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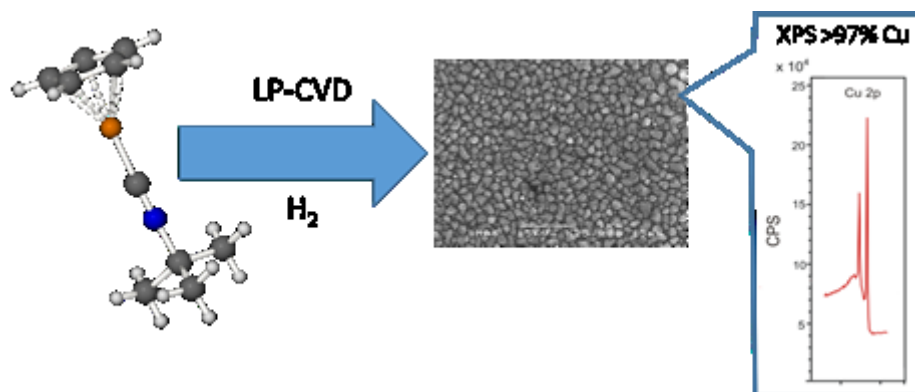
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Table of Content Abstract and Graphic

We report here the synthesis and characterization of a family of copper(I) metal precursors based around cyclopentadienyl and isocyanide ligands. By systematically varying substituents on both the cyclopentadienyl and isocyanide ligands we have investigated the stability of the complexes. For the *tert*-butyl isocyanide complexes ($[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cu}(\text{CN}^t\text{Bu})$ **2b**: R = H; **3b**: R = Me; **4b**: R = Et; **5b**: R = *i*Pr) we have investigated the effect of the cyclopentadienyl substituent on both vapor pressure and the stability of the complexes. Low pressure chemical vapor deposition (LP-CVD) has been employed using **2a** and **2b** to synthesize thin films of metallic copper on silicon and gold substrates at both 180 °C and 300 °C under an H_2 atmosphere. Thin films were also grown using LP-CVD on platinum substrates at 180 °C. Analysis of the thin films by SEM and AFM reveal temperature and substrate dependent growth features.



Tailoring Precursors for Deposition: Synthesis Structure and Thermal Studies of Cyclopentadienyl Copper(I) Isocyanide Complexes

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ABSTRACT:

We report here the synthesis and characterization of a family of copper(I) metal precursors based around cyclopentadienyl and isocyanide ligands. The molecular structure of the several complexes cyclopentadienyl-copper(I) isocyanide complexes have been unambiguously determined by single crystal X-ray diffraction analysis. Thermogravimetric analysis of the complexes highlighted the isopropyl isocyanide complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{CN}^i\text{Pr})]$ (**2a**) and the *tert*-butyl isocyanide complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{CN}^t\text{Bu})]$ (**2b**) as possible copper metal CVD precursors. Further modification of the precursors with variation of the substituents on the cyclopentadienyl ligand system (varying between H, Me, Et and ⁱPr) have allowed the affect these changes would have on features such as stability, volatility and decomposition to be investigated. As part of this study the vapor pressures of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{CN}^t\text{Bu})]$ (**2b**), $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Cu}(\text{CN}^t\text{Bu})]$ (**3b**), $[(\eta^5\text{-EtC}_5\text{H}_4)\text{Cu}(\text{CN}^t\text{Bu})]$

(4b) and $[(\eta^5\text{-iPrC}_5\text{H}_4)\text{Cu}(\text{CN}^t\text{Bu})]$ (**5b**) over a 40-65 °C temperature range have been determined. Low pressure chemical vapor deposition (LP-CVD) was employed using precursors **2a** and **2b**, to synthesize thin films of metallic copper on silicon, gold and platinum substrates, under an atmosphere of hydrogen (H₂). Analysis of the thin films deposited onto both silicon and gold substrates at substrate temperatures of 180 °C and 300 °C, by SEM and AFM reveal temperature dependent growth features: Films grown at 300 °C are continuous and pin hole free, whereas those films grown at 180 °C consist of highly crystalline nanoparticles. In contrast, deposition onto platinum substrates at 180 °C show a high degree of surface coverage with the formation of high density, continuous pin hole free thin films. Powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS) all show the films to be high purity metallic copper.

KEYWORDS: Copper, chemical vapor deposition, precursor, vapor pressure, organometallic.

Introduction

The development of copper precursors for the production of metallic thin films¹ by both chemical vapor deposition (CVD)² and atomic layer deposition (ALD)³ has been, and continues to be, an area of significant interest to those in the microelectronics industry, mainly due to the numerous potential applications in which these materials can be exploited.^{2d,2e,3a,3b} As the size downscaling of microelectronics continues, the use of copper as an interconnect material in integrated circuitry has increased.^{2c,2e,3b} The physical properties that make copper so desirable for such applications include its very low resistivity (significantly lower than aluminum and much lower than tungsten) and electromigration resistance that is far superior to that of aluminum (though inferior to tungsten).

The advantages of selective deposition and conformal coverage of surfaces gained when using CVD and ALD over other (physical) deposition techniques are derived from the molecular nature of these processes. While advances in the development of ALD precursors for copper metal deposition, most notably the reduction of copper(II) species to copper(0) metal in the presence of metal alkyls such as ZnEt_2 and AlMe_3 ,^{3i,4} have been made over the past 6-7 years, the significantly slower growth rate attributed to ALD processes compared to CVD means that the design and development of CVD precursors, specifically organometallic derivatives, is of interest.

In principle, copper(0) compounds would be the most desirable precursors; ligand dissociation would produce atomised metal, and any such process should lead to the formation of high-purity films, as is the case for the CVD of Pt metal from $\text{Pt}(\text{PF}_3)_4$.⁵ To date no such homoleptic Cu(0) complexes are known.

This leaves Cu(I) and Cu(II) compounds as potential precursors for the CVD of copper metal. While copper(II) species, and in particular the β -diketonate derivatives of 1,1,1,5,5,5-hexafluoroacetylacetone,^{2b,2d} have been used extensively for the CVD of copper, the inherent

instability of organometallic Cu(II) d^9 -species means that, to date, Cu(II) organometallic species are unknown. As already noted, the inherent instability in Cu(II) organometallics has been utilized by groups working on the development of ALD processes in which Cu(II) organometallics are formed *in-situ* to form nascent Cu metal,^{3i,4} but as CVD precursors their application has been limited.¹

In contrast, the organometallic chemistry of copper(I) species is considerably more extensive, with copper alkyl, copper aryl and copper alkynyl species all playing important roles in catalytic bond forming reactions,⁶ although the utility of these species in deposition are limited by their tendency to oligomerize, forming large aggregate species unsuitable for most CVD processes. Of the organometallic copper(I) systems known it is the cyclopentadienyl derivatives [Cp-Cu-L] (L = $2e^-$ donor ligand) which compete most effectively, in terms of stability and volatility, with β -diketonate copper systems as CVD precursors.⁷ The cyclopentadienyl ligand, which can occupy three coordination sites around the metal center, imparts a significant degree of thermal stability to complexes, not present in copper alkyl, [R-Cu-L], aryl, [Ar-Cu-L], or alkynyl, [R-C \equiv C-Cu-L], derivatives.^{2d,7}

The cyclopentadienyl copper phosphine adduct [Cp-Cu-PEt₃] was first described by Wilkinson *ca.* 1956,⁸ but it wasn't until the 1980-90s that this and related complexes were developed as MOCVD precursors.⁹ Subsequently, the number of copper cyclopentadienyl complexes has increased, but despite their utility the number of systems known in the literature (Chart 1) is still small, relative to β -diketonate copper systems.^{2d,7}

