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Group 11 Amidinates and Guanidinates: Potential Precursors for Vapour Deposition

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Several guanidinates of copper and silver, as well as amidinates and guanidinates of gold were synthesized as potential precursors for vapour deposition methods. These compounds were found to be dimers in the case of copper and gold, and trimers in the case of silver. The copper compounds showed good thermal and photostability, and were isolable by sublimation. The silver compounds proved to be very reactive to both heat and light, and were found to deposit silver metal when heated, suggesting that these sensitive compounds might be used as single source precursors. The gold compounds were found to exhibit some heat and light sensitivity, but were much more stable than their silver counterparts. Specifically, $[Au(NiPr)_2NMe_2]_2$ (**8**) was found to be sublimable at 85 °C and 20 mTorr, and deposited gold metal under higher temperatures. These metal-depositing thermal reactions were thought to abstract a hydrogen from the guanidinate ligand, which acts as the reducing agent. Interestingly, the gold amidinate compounds were found to produce diisopropylcarbodiimide when heated, suggesting that these compounds deinsert carbodiimide rather than abstract a hydrogen atom from the ligand.

Introduction

Group 11 compounds are interesting as potential precursors for chemical vapour deposition (CVD) or atomic layer deposition (ALD) of metal films. Thin films of copper are under intense scrutiny as an interconnect material for microelectronics because of copper's low bulk resistivity and excellent resistance to electromigration.[1] Silver and gold have strong surface plasmons, and thus can be employed in biosensors.[2] Amidinates and guanidinates are very promising ligands for these metal centres.[3] Our recent research interests have included a CVD process for copper metal from a guanidinatocopper(I) dimer,[4] and have extensively explored the thermal decomposition mechanism by infrared spectroscopy (employing matrix isolation), time-of-flight mass spectrometry, and calculational modelling.[5]

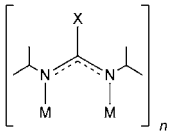
Amidinatocopper(I) dimers were first reported in 1988,[6] and used in ALD of copper films in 2006.[7] This same group reported a silver amidinate compound with a dimer-trimer equilibrium structure in 2003, but did not detail any thermal chemistry.[8] Gold amidinate complexes have previously been reported, although thermal data were not included.[9] We have thus undertaken the synthesis and thermal studies of the group 11 guanidinato species, as well as some novel amidinatogold(I) compounds.

It should also be generally noted that, although the copper compounds are stable with respect to heat and light, the analogous silver and gold compounds can show significant decompositions under these conditions.

Results and Discussion

Generally the syntheses of these group 11 compounds were facile by salt metathesis of amidinate or guanidinate ligands with a metal(I) chloride reactant, resulting in a variety of group 11 amidinates and guanidinates (Table 1). The

Table 1. The compounds reported in this article.



	Metal	X	R	*n*
1	Cu	NR_2	Et	2
2	Cu	NR_2	*i*Pr	2
3	Ag	NR_2	Me	3
4	Ag	NR_2	*i*Pr	3
5	Ag	NR_2	Et	3
6	Au	NR_2	*i*Pr	2
7	Au	NR_2	Et	2
8	Au	NR_2	Me	2
9	Au	R	Me	2
10	Au	R	*n*Bu	2

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yields were varied, ranging from 25% for $[Ag(NiPr)_2CNiPr_2]_2$ (**4**) to 95% for the analogous gold compound **6**.

For copper (**1** and **2**) and silver (**3**–**5**), the syntheses generally occurred in a straightforward manner, and were carried out by generating the ligand in situ by insertion of an amido into diisopropylcarbodiimide (CDI). This could be done in a one pot synthesis by stoichiometric addition of copper(I) chloride to the generated ligand. The copper species are particularly robust with respect to reaction conditions.

In the case of the gold compounds **6**–**10**, it was necessary to isolate and purify the amidinato or guanidinato ligand as the alkali salt. We suspect that a slight excess of alkyllithium (from the ligand formation) caused reduction of the gold(I) starting material. Suspending the purified ligand salt in the reaction solvent and adding gold chloride at reduced temperatures vastly improved the yields of these compounds.

A previous report showed the copper guanidinates to be dimers sharing bridging ligands in the solid state.[4] The single crystal data presented herein confirmed the dimeric structures of **1** and **2**, which was consistent with ^1H and ^{13}C NMR spectra. Compounds **1** and **2** (Table 2 and Table 3, Figure 1) have copper···copper separations comparable to reported compounds.[4] In each case, the metallocylic N–C–N angle of the ligand is close to 120°, and the sum of angles for the chelate nitrogen atoms are close to planarity, demonstrating full participation in π bond resonance. The similar Cu–N bond lengths for both compounds in the chelating amido moieties are also consistent with bond resonance and electron delocalization.

Table 2. Selected crystal data and structure refinement parameters for compounds **1**, **2**, and **3**.

