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Preventing thermolysis: precursor design for volatile copper compounds[†]

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A copper(1) iminopyrrolidinate was synthesized and evaluated by thermal gravimetric analysis (TGA), solution based ¹H NMR studies and surface chemistry to determine its thermal stability and decomposition mechanism. Copper(1) *tert*-butyl-imino-2,2dimethylpyrrolidinate (1) demonstrated superior thermal stability and showed negligible decomposition in TGA experiments up to 300 °C as well as no decomposition in solutions at 165 °C over 3 weeks.

Atomic layer deposition (ALD) is a deposition process that relies on successive self-limiting reactions between an entrained precursor gas and a solid substrate. Progress in ALD has relied on novel precursor chemistry to allow processes for thin film deposition to be defined for a variety of target films and process conditions.¹ In many cases, the "design" of the precursor entails selecting a new ligand and modifying it to provide volatility and thermal stability to a precursor. However, such ligands are often not tested and redesigned to improve on their original performance. More often, a new ligand is employed to overcome the failings of a previous ligand.

There have been several designs for precursors for the deposition of copper metal, a key element in the fabrication of microelectronic circuits.² One influential ligand used in copper ALD is the amidinate family, which includes both amidinates and guanidinates,³ including copper(1) alkylamidinates⁴ and copper(1) guanidinates⁵ (Fig. 1). These ligands suffer from two main thermal decomposition pathways: loss of carbodiimide (herein called "deinsertion") and β -hydrogen abstraction.⁶ These low temperature decompositions lead to the formation of copper metal, with the ligand acting as a reducing agent.

The redesign of the amidinate ligand was undertaken to prevent these thermolyses. By using a judiciously chosen pyrrolidinate, both thermal pathways could be eliminated (Fig. 2).

The deinsertion of carbodiimide (CDI) was prevented by tethering the alkyl group of the chelate position to the exocyclic group through use of a pyrrole ring. β -hydrogen abstraction was eliminated by using a *tert*-butyl group in the chelate



Fig. 1 Thermal decomposition pathways for copper(1) amidinates. Where R can be an alkyl or an amine.



Fig. 2 The synthetic procedure for producing the *tert*-butyl-imino-2,2-dimethylpyrrolidine ligand.

position as well as replacing the β -hydrogens on the ring with methyl groups. The ligand was made in high yield, and the copper(1) pyrrolidinate (1) was formed through simple salt metathesis. Recently, trimeric heteroleptic copper(1) guanidinates were isolated from the attempted synthesis of $[Me_2NC(N'Bu)_2Cu]_2$.⁷ Compared to this trimer, the ring of the iminopyrrolidinate reduced the steric bulk to permit the isolation of 1 as the more typical dimer, as seen by single crystal X-ray diffraction. The structure of 1 is consistent with previously known amidinate⁴ and guanidinate⁵ systems (Fig. 3, Table 1). The compound has a Cu–Cu distance of ~2.5 Å, with an approximately linear coordination geometry around each copper atom. The metallocycle core is planar with equivalent N–C bonds (1.34 Å) suggesting delocalization.

This compound showed excellent volatility: thermogravimetric analysis (TGA) showed it to be volatile as low as 165 °C at atmospheric pressure, with a residual mass of <2% of the sample mass. Compound 1 could also be quantitatively sublimed at 130 °C at a pressure of 20 mtorr. This indicated that the compound cleanly volatilizes at these temperatures with no thermal decomposition.

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Fig. 3 The structure of 1, with hydrogens removed for clarity, and the thermal ellipsoids shown at 30%.

Table 1 The selected bond lengths and angles for 1

Selected bond	Length (Å)
Cu-Cu	2.47
Cu-N1	1.87
Cu-N2	1.89
N1-C4	1.33
N2-C4	1.33
Selected angle	Angle (°)
N1–Cu–N2	175.6
N1–C4–N2	122.5

More importantly, a thermal stress test designed for this study showed **1** to be very resistant to thermal decomposition at higher temperatures. In this stress test, the compound is measured by TGA using the same temperature ramp rate $(10 \ ^{\circ}\text{C min}^{-1})$ but with different sample masses (Fig. 4).