Complex	R	R'	R''	Ref
	H	H	^t Bu	10
	H	H	Ph	11
	Me	H	^t Bu	10
	^t Bu	H	^t Bu	10
	CF ₃	H	^t Bu	10
	Me	Me	^t Bu	10
		H	H	Me
H		H	Et	13
H		H	Et/Et/Ph	14
H		H	ⁱ Pr	12
H		H	ⁿ Bu	13a
H		H	Ph	13a
H		H	OMe	13a
H		H	OEt	15
H		Me	Ph	16
Me		H	Me	17
Me		H	Et	18
ⁱ Pr		H	OMe	19
Me	Me	Me	12	

Complex	R	R'	R''	Ref
	Me	Me	Et	20
	Me	Me	ⁱ Pr	12
	Me	Me	Ph	20
	Ph	Ph	Et	21
	C(O)Me	H	Ph	21
	C(O)OMe	H	Ph	21
	CHCH ₂	H	Et	22
	CMeCH ₂	H	Et	22
	H	H	ⁱ Pr	23
	H	H	^t Bu	23
	H	H	Mes	23
	H	H	Dipp	23
	H	H	<i>c</i> - [CMe ₂ CH ₂] ₂ S	24
	H	H	-	25
	H	H	-	25
	H	Me	-	25

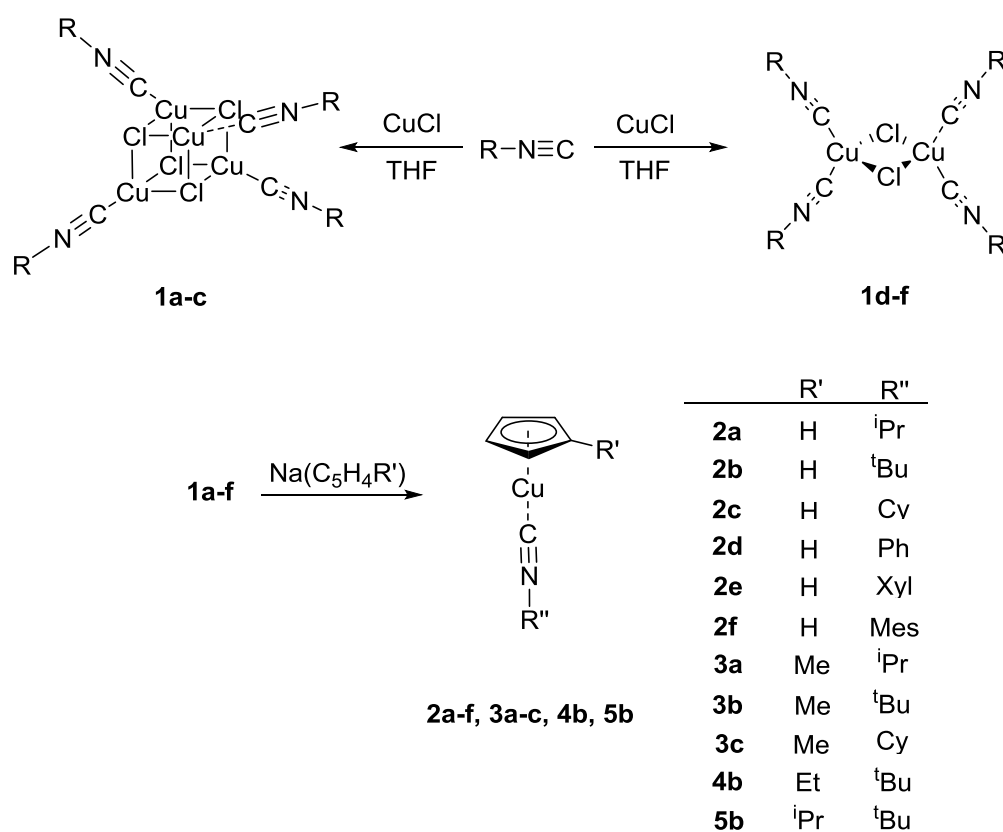
Chart 1: Stable copper(I) cyclopentadienyl complexes.

To date only the phosphine adduct [CpCu(PEt₃)] is commercially available and has been studied as a CVD precursor. The remaining N-heterocyclic carbene²³ and ylide²⁵ adducts have not been investigated as potential precursors, thus far.

However, to mass produce copper thin films laboratory methods must be scalable for commercial production. While the thermal behavior of [CpCu(PEt₃)] and MOCVD process of copper deposition from it is well established,^{9b,9c,26} [CpCu(PR₃)] systems are not considered by industry to be good Cu sources for commercial CVD processing because of a high degree of contamination of the copper thin films.^{9n,9o,9q,15} Other precursors such as Cu(hfac)(VTMS) (CupraSelect™) and Cu(hfac)(alkyne) systems are equally susceptible to contamination (specifically O and F) which results in poor adhesion to layers such as Ta or TiN.^{2b,2d,7} Consequently new precursors, which are preferably halogen free and contain as few heteroatoms as possible, have been sought. Foremost amongst these compounds is cyclopentadienyl copper *tert*-butyl isocyanide, originally described by Saegusa *et al.*

as a catalyst in alkylidene forming reactions in 1971.²⁷ Since then it has been used as a precursor for copper metal deposition,^{10,28} a vinyl polymerization catalyst²⁹ and a number of derivatives have been reported.^{28a-c}

As an extension of our continuing interest in the development of precursors for copper thin film formation,³⁰ we describe here the synthesis of a range of substituted cyclopentadienyl copper alkyl and aryl isocyanide complexes of the general form $[(\eta^5\text{-C}_5\text{H}_4\text{R}')\text{Cu}(\text{CNR}'')]$ (Scheme 1), in an attempt to optimize the volatility and stability of these prospective copper metal precursors, for application in the CVD of copper thin films.



Scheme 1: Synthetic procedure for the synthesis of copper(I) chloride isocyanide adducts (**1a-f**) and cyclopentadienyl copper(I) isocyanide adducts (**2a-f**, **3a-c**, **4b** and **5b**)

Results and Discussion

The formation of the cyclopentadienyl copper(I) *tert*-butyl isocyanide complex (**2b**) was originally reported in 1971,²⁷ from the reaction of Cu₂O with excess freshly distilled cyclopentadiene (which also acts as a solvent) in the presence of *tert*-butyl isocyanide, to afford the desired complex which

can be recrystallized to afford pure product. Despite this synthetically unpretentious strategy its utility is limited, as use of methyl, ethyl and other alkyl-substituted cyclopentadienyl systems are typically expensive, which prohibits their use as a solvent for the reaction. To this end we have investigated the salt metathesis synthesis of the cyclopentadienyl derivatives, by stoichiometrically reacting sodium cyclopentadienide and the methyl-, ethyl- and isopropyl-substituted derivatives respectively, with a range of alkyl and aryl isocyanide adducts of copper chloride.

Synthesis of isocyanide adducts of copper(I) chloride.

Copper chloride adducts of both alkyl and aryl isocyanides were initially synthesized from the stoichiometric reaction of the RNC ligand and copper(I) chloride in THF in a 1:1 ratio, followed by filtration to remove unreacted copper(I) chloride and recrystallization from THF. The resulting adducts were characterized by ^1H and ^{13}C NMR spectroscopy, with ^1H and ^{13}C NMR spectra showing no significant changes from the equivalent spectra of the free ligands upon complexation, apart from the ^{13}C chemical shifts for the divalent $\underline{\text{C}}\text{N}$ carbons; these are all reduced by approximately 20 ppm, which can be attributed to loss of the electron density associated with forming the metal-ligand bond. These observations are consistent with those reported previously in the literature.^{10,31} Because of the nature of these adducts the precise ratio of isocyanide ligand to copper chloride was impossible to ascertain from NMR analysis. Therefore elemental analysis was used to confirm the purity of the samples and where possible single crystal X-ray diffraction was used to unequivocally determine the molecular structure of the adducts.

