3.70 mmol) was diluted with 8 mL of hexanes and added dropwise to the suspension of LiNMe₂ at -30 °C. The cloudy, pale yellow suspension cleared to a homogeneous pale yellow solution over 2 h of stirring at room temperature. Owing to the photosensitivity of silver (I) chloride, the reaction was carried out with protection against light from this point on. Silver (I) chloride (0.530 g, 3.70 mmol) was added to the ligand suspension, and the mixture was stirred overnight, after which a light brown solid was filtered to afford a colorless solution. The volatiles were removed under reduced pressure to afford white solid 4 (0.85 g, 3.15 mmol, 85.0 % crude yield). This was dissolved in a minimal volume of hexanes and was kept at -35 °C overnight. Compound 4 was collected as white crystals (0.45 g, 1.62 mmol, 45 %). m.p. 78 °C (dec). Anal. Calcd for C₂₇H₆₀Ag₃N₉: C, 38.86; H, 7.25; N, 15.11. ¹H NMR (300 MHz, C₆D₆): 3.57 (sept, 4H, NCH(CH₃)₂), 2.62 (s, 12H, N(CH₃)₂), 1.34 (d, 24H NCH(CH₃)₂). ¹³C{¹H} NMR (75 MHz, C₆D₆): 169.38 (NCN), 48.19 ((CH₃)₂CHN), 40.83 ((CH₃)₂N), 27.76 ((CH₃)₂CHN).

Ag₃[(ⁱPrN)₂CN(Et)₂]₃ (11): Compound 11 was prepared in an analogous manner as compound 10 substituting: Diethylamine (0.523g, 7.20 mmol), MeLi (11.4 mL, 7.20 mmol), diisopropylcarbodiimide (0.442 g, 7.20 mmol), and silver(I) chloride (1.03 g, 7.20 mmol). Compound 6 was collected as white crystals (0.82 g, 2.62 mmol, 36.4% crude yield). m.p. 65 °C (dec). Anal. Calcd for C₃₃H₇₂Ag₃N₉: C, 43.15; H, 7.90; N, 13.72. ¹H NMR (300 MHz, C₆D₆): 3.65 (sept, 4H, NCH(CH₃)₂), 3.01 (q, 8H, N(CH₂CH₃)₂), 1.36 (d, 24H NCH(CH₃)₂), 0.95 (t, 12H,

$\text{N}(\text{CH}_2\text{CH}_3)_2$. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 168.40 (NCN), 48.62 ($(\text{CH}_3)_2\text{CHN}$), 43.91 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 27.85 ($(\text{CH}_3)_2\text{CHN}$), 13.44 ($\text{N}(\text{CH}_2\text{CH}_3)_2$).

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(^i\text{Pr})_2]_3$ (12): In a 100 mL flask, diisopropylamine (0.354 g, 3.50 mmol) was dissolved in 40 mL of hexanes at $-30\text{ }^\circ\text{C}$ and MeLi (2.19 mL, 3.50 mmol) was added dropwise to give white suspension after stirring for 2 hours. Diisopropylcarbodiimide (0.442 g, 3.50 mmol) was diluted with 10 mL of hexanes and added dropwise to the suspension of the lithiated amine at $-36\text{ }^\circ\text{C}$. Owing to the photosensitivity of silver(I) chloride, the reaction was carried out with protection against light from this point on. Silver(I) chloride (0.50 g, 3.50 mmol) was added, and the mixture was stirred overnight, after which a dark brown/grey solid was filtered to afford pale yellow solution. The volatiles were removed under reduced pressure to afford white solid 5 (0.819 g, 2.45 mmol, 70.0 % crude yield). The solid was dissolved in a minimal volume of hexanes and was kept at $-35\text{ }^\circ\text{C}$ overnight. Compound 5 was collected as white crystals (0.29 g, 0.87 mmol, 24.9 %). m.p. $73\text{ }^\circ\text{C}$ (dec). Anal. Calcd for $\text{C}_{39}\text{H}_{84}\text{Ag}_3\text{N}_9$: C, 46.71; H, 8.44; N, 12.57. ^1H NMR (300 MHz, C_6D_6): 3.85 (sept, 4H, $\text{NCH}(\text{CH}_3)_2$), 3.46 [sept, 4H, $\text{N}(\text{CH}(\text{CH}_3)_2)_2$], 1.33 [d, 24H $\text{NCH}(\text{CH}_3)_2$], 1.20 (d, 24H $\text{N}(\text{CH}(\text{CH}_3)_2)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 167.28 (NCN), 49.13 ($\text{NCH}(\text{CH}_3)_2$), 47.98 ($\text{N}(\text{CH}(\text{CH}_3)_2)_2$), 27.60 ($\text{NCH}(\text{CH}_3)_2$), 23.44 ($\text{N}(\text{CH}(\text{CH}_3)_2)_2$).

$\text{Ag}_3[(^i\text{PrN})_2\text{CN}(\text{TMS})_2]_3$ (13): In a 50 mL flask, $\text{KN}(\text{TMS})_2$ (0.542 g, 2.71 mmol) was suspended in 30 mL of hexanes. Diisopropylcarbodiimide (0.342 g, 2.71 mmol) was added dropwise and the homogeneous pale yellow solution turned cloudy, pale yellow over 2 h of stirring. Owing to the photosensitivity of silver (I) chloride, the reaction was carried out with protection against light from this point on. Silver (I) chloride (0.389 g, 2.71 mmol) was added, and the mixture was stirred overnight, after which a light brown/grey solid was filtered to afford colorless solution. Volatiles were removed under reduced pressure to afford white solid 7 (0.747 g, 1.89 mmol, 69.9 % crude yield). The solid was dissolved in a minimal volume of hexanes and was kept at $-35\text{ }^\circ\text{C}$ overnight. Compound 7 was collected as white microcrystalline material (0.445 g, 1.13 mmol, 41.6 %). m.p. $106\text{ }^\circ\text{C}$ (dec). Anal. Calcd for $\text{C}_{39}\text{H}_{96}\text{Ag}_3\text{N}_9\text{Si}_6$: C, 39.58; H, 8.18; N, 10.65. ^1H NMR (300 MHz, C_6D_6): 3.76 (sept, 4H, $\text{NCH}(\text{CH}_3)_2$), 1.11 [d, 24H $\text{NCH}(\text{CH}_3)_2$], 0.29 [s, 36H $\text{Si}(\text{CH}_3)_3$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 157.92 (NCN), 46.66 [$\text{NCH}(\text{CH}_3)_2$], 28.00 [$\text{NCH}(\text{CH}_3)_2$], 3.00 [$\text{Si}(\text{CH}_3)_3$].

7.5. Zinc (II) Complexes

$[\text{PrNC}(\text{N}^i\text{Pr})_2]_2\text{Zn}$ (**14**)

- Salt metathesis

In a 100mL round bottom flask, lithiated isopropyl guanidinate (0.549g, 3.01 mmol) was dissolved in Hexanes or Pentane (30mL). Zinc Chloride-THF (0.315 g, 1.51 mmol) was added while the solution was stirred rapidly. The solution remained colourless with undissolved ZnCl_2 . The solution was left to stir for 12h. The mixture became cloudy white with the precipitation of LiCl. The solution was filtered. Excess solvent was removed via a vacuum pump. A colourless resin was isolated which did not solidify at -30°C . (0.561g, 1.29mmol, 85%). ^1H NMR (300 MHz, C_6D_6): 3.63 (sept, 2H, $\text{CH}(\text{Me}_2)$), 3.49 (sept, 4H, $\text{CH}(\text{Me}_2)$), 1.24 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 164.35 $\text{NC}(\text{NMe}_2)\text{N}$, 45.77 $\text{CH}(\text{Me}_2)$, 45.33 $\text{CH}(\text{Me}_2)$, 26.31 ($\text{CH}(\text{CH}_3)_2$), 23.78 ($\text{CH}(\text{CH}_3)_2$).

- Alkane elimination

In a 100 mL round bottom flask, Isopropyl Guanidine (0.0.615g, 3.37 mmol) was dissolved in Hexanes or Pentane (30mL). Diethylzinc (1.0 M in hexane, 1.69 mL, 1.69 mmol) was added dropwise over 15min while the solution was stirred rapidly and left to stir for 12h. The mixture remained colourless. Excess solvent was removed via a vacuum pump. A colourless resin was isolated which did not solidify at -36°C . (0.647g, 1.49mmol, 88%). ^1H NMR (300 MHz, C_6D_6): 3.63 (sept, 2H, $\text{CH}(\text{Me}_2)$), 3.50 (sept, 4H, $\text{CH}(\text{Me}_2)$), 1.24 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 164.34 $\text{NC}(\text{NMe}_2)\text{N}$, 45.76 $\text{CH}(\text{Me}_2)$, 45.32 $\text{CH}(\text{Me}_2)$, 26.30 ($\text{CH}(\text{CH}_3)_2$), 23.76 ($\text{CH}(\text{CH}_3)_2$).

$[\text{PrNC}(\text{N}^i\text{Pr})_2]_3\text{Zn}_2\text{Cl}$ (**15**)

A 100mL flask, was charged with 30mL of diethyl ether (0.386g, 2.02 mmol) of lithium triisopropyl guanidinate was added. $\text{ZnCl}\cdot\text{THF}$ (0.237g, 1.37 mmol) was added to the suspension and allowed to stir overnight. LiCl was filtered, and ether removed under reduced pressure, yielding a white powder. **15** was isolated as by recrystallization in ether as clear colourless plates (0.396g, 0.55 mmol).

$[\text{}^i\text{PrHNC}(\text{}^i\text{Pr})_2]_2(\text{ZnEt})_4$ (16)

In a 100 mL round bottom flask, Isopropyl Guanidine (0.538g, 2.95 mmol) was dissolved in Hexanes (30mL). Diethylzinc (1.0 M in hexane, 2.95 mL, 2.95 mmol) was added dropwise over 15min while the solution was stirred rapidly. The solution remained colourless. The solution was left to stir for 12h. The mixture remained colourless. Excess solvent was removed under reduced pressure. Clear platy crystals were precipitated at -30°C then recrystallized in hexanes (0.507g, 0.69mmol, 47%). ^1H NMR (300 MHz, C_6D_6): 3.63 (sept, 1H, $\text{CH}(\text{Me}_2)$), 3.32 (sept, 2H, $\text{CH}(\text{Me}_2)$), 1.75 (t, 3H, CH_2CH_3), 1.17 (d, 12H, $\text{CH}(\text{CH}_3)_2$), 0.93 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 0.69 (q, 2H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): 162.20(NCN), 46.92 $\text{CH}(\text{Me}_2)$, 44.98 $\text{CH}(\text{Me}_2)$, 25.06 ($\text{CH}(\text{CH}_3)_2$), 24.57 ($\text{CH}(\text{CH}_3)_2$), 14.65 (CH_2CH_3), 3.23 (CH_2CH_3).

7.6. Thermolysis Experiments:

A screw cap NMR tube was charged with enough compound for an NMR experiment, typically a few milligrams. The bottom portion of the tube containing the compound was placed in an oil bath at 120°C for 2 hours with no solvent present. The sample tube was then cooled in liquid nitrogen (-196°C) to trap any volatile byproducts, then C_6D_6 was added and a ^1H NMR was collected.

7.7. Photodeposition Experiments

All experiments done in a nitrogen atmosphere drybox.

7.7.1. Film deposition on glass vials:

Recrystallized $\text{Au}_2[(\text{}^i\text{PrN})_2\text{CMe}]_2$ was dissolved in a volume of pentane in a 20mL glass vial until a supersaturated solution was achieved. The solution was placed in a freezer at -36°C for a minimum of 12hrs. A glass microscope slide was cut to 1 cm^2 and sonicated in acetone for 30 min then rinsed with distilled water dried and pumped into the drybox overnight then added to a 20 mL vial. A volume of the mother liquor from the $\text{Au}_2[(\text{}^i\text{PrN})_2\text{CMe}]_2$ recrystallization was transferred to the slide containing glass vial at room temperature. The vial was placed on a stainless steel shelf and left for a period of time ranging from a) 4 days, b) 7 days, c) 14 days. The remaining pentane was removed and the films rinsed with hexanes to remove any loosely bound particulates. The slides were then removed and characterized. Vials were also cut with a diamond tipped pen to be characterized.