	$C_{22}H_{48}Cu_2N_6$ (**1**)	$C_{26}H_{56}Cu_2N_6$ (**2**)	$C_{27}H_{60}Ag_3N_9$ (**3**)
FW	523.74	579.85	834.45
T (K)	120	120	200
λ [Å] (Mo-K_α)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	*Pbcn*	*Pbca*	$P\bar{1}$
a [Å]	10.459	10.02	10.36
b [Å]	21.77	11.77	11.86
c [Å]	11.93	25.3	15.30
α [°]	90	90	98.86
β [°]	90	90	91.26
γ [°]	90	90	105.5
V [Å^3]	2717	2987	1786
Z	4	4	2
ρ/g/cm^3	1.280	1.289	1.552
Abs. coeff. [mm^{-1}]	1.584	0.6608	1.658
R indices	$R_1 = 0.0669$	$R_1 = 0.0361$	$R_1 = 0.0505$
$[I>2\sigma(I)]$[a]	$wR_2 = 0.1055$	$wR_2 = 0.0885$	$wR_2 = 0.0741$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The "core twist" is defined as the degree the dimer is twisted as measured across the chelating nitrogen atoms in a "Z" pattern (see Scheme 1). A dimer of higher core twist would have participation of the exocyclic amide moiety in π resonance (demonstrated by greater planarization of this atom) and thus have a lower melting point. We have previously analysed copper guanidinates using this concept.[4]

Table 3. Selected bond lengths and angles for compounds **1** and **2**.

Selected bond lengths [Å]			
1		**2**	
Cu–N1	1.872(3)	Cu–N1	1.8818(17)
Cu–N3	1.878(3)	Cu–N2	1.8854(16)
Cu–CuA	2.4294(8)	Cu–CuA	2.4209(8)
N2–C1	1.405(6)	N3–C1	1.445(3)
N4–C7	1.394(6)		
N1–C1	1.335(3)	N1–C1	1.326(3)
N3–C7	1.341(3)	N2–C1	1.331(3)
Selected bond angles [°]			
1		**2**	
N1–C1–N2	120.46(17)	N1–Cu–N2	176.22(7)
N1–C1–N1A	120.1(4)	N1–Cu–N3	175.78(12)
N3–C7–N3A	120.9(4)		
Sum of angles [°]			
1		**2**	
N1	358.9	N1	359.8
N3	358.2	N2	358.8
N2	360	N3	355.9
N4	360.1		
Torsion angles [°]			
1		**2**	
N1–N1A–N3–N3A	22.4	N1–N2A–N2–N1A	0
C11–N4–C7–N3	52.8	C11–N3–C1–N2	71.3
C5–N2–C1–N1	56.7		

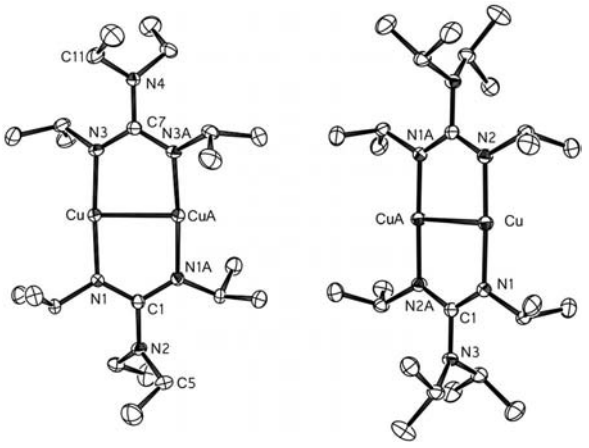
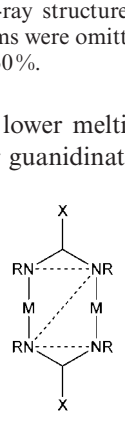


Figure 1. Single crystal X-ray structures for compounds **1** and **2** respectively. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.



Scheme 1. Torsion angle of the core as measured in a "Z" pattern across the chelating groups.

Compound **1** displays a higher core twist than **2** (22° and 0°). The bond length between the bridgehead carbon of the guanidinate moiety and the exocyclic nitrogen is significantly shorter in **1** than in **2**. The chelating nitrogen atoms are more pyramidalized in **1**, while the exocylic nitrogen atom is more pyramidalized in **2**. These observations suggest that the exocyclic amide in **1** is participating in π bonding to a greater degree than in **2**. Perhaps these structural differences arise from the steric crowding contributed by the larger alkyl groups at the exocyclic amido group, causing further out-of-plane bending of the ligand for **2** (71.3°) than for **1** (53–58 °C) and thereby frustrating π interaction. The observed melting points of **1** and **2** adhere to the previously reported melting point trend.[4]

Amidinatosilver species have previously shown a dimer-trimer equilibrium in solution (by ^{1}H NMR), with these species cocrystallizing in the solid phase.[8] In contrast, compounds **3**–**5** have spectra analogous to the copper species, suggesting that there was only one oligomer in solution in every case on the NMR time-frame. Single crystal structural determination determined compound **3** to be a trimer (Figure 2, Tables 2 and 4), and it is reasonable to suppose that all of the reported silver compounds are trimers, since the larger metallocylic N–C–N angle of guanidinate ligands (compared to the range for amidinates) would accommodate these higher order oligomers.