Direct reaction of copper chloride with the alkyl isocyanides, **a-c** (**a**: isopropyl isocyanide, **b**: *tert*-butyl isocyanide and **c**: cyclohexyl isocyanide) results in the formation colorless crystalline materials in moderate to high yields (56-89%), which were identified by elemental analysis as the 1:1 adducts (**1a-c**)^{10,31a,31b} with what is assumed to be a cubane-like molecular structure. Comparable cubane-like structures are well-known for copper(I) complexes and it has been shown for phosphine complexes

of the general form $[\text{CuX}(\text{PR}_3)]$ that their structure in the solid state depends not only on the complex itself but also on the solvent used for growing the crystal.³² While pure microcrystalline samples of **1a-c** could be isolated in moderate yields, crystals suitable for single crystal X-ray diffraction analysis were not obtained.

In contrast, reaction of aryl isocyanides (**d-f**) with copper(I) chloride in THF (1:1), followed by hot filtration and recrystallization, results in the formation of complexes which by elemental analysis are consistent with the form $[\text{ClCu}(\text{CNAr})_2]$.^{31c,31f} Amendment of the reaction stoichiometries allowed the isolation of the *bis*-isocyanide adducts (**1d-f**) in high yield (73-88%) as colorless crystalline products. In all cases crystals suitable for single crystal X-ray diffraction analysis were obtained. Figure 1 shows the molecular structure of complex **1e**, which crystallizes in the *P-1* space group with half of a molecule of the complex in the asymmetric unit cell. The complexes **1d-f** are isotactic and isostructural in the solid state and display the same gross structural features; for this reason only the molecular structure of **1e** is described here.

In the solid state complex **1e** forms a halogen-bridged complex with two isocyanide ligands completing the *pseudo* tetrahedral coordination of the copper atoms. The dimers **1d-f** all have an imposed crystallographic C_i symmetry and contain $\text{Cu}\cdots\text{Cu}$ units separated by distances between ~ 3.20 - 3.22 Å. The Cu-Cl bond distances in **1e** show an asymmetry of the binuclear unit [$\text{Cu}(1)\text{-Cl}(1) = 2.4796(5)$ Å; $\text{Cu}(1)\text{-Cl}(1A) = 2.3641(5)$ Å], a feature which has been noted previously within related complexes.^{31c,31f} The Cu-C bond lengths [$\text{Cu}(1)\text{-C}(11) = 1.896(2)$ Å, $\text{Cu}(1)\text{-C}(21) = 1.903(2)$ Å] are similarly comparable to related systems in the literature. The molecular structures of the complexes **1d** and **1f** are included in supplementary information and need no further comment here.

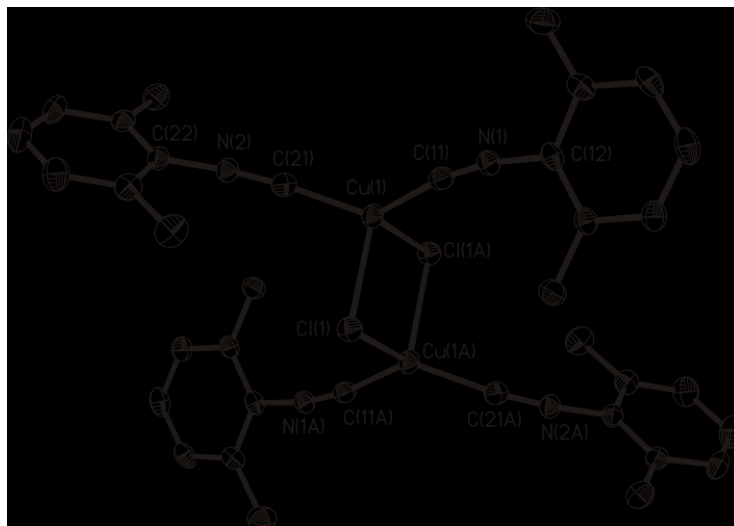


Figure 1: Molecular structure of the copper(I)chloride *bis*-xylylisocyanide dimer, **1e**, showing the labelling scheme used in the text; Hydrogen atoms have been omitted for clarity and thermal ellipsoids are at the 30% probability level. Symmetry operation: 1-x, 1-y,-z.

Synthesis of cyclopentadienyl copper(I) isocyanide adducts

An attractive feature of the $[(\eta^5\text{-Cp})\text{Cu}(\text{CNR})]$ complexes is that the sterics and electronics of the complexes can be tuned by altering the substituents of either the Cp ring or the R group of the isocyanide ligand, to make a suitable precursor for copper CVD (or ALD). It has been previously suggested that the size of the ligands (esp. Cp ligands) associated with particular precursors can play important role in determining its suitability.³³

Reaction of the copper(I) chloride isocyanide adducts with either sodium cyclopentadienide (NaCp), sodium methyl-cyclopentadienide (NaCp-Me) sodium ethyl-cyclopentadienide (NaCp-Et) or sodium isopropyl-cyclopentadienide (NaCp-*i*Pr) in stoichiometric ratios results in the formation of the η^5 -cyclopentadienyl copper complexes **2a-2f**, **3a-3c**, **4b** and **5b** respectively (Scheme 1) in quantitative yields. We have reported elsewhere the intriguing reactivity of the aryl isocyanide adducts **2d** and **2f**,^{31d} along with the *para*-fluorinated and nitrated derivatives $[(\eta^5\text{-C}_5\text{H}_5)\text{CuCNC}_6\text{H}_4\text{F}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{CuCNC}_6\text{H}_4\text{NO}_2]$,³⁴ with excess isocyanide ligand, to form 6-aminofulvene-2-alimine complexes.^{31b} Reduced reaction times (<2hrs) between sodium cyclopentadienide and the isocyanide adducts **1d-f** limits the formation of these complexes, and selective crystallization from hexane solution at -28 °C allows the complexes **2d-f** to be isolated pure and in moderate yields.

In an attempt to probe the effect of the R group of the isocyanide ligand on the precursor's suitability for copper CVD our initial studies focused on the synthesis of a family of complexes in which this substituent was varied. Thus the complexes **2a** [$(\eta^5\text{-Cp})\text{Cu}(\text{CN}^i\text{Pr})$], **2b** [$(\eta^5\text{-Cp})\text{Cu}(\text{CN}^i\text{Bu})$], **2c** [$(\eta^5\text{-Cp})\text{Cu}(\text{CNCy})$], **2d** [$(\eta^5\text{-Cp})\text{Cu}(\text{CNPh})$], **2e** [$(\eta^5\text{-Cp})\text{Cu}(\text{CNXyl})$] and **2f** [$(\eta^5\text{-Cp})\text{Cu}(\text{CNMes})$] were prepared. In all cases the ^1H NMR and ^{13}C NMR spectra of these systems (**2a-f**) show a singlet resonance associated with the {Cp} moiety: ^1H NMR; $\delta = 5.89 - 5.96$ ppm respectively (integrating to five H atoms), ^{13}C NMR; between $\delta = 94.62 - 94.83$ ppm. The ^1H and ^{13}C NMR spectral resonances associated with the isocyanide groups show no significant change upon substitution of Cl for Cp. Unfortunately, due to the fast relaxation time of quaternary carbon atoms and ^{14}N coupling, the $\underline{\text{CN}}$ resonances are not observed in the ^{13}C NMR spectra.

Crystalline materials suitable for single crystal X-ray diffraction experiments were isolated for **2a-d** and **2f**. In the solid state, **2a-d** and **2f** form discrete monomers with one-legged piano stool (pogo stick) type geometries (Fig. 2). In all cases, the central Cu atom of the complexes are bound to the {C₅H₅} ligands in a η^5 -fashion and the isocyanide ligand by the carbon atom in a κ^1 coordination mode. If we consider the {C₅H₅} ligands as occupying a single coordination site, the individual copper geometries are almost linear with $\text{Cp}_{\text{centroid}}\text{-Cu-C}$ angles between $168.69\text{-}176.15^\circ$. This variance in angle is most likely a consequence of packing forces rather than a reflection of anything significant in the bonding description. The remaining metrical data for complexes **2a-d** and **2f** (Table 1) is in good agreement with other Cp and substituted Cp-copper complexes, reflecting an apparent indifference to the nature of the isocyanide.