Figure 68: Schematic of photodeposition apparatus

7.7.2. Deposition on Fibre Bragg Gratings (FBG):

A fibre Bragg grating (FBG) filament was sonicated for 30 min in acetone to remove the polymeric protective jacket. The FBG filament mount was adhered to a hole in a 20mL vial cap. The filament was then mounted within the lid assembly. The vial was filled to the top with precursor pentane solution (as prepared in 7.7.1.). The filament-lid assembly was screwed to the top of the filled vial, making sure that the entire filament was submerged. The vial was then wrapped in aluminum foil to ensure no ambient light penetrated the vial. The FBG filament was plugged into a white light source via fibre optic cable and allowed to run for 7 days. The FBG filament was then removed from the apparatus and the source, rinsed in pentane and characterized via optical microscopy as well as SEM.

Figure 69: Schematic of Fibre Bragg Grating photodeposition apparatus

7.8. CVD Experiments

Figure 70: Schematic of CVD deposition apparatus

7.8.1. Substrate Cleaning Procedure

The following steps were undertaken to clean the Si(100) substrates

- i) Sonicated for 20 minutes at highest power level in acetone
- ii) Rinsed with distilled water
- iii) Placed in a freshly prepared mixture of concentrated 10:10:1 ratio of $\text{H}_2\text{O}:\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ for 30 minutes then rinsed with distilled water.
- iv) Sonicated for 10 minutes at highest power level in distilled water
- v) Placed in a freshly prepared mixture of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ in a ratio of 4:1 for 10 minutes then rinsed with distilled water.
- vi) Placed in freshly prepared 1:1:6 ratio of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ for 10 minutes, then rinsed with distilled water.
- vii) Dried with a kim wipe and placed under a UV Ozone lamp for 30 seconds.

7.8.2. CVD Deposition Procedure

For all depositions Si(100) was used as the substrate. The substrate was placed so as to have the (100) face down so as to incur a "line of site" type CVD film. All depositions occurred using approximately 1g of purified then powdered $\text{Au}_2[(^i\text{PrN})_2\text{CN}(\text{Me})_2]_2$ as the gold source.

Heating zones #1 and #2 were heated to the desired temperatures using heating tape, then precursor introduced via the endcap into the lower portion of the apparatus. The substrate was then placed polished side down facing the precursor. The endcap was replaced and dynamic vacuum applied via roughing pump (20 mtorr). The experiment was allowed to proceed from a period of 2-12 hours.

8. Conclusions

Novel monovalent gold complexes of amidinates and guanidines were synthesized in order to study their thermal chemistry for the purposes of application as CVD precursors. These compounds were $[\text{RC}(\text{N}^i\text{Pr})_2]_2\text{Au}_2$ where $\text{R} = n\text{Bu}$, Me , NMe_2 , NEt_2 , N^iPr_2 and $\text{N}(\text{TMS})_2$. It was found that these compounds decomposed to metallic gold in the presence of light. This resulted in the solution phase deposition of gold metal films using the $\text{R} = \text{Me}$ derivative as the gold source. The films were characterized by SEM, EDS, and XRD.

Gold (I) dimethyl guanidinate ($\text{R} = \text{NMe}_2$) proved to be the only sublimable compound. For this reason it was used as a single source precursor in the deposition of gold metal films by thermal CVD. This was obtained at lower operating temperatures than those previously reported in literature. The films were studied by SEM and EDS.

Monovalent silver guanidines were synthesized for the same purposes as the gold analogues. These were found to be too unstable to reach the vapour phase and made for poor CVD precursors. The crystal structure of silver (I) dimethyl guanidinate proved to be a trimeric complex.

Novel zinc (II) triisopropyl structures showed interesting geometry and helped to better understand the chemistry behind alkane elimination reactions. The complex NMR data showed that the zinc (II) lantern structure exists as a dimer in solution as well as another chloride containing zinc (II) guanidinate complex.

9. References

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10. Appendices

Crystallographic Data

Compound 1

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 $F^2 > 2\sigma(F^2)$  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)+(0.0220P)^2+8.5300P] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment constr
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?

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_refine_ls_number_restraints   0
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_refine_ls_wR_factor_ref       0.0507
_refine_ls_wR_factor_gt        0.0491
_refine_ls_goodness_of_fit_ref 1.017
_refine_ls_restrained_S_all    1.017
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_atom_site_refinement_flags
_atom_site_disorder_assembly
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Au2 Au 0.016646(8) 0.552468(13) 0.076427(10) 0.01006(5) Uani 1 1 d...
N1 N 0.30641(18) 0.2279(3) 0.4419(2) 0.0135(7) Uani 1 1 d...
N2 N 0.22547(17) 0.0853(3) 0.4044(2) 0.0123(7) Uani 1 1 d...
N3 N 0.09132(17) 0.4251(3) 0.1554(2) 0.0109(7) Uani 1 1 d...
N4 N 0.06325(17) 0.3351(3) 0.0198(2) 0.0114(7) Uani 1 1 d...
C1 C 0.2759(2) 0.1225(4) 0.4069(3) 0.0122(8) Uani 1 1 d...
C2 C 0.2985(3) 0.0411(4) 0.3674(3) 0.0204(10) Uani 1 1 d...
H2A H 0.3488 0.0473 0.4077 0.031 Uiso 1 1 calc R..
H2B H 0.2751 0.0648 0.3015 0.031 Uiso 1 1 calc R..
H2C H 0.2863 -0.0414 0.3677 0.031 Uiso 1 1 calc R..
C3 C 0.3604(2) 0.2689(4) 0.4412(3) 0.0176(9) Uani 1 1 d...
H3A H 0.3595 0.2157 0.3976 0.021 Uiso 1 1 calc R..
C4 C 0.3429(2) 0.3950(4) 0.4011(3) 0.0244(10) Uani 1 1 d...
H4A H 0.2974 0.3955 0.3357 0.037 Uiso 1 1 calc R..
H4B H 0.3781 0.4228 0.3999 0.037 Uiso 1 1 calc R..
H4C H 0.3421 0.4479 0.4419 0.037 Uiso 1 1 calc R..
C5 C 0.4314(2) 0.2614(5) 0.5408(4) 0.0265(11) Uani 1 1 d...
H5A H 0.4425 0.1780 0.5614 0.040 Uiso 1 1 calc R..
H5B H 0.4319 0.3074 0.5857 0.040 Uiso 1 1 calc R..
H5C H 0.4659 0.2941 0.5398 0.040 Uiso 1 1 calc R..
C6 C 0.1853(2) -0.0242(4) 0.3511(3) 0.0158(9) Uani 1 1 d...

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H6A H 0.1874 -0.0393 0.3004 0.019 Uiso 1 1 calc R..
 C7 C 0.2153(3) -0.1318(4) 0.4177(3) 0.0261(11) Uani 1 1 d...
 H7A H 0.2639 -0.1425 0.4488 0.039 Uiso 1 1 calc R..
 H7B H 0.1889 -0.2032 0.3804 0.039 Uiso 1 1 calc R..
 H7C H 0.2125 -0.1190 0.4668 0.039 Uiso 1 1 calc R..
 C8 C 0.1101(2) -0.0060(5) 0.3026(3) 0.0266(11) Uani 1 1 d...
 H8A H 0.0904 0.0599 0.2566 0.040 Uiso 1 1 calc R..
 H8B H 0.1075 0.0128 0.3512 0.040 Uiso 1 1 calc R..
 H8C H 0.0838 -0.0790 0.2686 0.040 Uiso 1 1 calc R..
 C9 C 0.09833(19) 0.3371(3) 0.1146(3) 0.0103(8) Uani 1 1 d...
 C10 C 0.1481(2) 0.2354(4) 0.1772(3) 0.0171(9) Uani 1 1 d...
 H10A H 0.1484 0.2202 0.2290 0.026 Uiso 1 1 calc R..
 H10B H 0.1948 0.2572 0.2048 0.026 Uiso 1 1 calc R..
 H10C H 0.1331 0.1635 0.1379 0.026 Uiso 1 1 calc R..
 C11 C 0.1318(2) 0.4267(4) 0.2603(3) 0.0152(9) Uani 1 1 d...
 H11A H 0.1723 0.3718 0.2928 0.018 Uiso 1 1 calc R..
 C12 C 0.0869(2) 0.3844(5) 0.2806(3) 0.0254(11) Uani 1 1 d...
 H12A H 0.0718 0.3024 0.2577 0.038 Uiso 1 1 calc R..
 H12B H 0.0463 0.4363 0.2472 0.038 Uiso 1 1 calc R..
 H12C H 0.1138 0.3874 0.3499 0.038 Uiso 1 1 calc R..
 C13 C 0.1584(2) 0.5524(4) 0.2990(3) 0.0235(10) Uani 1 1 d...
 H13A H 0.1870 0.5785 0.2852 0.035 Uiso 1 1 calc R..
 H13B H 0.1863 0.5528 0.3686 0.035 Uiso 1 1 calc R..
 H13C H 0.1190 0.6067 0.2681 0.035 Uiso 1 1 calc R..
 C14 C 0.0768(2) 0.2420(4) -0.0215(3) 0.0207(10) Uani 1 1 d...
 H14A H 0.1249 0.2113 0.0304 0.025 Uiso 1 1 calc R..
 C15 C 0.0719(3) 0.2944(6) -0.1004(4) 0.0389(15) Uani 1 1 d...
 H15A H 0.1056 0.3591 -0.0741 0.058 Uiso 1 1 calc R..
 H15B H 0.0251 0.3257 -0.1516 0.058 Uiso 1 1 calc R..
 H15C H 0.0817 0.2324 -0.1267 0.058 Uiso 1 1 calc R..
 C16 C 0.0263(3) 0.1391(4) -0.0585(4) 0.0322(13) Uani 1 1 d...
 H16A H 0.0348 0.1006 -0.0045 0.048 Uiso 1 1 calc R..
 H16B H 0.0329 0.0810 -0.0909 0.048 Uiso 1 1 calc R..
 H16C H -0.0213 0.1694 -0.1041 0.048 Uiso 1 1 calc R..

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 _atom_site_aniso_U_23
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 Au2 0.01098(8) 0.00953(8) 0.00772(7) 0.00051(5) 0.00544(6) 0.00255(6)
 N1 0.0189(18) 0.0091(17) 0.0196(18) 0.0008(14) 0.0158(16) -0.0006(14)
 N2 0.0158(17) 0.0071(17) 0.0133(17) -0.0019(13) 0.0095(15) -0.0007(13)
 N3 0.0099(16) 0.0126(17) 0.0066(15) 0.0023(13) 0.0040(14) 0.0016(13)

N4 0.0099(16) 0.0117(18) 0.0104(16) 0.0012(13) 0.0059(14) 0.0028(13)
 C1 0.0133(19) 0.010(2) 0.0084(18) 0.0029(15) 0.0053(17) 0.0053(16)
 C2 0.030(3) 0.010(2) 0.031(3) -0.0016(18) 0.025(2) 0.0045(18)
 C3 0.021(2) 0.017(2) 0.023(2) -0.0022(18) 0.018(2) -0.0018(18)
 C4 0.022(2) 0.030(3) 0.025(2) 0.006(2) 0.018(2) -0.005(2)
 C5 0.016(2) 0.029(3) 0.034(3) 0.010(2) 0.016(2) 0.0037(19)
 C6 0.021(2) 0.010(2) 0.014(2) -0.0036(16) 0.0103(19) -0.0033(17)
 C7 0.034(3) 0.010(2) 0.028(3) -0.0023(19) 0.018(2) -0.008(2)
 C8 0.020(2) 0.026(3) 0.022(2) -0.006(2) 0.009(2) -0.011(2)
 C9 0.0075(18) 0.010(2) 0.0112(19) -0.0012(15) 0.0055(16) -0.0018(15)
 C10 0.021(2) 0.009(2) 0.015(2) 0.0034(16) 0.0098(19) 0.0058(17)
 C11 0.014(2) 0.019(2) 0.0081(19) 0.0010(16) 0.0054(17) 0.0047(17)
 C12 0.030(3) 0.033(3) 0.020(2) 0.007(2) 0.019(2) 0.005(2)
 C13 0.025(2) 0.025(3) 0.015(2) -0.0054(19) 0.011(2) -0.004(2)
 C14 0.019(2) 0.023(2) 0.016(2) -0.0010(18) 0.0095(19) 0.0106(18)
 C15 0.043(3) 0.057(4) 0.027(3) 0.014(3) 0.028(3) 0.031(3)
 C16 0.027(3) 0.019(3) 0.027(3) -0.010(2) 0.009(2) 0.006(2)

_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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 Au1 N1 2.044(3) . ?
 Au1 Au1 2.6529(5) 7_556 ?
 Au2 N4 2.036(3) 5_565 ?
 Au2 N3 2.039(3) . ?
 Au2 Au2 2.6486(6) 5_565 ?
 N1 C1 1.328(5) . ?
 N1 C3 1.483(5) . ?
 N2 C1 1.346(5) . ?
 N2 C6 1.485(5) . ?
 N2 Au1 2.037(3) 7_556 ?
 N3 C9 1.334(5) . ?
 N3 C11 1.483(5) . ?
 N4 C9 1.349(5) . ?