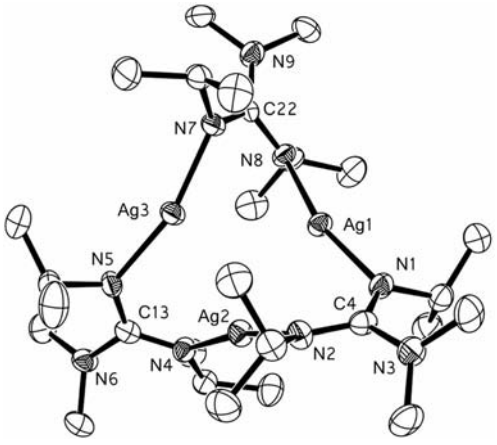


Figure 2. Single crystal X-ray structures for compound **3**. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

The structure of compound **3** (Figure 2) shows an approximately isosceles triangular arrangement of the silver atoms. The metal-metal distances for Ag1–Ag2 or Ag2–Ag3 were comparable with the amidinate trimer,[8] while Ag1 and Ag3 were significantly further apart. This distortion was due to the arrangement of the ligands. Consider a plane described by the silver centres and C22 (which is coplanar with the silver triangle within ca. 6°): the plane of the ligand containing C22 intersects the silver plane at an angle of 67.5°, differentiating this ligand from the other two ligands in the complex. The ligands containing the C4 and C13 quaternary carbons are wholly above and below the plane of the silver atoms, respectively. The C22-containing ligand has a smaller bite angle but much larger torsion angle (considered through the silver and nitrogen centres) than the other two ligands.

Table 4. Selected bond lengths and angles for compound **3**.

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		

The three ligands are each planar, and the Ag–N and cyclic C–N bond lengths are comparable to the amidinatosilver trimer,[8] while the exocyclic N–C bond lengths were all longer than the chelate N–C bond lengths. This suggests that the exocyclic nitrogens do not participate fully in the π systems of the ligands in this structure.

Since the gold(I) ion is smaller than the silver(I) ion, it is reasonable to expect that gold might more easily form dimers instead of trimers in the solid phase. The gold com-

Table 5. Selected crystal data and structure refinement parameters for the gold compounds.

	$C_{18}H_{40}Au_2N_6$ (**8**)	$C_{16}H_{34}Au_2N_4$ (**9**)	$C_{22}H_{46}Au_2N_4$ (**10**)
FW	734.49	676.40	760.56
T [K]	200	120	120
λ [Å] (Mo-K_α)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	19.48	25.98	7.851
b [Å]	11.35	11.23	8.88
c [Å]	12.08	18.72	10.21
α [°]	90	90	104.22
β [°]	113.21	131.98	102.47
γ [°]	90	90	105.08
V [Å^3]	2454	4059	635
Z	4	8	1
ρ (calcd.) [g/cm^3]	1.988	2.214	1.987
Abs. coeff. [mm^{-1}]	11.96	14.443	11.54
R indices	R_1 = 0.0184	R_1 = 0.0276	R_1 = 0.0325
[$I > 2s(I)$][a]	wR_2 = 0.0500	wR_2 = 0.0507	wR_2 = 0.0681

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 6. Selected bond lengths and angles for compounds **8**, **9** and **10**.

8		**9**		**10**	
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–Au1A	2.6559(6)	Au1–Au1A	2.6529(5)	Au1–Au1A	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(9)	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–N1A–N2A	0	N1–N2–N2A–N1A	0	N1–N2–N2A–N1A	0

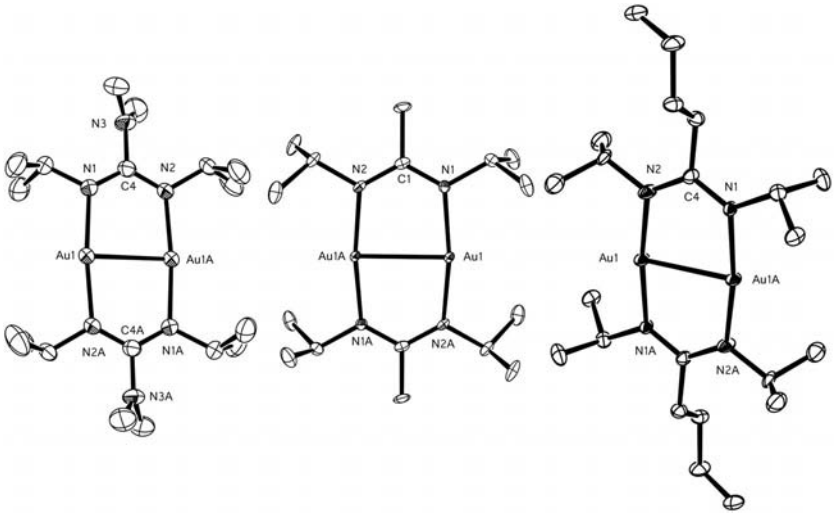
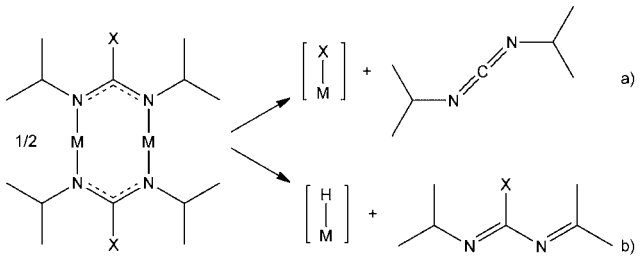