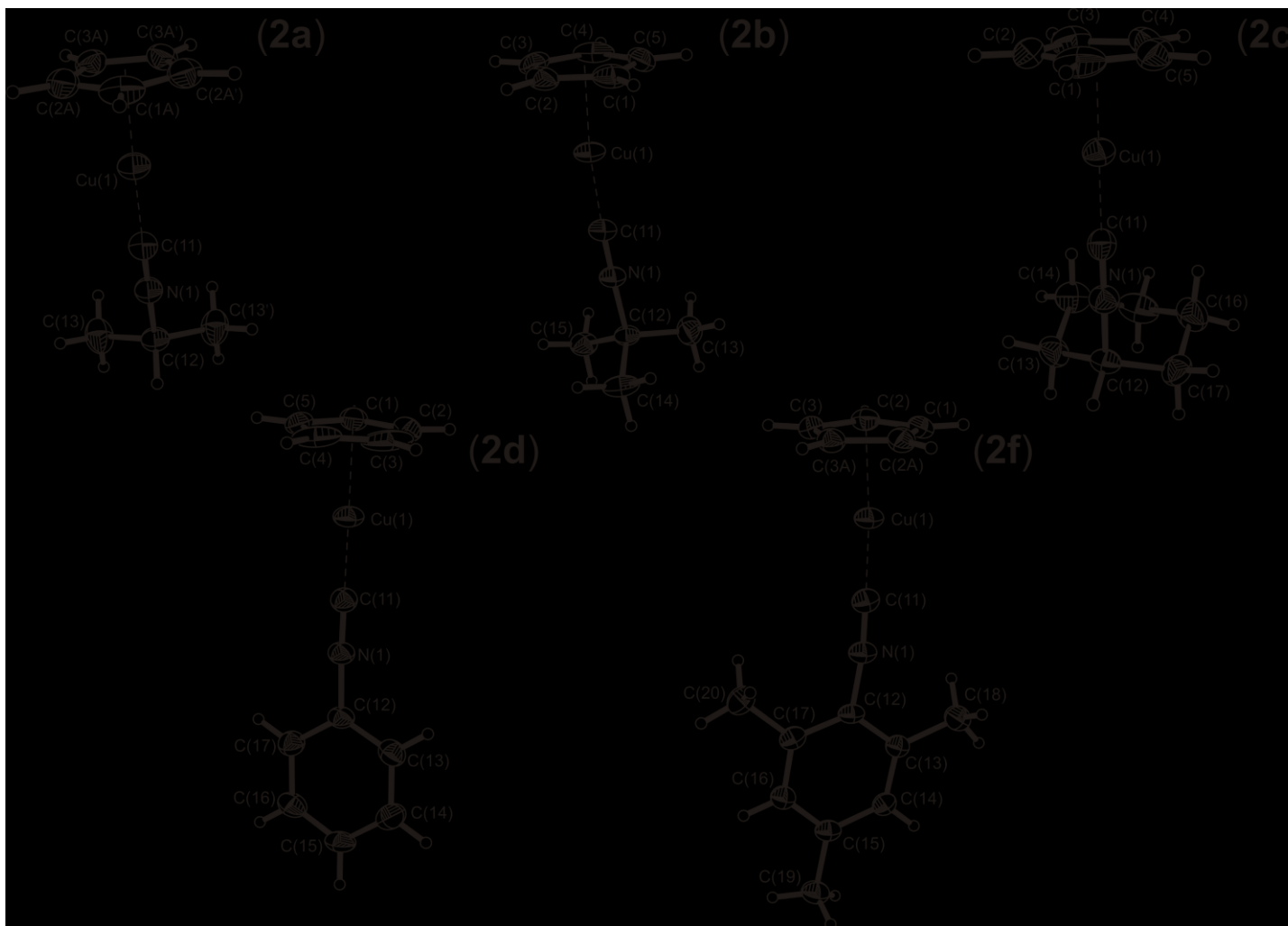


Figure 2: Diagram showing the molecular structures of the complexes **2a-d** and **2f** (50% probability ellipsoids). Symmetry transformations used to generate equivalent atoms in **2a**: $x, -y+3/2, z$; **2f**: $-x+1/2, y, z$.

Table 1: Selected bond lengths and angles for **2a-d** and **2f**.

	2a	2b	2c	2d	2f
Cu(1)-C(11)	1.816(2) Å	1.815(2) Å	1.810(2) Å	1.798(3) Å	1.805(3) Å
Cu(1)-Cp _{cent}	1.833(5) Å	1.849(3) Å	1.846(4) Å	1.843(4) Å	1.852(3) Å
Ave Cu-C _{cp}	2.1846 Å	2.198 Å	2.196 Å	2.194 Å	2.209 Å
Ave C-C _{cp}	1.398 Å	1.398 Å	1.399 Å	1.399 Å	1.415 Å
Cp _{cent} -Cu(1)-C(11)	168.69(22) °	173.06(22) °	173.24(20) °	176.15(19) °	175.70(19) °
Cu(1)-C(11)-N(1)	174.40(18) °	177.48(19) °	176.11(19) °	176.9(3) °	178.9(3) °
C(11)-N(1)-C(12)	175.34(19) °	177.22(19) °	174.0(2) °	176.4(3) °	172.6(3) °

It is also noteworthy that complexes **2a-d** and **2f** are scarce examples of structurally characterized Cu-Cp systems with the general form $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu-L}]$ (L = 2e- donor ligand).

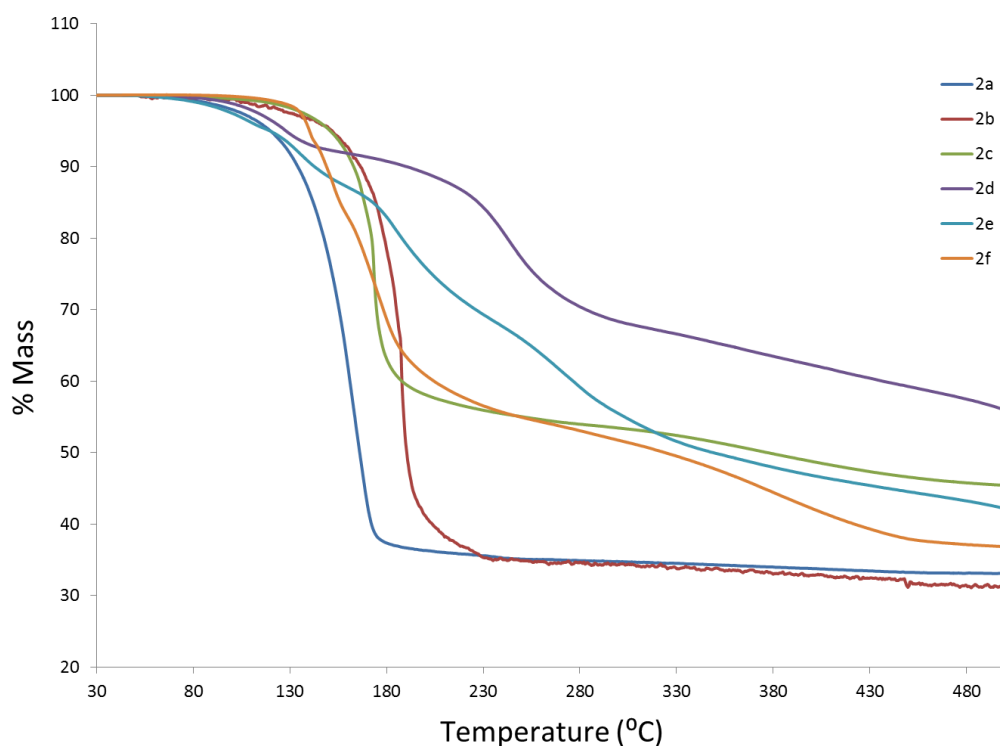


Figure 3: Thermogravimetric analysis traces of **2a-f** from 30 to 500 °C. Experiments were run under N₂ (50 mL/min) at a ramp rate of 20 °C/min.