N4 C14 1.475(5) . ?
 N4 Au2 2.036(3) 5_565 ?
 C1 C2 1.519(6) . ?
 C3 C5 1.512(6) . ?
 C3 C4 1.523(6) . ?
 C6 C8 1.520(6) . ?
 C6 C7 1.525(6) . ?
 C9 C10 1.523(5) . ?
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 C14 C15 1.515(7) . ?
 C14 C16 1.523(7) . ?

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 _geom_angle_site_symmetry_3
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 N2 Au1 Au1 85.69(10) 7_556 7_556 ?
 N1 Au1 Au1 85.65(10) . 7_556 ?
 N4 Au2 N3 171.46(13) 5_565 . ?
 N4 Au2 Au2 85.24(9) 5_565 5_565 ?
 N3 Au2 Au2 86.34(9) . 5_565 ?
 C1 N1 C3 121.9(3) . . ?
 C1 N1 Au1 122.5(3) . . ?
 C3 N1 Au1 114.9(3) . . ?
 C1 N2 C6 120.6(3) . . ?
 C1 N2 Au1 122.2(3) . 7_556 ?
 C6 N2 Au1 117.0(3) . 7_556 ?
 C9 N3 C11 121.3(3) . . ?
 C9 N3 Au2 122.2(3) . . ?
 C11 N3 Au2 116.1(3) . . ?
 C9 N4 C14 120.9(3) . . ?
 C9 N4 Au2 123.1(3) . 5_565 ?
 C14 N4 Au2 115.8(3) . 5_565 ?
 N1 C1 N2 122.6(4) . . ?
 N1 C1 C2 118.6(4) . . ?
 N2 C1 C2 118.8(4) . . ?
 N1 C3 C5 110.7(4) . . ?
 N1 C3 C4 108.8(3) . . ?
 C5 C3 C4 112.0(4) . . ?
 N2 C6 C8 109.5(4) . . ?
 N2 C6 C7 111.2(3) . . ?
 C8 C6 C7 110.2(4) . . ?

N3 C9 N4 122.4(4) . . ?
 N3 C9 C10 119.0(3) . . ?
 N4 C9 C10 118.6(3) . . ?
 N3 C11 C13 109.6(3) . . ?
 N3 C11 C12 110.0(3) . . ?
 C13 C11 C12 110.4(4) . . ?
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 N4 C14 C16 110.0(4) . . ?
 C15 C14 C16 111.4(4) . . ?

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 _geom_torsion_site_symmetry_3
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 N2 Au1 N1 C1 7.8(11) 7_556 . . . ?
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 N2 Au1 N1 C3 -162.7(8) 7_556 . . . ?
 Au1 Au1 N1 C3 -174.7(3) 7_556 . . . ?
 N4 Au2 N3 C9 6.6(11) 5_565 . . . ?
 Au2 Au2 N3 C9 -3.3(3) 5_565 . . . ?
 N4 Au2 N3 C11 -166.0(8) 5_565 . . . ?
 Au2 Au2 N3 C11 -175.9(3) 5_565 . . . ?
 C3 N1 C1 N2 -178.1(4) ?
 Au1 N1 C1 N2 12.1(5) ?
 C3 N1 C1 C2 1.5(6) ?
 Au1 N1 C1 C2 -168.3(3) ?
 C6 N2 C1 N1 170.3(4) ?
 Au1 N2 C1 N1 -14.5(5) 7_556 . . . ?
 C6 N2 C1 C2 -9.3(5) ?
 Au1 N2 C1 C2 165.9(3) 7_556 . . . ?
 C1 N1 C3 C5 -105.0(5) ?
 Au1 N1 C3 C5 65.6(4) ?
 C1 N1 C3 C4 131.5(4) ?
 Au1 N1 C3 C4 -57.9(4) ?
 C1 N2 C6 C8 -142.3(4) ?
 Au1 N2 C6 C8 42.3(4) 7_556 . . . ?
 C1 N2 C6 C7 95.8(5) ?
 Au1 N2 C6 C7 -79.7(4) 7_556 . . . ?
 C11 N3 C9 N4 -178.4(3) ?
 Au2 N3 C9 N4 9.3(5) ?
 C11 N3 C9 C10 1.1(6) ?

Au2 N3 C9 C10 -171.1(3) . . . ?
C14 N4 C9 N3 174.6(4) . . . ?
Au2 N4 C9 N3 -11.4(5) 5_565 . . . ?
C14 N4 C9 C10 -4.9(6) . . . ?
Au2 N4 C9 C10 169.1(3) 5_565 . . . ?
C9 N3 C11 C13 137.3(4) . . . ?
Au2 N3 C11 C13 -50.0(4) . . . ?
C9 N3 C11 C12 -101.1(4) . . . ?
Au2 N3 C11 C12 71.6(4) . . . ?
C9 N4 C14 C15 -143.0(4) . . . ?
Au2 N4 C14 C15 42.5(5) 5_565 . . . ?
C9 N4 C14 C16 93.9(5) . . . ?
Au2 N4 C14 C16 -80.6(4) 5_565 . . . ?

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_diffraction_reflns_theta_full 25.00
_diffraction_measured_fraction_theta_full 0.999
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_refine_diff_density_min -1.249
_refine_diff_density_rms 0.172

Compound 2

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?
;
_chemical_name_common      ?
_chemical_melting_point    ?
_chemical_formula_moiety   ?
_chemical_formula_sum
'C30 H30 Au Cl N2'
_chemical_formula_weight   650.98

loop_
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_atom_type_description
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_atom_type_scatter_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'
'Cl' 'Cl' 0.1484 0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Au' 'Au' -2.0133 8.8022
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting     Triclinic
_symmetry_space_group_name_H-M P-1

loop_
_symmetry_equiv_pos_as_xyz
'x, y, z'
'-x, -y, -z'

_cell_length_a             7.8512(11)
_cell_length_b             8.8808(12)
_cell_length_c             10.2077(14)
_cell_angle_alpha          104.223(2)
_cell_angle_beta           102.470(2)
_cell_angle_gamma          105.080(2)
_cell_volume               635.68(15)
_cell_formula_units_Z      1
_cell_measurement_temperature 120(2)

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_exptl_crystal_F_000            320
_exptl_absorpt_coefficient_mu   5.912
_exptl_absorpt_correction_type  multi-scan
_exptl_absorpt_correction_T_min 0.5348
_exptl_absorpt_correction_T_max 0.8711
_exptl_absorpt_process_details  'SADABS (Sheldrick, 2003)'

_exptl_special_details
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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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_diffn_radiation_monochromator  graphite
_diffn_measurement_device_type  'Bruker AXS APEX diffractometer'
_diffn_measurement_method       \w
_diffn_detector_area_resol_mean 836.6
_diffn_standards_number         0
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_diffn_standards_decay_%        1
_diffn_reflns_number            5433
_diffn_reflns_av_R_equivalents  0.0352
_diffn_reflns_av_sigmal/netl    0.0485
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_diffrn_reflms_theta_max     25.00
_reflms_number_total         2242
_reflms_number_gt            2083
_reflms_threshold_expression  >2sigma(I)

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_computing_data_reduction     SAINT
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
_computing_publication_material 'SHELXTL (Sheldrick, 2001)'

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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_weighting_details
'calc w=1/[ $s^2(F_o^2) + (0.0330P)^2$ ] where  $P=(F_o^2+2F_c^2)/3$ '
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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_reflms        2242
_refine_ls_number_parameters     127
_refine_ls_number_restraints     0
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_atom_site_symmetry_multiplicity
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_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
Au1 Au 0.47307(3) 1.03058(3) 0.12595(3) 0.01765(10) Uani 1 1 d ...
N1 N 0.6617(7) 0.8180(6) -0.0655(6) 0.0158(11) Uani 1 1 d ...
N2 N 0.6151(8) 0.8733(6) 0.1587(6) 0.0199(12) Uani 1 1 d ...
C1 C 0.7360(9) 0.7321(8) -0.1725(7) 0.0184(14) Uani 1 1 d ...
H1A H 0.7749 0.6456 -0.1396 0.022 Uiso 1 1 calc R..
C2 C 0.5878(9) 0.6477(8) -0.3141(7) 0.0216(14) Uani 1 1 d ...
H2A H 0.4807 0.5721 -0.3025 0.032 Uiso 1 1 calc R..
H2B H 0.6366 0.5858 -0.3815 0.032 Uiso 1 1 calc R..
H2C H 0.5503 0.7306 -0.3498 0.032 Uiso 1 1 calc R..
C3 C 0.9059(9) 0.8514(8) -0.1867(8) 0.0267(16) Uani 1 1 d ...
H3A H 0.9998 0.9045 -0.0940 0.040 Uiso 1 1 calc R..
H3B H 0.8701 0.9354 -0.2217 0.040 Uiso 1 1 calc R..
H3C H 0.9564 0.7906 -0.2534 0.040 Uiso 1 1 calc R..
C4 C 0.6948(8) 0.8069(7) 0.0649(7) 0.0160(13) Uani 1 1 d ...
C5 C 0.8310(9) 0.7219(8) 0.1121(7) 0.0188(14) Uani 1 1 d ...
H5A H 0.9208 0.7309 0.0573 0.023 Uiso 1 1 calc R..
H5B H 0.9007 0.7809 0.2132 0.023 Uiso 1 1 calc R..
C6 C 0.7425(9) 0.5420(7) 0.0941(7) 0.0191(14) Uani 1 1 d ...
H6A H 0.6855 0.4802 -0.0082 0.023 Uiso 1 1 calc R..
H6B H 0.6426 0.5312 0.1396 0.023 Uiso 1 1 calc R..
C7 C 0.8785(10) 0.4649(8) 0.1574(8) 0.0266(16) Uani 1 1 d ...
H7A H 0.8158 0.3446 0.1290 0.032 Uiso 1 1 calc R..
H7C H 0.9828 0.4830 0.1167 0.032 Uiso 1 1 calc R..
C8 C 0.9548(10) 0.5318(9) 0.3171(8) 0.0286(16) Uani 1 1 d ...
H8D H 1.0407 0.4766 0.3497 0.043 Uiso 1 1 calc R..
H8A H 0.8530 0.5118 0.3587 0.043 Uiso 1 1 calc R..
H8B H 1.0203 0.6505 0.3465 0.043 Uiso 1 1 calc R..
C9 C 0.6436(10) 0.8526(8) 0.2990(7) 0.0221(15) Uani 1 1 d ...
H9A H 0.7025 0.7657 0.3009 0.026 Uiso 1 1 calc R..
C10 C 0.7699(11) 1.0119(10) 0.4143(8) 0.0330(18) Uani 1 1 d ...
H10A H 0.8888 1.0470 0.3955 0.050 Uiso 1 1 calc R..
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H10B H 0.7899 0.9937 0.5065 0.050 Uiso 1 1 calc R . .
H10D H 0.7122 1.0975 0.4151 0.050 Uiso 1 1 calc R . .
C11 C 0.4596(10) 0.7979(9) 0.3275(8) 0.0288(16) Uani 1 1 d . . .
H11A H 0.3786 0.6954 0.2531 0.043 Uiso 1 1 calc R . .
H11B H 0.4017 0.8833 0.3282 0.043 Uiso 1 1 calc R . .
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N1 0.022(3) 0.018(3) 0.015(3) 0.009(2) 0.009(2) 0.013(2)
N2 0.027(3) 0.018(3) 0.020(3) 0.009(2) 0.005(2) 0.014(2)
C1 0.022(3) 0.015(3) 0.023(4) 0.008(3) 0.010(3) 0.009(3)
C2 0.028(4) 0.018(3) 0.015(3) 0.002(3) 0.003(3) 0.009(3)
C3 0.026(4) 0.024(3) 0.037(4) 0.013(3) 0.020(3) 0.008(3)
C4 0.017(3) 0.017(3) 0.010(3) 0.002(3) 0.001(3) 0.004(3)
C5 0.021(3) 0.021(3) 0.017(4) 0.006(3) 0.006(3) 0.011(3)
C6 0.022(3) 0.018(3) 0.016(3) 0.002(3) 0.002(3) 0.011(3)
C7 0.033(4) 0.025(4) 0.030(4) 0.014(3) 0.007(3) 0.019(3)
C8 0.029(4) 0.035(4) 0.028(4) 0.017(4) 0.004(3) 0.018(3)
C9 0.038(4) 0.030(4) 0.018(4) 0.018(3) 0.017(3) 0.026(3)
C10 0.043(4) 0.043(4) 0.022(4) 0.013(4) 0.011(4) 0.025(4)
C11 0.037(4) 0.030(4) 0.026(4) 0.013(3) 0.012(3) 0.017(3)

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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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Au1 N2 2.046(5) . ?