Figure 3. Single crystal X-ray structures for compounds **8**, **9** and **10**, respectively. Hydrogen atoms were omitted for clarity, and the thermal ellipses are shown at 30%.

pounds show NMR spectra that indicate that they each form a single, symmetric product, in general agreement with the dimer formation seen in the case of the copper analogues. This is also typical of previously-reported similar gold compounds.[9] Again, single-crystal X-ray structures of **8**–**10** also confirm these compounds to be dimers (Tables 5 and 6, Figure 3).

Considering these three structures, the bite angles on the bridging ligand are in the range 122–124°, with the guanidinato adopting the largest bite angle, as expected. The Au–N bonds are all very similar, around 2.04 Å, which agrees with known gold guanidinate compounds.[9] The Au–Au separations are similar for all three cases with a slight deviation from a linear geometry at the metal centres. The nitrogen atoms in **9** and **10** show very planar geometries, demonstrating the resonance of the π bond between the chelating nitrogen atoms. The exocyclic nitrogen in compound **8** also shows itself to be very planar, but the chelating nitrogens are only slightly deviated from planarity, suggesting the π system is shared with the exocyclic position. However, the longer C4–N3 bond length suggests that the exocyclic nitrogen does not participate in the π system as fully as the chelate nitrogen atoms. The fact that the C–N bond lengths in the metallocycle of **8** are similar to those of **9** and **10**, and that the core was planar in all cases corroborates this conclusion.

The thermolysis studies were quite encouraging to consider these compounds as precursors for vapour deposition of thin metal films. Thermolysis produced the reduced metal either as a deposited mirror or as finely divided metal particles for every compound reported herein. In the thermolysis studies, two general decomposition pathways are known for compounds of this nature: CDI deinsertion and β-hydrogen elimination (Scheme 2).[5]



Scheme 2. Different decomposition pathways of diisopropyl amidinates and guanidinates. a) carbodiimide deinsertion, and b) β-hydrogen elimination.

With respect to the thermal decomposition pathways, there are some general considerations that require illumination. Firstly, the products of β-hydrogen elimination can quite easily generate free guanidine when the transient "metal hydride" reacts with an intact metal guanidinate species, which would result in reduced metal. Secondly, guanidines themselves can undergo deinsertion to produce an amine and carbodiimide, and so this decomposition had to be investigated for the ligands used in this study. For example, a thermolysis experiment of tetraisopropylguanidine in C_6D_6 in an NMR tube at 120 °C showed a ^1H spectrum that contained peaks characteristic of diisopropyl CDI (i.e., a doublet at δ = 1.04 ppm and a septet at δ = 3.33 ppm) as well as peaks characteristic of diisopropylamine. The same reactivity was found in the dimethyl analogue at 155 °C. This can confuse the decomposition pathway for a given compound, and careful consideration was necessary to determine which pathway was followed.

The copper dimers **1** and **2** and the gold compound **8** were sufficiently thermally stable to allow sublimation, while the remaining compounds could not be isolated by sublimation, even when the sublimation was performed in the absence of light (Table 7). In the case of **3**–**7**, **9** and **10**, attempted sublimation resulted in a metallic mirror in the sublimation pot.

Table 7. The thermal parameters for **1**–**10**.

	Sublimation temp. [°C] @ *p* [mTorr]	Onset of thermolysis[a] [°C]	Residual mass[b] [%]
1	130 @ 85	78.1	19.1 (24.3)
2	130 @ 80	87.5	21.4 (21.9)
3		114.9	41.0 (37.2)
4		58.4	33.8 (32.3)
5		99.4	36.0 (35.2)
6		25.5	46.0 (47.5)
7		100.5	50.0 (49.8)
8	85 @ 20	52.0	4.0 (53.6)
9		79.5	14.2 (58.2)
10		132.3	54.1 (51.8)

[a] The onset of thermolysis reported at 99.5% mass from thermogravimetric analysis. [b] The number in brackets is the percent mass of metal in the compound.

The copper compounds show straight-forward thermal chemistry, with their thermogravimetric (TG) analysis curves demonstrating a combination of volatilization and thermal decomposition. Although compound **2** showed a residual mass very close to the percent mass of the metal in the compound, visual inspection determined there to be no metal left at the end of this experiment, and that the residual was coincidentally close to 21.9% (Table 7).

This contrasted with the silver (**3**–**5**) and the gold guanidinate species (**6**–**8**), which showed reduced metal in the TG pans at the conclusion of the experiment. This suggests that these compounds underwent a redox process whereby the ligand was oxidised, and the metal was reduced. For compounds **3**–**7**, there was likely very little or no volatilization during this reaction, as their residual masses matched very closely to the percent mass of the metal in the compound. This suggests that these compounds were quantitatively reduced. In contrast, compound **8** showed a very low residual mass (although gold metal was obviously left behind). This suggests that the material mostly sublimed, and the derivative TG curve did indeed show a characteristic shape for sublimation, where there is an exponential ascent and rapid, almost asymptotic descent (Figure 4). This combination of volatility and reactivity suggests that compound **8** will be a suitable precursor for the vapour deposition of gold, and this research is presently being undertaken.