Due to the kinetics of volatilization, as sample mass is increased, more sample becomes exposed to higher temperatures. This valuable test can be used to gauge the behaviour of a compound with respect to thermal handling during a deposition process. As seen in Fig. 4, varying the sample weights of **1** gave no deviation in residual mass, whereas performing the same stress test on the similar N',N''-diisopropyl-*N*-dimethylguani-dinatocopper⁵ (**2**) compound showed a marked increase of



Fig. 4 Thermal stress test of compounds (a) 1 and (b) 2, showing effect on residual mass as starting mass was increased.

residual mass of <2% to 9.0% of the initial mass as the sample mass was increased from 10 mg to 63 mg. It has been previously demonstrated that **2** undergoes CDI deinsertion at lower temperatures, a process which has been prevented through this ligand design.⁴

This contrast in thermal behaviour was highlighted by the decomposition kinetics of these two compounds at 165 °C. Compound **2** was found to decompose following first order decomposition kinetics with a calculated half-life of 33.8 hours while **1** showed no appreciable decomposition over 20 days at 165 °C.

To test compound 1 for vapour phase stability, it was heated in a bubbler at 160 °C and the evolved vapour was entrained over high surface area silica for 17 hours to saturate the silica with a chemisorbed monolayer. Characterization was undertaken using ¹H/¹³C cross-polarized magic-angle spinning solid state NMR, and there was only physisorbed species detected up to 200 °C. At a deposition temperature of 275 °C, solid state ¹³C NMR showed signals attributable to the copper precursor (Fig. 5a, top trace). These signals were similar to the high resolution ¹³C NMR of 1 in deuterated benzene (Fig. 5a, bottom trace). There was excellent corroboration between the solution NMR and the solid-state NMR. Although this suggested that the precursor chemisorbed "whole" at the surface, literature suggests that the alkyl group at the chelate position might be lost at high temperatures.⁷ The line width of the solid-state NMR did not permit unambiguous identification of the *tert*-butyl moiety, so another experiment was needed.

The silica with the deposited monolayer was rinsed with D₂O to etch off the surface species, and a high resolution ¹H NMR was collected (Fig. 5b, top trace), showing a singular surface species. Although the chemical shifts were different because of the necessity of using different solvents, the integration of the peaks for the surface species showed loss of the tert-butyl group: integrations of 2.1, 2.0, and 5.7 for the peaks at 2.94 ppm, 2.07 ppm, and 1.36 ppm respectively. The ¹H NMR of the ligand in deuterated chloroform clearly showed a singlet for the tert-butyl group (Fig. 5b, bottom trace) with integration ratios of 2.0, 2.0, 9.4, and 6.1 for the peaks at 2.42 ppm, 1.57 ppm, 1.32 ppm, and 1.18 ppm respectively. As well, ²⁹Si SS-NMR of the silica showed no additional signals for silicon beyond what was detected for pure silica, suggesting nucleation did not occur at a silicon atom. This is reasonable, considering that the most likely nucleation point for this precursor on silica surface is at the oxygen of a silanol group. Given these data, nucleation likely occurs through the copper atom to a surface oxygen, and subsequently undergoes butene elimination (Fig. 5c). This elimination occurs at 300 °C higher in temperature than shown for the copper amidinate,8 and highlights the excellent thermal stability designed into this ligand.

In summary, a new volatile precursor for copper metal deposition was synthesized with its ligand designed to prevent two known, low temperature decomposition pathways. The precursor 1 showed excellent stability both in the solid state, in solution, and as a vapour species. Surface analysis suggested that the precursor undergoes an alkene elimination from the chelating nitrogen atom during chemisorption on silica at 275 °C. This novel precursor suggests that a family of iminopyrrolidinates of copper might be



Fig. 5 Reactivity of **1** with silica: (a) shows the SS-¹³C NMR of silica after deposition of **1** at 275 °C (top trace) compared to the HR-¹³C NMR of **1** in deuterated benzene (bottom trace). (b) Shows the HR-¹H NMR of the surface species etched from the silica with D₂O (in D₂O; top trace) compared to the HR-¹H NMR of **1** in CDCl₃ (bottom trace). (c) Shows the proposed nucleation and chemisorption of **1** at a silanol group on a silica surface.

synthesized with various β -hydrogen atoms, which would allow tuning of the precursors thermal reactivity.

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