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Au1 Au1 2.6436(6) 2_675 ?

N1 C4 1.333(8) . ?

N1 C1 1.487(8) . ?

N1 Au1 2.043(5) 2_675 ?

N2 C4 1.352(8) . ?

N2 C9 1.465(8) . ?

C1 C2 1.514(9) . ?

C1 C3 1.532(8) . ?

C4 C5 1.523(9) . ?

C5 C6 1.514(9) . ?

C6 C7 1.525(9) . ?

C7 C8 1.512(10) . ?

C9 C11 1.514(9) . ?

C9 C10 1.522(10) . ?

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N1 Au1 N2 171.7(2) 2_675 . ?

N1 Au1 Au1 86.31(14) 2_675 2_675 ?

N2 Au1 Au1 85.40(16) . 2_675 ?

C4 N1 C1 121.8(5) . . ?

C4 N1 Au1 122.5(4) . 2_675 ?

C1 N1 Au1 115.5(4) . 2_675 ?

C4 N2 C9 121.7(5) . . ?

C4 N2 Au1 123.0(4) . . ?

C9 N2 Au1 114.9(4) . . ?

N1 C1 C2 110.5(5) . . ?

N1 C1 C3 111.2(5) . . ?

C2 C1 C3 110.9(6) . . ?

N1 C4 N2 122.0(6) . . ?

N1 C4 C5 119.4(5) . . ?

N2 C4 C5 118.6(6) . . ?

C6 C5 C4 114.4(5) . . ?

C5 C6 C7 113.4(5) . . ?

C8 C7 C6 114.3(6) . . ?

N2 C9 C11 110.0(6) . . ?

N2 C9 C10 111.1(6) . . ?

C11 C9 C10 109.7(6) . . ?

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Au1 Au1 N2 C4 5.0(5) 2_675 ... ?
N1 Au1 N2 C9 176.0(12) 2_675 ... ?
Au1 Au1 N2 C9 178.1(4) 2_675 ... ?
C4 N1 C1 C2 134.9(6) .... ?
Au1 N1 C1 C2 -50.5(6) 2_675 ... ?
C4 N1 C1 C3 -101.6(7) .... ?
Au1 N1 C1 C3 73.1(6) 2_675 ... ?
C1 N1 C4 N2 -174.4(5) .... ?
Au1 N1 C4 N2 11.4(8) 2_675 ... ?
C1 N1 C4 C5 7.6(9) .... ?
Au1 N1 C4 C5 -166.7(4) 2_675 ... ?
C9 N2 C4 N1 176.4(5) .... ?
Au1 N2 C4 N1 -11.0(9) .... ?
C9 N2 C4 C5 -5.5(9) .... ?
Au1 N2 C4 C5 167.0(4) .... ?
N1 C4 C5 C6 -95.0(7) .... ?
N2 C4 C5 C6 86.8(7) .... ?
C4 C5 C6 C7 -173.4(5) .... ?
C5 C6 C7 C8 67.0(8) .... ?
C4 N2 C9 C11 -131.3(6) .... ?
Au1 N2 C9 C11 55.6(6) .... ?
C4 N2 C9 C10 107.0(7) .... ?
Au1 N2 C9 C10 -66.1(6) .... ?

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_diffrn_reflns_theta_full 25.00
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Compound 3

_audit_creation_method SHELXL-97

_chemical_name_systematic

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_chemical_name_common ?

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_chemical_formula_moiety ?

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'C18 H40 Au2 N6'

_chemical_formula_weight 734.49

loop_

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_atom_type_scatter_dispersion_imag

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'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'

'Au' 'Au' -2.0133 8.8022

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M C2/c

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_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'

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_cell_length_b 11.349(3)

_cell_length_c 12.080(3)

_cell_angle_alpha 90.00

_cell_angle_beta 113.214(3)

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_cell_angle_gamma      90.00
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_cell_measurement_reflns_used 991
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_exptl_crystal_F_000 1392
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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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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 $F^2 > 2\text{sigma}(F^2)$ 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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'calc w=1/(\s^2*(Fo^2)+(0.0324P)^2+2.8568P) 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_reflms 3046
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Au1 Au 0.314565(5) 0.198843(8) 0.016095(8) 0.02769(5) Uani 1 1 d ...
N1 N 0.28473(12) 0.0730(2) 0.1094(2) 0.0316(5) Uani 1 1 d ...
N2 N 0.16680(12) 0.1578(2) 0.0699(2) 0.0304(4) Uani 1 1 d ...
N3 N 0.20229(16) -0.0169(3) 0.1828(3) 0.0480(7) Uani 1 1 d ...
C1 C 0.34653(15) 0.0000(3) 0.1916(3) 0.0360(6) Uani 1 1 d ...
H1A H 0.3257 -0.0579 0.2326 0.043 Uiso 1 1 calc R..
C2 C 0.40381(19) 0.0765(3) 0.2871(3) 0.0506(8) Uani 1 1 d ...
H2A H 0.3805 0.1140 0.3366 0.076 Uiso 1 1 calc R..
H2B H 0.4221 0.1373 0.2479 0.076 Uiso 1 1 calc R..
H2C H 0.4457 0.0274 0.3382 0.076 Uiso 1 1 calc R..
C3 C 0.3820(2) -0.0679(3) 0.1190(3) 0.0511(8) Uani 1 1 d ...
H3A H 0.3455 -0.1234 0.0653 0.077 Uiso 1 1 calc R..
H3B H 0.4256 -0.1113 0.1740 0.077 Uiso 1 1 calc R..
H3C H 0.3976 -0.0126 0.0712 0.077 Uiso 1 1 calc R..
C4 C 0.21840(15) 0.0743(2) 0.1182(2) 0.0304(5) Uani 1 1 d ...
C5 C 0.1989(2) -0.1378(3) 0.1453(5) 0.0701(13) Uani 1 1 d ...
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H5B H 0.1466 -0.1628 0.1074 0.105 Uiso 1 1 calc R..
H5C H 0.2254 -0.1875 0.2156 0.105 Uiso 1 1 calc R..
C6 C 0.1837(2) 0.0094(5) 0.2847(4) 0.0697(13) Uani 1 1 d ...
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H6B H 0.2169 -0.0348 0.3552 0.105 Uiso 1 1 calc R..
H6C H 0.1317 -0.0133 0.2660 0.105 Uiso 1 1 calc R..
C7 C 0.08776(14) 0.1345(2) 0.0467(2) 0.0318(5) Uani 1 1 d ...
H7A H 0.0853 0.0607 0.0901 0.038 Uiso 1 1 calc R..
C8 C 0.0557(2) 0.2338(4) 0.0945(5) 0.0637(11) Uani 1 1 d ...
H8A H 0.0820 0.2380 0.1823 0.095 Uiso 1 1 calc R..

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H8B H 0.0025 0.2194 0.0737 0.095 Uiso 1 1 calc R . .
H8C H 0.0620 0.3083 0.0587 0.095 Uiso 1 1 calc R . .
C9 C 0.04236(19) 0.1160(4) -0.0870(3) 0.0512(8) Uani 1 1 d . . .
H9A H 0.0599 0.0449 -0.1138 0.077 Uiso 1 1 calc R . .
H9B H 0.0484 0.1843 -0.1320 0.077 Uiso 1 1 calc R . .
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N1 0.0257(10) 0.0325(11) 0.0358(11) 0.0109(9) 0.0114(9) 0.0013(9)
N2 0.0228(10) 0.0330(11) 0.0344(11) 0.0092(9) 0.0100(9) -0.0021(9)
N3 0.0439(15) 0.0417(15) 0.0674(18) 0.0278(14) 0.0316(14) 0.0053(12)
C1 0.0277(13) 0.0351(13) 0.0432(15) 0.0122(12) 0.0118(11) 0.0041(11)
C2 0.0404(17) 0.053(2) 0.0452(18) 0.0080(15) 0.0023(14) 0.0032(14)
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C4 0.0287(12) 0.0318(13) 0.0296(12) 0.0052(10) 0.0104(10) -0.0040(10)
C5 0.052(2) 0.044(2) 0.101(3) 0.024(2) 0.016(2) -0.0141(17)
C6 0.058(2) 0.103(3) 0.051(2) 0.040(2) 0.0236(18) 0.000(2)
C7 0.0240(12) 0.0370(13) 0.0358(13) 0.0043(11) 0.0131(10) -0.0059(10)
C8 0.044(2) 0.071(2) 0.090(3) -0.021(2) 0.042(2) -0.0070(19)
C9 0.0363(16) 0.069(2) 0.0418(17) -0.0040(15) 0.0086(13) -0.0184(16)

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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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Au1 N1 2.041(2) . ?
Au1 Au1 2.6559(6) 7 ?

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N1 C4 1.337(3) . ?
 N1 C1 1.477(3) . ?
 N2 C4 1.337(4) . ?
 N2 C7 1.476(3) . ?
 N2 Au1 2.038(2) 7 ?
 N3 C4 1.404(3) . ?
 N3 C5 1.438(5) . ?
 N3 C6 1.445(6) . ?
 C1 C2 1.521(4) . ?
 C1 C3 1.521(5) . ?
 C7 C8 1.508(5) . ?
 C7 C9 1.519(4) . ?

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 _geom_angle_atom_site_label_3
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 N2 Au1 N1 170.64(10) 7 . ?
 N2 Au1 Au1 85.69(7) 7 7 ?
 N1 Au1 Au1 85.83(6) . 7 ?
 C4 N1 C1 120.6(2) . . ?
 C4 N1 Au1 122.06(17) . . ?
 C1 N1 Au1 115.49(17) . . ?
 C4 N2 C7 120.3(2) . . ?
 C4 N2 Au1 122.30(17) . 7 ?
 C7 N2 Au1 115.36(17) . 7 ?
 C4 N3 C5 121.4(3) . . ?
 C4 N3 C6 120.5(3) . . ?
 C5 N3 C6 118.0(3) . . ?
 N1 C1 C2 110.4(2) . . ?
 N1 C1 C3 109.4(2) . . ?
 C2 C1 C3 111.2(3) . . ?
 N2 C4 N1 123.8(2) . . ?
 N2 C4 N3 118.1(2) . . ?
 N1 C4 N3 118.1(2) . . ?
 N2 C7 C8 110.6(2) . . ?
 N2 C7 C9 110.6(2) . . ?
 C8 C7 C9 110.8(3) . . ?

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_geom_torsion_site_symmetry_3
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N2 Au1 N1 C4 29.2(7) 7...?
Au1 Au1 N1 C4 4.1(2) 7...?
N2 Au1 N1 C1 -135.5(5) 7...?
Au1 Au1 N1 C1 -160.6(2) 7...?
C4 N1 C1 C2 -104.3(3) ....?
Au1 N1 C1 C2 60.7(3) ....?
C4 N1 C1 C3 133.0(3) ....?
Au1 N1 C1 C3 -62.0(3) ....?
C7 N2 C4 N1 159.2(3) ....?
Au1 N2 C4 N1 -3.7(4) 7...?
C7 N2 C4 N3 -21.4(4) ....?
Au1 N2 C4 N3 175.7(2) 7...?
C1 N1 C4 N2 162.5(3) ....?
Au1 N1 C4 N2 -1.5(4) ....?
C1 N1 C4 N3 -16.9(4) ....?
Au1 N1 C4 N3 179.1(2) ....?
C5 N3 C4 N2 118.6(3) ....?
C6 N3 C4 N2 -57.2(4) ....?
C5 N3 C4 N1 -61.9(4) ....?
C6 N3 C4 N1 122.2(4) ....?
C4 N2 C7 C8 131.7(3) ....?
Au1 N2 C7 C8 -64.2(3) 7...?
C4 N2 C7 C9 -105.1(3) ....?
Au1 N2 C7 C9 59.0(3) 7...?