Table 2: Expected % residue, % of non-volatile residue and onset of volatilisation/decomposition temperature for **2a-f**.

Precursor	Expected % for Cu	% Non-volatile Residue (Temp.)	Onset Temp. [§]
2a	32.1%	36.0% (200 °C)	100 °C
2b	30.0%	34.8% (280 °C)	121 °C
2c	26.7%	45.4% (500 °C) †	119 °C
2d	27.4%	55.9% (500 °C) †	98 °C
2e	24.5%	42.2% (500 °C) †	82 °C
2f	23.2%	36.8% (500 °C)	125 °C

[§] The temperature at which 1% mass loss has occurred. † % weight at 500 °C (stable residue not achieved).

Thermogravimetric analyses (TGA) of complexes **2a-f** are shown in Figure 3. Of the compounds analyzed only **2a-b** and **2f** were found to produce stable residues below 500°C. Compounds **2a-b** were found to undergo mass loss to yield stable residues of 36.0% and 34.8% respectively, which are slightly higher than the expected values for copper metal from each respective complex (Table 2), indicating a significant degree of incomplete decomposition or incorporation of carbon into the residue. While **2a-b** have single step decomposition pathways, **2c-f** display multistep decomposition pathways. For complexes **2c-e** stable residues were not achieved even at 600 °C. Of the complexes investigated complexes **2a** and **2b** show the greatest promise as potential copper metal precursors with **2b** showing a higher degree of thermal stability.

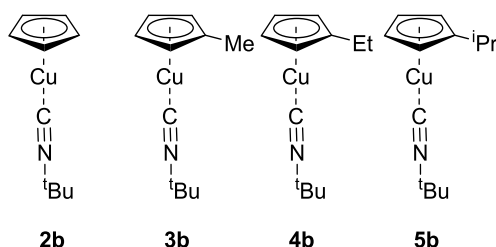


Chart 2:

In an effort to ascertain the effect of derivatizing the cyclopentadienyl moiety on features such as stability, volatility and decomposition, a series of complexes were produced (Chart 2) in which the

isocyanide moiety was kept the same (*i.e.* CN^tBu) and the substituent group on the cyclopentadienyl group was modified.

Complexes **3b**, **4b** and **5b** were synthesized using a modification of the preparative method used for **2b**. In these cases analytically pure samples were obtained from either recrystallization from hexane (**4b**) or sublimation at reduced pressure (**3b** and **5b**).

The ¹H NMR spectra for the complexes **3-5b** each contain an unresolvable multiplet resonance between $\delta = 5.70 - 5.73$ ppm for the C₅H₄-R hydrogen protons, which correlate to resonances between $\delta = 91.69 - 92.17$, $92.62 - 95.38$ and $109.86 - 124.42$ ppm, for the three equivalent carbon atoms in the { η^5 -C₅H₄-R} rings in the ¹³C NMR spectra. Analysis of the ¹H and ¹³C NMR spectra for these complexes show very little change in the resonances associated with the ^tBuNC ligand, compared to both **1b** and **2b**. As with complexes **2a-f**, the CN resonances are not observed in the ¹³C NMR spectra.

For **3b** and **4b** crystals suitable for single crystal X-ray diffraction studies were obtained, the molecular structures of which are shown in Figure 4, with selected bond lengths and angles shown in Table 3.

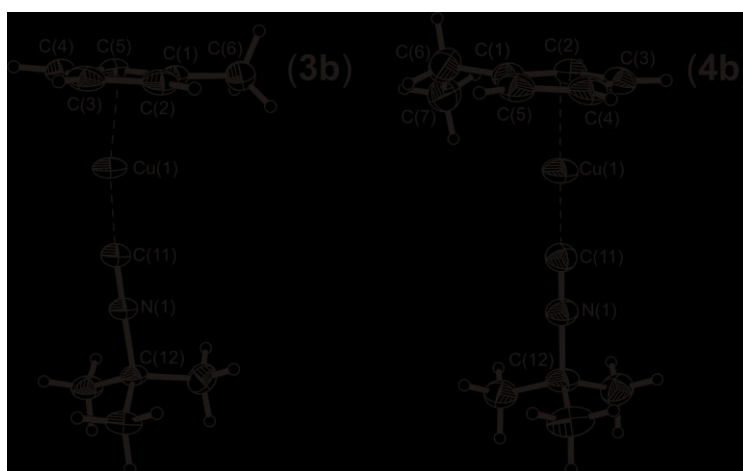


Figure 4: Diagram showing the molecular structures of the methyl- and ethyl-cyclopentadienyl copper (*tert*-butyl isocyanide) complexes **3b** and **4b** (50% probability ellipsoids).

Table 3: Selected bond lengths and angles for **2a-d** and **2f**.

	3b	4b
Cu(1)-C(11)	1.810(2)	1.809(2) Å
Cu(1)-Cp _{cent}	1.850(4)	1.845(5) Å
Cp _{cent} -Cu(1)-C(11)	169.86(17)	175.87(16) °
Cu(1)-C(11)-N(1)	175.74(16)	178.1(2) °

While there is little obvious effect on the metrical data when the molecular structures of **2b**, **3b** and **4b** are compared, there is an obvious increase in reactivity of the complexes as the Cp-substituent changes from H-Cp < Me-Cp < Et-Cp < ⁱPr-Cp with the general sensitivity of these systems increasing throughout the series, which correlates with the steric bulk of the Cp ligands. What is most obvious from Figure 4 is the variation in the Cp_{cent}-Cu-C(11) angle, which again is thought to be a consequence of packing forces.

Thermogravimetric analysis (TGA) traces of complexes **2-5b** are shown in Figure 5, the most striking feature of which appears in the TGA trace of complex **3b**; showing a very clear, and distinct, two step decomposition pathway with an initial onset of mass loss of 33.8% (to 66.2%) between 107-114 °C, followed by a further mass loss of 44.5% (down to 21.7%) between 130-218 °C. With a residual % mass of 21.7% at 218 °C (which is lower than the expected residual mass for pure copper) complex **2b** appears to possess a small degree of volatility.

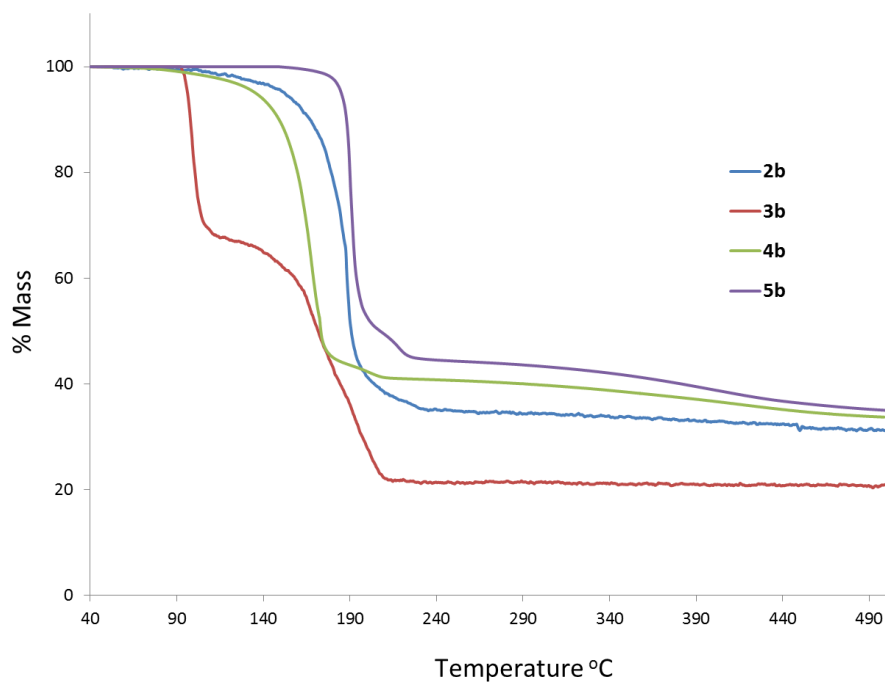


Figure 5: Thermogravimetric analysis traces of **2-5b** from 40 to 500 °C. Experiments were run under N₂ (50 mL/min) at a ramp rate of 20 °C/min.