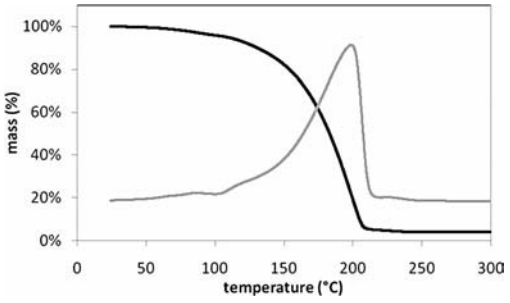


Figure 4. The thermogravimetric curve (black) and its derivative curve (grey) for compound **8**.

The fact that compounds **3**–**5**, **7** and **8** undergo reduction upon heating suggests that the ligand system might be becoming oxidised. This in turn suggests that the primary thermal reaction pathway for these compounds is either via CDI elimination and subsequent reduction of the copper by the transient amido moiety (Scheme 2, a) or by β-hydrogen elimination followed by elimination of the metal hydride (Scheme 2, b). Further thermolysis was studied by heating these compounds in a deuterated benzene solution in sealed NMR tubes, and monitoring thermal by-products by ^1H NMR spectroscopy. In every case, the free parent guanidine was found to evolve when the thermolysis was allowed to run at 120 °C overnight. Production of free guanidine implies the production of an "oxidised" guanidine species as a hydrogen source (Scheme 2). No evidence of this compound was found in the ^1H NMR spectra, although thermolysis also resulted in a flocculent solid that might contain the oxidised guanidine species.

When compound **6** was heated at 120 °C for 2 h, diisopropylcarbodiimide and diisopropylamine were both evident in the thermolysis NMR, similar to what is observed

for the thermolysis of the parent guanidine under similar conditions. Thus, it is possible that the free guanidine was produced (as above), and it subsequently underwent thermolysis to produce the carbodiimide. However, this does not rule out carbodiimide deinsertion.

Compounds **9** and **10** both showed CDI as a thermolysis by-product by ^{1}H NMR when heated overnight at 120 °C in the conditions described above. However, the parent amidines showed no inclination to produce the carbodiimide under these conditions. This suggests that the gold amidinate compounds themselves thermally decomposed by CDI deinsertion (Scheme 2, a). This was somewhat surprising, because these ligands have to undergo the cleavage of a much stronger C–C bond in order for CDI to deinsert, as compared to guanidinate ligands wherein a weaker N–C bond would break. However, the TG curve for compound **9** showed an inflection at 64.6%, which matches closely to the percent mass loss of CDI from this compound (Figure 5). The symmetry of the derivative curve features showed these events to be decomposition or thermal reactions, rather than straightforward sublimation. Thus, it is likely that **9** is undergoing sublimation and decomposition in the same temperature range.

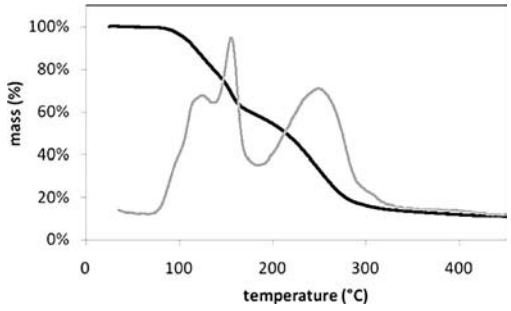


Figure 5. The thermogravimetric curve (black) and its derivative curve (grey) for compound **9**.

Conclusions

Guanidinato complexes of copper and silver gold were shown to be potential precursors for chemical vapour deposition of these metals. Both the silver and gold compounds were found to produce the reduced metal upon thermolysis (and photolysis in the case of silver), with the ligand acting as a reducing agent through β-hydrogen elimination. This promising chemistry opens the door to single-source silver and gold deposition processes.

The preferred oligomeric species appears to be dimers in the case of copper and gold, and trimers in the case of silver, which nicely follows the periodic trend in atomic radii. The silver trimer showed an interesting isosceles arrangement of the silver centres, which can be attributed to the peculiar ligand bonding arrangement.

Compound **8** showed the best promise as a gold precursor, subliming well at 85 °C while also producing gold metal at higher temperatures. The amidinates **9** and **10** of gold appeared to undergo thermolysis by deinsertion of CDI, which was unexpected given that the amidinate ligand must cleave a C–C bond to do so.