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_diffrn_reflns_theta_full 25.00
_diffrn_measured_fraction_theta_full 1.000
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_refine_diff_density_rms 0.127

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Compound 10

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;
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'C27 H60 Ag3 N9'
_chemical_formula_weight    834.45

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'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'
'Ag' 'Ag' -0.8971 1.1015
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting      Triclinic
_symmetry_space_group_name_H-M P-1

loop_
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'x, y, z'
'-x, -y, -z'

_cell_length_a              10.3566(15)
_cell_length_b              11.8649(18)
_cell_length_c              15.297(2)
_cell_angle_alpha           98.855(2)
_cell_angle_beta            91.259(2)
_cell_angle_gamma           105.500(2)
_cell_volume                 1785.8(5)
_cell_formula_units_Z        2
_cell_measurement_temperature 200(2)
_cell_measurement_reflns_used 1021
_cell_measurement_theta_min  2.43

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_exptl_crystal_size_mid        0.23
_exptl_crystal_size_min        0.19
_exptl_crystal_density_meas    ?
_exptl_crystal_density_diffn   1.552
_exptl_crystal_density_method  'not measured'
_exptl_crystal_F_000           852
_exptl_absorpt_coefficient_mu   1.658
_exptl_absorpt_correction_type  multi-scan
_exptl_absorpt_correction_T_min 0.5945
_exptl_absorpt_correction_T_max 0.7424
_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

_exptl_special_details
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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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_diffn_radiation_monochromator   graphite
_diffn_measurement_device_type  'Bruker AXS APEX diffractometer'
_diffn_measurement_method       \w
_diffn_detector_area_resol_mean 836.6
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_diffn_reflns_number            17272
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_diffn_reflns_av_sigmal/netl    0.0483
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_diffn_reflns_limit_h_max       13
_diffn_reflns_limit_k_min       -15
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_diffn_reflns_limit_l_min       -20

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_reflms_number_gt           7009
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_computing_cell_refinement   'SAINT (Bruker, 2002)'
_computing_data_reduction    SAINT
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
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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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_refine_ls_structure_factor_coef Fsqd
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_refine_ls_weighting_details
'calc w=1/[s^2*(Fo^2)+(0.0258P)^2] where P=(Fo^2+2Fc^2)/3'
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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_reflms       8794
_refine_ls_number_parameters    370
_refine_ls_number_restraints    0
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_refine_ls_R_factor_gt         0.0366
_refine_ls_wR_factor_ref        0.0741
_refine_ls_wR_factor_gt        0.0683
_refine_ls_goodness_of_fit_ref  1.045
_refine_ls_restrained_S_all     1.045
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_refine_ls_shift/su_mean        0.000