Table 4: Expected % residue, % of non-volatile residue and onset of volatilization/decomposition temperature for **2-5b**.

Precursor	Expected % for Cu	% Non-volatile Residue (Temp.)	Onset Temp. [§]	mp / Subl. pt.
2b	30.0%	34.8% (280 °C)	121 °C	95 °C / 40 °C 0.1Torr
3b	28.1%	21.7% (218 °C)	107 °C	dec./70 °C 0.1Torr
4b	26.5%	33.6% (500 °C)†	90 °C	dec./ 80 °C 0.1Torr
5b	25.0%	34.9% (500 °C)†	171 °C	dec./ 80 °C 0.1Torr

[§] The temperature at which 1% mass loss has occurred. † % weight at 500 °C (stable residue not achieved).

Despite a clear two-step decomposition process for **3b**, assignment of each thermal event, (Cp-Me vs CN^tBu loss) has not been possible because of the volatility of this complex, making assignment of the thermal events problematic. However, works by others has suggested loss of the neutral donor ligand (in this case CN^tBu) occurs initially to form {CuCp} species.^{2d,35} Furthermore, such a chemisorption mechanism is consistent with related studies by Coyle *et al.* who have shown that

carbene stabilized Cu(I) silylamide precursors work most efficiently at elevated temperatures (>170 °C) in order to provide sufficient energy to break the C-carbene bond, or in our case the Cu-isocyanide bond, to form surface chemisorbed Cu(I) species which then react with hydrogen coreagent.^{3m,3n}

For **4b** and **5b** mass loss continued up to, and beyond, 500 °C and in both cases the % mass residue at 500 °C was greater than that expected for the formation of copper metal.

As part of our study, vapor pressure measurements were carried out on **2-5b** using a previously reported method and apparatus.³⁶ Details of these analyses are supplied in the supporting information. The results of the vapor pressure measurements of **2-5b** are depicted in Figure 6 and the numerical results shown in Table 5. Each set of data was obtained at temperatures below the melting points of the precursors. The vapor pressures of **2-5b** obey the general equation $\log P = A - B/T$; where A and B are free parameters, with the corresponding enthalpy of vaporization or sublimation being deduced from the parameter B (Table 5).³⁷

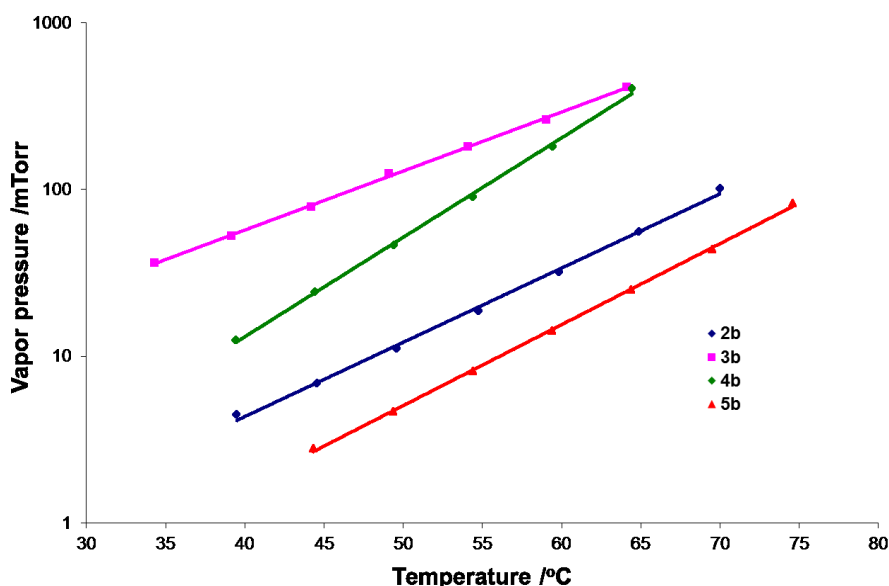


Figure 6: Vapor pressure measurements of **2-5b**.

Table 5: Vapor pressure data for the copper metal precursors **2-5b**. Data are fitted to $\log P$ (mTorr) = $A - (1000 \cdot B)/(T/K)$. Error margins are established by a linear regression method and given at the 95% confidence interval.

Precursor	A	$B \times 10^{-3}$	ΔH_{sub} [kJ mol ⁻¹]	Temp. range of measurement [°C]	Calc. vapor pressure @ 60 °C [mTorr]
2b	15.9 ± 0.5	4.77 ± 0.16	39.7 ± 1.4	35-70	33.76
3b	13.5 ± 0.2	3.67 ± 0.06	30.5 ± 0.5	30-65	290.99
4b	21.2 ± 0.6	6.29 ± 0.19	52.3 ± 1.6	35-65	203.93
5b	17.3 ± 0.4	5.36 ± 0.12	44.6 ± 1.0	40-75	15.48

As can be seen from the calculated vapor pressures of complexes **2-5b** at 60 °C, shown in Table 6, the order of volatility is **3b**>**4b**>>**2b**>**5b**, which is attributed to the difference in cyclopentadienyl substituent such that the order of volatility can be viewed as Me-Cp > Et-Cp > H-Cp > ⁱPr-Cp; in fact comparison of the vapor pressures of **3b** and **4b** at 60 °C with commercially available copper precursors, specifically Cyclopentadienyl(triethylphosphine)copper(I) and CupraSelect™ (200 mTorr and 150 mTorr respectively) shows **3b** and **4b** to be more volatile at these operating temperatures.^{35,38}

Despite the significant effects of the both the methyl- and ethyl- substituents on the volatility of the cyclopentadienyl (tert-butyl isocyanide) copper(I) systems **3b** and **4b**, the stability of complex **4b** was found to be low, and the compound was observed to decompose on standing at room temperature over a period of weeks, producing a black micro-crystalline powder identified as copper metal. More significantly, attempts to synthesize the corresponding methyl and ethyl-cyclopentadienyl (iso-propylisocyanide) copper (I) complexes (**3a** and **4a**) and the methyl-cyclopentadienyl (cyclo-hexyl isocyanide) copper (I) complex (**3c**) in the hope that these compounds would be suitable and possibly liquid precursors were met with mixed results; compound **4a** could not be synthesized and multiple attempts to produce the complex under varied conditions met with the formation of copper metal. Although compounds **3a** and **3c** could be synthesized in adequate

yields, using the methodology outlined previously (Scheme 1), the complexes were only stable for prolonged periods of time under an argon atmosphere at -28 °C, features which inhibited full characterization of the products by elemental analysis and TGA. However, single crystals suitable for X-ray diffraction analysis of both **3a** and **3c** were obtained, and the molecular structures (which are included in the ESI) determined, which show matching features to the complexes already described.

The reduced stability of the methyl cyclopentadienyl derivatives **3a-c** and the ethyl-system **4a** is attributed, in part, to the increased electron donor capacity of the substituted cyclopentadienyl derivatives compared to {C₅H₅}.