The mechanism of these thermolyses require further investigation, and a careful study similar to our previous work with the (dimethylguanidinato)copper is underway.[4]

Experimental Section

General: All manipulations were performed in an MBraun Unilab inert atmosphere 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, diethylamine, diisopropylamine, butyllithium (2.5 M in hexanes), methyllithium (1.6 M in diethyl ether), copper(I) chloride, silver(I) chloride, and lithium dimethyl amide were purchased from Aldrich Chemical Co. and used as received. The gold(I) starting material AuCl·THT was synthesised by literature methods.[10] The compounds Li[(*i*PrN)$_2$CN(*i*Pr)$_2$], Li[(*i*PrN)$_2$CN(Et)$_2$], Li[(*i*PrN)$_2$CN(Me)$_2$], Li[(*i*PrN)$_2$CMe], and Li[(*i*PrN)C*n*Bu] were prepared by literature methods.[11] Nuclear Magnetic Resonance was done on 300 MHz Avance 3 and 400 MHz Bruker AMX. Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Guelph Chemical Laboratories performed combustion analysis. Thermogravimetric analysis was performed on a TA Instruments Q50 apparatus located in an MBraun Labmaster 130 Dry box under a nitrogen atmosphere.

[Cu(N*i*Pr)$_2$CNEt$_2$]$_2$ (1): In a 50 mL flask, HNEt$_2$ (0.0.283 g, 3.87 mmol) was diluted in 20 mL of ethyl ether. Butyllithium (1.53 mL, 3.82 mmol) was added dropwise to the amine solution and stirred for 1.5 h. Diisopropylcarbodiimide (0.482 g, 3.82 mmol) was diluted in 5 mL of ethyl ether and added dropwise to the solution of lithiated amine. The solution was stirred for 3 h during which time a colourless precipitate formed. Copper(I) chloride (0.391 g, 3.95 mmol) was added and the mixture was stirred for 18 h, after which the cloudy solution was filtered to afford a light green solid and a slightly pale yellow solution. The filtrate was evacuated to dryness to afford an off-white solid of **1** (0.923 g, 92.3% crude yield). The solid was purified by sublimation (T_{sub} = 130 °C, 85 mTorr) and collected as clear, colourless crystals (0.811 g, 81.1%); m.p. 154 °C. $C_{22}H_{48}Cu_2N_6$ (523.75): calcd. C 50.45, H 9.24, N 16.05; found C 50.77, H 9.26, N 16.22. Mass spectra *m*/*z*: 524 M$^+$. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 7.1 Hz for ethyl; 6.2 Hz for isopropyl]: δ = 3.50 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 2.94 [q, 8 H, C*H*$_2$CH$_3$], δ = 1.30 [d, 24 H, CH(C*H*$_3$)$_2$], δ = 0.89 [t, 12 H, CH$_2$C*H*$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 170.9 [N*C*N], δ = 48.5 [*C*H(CH$_3$)$_2$], δ = 43.7, [*C*H$_2$CH$_3$], δ = 27.57 [CH(*C*H$_3$)$_2$], δ = 13.4 [CH$_2$*C*H$_3$] ppm.

[Cu(N*i*Pr)$_2$CN*i*Pr$_2$]$_2$ (2): Compound **2** was prepared in a analogous manner as compound **1**, substituting HN*i*Pr$_2$ for HNEt$_2$ (0.359 g, 3.55 mmol) and using 1.38 mL of 2.5 M BuLi. Crude yield was 89.8%. Compound **2** was purified by sublimation (T_{sub} = 130 °C, 80 mTorr) and collected as clear, colourless crystals of **2** (0.630 g, 63.0%); m.p. 157 °C. $C_{26}H_{56}Cu_2N_6$ (579.86): calcd. C 53.85, H 9.73, N 14.49; found C 53.85, H 9.45, N 14.82. Mass spectra m/e: 580 M$^+$. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.5 Hz for exocyclic isopropyl; 6.2 Hz for metallocyclic isopropyl]: δ = 3.73 {sept, 4 H, N[C*H*(CH$_3$)$_2$]$_2$}, δ = 3.33 [sept, 4 H, NC*H*(CH$_3$)$_2$], δ = 1.31 {d, 24 H, N[CH(C*H*$_3$)$_2$]$_2$}, δ = 1.12 [d, 24 H, NCH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 168.3 [N*C*N], δ = 48.4 [NCH(CH$_3$)$_2$], δ = 47.4 {N[*C*H(CH$_3$)$_2$]$_2$}, δ = 27.6 {N[CH(*C*H$_3$)$_2$]$_2$}, δ = 23.13 [NCH(*C*H$_3$)$_2$] ppm.

[Ag(N*i*Pr)$_2$CNMe$_2$]$_3$ (3): 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 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, further reaction was carried out with protection against light. 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 **3** (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 **3** was collected as white crystals (0.45 g, 1.62 mmol, 45%). $C_{18}H_{40}Ag_2N_6$ (556.29): calcd. C 38.86, H 7.25, N 15.11; found C 38.53, H 7.40, N 15.49. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.2 Hz for all peaks]: δ = 3.57 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 2.62 [s, 12 H, N(C*H*$_3$)$_2$], δ = 1.34 [d, 24 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 169.4 [N*C*N], δ = 48.2 [*C*H(CH$_3$)$_2$], δ = 40.8 [N(*C*H$_3$)$_2$], δ = 27.8 [CH(*C*H$_3$)$_2$] ppm.