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  _atom_site_adp_type
  _atom_site_occupancy
  _atom_site_symmetry_multiplicity
  _atom_site_calc_flag
  _atom_site_refinement_flags
  _atom_site_disorder_assembly
  _atom_site_disorder_group
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Ag2 Ag 0.17064(3) 0.57211(2) 0.341294(16) 0.03032(7) Uani 1 1 d ...
Ag3 Ag 0.39107(2) 0.77439(2) 0.301101(16) 0.02991(7) Uani 1 1 d ...
N1 N -0.0256(3) 0.5121(2) 0.16575(17) 0.0306(6) Uani 1 1 d ...
N2 N 0.1236(3) 0.4329(2) 0.23438(17) 0.0302(6) Uani 1 1 d ...
N3 N -0.0516(3) 0.3053(2) 0.13419(18) 0.0366(7) Uani 1 1 d ...
N4 N 0.2080(3) 0.6857(2) 0.46350(17) 0.0298(6) Uani 1 1 d ...
N5 N 0.4302(3) 0.7550(2) 0.43258(16) 0.0300(6) Uani 1 1 d ...
N6 N 0.3742(3) 0.7685(2) 0.58144(17) 0.0345(7) Uani 1 1 d ...
N7 N 0.4008(3) 0.8382(2) 0.17890(16) 0.0293(6) Uani 1 1 d ...
N8 N 0.1916(2) 0.8666(2) 0.19807(17) 0.0279(6) Uani 1 1 d ...
N9 N 0.3490(3) 0.9990(2) 0.12617(18) 0.0340(7) Uani 1 1 d ...
C1 C -0.1693(3) 0.4981(3) 0.1457(2) 0.0340(8) Uani 1 1 d ...
H1 H -0.2164 0.4116 0.1307 0.041 Uiso 1 1 calc R ..
C2 C -0.1913(4) 0.5575(3) 0.0675(2) 0.0446(9) Uani 1 1 d ...
H2A H -0.1430 0.6420 0.0805 0.067 Uiso 1 1 calc R ..
H2B H -0.2875 0.5488 0.0571 0.067 Uiso 1 1 calc R ..
H2C H -0.1578 0.5201 0.0144 0.067 Uiso 1 1 calc R ..
C3 C -0.2281(4) 0.5506(3) 0.2267(2) 0.0456(9) Uani 1 1 d ...
H3A H -0.2139 0.5119 0.2768 0.068 Uiso 1 1 calc R ..
H3B H -0.3246 0.5382 0.2143 0.068 Uiso 1 1 calc R ..
H3C H -0.1839 0.6359 0.2414 0.068 Uiso 1 1 calc R ..
C4 C 0.0173(3) 0.4187(3) 0.1786(2) 0.0291(7) Uani 1 1 d ...
C5 C -0.0949(4) 0.2825(3) 0.0415(2) 0.0467(10) Uani 1 1 d ...
H5A H -0.0739 0.3574 0.0182 0.070 Uiso 1 1 calc R ..
H5B H -0.1920 0.2455 0.0341 0.070 Uiso 1 1 calc R ..
H5C H -0.0483 0.2290 0.0089 0.070 Uiso 1 1 calc R ..
C6 C -0.0745(4) 0.2026(3) 0.1772(3) 0.0461(10) Uani 1 1 d ...
H6A H -0.0245 0.1489 0.1490 0.069 Uiso 1 1 calc R ..
H6B H -0.1707 0.1614 0.1718 0.069 Uiso 1 1 calc R ..
H6C H -0.0440 0.2274 0.2400 0.069 Uiso 1 1 calc R ..
C7 C 0.2138(3) 0.3556(3) 0.2170(2) 0.0350(8) Uani 1 1 d ...
H7 H 0.1674 0.2847 0.1722 0.042 Uiso 1 1 calc R ..

```

C8 C 0.3401(4) 0.4235(3) 0.1796(3) 0.0488(10) Uani 1 1 d ...
H8A H 0.3164 0.4471 0.1241 0.073 Uiso 1 1 calc R ...
H8B H 0.4008 0.3729 0.1682 0.073 Uiso 1 1 calc R ...
H8C H 0.3848 0.4945 0.2224 0.073 Uiso 1 1 calc R ...
C9 C 0.2480(4) 0.3144(3) 0.3016(2) 0.0473(10) Uani 1 1 d ...
H9A H 0.2912 0.3835 0.3465 0.071 Uiso 1 1 calc R ...
H9B H 0.3093 0.2646 0.2893 0.071 Uiso 1 1 calc R ...
H9C H 0.1655 0.2685 0.3237 0.071 Uiso 1 1 calc R ...
C10 C 0.0990(3) 0.7035(3) 0.5207(2) 0.0321(7) Uani 1 1 d ...
H10 H 0.1011 0.6611 0.5722 0.039 Uiso 1 1 calc R ...
C11 C -0.0343(3) 0.6475(4) 0.4673(2) 0.0473(10) Uani 1 1 d ...
H11A H -0.0383 0.6883 0.4167 0.071 Uiso 1 1 calc R ...
H11B H -0.1080 0.6545 0.5050 0.071 Uiso 1 1 calc R ...
H11C H -0.0426 0.5635 0.4458 0.071 Uiso 1 1 calc R ...
C12 C 0.1110(4) 0.8332(3) 0.5564(2) 0.0452(9) Uani 1 1 d ...
H12A H 0.1908 0.8659 0.5975 0.068 Uiso 1 1 calc R ...
H12B H 0.0309 0.8393 0.5876 0.068 Uiso 1 1 calc R ...
H12C H 0.1189 0.8778 0.5070 0.068 Uiso 1 1 calc R ...
C13 C 0.3360(3) 0.7358(3) 0.4912(2) 0.0293(7) Uani 1 1 d ...
C14 C 0.3286(4) 0.6886(3) 0.6435(2) 0.0432(9) Uani 1 1 d ...
H14A H 0.2669 0.7183 0.6825 0.065 Uiso 1 1 calc R ...
H14B H 0.4059 0.6833 0.6792 0.065 Uiso 1 1 calc R ...
H14C H 0.2819 0.6098 0.6109 0.065 Uiso 1 1 calc R ...
C15 C 0.4684(4) 0.8812(3) 0.6166(2) 0.0445(9) Uani 1 1 d ...
H15A H 0.4984 0.9248 0.5679 0.067 Uiso 1 1 calc R ...
H15B H 0.5460 0.8677 0.6468 0.067 Uiso 1 1 calc R ...
H15C H 0.4247 0.9275 0.6588 0.067 Uiso 1 1 calc R ...
C16 C 0.5644(3) 0.7428(3) 0.4556(2) 0.0359(8) Uani 1 1 d ...
H16 H 0.5747 0.7481 0.5214 0.043 Uiso 1 1 calc R ...
C17 C 0.5743(4) 0.6223(4) 0.4130(3) 0.0627(13) Uani 1 1 d ...
H17A H 0.5053 0.5607 0.4346 0.094 Uiso 1 1 calc R ...
H17B H 0.6633 0.6140 0.4281 0.094 Uiso 1 1 calc R ...
H17C H 0.5605 0.6139 0.3484 0.094 Uiso 1 1 calc R ...
C18 C 0.6752(4) 0.8413(4) 0.4286(3) 0.0605(12) Uani 1 1 d ...
H18A H 0.6656 0.8388 0.3644 0.091 Uiso 1 1 calc R ...
H18B H 0.7628 0.8306 0.4446 0.091 Uiso 1 1 calc R ...
H18C H 0.6686 0.9182 0.4594 0.091 Uiso 1 1 calc R ...
C19 C 0.4990(3) 0.8237(3) 0.1133(2) 0.0333(8) Uani 1 1 d ...
H19 H 0.5024 0.8818 0.0720 0.040 Uiso 1 1 calc R ...
C20 C 0.4552(4) 0.6992(4) 0.0601(3) 0.0528(11) Uani 1 1 d ...
H20A H 0.4553 0.6414 0.0995 0.079 Uiso 1 1 calc R ...
H20B H 0.5176 0.6915 0.0137 0.079 Uiso 1 1 calc R ...
H20C H 0.3645 0.6844 0.0328 0.079 Uiso 1 1 calc R ...
C21 C 0.6377(4) 0.8470(4) 0.1579(3) 0.0534(11) Uani 1 1 d ...
H21A H 0.6654 0.9278 0.1914 0.080 Uiso 1 1 calc R ...
H21B H 0.7016 0.8380 0.1128 0.080 Uiso 1 1 calc R ...
H21C H 0.6359 0.7902 0.1984 0.080 Uiso 1 1 calc R ...
C22 C 0.3150(3) 0.8996(3) 0.16691(19) 0.0234(6) Uani 1 1 d ...

C23 C 0.4812(3) 1.0815(3) 0.1370(2) 0.0418(9) Uani 1 1 d ...
 H23A H 0.5357 1.0613 0.1822 0.063 Uiso 1 1 calc R..
 H23B H 0.4736 1.1622 0.1556 0.063 Uiso 1 1 calc R..
 H23C H 0.5240 1.0771 0.0805 0.063 Uiso 1 1 calc R..
 C24 C 0.2522(4) 1.0311(3) 0.0710(2) 0.0400(9) Uani 1 1 d ...
 H24A H 0.1667 0.9690 0.0645 0.060 Uiso 1 1 calc R..
 H24B H 0.2866 1.0392 0.0125 0.060 Uiso 1 1 calc R..
 H24C H 0.2382 1.1065 0.0991 0.060 Uiso 1 1 calc R..
 C25 C 0.1274(3) 0.9549(3) 0.2411(2) 0.0348(8) Uani 1 1 d ...
 H25 H 0.1737 1.0344 0.2262 0.042 Uiso 1 1 calc R..
 C26 C 0.1413(4) 0.9600(4) 0.3409(2) 0.0505(10) Uani 1 1 d ...
 H26A H 0.0954 0.8825 0.3558 0.076 Uiso 1 1 calc R..
 H26B H 0.1008 1.0202 0.3707 0.076 Uiso 1 1 calc R..
 H26C H 0.2366 0.9807 0.3606 0.076 Uiso 1 1 calc R..
 C27 C -0.0198(3) 0.9224(3) 0.2099(3) 0.0482(10) Uani 1 1 d ...
 H27A H -0.0280 0.9214 0.1458 0.072 Uiso 1 1 calc R..
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 H27C H -0.0651 0.8437 0.2231 0.072 Uiso 1 1 calc R..

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 _atom_site_aniso_U_12

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 Ag3 0.03126(14) 0.03572(15) 0.02486(13) 0.00924(10) 0.00273(10) 0.01037(11)
 N1 0.0292(15) 0.0240(14) 0.0355(16) 0.0039(12) -0.0013(12) 0.0028(12)
 N2 0.0352(16) 0.0263(15) 0.0289(15) -0.0002(12) -0.0021(12) 0.0109(12)
 N3 0.0443(18) 0.0239(15) 0.0364(17) 0.0002(12) -0.0048(14) 0.0035(13)
 N4 0.0276(15) 0.0331(16) 0.0259(15) 0.0013(12) 0.0018(12) 0.0055(12)
 N5 0.0267(15) 0.0392(17) 0.0235(14) 0.0040(12) -0.0030(11) 0.0094(12)
 N6 0.0432(17) 0.0337(16) 0.0220(15) 0.0047(12) -0.0009(12) 0.0030(13)
 N7 0.0283(15) 0.0367(16) 0.0251(14) 0.0110(12) 0.0033(11) 0.0095(12)
 N8 0.0234(14) 0.0232(14) 0.0362(16) 0.0078(12) 0.0018(12) 0.0031(11)
 N9 0.0301(16) 0.0280(16) 0.0416(17) 0.0073(13) -0.0009(13) 0.0035(12)
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 C3 0.037(2) 0.046(2) 0.053(2) 0.0108(19) 0.0065(18) 0.0094(18)
 C4 0.0357(19) 0.0220(17) 0.0275(17) 0.0020(13) 0.0057(14) 0.0054(14)
 C5 0.052(2) 0.039(2) 0.040(2) -0.0081(17) -0.0074(18) 0.0065(19)
 C6 0.049(2) 0.0232(19) 0.060(3) 0.0045(17) 0.0007(19) 0.0008(17)
 C7 0.042(2) 0.0272(18) 0.037(2) 0.0011(15) 0.0002(16) 0.0135(16)
 C8 0.048(2) 0.051(3) 0.050(2) 0.0068(19) 0.0089(19) 0.017(2)
 C9 0.051(2) 0.046(2) 0.054(3) 0.0170(19) 0.0035(19) 0.0229(19)

C10 0.0326(19) 0.0338(19) 0.0293(18) 0.0030(14) 0.0043(14) 0.0092(15)
 C11 0.031(2) 0.059(3) 0.049(2) 0.001(2) 0.0050(17) 0.0119(19)
 C12 0.053(2) 0.043(2) 0.041(2) 0.0017(17) 0.0106(18) 0.0169(19)
 C13 0.039(2) 0.0247(17) 0.0247(17) 0.0033(13) 0.0022(15) 0.0104(15)
 C14 0.053(2) 0.052(2) 0.0282(19) 0.0148(17) 0.0026(17) 0.0147(19)
 C15 0.049(2) 0.042(2) 0.034(2) -0.0047(17) -0.0052(17) 0.0032(18)
 C16 0.0258(18) 0.054(2) 0.0275(18) 0.0068(16) -0.0010(14) 0.0098(16)
 C17 0.044(2) 0.065(3) 0.080(3) -0.007(2) -0.011(2) 0.027(2)
 C18 0.029(2) 0.081(3) 0.066(3) 0.024(3) -0.005(2) 0.001(2)
 C19 0.0300(18) 0.043(2) 0.0296(18) 0.0114(15) 0.0050(14) 0.0122(16)
 C20 0.051(3) 0.055(3) 0.052(3) -0.003(2) 0.006(2) 0.020(2)
 C21 0.033(2) 0.081(3) 0.051(3) 0.019(2) 0.0061(18) 0.019(2)
 C22 0.0218(16) 0.0259(16) 0.0194(15) 0.0048(12) -0.0049(12) 0.0013(13)
 C23 0.045(2) 0.040(2) 0.036(2) 0.0142(17) 0.0064(17) -0.0012(17)
 C24 0.052(2) 0.034(2) 0.036(2) 0.0123(16) -0.0013(17) 0.0130(17)
 C25 0.036(2) 0.0260(18) 0.043(2) 0.0071(15) 0.0073(16) 0.0077(15)
 C26 0.059(3) 0.045(2) 0.047(2) 0.0014(19) 0.012(2) 0.016(2)
 C27 0.035(2) 0.037(2) 0.078(3) 0.015(2) 0.004(2) 0.0160(17)

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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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Ag1 Ag3 3.2173(5) . ?

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Ag2 N4 2.091(3) . ?

Ag2 Ag3 2.9896(5) . ?

Ag3 N5 2.102(2) . ?

Ag3 N7 2.117(2) . ?

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N2 C7 1.475(4) . ?

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Compound 14

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

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\ 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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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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Cl1 Cl 0.06074(6) 0.156300(19) 0.85239(6) 0.02667(15) Uani 1 1 d ...
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H3A H -0.0939 0.1310 0.3374 0.024 Uiso 1 1 calc R ..
N4 N 0.41927(19) 0.15983(6) 0.58221(19) 0.0183(4) Uani 1 1 d ...
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H6B H 0.4737 0.2286 0.7630 0.024 Uiso 1 1 calc R ..
N7 N 0.19854(18) 0.07665(6) 0.73547(19) 0.0179(4) Uani 1 1 d ...
N8 N 0.39520(19) 0.06961(6) 0.68636(19) 0.0187(4) Uani 1 1 d ...
N9 N 0.3214(2) 0.02032(6) 0.8042(2) 0.0232(5) Uani 1 1 d ...
H9D H 0.3081 0.0191 0.8830 0.028 Uiso 1 1 calc R ..
C1 C -0.0374(2) 0.07384(8) 0.6605(3) 0.0289(6) Uani 1 1 d ...
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H1B H -0.0481 0.1001 0.6900 0.043 Uiso 1 1 calc R ..
H1C H -0.1133 0.0585 0.6637 0.043 Uiso 1 1 calc R ..
C2 C 0.0337(3) 0.18950(7) 0.5146(3) 0.0246(6) Uani 1 1 d ...
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C5 C 0.6752(3) 0.25109(8) 0.6969(3) 0.0345(7) Uani 1 1 d ...
H5A H 0.6170 0.2589 0.6142 0.052 Uiso 1 1 calc R ..
H5B H 0.7643 0.2521 0.6888 0.052 Uiso 1 1 calc R ..
H5C H 0.6650 0.2686 0.7662 0.052 Uiso 1 1 calc R ..
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H7A H 0.5371 0.0350 0.7877 0.028 Uiso 1 1 calc R . .
C8 C 0.0692(3) 0.05453(8) 0.8907(3) 0.0352(7) Uani 1 1 d . . .
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H8B H -0.0061 0.0391 0.8953 0.053 Uiso 1 1 calc R . .
H8C H 0.0591 0.0808 0.9208 0.053 Uiso 1 1 calc R . .
C9 C 0.2426(3) -0.03877(8) 0.6797(3) 0.0330(7) Uani 1 1 d . . .
H9A H 0.1879 -0.0231 0.6108 0.050 Uiso 1 1 calc R . .
H9B H 0.1937 -0.0464 0.7427 0.050 Uiso 1 1 calc R . .
H9C H 0.2708 -0.0619 0.6412 0.050 Uiso 1 1 calc R . .
C10 C 0.0886(2) 0.12928(7) 0.4279(2) 0.0184(5) Uani 1 1 d . . .
C11 C 0.6433(2) 0.21021(7) 0.7302(2) 0.0222(5) Uani 1 1 d . . .
H11A H 0.6557 0.1927 0.6592 0.027 Uiso 1 1 calc R . .
C12 C 0.3305(3) 0.18889(8) 0.3653(2) 0.0275(6) Uani 1 1 d . . .
H12A H 0.2722 0.2049 0.4012 0.041 Uiso 1 1 calc R . .