Copper Deposition and Thin Film Analysis

The results of structural and thermal studies led us to focus initially on the production of the cyclopentadienyl and methyl-cyclopentadienyl copper derivatives **2a-b** and **3a-b** on multi-gram scales for deposition studies. However, attempts to up-scale the production of systems **3a-b** resulted in significantly lower yielding reactions. Focus was therefore directed to the production of complexes **2a** and **2b**, both of which are stable under inert conditions for weeks to months and could be successfully produced on a 5-10 g scale.

Table 6: The general physical parameters for the low pressure CVD (LP-CVD) of complex **2a-b**.

CVD parameters	2a	2b	2a	2b
Substrate Temperature (°C)	180	180	300	300
Operating pressure (Torr)	40	40	40	40
Carrier Gas	H ₂	H ₂	H ₂	H ₂
Carrier flow rate (L min ⁻¹)	0.3	0.3	0.3	0.3
Bubbler flow rate (L min ⁻¹)	0.3	0.3	0.3	0.3
Temp. of bubbler (°C)	60	60	60	60
Temp. of gas lines (°C)	75	75	75	75
Deposition duration (mins)	60	60	60	60

Copper was initially deposited onto silicon (400) wafers using complex **2a** and **2b** respectively at low pressure (40 Torr) using a cold-walled ElectroGas CVD apparatus. However, because copper has been shown to adhere poorly to Si, Au on silicon was also investigated as a suitable substrate. Copper metal was deposited on both substrates at both 180 °C and 300 °C. In all of the deposition runs the precursor was heated to 60 °C and the carrier gas lines were externally heated to 75 °C. The pressure during deposition was maintained at 40 Torr, using H₂ as the carrier gas at a flow rate of 0.3 L min⁻¹. Typically H₂ is used a reductant for Cu precursors, as it can homolytically dissociate into hydrogen adatoms on clean substrate surfaces.^{1,30a} Table 6 shows the general physical parameters used throughout the deposition experiments. In all cases films deposited using **2a** or **2b** under identical conditions were indistinguishable from each other; for this reason subsequent discussion is limited to films deposited using **2b**.

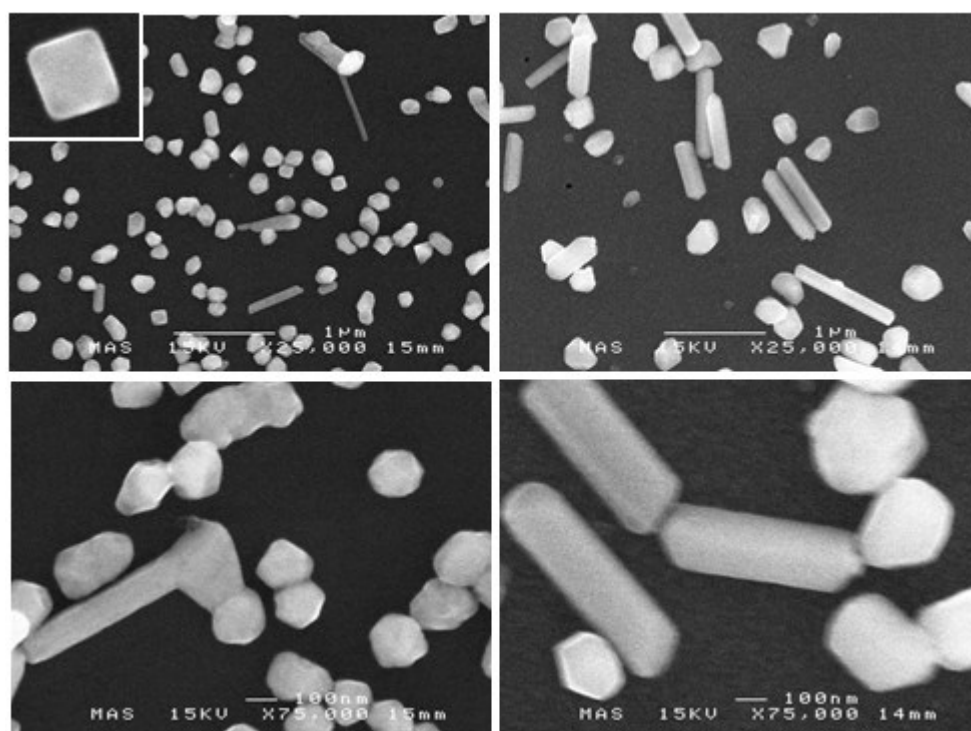


Figure 7: Micrographs of copper films deposited on Au/Si (left) and Si (right) at a substrate temperature of 180 °C.

Films deposited at 180 °C for both precursors appeared silvery-blue in color and discontinuous to the naked eye, a feature which is confirmed by SEM analysis of the films (Figure 7) which reveals the

presence of single crystals of copper metal between 400 nm-1 μm long, dispersed over the surface of the substrates.

In stark contrast those films deposited at 300 °C possessed a metallic luster and appeared continuous on both Si and Au/Si substrates. It should be noted that deposition runs at temperatures below 180 °C failed to provide films with sufficient coverage for analysis, and have not been discussed here; at intermediate temperatures between 180-300 °C LP-CVD copper films were discontinuous and comparable to those grown at 180 °C. Only at 300 °C, and above, were continuous pinhole free films observed.

SEM analysis of films deposited onto Au/Si at 300 °C show the films to be continuous and comprise of uniformly granular shaped particles (Fig. 8) of approximately 200 nm thickness. While films deposited onto Si at 300 °C were somewhat similar, larger particles of material on the film were also present (Fig. 8), likely to be a result of thermal mobility of the copper, leading to particle agglomeration.^{30a}

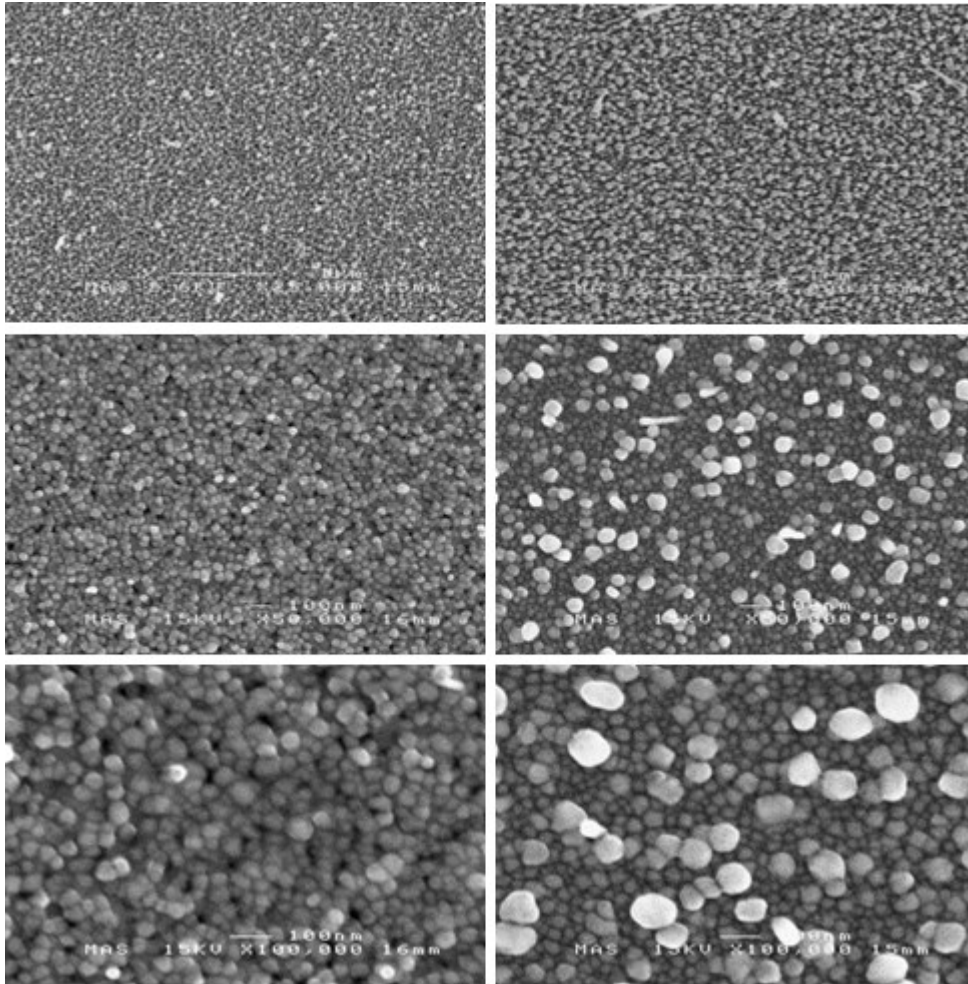


Figure 8: Micrographs of copper films deposited on Au/Si (left) and Si (right) at a substrate temperature of 300 °C.