[Ag(N*i*Pr)$_2$CN*i*Pr$_2$]$_3$ (4): In a 50 mL flask, diisopropylamine (0.354 g, 3.50 mmol) was dissolved in 40 mL of hexanes at –30 °C and MeLi (2.19 mL, 3.50 mmol) was added dropwise and stirred for two hours, giving a white suspension. Diisopropylcarbodiimide (0.442 g, 3.50 mmol) was diluted with 10 mL of hexanes and added dropwise to this suspension at –30 °C. Owing to the photosensitivity of silver(I) chloride, further reaction was carried out with protection against light. 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 **4** (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 °C overnight. Compound **4** was collected as white crystals (0.29 g, 0.28 mmol, 24.9%). $C_{26}H_{56}Ag_2N_6$ (668.50): calcd. C 46.71, H 8.44, N 12.57; found C 46.98, H 8.43, N 12.53. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.2 Hz for all peaks]: δ = 3.85 [sept, 4 H, NC*H*(CH$_3$)$_2$], δ = 3.46 {sept, 4 H, N[C*H*(CH$_3$)$_2$]$_2$}, δ = 1.33 [d, 24 H, NCH(C*H*$_3$)$_2$] δ = 1.20 {d, 24 H, N[CH(C*H*$_3$)$_2$]$_2$} ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 167.3 [N*C*N], δ = 49.1 [N*C*H(CH$_3$)$_2$], δ = 48.0 {N[*C*H(CH$_3$)$_2$]$_2$}, δ = 27.6 [NCH(*C*H$_3$)$_2$], δ = 23.4 {N[CH(*C*H$_3$)$_2$]$_2$} ppm.

[Ag(N*i*Pr)$_2$CNEt$_2$]$_3$ (5): Compound **5** was prepared in a analogous manner as compound **4** substituting: Diethylamine (0.523 g, 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% yield). $C_{22}H_{48}Ag_2N_6$ (612.40): calcd. C 43.15, H 7.90, N 13.72; found C 43.28, H 8.10, N 13.91. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 7.1 Hz for ethyl; 6.2 Hz for isopropyl]: δ = 3.65 [sept, 6 H, C*H*(CH$_3$)$_2$], δ = 3.01 [q, 12 H, C*H*$_2$CH$_3$], δ = 1.36 [d, 36 H, CH(C*H*$_3$)$_2$], δ = 0.95 [t, 18 H, CH$_2$C*H*$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 168.4 [N*C*N], δ = 48.6 [N(*C*H(CH$_3$)], δ = 43.9 [N(*C*H$_2$CH$_3$)$_2$], δ = 27.8 [N(CH(*C*H$_3$)], δ = 13.4 [N(CH$_2$*C*H$_3$)$_2$] ppm.

[Au(N*i*Pr)$_2$CN*i*Pr$_2$]$_2$ (6): In a 100 mL round bottomed flask, AuCl·THT (0.85 g, 2.64 mmol) was suspended in 50 mL of hexanes. The slurry was cooled to –36 °C. Solid Li[(*i*PrN)$_2$CN(*i*Pr)$_2$] (0.62 g, 2.64 mmol) was added to the solution and allowed to react in a freezer at –35 °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 h. A white precipitate of 6 formed. (1.02 g, 2.41 mmol, 91.1%); m.p. 87 °C (dec.). $C_{26}H_{56}Au_2N_6$ (846.70): calcd. C 36.88, H 6.67, N 9.93; found C 36.79, H 7.06, N 10.03. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.2 Hz for all peaks]: δ = 3.96 [sept, 4 H, NC*H*(CH$_3$)$_2$], δ = 3.26 [sept, 4 H, N(C*H*(CH$_3$)$_2$)$_2$], δ = 1.39 [d, 24 H, NCH(C*H*$_3$)$_2$], δ = 1.06 [d, 24 H, N(CH(C*H*$_3$)$_2$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 166.6 [N*C*N], δ = 50.1 [N*C*H(CH$_3$)2], δ = 48.5 [N(*C*H(CH$_3$)$_2$)$_2$], δ = 27.2 [NCH(*C*H$_3$)$_2$], δ = 22.6 [N(CH(*C*H$_3$)$_2$)$_2$] ppm.

[Au(N*i*Pr)$_2$CNEt$_2$]$_2$ (7): Compound **7** was prepared in a analogous manner as compound **6** substituting: AuCl·THT (0.71 g, 2.23 mmol), Li[(*i*PrN)$_2$CN(Et)$_2$] (0.46 g, 2.23 mmol). Compound **6** was isolated by recrystallisation (0.71 g, 1.80 mmol, 80.6% yield); m.p. 72 °C (dec.). $C_{22}H_{48}Au_2N_6$ (790.59): calcd. C 33.42, H 6.12, N 10.63; found C 33.74, H 6.23, N 10.33. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 7.0 Hz for ethyl; 6.2 Hz for isopropyl]: δ = 3.80 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 2.85 [q, 8 H, C*H*$_2$CH$_3$], δ = 1.39 [d, 24 H, CH(C*H*$_3$)$_2$], δ = 0.83 [t, 12 H, CH$_2$C*H*$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 166.4 [N*C*N], δ = 50.5 [*C*H(CH$_3$)$_2$], δ = 44.2 [*C*H$_2$CH$_3$], δ = 27.1 [CH(*C*H$_3$)$_2$], δ = 13.3 [CH$_2$*C*H$_3$] ppm.