H12B H 0.2876 0.1647 0.3326 0.041 Uiso 1 1 calc R . .
H12C H 0.3540 0.2027 0.2936 0.041 Uiso 1 1 calc R . .
C13 C 0.2607(3) 0.06662(8) 0.2654(3) 0.0314(6) Uani 1 1 d . . .
H13A H 0.2629 0.0902 0.2148 0.047 Uiso 1 1 calc R . .
H13B H 0.2436 0.0444 0.2064 0.047 Uiso 1 1 calc R . .
H13C H 0.3438 0.0632 0.3283 0.047 Uiso 1 1 calc R . .
C14 C 0.6145(2) 0.09005(8) 0.7997(3) 0.0288(6) Uani 1 1 d . . .
H14A H 0.5845 0.0975 0.8765 0.043 Uiso 1 1 calc R . .
H14B H 0.6094 0.1123 0.7415 0.043 Uiso 1 1 calc R . .
H14C H 0.7039 0.0812 0.8272 0.043 Uiso 1 1 calc R . .
C15 C 0.5784(3) 0.04612(9) 0.6100(3) 0.0356(7) Uani 1 1 d . . .
H15A H 0.5250 0.0251 0.5637 0.053 Uiso 1 1 calc R . .
H15B H 0.6679 0.0375 0.6383 0.053 Uiso 1 1 calc R . .
H15C H 0.5732 0.0683 0.5517 0.053 Uiso 1 1 calc R . .
C16 C 0.3593(3) -0.01540(7) 0.7486(3) 0.0250(6) Uani 1 1 d . . .
H16A H 0.4089 -0.0083 0.6834 0.030 Uiso 1 1 calc R . .
C17 C 0.4512(2) 0.18031(7) 0.4715(2) 0.0218(5) Uani 1 1 d . . .
H17A H 0.4946 0.2052 0.5037 0.026 Uiso 1 1 calc R . .
C19 C 0.3878(3) 0.13413(7) 0.9993(2) 0.0272(6) Uani 1 1 d . . .
H19A H 0.4263 0.1112 0.9699 0.041 Uiso 1 1 calc R . .
H19B H 0.2951 0.1302 0.9863 0.041 Uiso 1 1 calc R . .
H19C H 0.4270 0.1385 1.0920 0.041 Uiso 1 1 calc R . .
C20 C -0.0109(3) 0.18185(7) 0.1558(2) 0.0270(6) Uani 1 1 d . . .
H20A H 0.0608 0.1947 0.2164 0.040 Uiso 1 1 calc R . .
H20B H -0.0924 0.1930 0.1644 0.040 Uiso 1 1 calc R . .
H20C H -0.0028 0.1854 0.0663 0.040 Uiso 1 1 calc R . .
C21 C -0.1003(3) 0.18834(9) 0.5389(3) 0.0368(7) Uani 1 1 d . . .
H21A H -0.1523 0.1690 0.4821 0.055 Uiso 1 1 calc R . .
H21B H -0.1409 0.2137 0.5200 0.055 Uiso 1 1 calc R . .
H21C H -0.0940 0.1816 0.6302 0.055 Uiso 1 1 calc R . .
C22 C 0.5438(3) 0.15553(8) 0.4176(3) 0.0302(6) Uani 1 1 d . . .
H22A H 0.6211 0.1503 0.4869 0.045 Uiso 1 1 calc R . .

H22B H 0.5678 0.1692 0.3461 0.045 Uiso 1 1 calc R . .
 H22C H 0.5019 0.1311 0.3851 0.045 Uiso 1 1 calc R . .
 C23 C 0.4116(2) 0.16924(7) 0.9205(2) 0.0209(5) Uani 1 1 d . . .
 H23A H 0.5066 0.1732 0.9379 0.025 Uiso 1 1 calc R . .
 C24 C 0.1496(3) 0.03287(7) 0.4148(3) 0.0270(6) Uani 1 1 d . . .
 H24A H 0.0804 0.0349 0.4601 0.040 Uiso 1 1 calc R . .
 H24B H 0.2319 0.0292 0.4788 0.040 Uiso 1 1 calc R . .
 H24C H 0.1331 0.0109 0.3549 0.040 Uiso 1 1 calc R . .
 C25 C 0.4462(3) -0.03907(8) 0.8560(3) 0.0374(7) Uani 1 1 d . . .
 H25A H 0.5216 -0.0237 0.8982 0.056 Uiso 1 1 calc R . .
 H25B H 0.4740 -0.0624 0.8183 0.056 Uiso 1 1 calc R . .
 H25C H 0.3988 -0.0463 0.9207 0.056 Uiso 1 1 calc R . .
 C26 C 0.1161(3) 0.21983(7) 0.6006(3) 0.0312(6) Uani 1 1 d . . .
 H26A H 0.2014 0.2205 0.5824 0.047 Uiso 1 1 calc R . .
 H26B H 0.1249 0.2133 0.6924 0.047 Uiso 1 1 calc R . .
 H26C H 0.0752 0.2451 0.5821 0.047 Uiso 1 1 calc R . .
 C27 C -0.0086(2) 0.13900(7) 0.1873(2) 0.0209(5) Uani 1 1 d . . .
 H27A H 0.0746 0.1280 0.1771 0.025 Uiso 1 1 calc R . .
 C28 C 0.0817(2) 0.05578(7) 0.7492(3) 0.0250(6) Uani 1 1 d . . .
 H28A H 0.0880 0.0286 0.7197 0.030 Uiso 1 1 calc R . .
 C29 C 0.7329(2) 0.19725(8) 0.8571(3) 0.0302(6) Uani 1 1 d . . .
 H29A H 0.7110 0.1709 0.8769 0.045 Uiso 1 1 calc R . .
 H29B H 0.7238 0.2145 0.9276 0.045 Uiso 1 1 calc R . .
 H29C H 0.8219 0.1980 0.8489 0.045 Uiso 1 1 calc R . .
 C50 C 0.3528(3) 0.20538(7) 0.9662(3) 0.0280(6) Uani 1 1 d . . .
 H50A H 0.3688 0.2277 0.9156 0.042 Uiso 1 1 calc R . .
 H50B H 0.3923 0.2098 1.0589 0.042 Uiso 1 1 calc R . .
 H50C H 0.2599 0.2018 0.9534 0.042 Uiso 1 1 calc R . .
 C51 C -0.1184(3) 0.11802(8) 0.0937(2) 0.0284(6) Uani 1 1 d . . .
 H51A H -0.1152 0.0906 0.1159 0.043 Uiso 1 1 calc R . .
 H51B H -0.1097 0.1212 0.0042 0.043 Uiso 1 1 calc R . .
 H51C H -0.2007 0.1289 0.1009 0.043 Uiso 1 1 calc R . .

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 Zn2 0.01792(16) 0.01650(15) 0.01927(16) -0.00108(11) 0.00665(11) -0.00054(10)
 Cl1 0.0262(3) 0.0294(3) 0.0283(3) -0.0042(3) 0.0143(3) -0.0003(3)
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 N2 0.0176(10) 0.0151(10) 0.0189(10) -0.0021(8) 0.0044(8) 0.0003(8)
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 N7 0.0153(10) 0.0175(10) 0.0214(11) -0.0020(8) 0.0053(8) -0.0027(8)
 N8 0.0170(10) 0.0160(10) 0.0226(11) 0.0009(8) 0.0039(8) 0.0003(8)
 N9 0.0298(12) 0.0183(11) 0.0223(11) 0.0032(9) 0.0081(9) 0.0027(9)
 C1 0.0207(14) 0.0243(14) 0.0425(17) -0.0027(12) 0.0091(12) -0.0051(11)
 C2 0.0294(14) 0.0197(13) 0.0251(13) 0.0028(10) 0.0075(11) 0.0096(11)
 C3 0.0223(13) 0.0175(12) 0.0169(12) -0.0021(9) 0.0033(10) -0.0030(9)
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 C5 0.0264(15) 0.0272(15) 0.0500(19) 0.0040(13) 0.0099(13) -0.0065(12)
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 C11 0.0199(13) 0.0224(13) 0.0262(13) -0.0036(10) 0.0093(10) -0.0036(10)
 C12 0.0317(15) 0.0272(14) 0.0225(13) 0.0034(11) 0.0049(11) -0.0061(11)
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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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N4 C17 1.481(3) . ?
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C11 C29 1.515(4) . ?
C12 C17 1.521(3) . ?
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C17 C22 1.525(4) . ?
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C3 N8 Zn1 113.38(16) . . ?
C7 N8 Zn1 123.76(16) . . ?
C3 N9 C16 124.8(2) . . ?
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 Zn1 Zn2 N7 C28 -143.07(17) ?
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 Zn2 N1 C2 C21 -81.4(2) ?
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 Zn2 N1 C2 C26 42.8(3) ?
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 Zn1 N8 C3 N7 -17.3(3) ?
 C7 N8 C3 N9 -24.3(3) ?
 Zn1 N8 C3 N9 162.48(17) ?
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 Zn2 N7 C3 N9 152.89(17) ?
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 C16 N9 C3 N7 130.7(2) ?
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 Zn2 N5 C4 N6 147.62(17) ?
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 Zn1 N8 C7 C15 -57.1(3) ?
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 C6 N2 C10 N3 -20.4(3) ?
 Zn1 N2 C10 N3 167.37(16) ?
 C2 N1 C10 N2 154.4(2) ?
 Zn2 N1 C10 N2 -30.7(3) ?
 C2 N1 C10 N3 -26.6(3) ?
 Zn2 N1 C10 N3 148.25(17) ?
 C27 N3 C10 N2 -54.2(3) ?
 C27 N3 C10 N1 126.8(2) ?
 C4 N6 C11 C29 -90.6(3) ?
 C4 N6 C11 C5 146.4(2) ?

C3 N9 C16 C25 144.1(2) ?
C3 N9 C16 C9 -93.2(3) ?
C4 N4 C17 C12 -110.1(3) ?
Zn1 N4 C17 C12 60.2(3) ?
C4 N4 C17 C22 128.2(2) ?
Zn1 N4 C17 C22 -61.5(3) ?
C4 N5 C23 C19 -143.5(2) ?
Zn2 N5 C23 C19 43.1(2) ?
C4 N5 C23 C50 93.2(3) ?
Zn2 N5 C23 C50 -80.2(2) ?
C10 N3 C27 C20 -91.9(3) ?
C10 N3 C27 C51 145.3(2) ?
C3 N7 C28 C1 -143.6(2) ?
Zn2 N7 C28 C1 40.1(3) ?
C3 N7 C28 C8 92.6(3) ?
Zn2 N7 C28 C8 -83.7(2) ?

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_diffn_reflns_theta_full 25.00
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_refine_diff_density_max 0.803
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Compound 16

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'C28 H60 N6 Zn4'
_chemical_formula_weight    742.30

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'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'
'Zn' 'Zn' 0.2839 1.4301
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M P2(1)/c

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

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_cell_length_c              17.350(8)
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_exptl_crystal_size_min 0.36
_exptl_crystal_density_meas ?
_exptl_crystal_density_diffn 1.403
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000 780
_exptl_absorpt_coefficient_mu 2.723
_exptl_absorpt_correction_type multi-scan
_exptl_absorpt_correction_T_min 0.3859
_exptl_absorpt_correction_T_max 0.4449
_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

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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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_diffn_radiation_monochromator graphite
_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'
_diffn_measurement_method \w
_diffn_detector_area_resol_mean 836.6
_diffn_standards_number 0
_diffn_standards_interval_count 0
_diffn_standards_interval_time 0
_diffn_standards_decay_% 1
_diffn_reflns_number 12050
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_diffn_reflns_av_sigmal/netl 0.0416
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_diffn_reflns_limit_h_max 11

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_reflms_number_total          3097
_reflms_number_gt             2517
_reflms_threshold_expression   >2sigma(l)

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_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 (Sheldrick, 2001)'

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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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_refine_ls_weighting_details
'calc w=1/[\s^2*(Fo^2)+(0.0440P)^2] where P=(Fo^2+2Fc^2)/3'
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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_reflms        3097
_refine_ls_number_parameters     262
_refine_ls_number_restraints     0
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_refine_ls_R_factor_gt           0.0314
_refine_ls_wR_factor_ref         0.0838
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_refine_ls_shift/su_max        0.001
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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
Zn1 Zn 0.77884(3) 0.07584(3) 0.149168(19) 0.01945(13) Uani 1 1 d...
Zn2 Zn 0.48633(3) 0.07359(3) 0.099568(18) 0.01672(12) Uani 1 1 d...
N1 N 0.6484(2) -0.0229(2) 0.06516(13) 0.0156(5) Uani 1 1 d...
N2 N 0.7853(2) 0.1468(2) 0.04416(13) 0.0165(5) Uani 1 1 d...
N3 N 0.6763(2) 0.0265(2) -0.06688(13) 0.0168(5) Uani 1 1 d...
C1 C 0.7054(3) 0.0548(3) 0.00828(17) 0.0163(6) Uani 1 1 d...
C2 C 0.8285(3) 0.2739(3) 0.01113(18) 0.0218(7) Uani 1 1 d...
H7 H 0.880(3) 0.255(3) -0.0315(19) 0.026 Uiso 1 1 d...
C3 C 0.7131(3) 0.3632(3) -0.0180(2) 0.0288(8) Uani 1 1 d...
H1 H 0.657(4) 0.391(3) 0.024(2) 0.043 Uiso 1 1 d...
H2 H 0.657(3) 0.319(4) -0.056(2) 0.043 Uiso 1 1 d...
H3 H 0.747(3) 0.443(4) -0.044(2) 0.043 Uiso 1 1 d...
C4 C 0.9136(3) 0.3484(4) 0.0745(2) 0.0284(8) Uani 1 1 d...
H4 H 0.990(3) 0.298(4) 0.0973(19) 0.043 Uiso 1 1 d...
H5 H 0.945(3) 0.440(4) 0.061(2) 0.043 Uiso 1 1 d...
H6 H 0.864(4) 0.368(4) 0.113(2) 0.043 Uiso 1 1 d...
C5 C 0.5181(3) 0.2382(3) 0.16396(19) 0.0232(7) Uani 1 1 d...
H10 H 0.520(3) 0.207(3) 0.217(2) 0.028 Uiso 1 1 d...
H11 H 0.606(3) 0.274(3) 0.1553(18) 0.028 Uiso 1 1 d...
C6 C 0.4180(4) 0.3506(4) 0.1465(2) 0.0386(10) Uani 1 1 d...
H8 H 0.435(4) 0.425(4) 0.174(2) 0.046 Uiso 1 1 d...
H9 H 0.341(4) 0.323(4) 0.149(2) 0.046 Uiso 1 1 d...
C7 C 0.7632(3) 0.0725(3) -0.12526(17) 0.0201(7) Uani 1 1 d...
H18 H 0.773(3) 0.172(3) -0.1224(17) 0.024 Uiso 1 1 d...
C8 C 0.9012(3) 0.0161(4) -0.10833(19) 0.0228(7) Uani 1 1 d...
H12 H 0.897(3) -0.077(4) -0.1131(19) 0.034 Uiso 1 1 d...
H13 H 0.958(3) 0.056(3) -0.149(2) 0.034 Uiso 1 1 d...
H14 H 0.938(3) 0.030(3) -0.055(2) 0.034 Uiso 1 1 d...
C9 C 0.7072(3) 0.0252(4) -0.20514(18) 0.0243(7) Uani 1 1 d...
H15 H 0.754(3) 0.056(3) -0.241(2) 0.036 Uiso 1 1 d...

```

H16 H 0.624(4) 0.066(3) -0.218(2) 0.036 Uiso 1 1 d ...
 H17 H 0.707(3) -0.073(4) -0.211(2) 0.036 Uiso 1 1 d ...
 C10 C 0.6443(3) -0.1718(3) 0.05693(17) 0.0184(6) Uani 1 1 d ...
 H25 H 0.580(3) -0.202(3) 0.0153(17) 0.022 Uiso 1 1 d ...
 C11 C 0.6010(3) -0.2326(4) 0.13093(19) 0.0248(7) Uani 1 1 d ...
 H19 H 0.599(3) -0.327(4) 0.1264(18) 0.037 Uiso 1 1 d ...
 H20 H 0.512(3) -0.200(3) 0.1384(18) 0.037 Uiso 1 1 d ...
 H21 H 0.660(3) -0.209(3) 0.172(2) 0.037 Uiso 1 1 d ...
 C12 C 0.7767(3) -0.2303(3) 0.0413(2) 0.0262(7) Uani 1 1 d ...
 H22 H 0.804(3) -0.197(3) -0.008(2) 0.039 Uiso 1 1 d ...
 H23 H 0.839(3) -0.209(3) 0.086(2) 0.039 Uiso 1 1 d ...
 H24 H 0.772(3) -0.325(4) 0.0409(19) 0.039 Uiso 1 1 d ...
 C13 C 0.8408(3) 0.0649(4) 0.25877(19) 0.0286(8) Uani 1 1 d ...
 H29 H 0.765(3) 0.096(3) 0.280(2) 0.034 Uiso 1 1 d ...
 H30 H 0.850(3) -0.026(4) 0.2700(19) 0.034 Uiso 1 1 d ...
 C14 C 0.9608(3) 0.1483(4) 0.2853(2) 0.0316(8) Uani 1 1 d ...
 H26 H 1.036(4) 0.126(4) 0.259(2) 0.047 Uiso 1 1 d ...
 H27 H 0.953(4) 0.242(4) 0.272(2) 0.047 Uiso 1 1 d ...
 H28 H 0.983(3) 0.147(4) 0.341(2) 0.047 Uiso 1 1 d ...

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 Zn2 0.0155(2) 0.0197(2) 0.0149(2) -0.00162(14) 0.00095(14) 0.00120(13)
 N1 0.0147(11) 0.0181(13) 0.0142(12) 0.0009(10) 0.0027(9) 0.0012(10)
 N2 0.0162(12) 0.0185(14) 0.0149(12) -0.0005(10) 0.0019(10) 0.0006(10)
 N3 0.0165(12) 0.0189(13) 0.0151(12) 0.0024(11) 0.0013(10) 0.0013(10)
 C1 0.0101(13) 0.0198(16) 0.0194(16) 0.0006(13) 0.0033(11) 0.0052(11)
 C2 0.0220(15) 0.0192(16) 0.0250(17) -0.0002(14) 0.0055(13) -0.0039(13)
 C3 0.0330(19) 0.0202(19) 0.033(2) 0.0022(16) 0.0006(16) 0.0008(15)
 C4 0.0280(18) 0.025(2) 0.031(2) -0.0024(16) 0.0001(15) -0.0054(15)
 C5 0.0215(16) 0.0258(19) 0.0217(17) -0.0062(14) -0.0009(13) -0.0001(13)
 C6 0.0329(19) 0.027(2) 0.053(2) -0.0187(18) -0.0084(18) 0.0097(16)
 C7 0.0193(15) 0.0235(18) 0.0174(16) 0.0046(13) 0.0014(12) 0.0026(12)
 C8 0.0172(15) 0.0303(19) 0.0216(17) 0.0028(15) 0.0051(13) 0.0032(14)
 C9 0.0201(17) 0.036(2) 0.0178(16) 0.0037(15) 0.0051(13) 0.0007(15)
 C10 0.0191(15) 0.0184(16) 0.0172(15) 0.0003(13) -0.0011(12) 0.0009(12)
 C11 0.0268(17) 0.0251(18) 0.0217(18) 0.0048(15) -0.0020(14) 0.0005(15)
 C12 0.0287(17) 0.0191(17) 0.0314(19) 0.0016(16) 0.0063(15) 0.0048(14)
 C13 0.0273(18) 0.037(2) 0.0205(18) 0.0009(15) -0.0039(14) -0.0031(15)
 C14 0.0259(18) 0.040(2) 0.027(2) -0.0095(17) -0.0036(15) -0.0005(16)

_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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Zn1 N2 1.959(2) . ?

Zn1 N1 2.124(2) . ?

Zn1 C1 2.499(3) . ?

Zn1 Zn2 3.0487(14) . ?

Zn2 N3 1.980(2) 3_655 ?

Zn2 C5 1.985(3) . ?

Zn2 N1 2.056(2) . ?

N1 C1 1.420(4) . ?

N1 C10 1.481(4) . ?

N2 C1 1.340(4) . ?

N2 C2 1.469(4) . ?

N3 C1 1.340(4) . ?

N3 C7 1.483(4) . ?

N3 Zn2 1.980(2) 3_655 ?

C2 C3 1.527(4) . ?

C2 C4 1.528(4) . ?

C5 C6 1.526(4) . ?

C7 C9 1.524(4) . ?

C7 C8 1.527(4) . ?

C10 C11 1.522(4) . ?

C10 C12 1.526(4) . ?

C13 C14 1.519(5) . ?

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 N2 Zn1 C1 32.18(9) . . ?
 N1 Zn1 C1 34.58(9) . . ?
 C13 Zn1 Zn2 119.90(11) . . ?
 N2 Zn1 Zn2 81.85(6) . . ?
 N1 Zn1 Zn2 42.30(6) . . ?
 C1 Zn1 Zn2 61.53(6) . . ?
 N3 Zn2 C5 131.47(11) 3_655 . ?
 N3 Zn2 N1 111.67(10) 3_655 . ?
 C5 Zn2 N1 116.70(11) . . ?
 N3 Zn2 Zn1 150.25(7) 3_655 . ?
 C5 Zn2 Zn1 74.27(9) . . ?
 N1 Zn2 Zn1 44.06(7) . . ?
 C1 N1 C10 118.8(2) . . ?
 C1 N1 Zn2 110.37(17) . . ?
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 C10 N1 Zn1 122.30(16) . . ?
 Zn2 N1 Zn1 93.64(10) . . ?
 C1 N2 C2 126.5(2) . . ?
 C1 N2 Zn1 96.67(18) . . ?
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 C7 N3 Zn2 120.25(18) . 3_655 ?
 N3 C1 N2 131.7(3) . . ?
 N3 C1 N1 119.6(2) . . ?
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 N1 C1 Zn1 58.11(13) . . ?
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 N2 C2 C4 107.8(2) . . ?
 C3 C2 C4 109.5(3) . . ?
 C6 C5 Zn2 114.5(2) . . ?
 N3 C7 C9 109.0(2) . . ?
 N3 C7 C8 111.3(2) . . ?
 C9 C7 C8 109.1(3) . . ?
 N1 C10 C11 108.7(2) . . ?
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 C11 C10 C12 109.6(3) . . ?
 C14 C13 Zn1 116.6(2) . . ?

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 C1 Zn1 Zn2 N3 79.70(15) ... 3_655 ?
 C13 Zn1 Zn2 C5 62.17(17) ... ?
 N2 Zn1 Zn2 C5 -100.45(13) ... ?
 N1 Zn1 Zn2 C5 -164.22(14) ... ?
 C1 Zn1 Zn2 C5 -126.94(13) ... ?
 C13 Zn1 Zn2 N1 -133.61(16) ... ?
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 Zn1 Zn2 N1 C1 -88.48(18) ... ?
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 C5 Zn2 N1 C10 147.0(2) ... ?
 Zn1 Zn2 N1 C10 130.0(2) ... ?
 N3 Zn2 N1 Zn1 -158.89(9) 3_655 ... ?
 C5 Zn2 N1 Zn1 17.04(15) ... ?
 C13 Zn1 N1 C1 -169.4(2) ... ?
 N2 Zn1 N1 C1 5.85(15) ... ?
 Zn2 Zn1 N1 C1 110.26(17) ... ?
 C13 Zn1 N1 C10 -46.7(3) ... ?
 N2 Zn1 N1 C10 128.6(2) ... ?
 C1 Zn1 N1 C10 122.7(3) ... ?
 Zn2 Zn1 N1 C10 -127.0(2) ... ?
 C13 Zn1 N1 Zn2 80.3(2) ... ?
 N2 Zn1 N1 Zn2 -104.41(11) ... ?
 C1 Zn1 N1 Zn2 -110.26(17) ... ?
 C13 Zn1 N2 C1 167.1(3) ... ?
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 Zn2 Zn1 N2 C1 -47.42(15) ... ?
 C13 Zn1 N2 C2 -28.0(4) ... ?
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 C1 Zn1 N2 C2 164.8(3) ... ?
 Zn2 Zn1 N2 C2 117.4(2) ... ?
 C7 N3 C1 N2 18.5(4) ... ?
 Zn2 N3 C1 N2 -160.1(2) 3_655 ... ?
 C7 N3 C1 N1 -160.0(2) ... ?

Zn2 N3 C1 N1 21.4(3) 3_655 ... ?
 C7 N3 C1 Zn1 -87.9(14) ... ?
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 Zn1 N2 C1 N1 9.0(2) ... ?
 C2 N2 C1 Zn1 -166.7(3) ... ?
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 Zn2 N1 C1 N3 -96.6(3) ... ?
 Zn1 N1 C1 N3 170.5(2) ... ?
 C10 N1 C1 N2 -134.1(2) ... ?
 Zn2 N1 C1 N2 84.6(2) ... ?
 Zn1 N1 C1 N2 -8.3(2) ... ?
 C10 N1 C1 Zn1 -125.8(2) ... ?
 Zn2 N1 C1 Zn1 92.89(13) ... ?
 C13 Zn1 C1 N3 -20.5(19) ... ?
 N2 Zn1 C1 N3 113.2(15) ... ?
 N1 Zn1 C1 N3 -76.9(14) ... ?
 Zn2 Zn1 C1 N3 -122.8(14) ... ?
 C13 Zn1 C1 N2 -133.7(8) ... ?
 N1 Zn1 C1 N2 169.9(2) ... ?
 Zn2 Zn1 C1 N2 123.99(17) ... ?
 C13 Zn1 C1 N1 56.4(9) ... ?
 N2 Zn1 C1 N1 -169.9(2) ... ?
 Zn2 Zn1 C1 N1 -45.91(13) ... ?
 C1 N2 C2 C3 57.1(4) ... ?
 Zn1 N2 C2 C3 -104.1(3) ... ?
 C1 N2 C2 C4 177.5(3) ... ?
 Zn1 N2 C2 C4 16.3(4) ... ?
 N3 Zn2 C5 C6 -42.6(3) 3_655 ... ?
 N1 Zn2 C5 C6 142.4(2) ... ?
 Zn1 Zn2 C5 C6 154.6(3) ... ?
 C1 N3 C7 C9 179.4(3) ... ?
 Zn2 N3 C7 C9 -2.1(3) 3_655 ... ?
 C1 N3 C7 C8 58.9(4) ... ?
 Zn2 N3 C7 C8 -122.5(2) 3_655 ... ?
 C1 N1 C10 C11 170.4(2) ... ?
 Zn2 N1 C10 C11 -51.3(3) ... ?
 Zn1 N1 C10 C11 63.9(3) ... ?
 C1 N1 C10 C12 49.1(3) ... ?
 Zn2 N1 C10 C12 -172.6(2) ... ?
 Zn1 N1 C10 C12 -57.4(3) ... ?
 N2 Zn1 C13 C14 -3.2(5) ... ?
 N1 Zn1 C13 C14 167.2(2) ... ?
 C1 Zn1 C13 C14 119.3(8) ... ?
 Zn2 Zn1 C13 C14 -142.8(2) ... ?

_diffraction_measured_fraction_theta_max 1.000
_diffraction_reflections_theta_full 25.00
_diffraction_measured_fraction_theta_full 1.000
_refinement_diff_density_max 0.714
_refinement_diff_density_min -0.365
_refinement_diff_density_rms 0.082