[Au(N*i*Pr)$_2$CNMe$_2$]$_2$ (8): Compound **8** was prepared in a analogous manner as compound **6** substituting: AuCl·THT (0.99 g, 3.09 mmol), Li[(*i*PrN)$_2$CN(Me)$_2$] (0.548 g, 3.09 mmol). Compound **8** was isolated by recrystallisation (0.99 g, 2.70 mmol, 87.4%); m.p. 83 °C (dec.). $C_{18}H_{40}Au_2N_6$ (734.49): calcd. C 29.43, H 5.49, N 11.44; found C 29.45, H 5.34, N 11.10. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.2 Hz for all peaks]: δ = 3.80 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 2.43 [s, 12 H, N(C*H*$_3$)$_2$], δ = 1.37 [d, 24 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 170.7 [N*C*N], δ = 50.3 [*C*H(CH$_3$)$_2$], δ = 40.9 [N(*C*H$_3$)$_2$], δ = 27.21 [CH(*C*H$_3$)$_2$] ppm.

[Au(N*i*Pr)$_2$CNMe]$_2$ (9): Compound **9** was prepared in a analogous manner as compound **6** substituting: AuCl·THT (0.57 g, 1.78 mmol) Li[(*i*PrN)$_2$CCH$_3$] (0.27 g, 1.78 mmol); Compound **9** was isolated by recrystallisation (0.43 g, 1.28 mmol, 71.8%); m.p. 79 °C (dec.). $C_{16}H_{34}Au_2N_4$ (676.40): calcd. C 28.41, H 5.07, N 8.28; found C 28.27, H 5.28, N 8.44. ^{1}H NMR [300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 6.2 Hz for isopropyl]: δ = 3.57 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 1.62 [s, 6 H, (NCC*H*$_3$)], δ = 1.25 [d, 24 H, (CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 168.5 [N*C*N], δ = 51.0 [*C*H(CH$_3$)], δ = 26.8 [CH(*C*H$_3$)$_2$], δ = 16.1 [NC*C*H$_3$] ppm.

[Au(N*i*Pr)$_2$CN*n*Bu]$_2$ (10): Compound **10** was prepared in a analogous manner as compound **6** substituting: AuCl·THT (1.01 g, 3.15 mmol) Li[(*i*PrN)$_2$C*n*Bu] (0.60 g, 3.15 mmol); Compound **10** was isolated by recrystallisation (0.30 g, 0.79 mmol, 25.0%); m.p. 96 °C (dec.). $C_{22}H_{26}Au_2N_4$ (740.41): calcd. C 34.74, H 6.10, N 7.37; found C 34.60, H 6.15, N 7.69. ^{1}H NMR (300 MHz, C_6D_6, $^3J(^1H,^1H)$ = 7.1 Hz for butyl; 6.2 Hz for isopropyl): δ = 3.74 [sept, 4 H, C*H*(CH$_3$)$_2$], δ = 2.26 [t, 4 H, C*H*$_2$CH$_2$CH$_2$CH$_3$], δ = 1.44 [q, 4H CH$_2$C*H*$_2$CH$_2$CH$_3$], δ = 1.33 [d, 24 H, CH(C*H*$_3$)], δ = 1.17 (sex, 4 H, CH$_2$CH$_2$C*H*$_2$CH$_3$], δ = 0.80 [t, 6 H, CH$_2$CH$_2$CH$_2$C*H*$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 171.55 [N*C*N], δ = 50.61 [*C*H(CH$_3$)$_2$], δ = 30.73 [C*C*H$_2$CH$_2$CH$_2$CH$_3$], δ = 29.85 [CH$_2$*C*H$_2$CH$_2$CH$_3$] δ = 27.20 [CH(*C*H$_3$)$_2$], 23.06 [CH$_2$CH$_2$*C*H$_2$CH$_3$], 13.92 [CH$_2$CH$_2$CH$_2$*C*H$_3$] ppm.

X-ray Structural Analysis for 1, 2, 3, 8, 9 and 10: Crystals were mounted using viscous oil onto plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald

sphere. The systematic absences in the diffraction data are consistent with *Cc* and *C*2/*c* for **8** and **9**, and, uniquely, for *Pbcn* for **1** and *Pbca* for **2**. No symmetry higher than triclinic was observed for **3** and **10**. Solution in the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with SADABS11 absorption corrections based on redundant multiscan data. The structures were solved by direct methods and refined with full-matrix, least-squares procedures on *F*2. For **1**, the compound molecule is located at a twofold axis. For **2**, **8**, **9** and **10**, each compound molecule (two symmetry unique molecules for **9**) was located on an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library.[12]

CCDC-782066 (for **1**), -782067 (for **2**), -782068 (for **3**), -782069 (for **8**), -782070 (for **9**), -782071 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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