EDX spectroscopy of all films demonstrated the presence of copper as well as peaks associated with the relevant substrates; an exemplar EDX plot is shown in Figure 9.

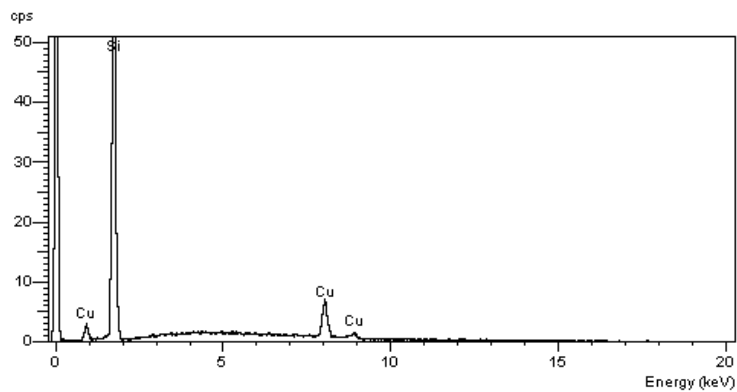


Figure 9: A typical EDX plot of copper films grown on Si (400) wafer from 2a.

XPS analysis of the as-deposited films revealed the presence of significant peaks associated with carbon ($1s = 284\text{eV}$) and oxygen ($1s = 532\text{eV}$) on the surface. The Cu LMM auger ionization energy, which is a clearer indicator of copper oxidation state,³⁹ indicates the presence of Cu_2O on the surface (570.72 eV (Au/Si) and 570.77 eV (Si)) of the deposited materials. However following an argon etch, the Cu LMM peak associated with Cu_2O disappears and is replaced with that associated with metallic copper (567.8 eV (Au/Si) and 567.7 eV (Si)), while peaks associated with carbon and oxygen are reduced. Figure 10 shows a typical example of a copper XPS spectrum. Table 7 shows the elemental profiles of the films after a four minute argon etch, as a function of substrate and deposition temperature. Analysis shows that films deposited from **2a** and **2b** at $300\text{ }^\circ\text{C}$ contain a small amount of oxygen (1.8-3.1 at.%) but significant carbon contamination still remains (14.4-21.5%), which can arise from decomposition of cyclopentadienyl ligand,^{9b,9o} even in the presence of H_2 ⁴⁰ when relatively high deposition temperatures are needed to induce precursor decomposition.

However, if background elements (Si and Au) were removed from the elemental analysis, we find that the films produced are of moderately high purity (71 and 82 at.% of Cu respectively), although still with a significant degree of carbon inclusion. XPS data for films deposited onto Si and Au/Si from complex **2a-b** at $180\text{ }^\circ\text{C}$ are not reported, due to the inability to obtain reliable measurements as a consequence of the significantly reduced surface coverage and larger particle size.

Table 7: Elemental analysis for etched copper films deposited from **2b**

Substrate (Temp. °C)	Atomic %					
	Cu	O	C	Au	Si	Pt
Si (300)	60.39	3.08	21.51	-	14.01	-
Au/Si (300)	74.33	1.81	14.43	9.42	-	-
Pt/Si (180)	54.66	0.33	1.15	-	-	43.86

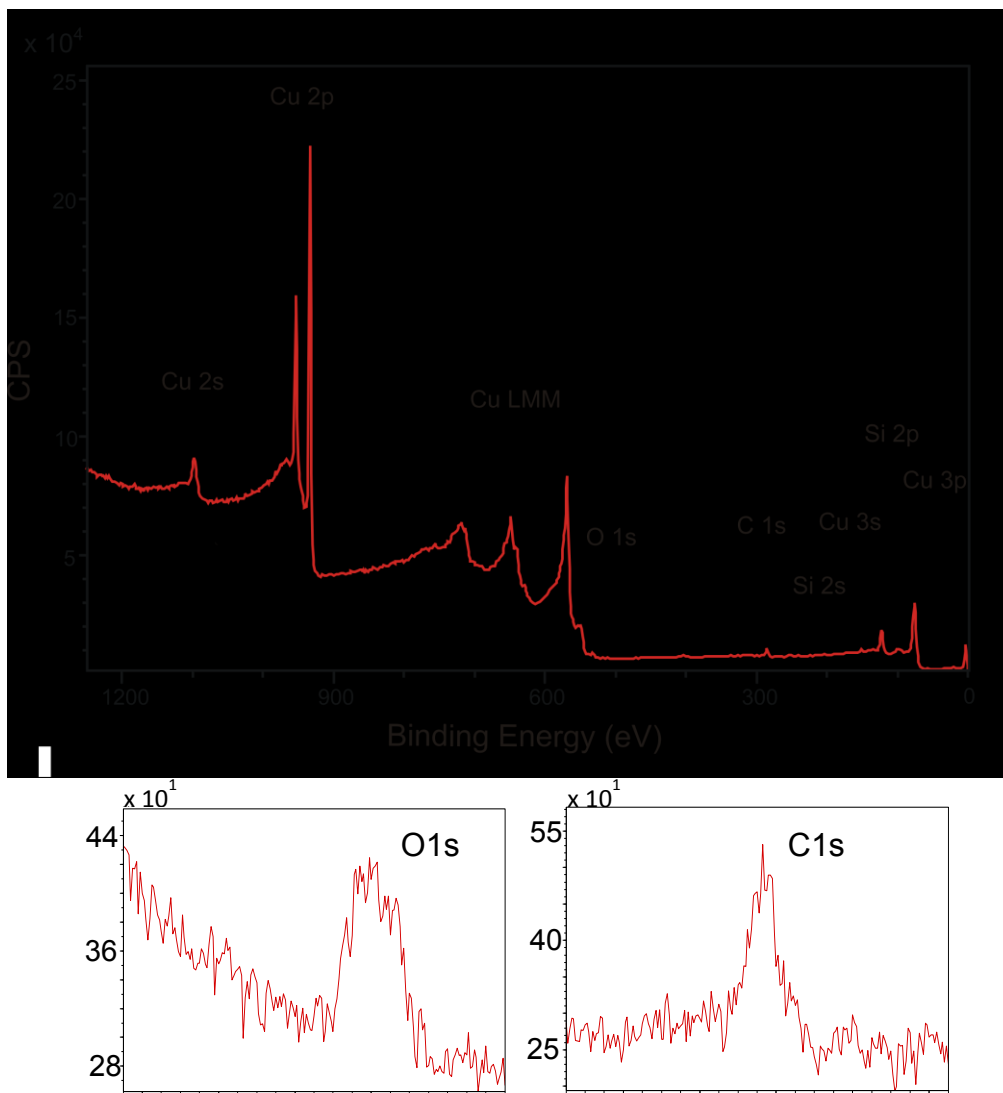


Figure 10: The XPS profile of a film deposited at a substrate temperature of 300°C on Si.

Magnified regions for oxygen (left) and carbon (right) are also shown.

In an attempt to reduce carbon content within the deposited films Pt substrates (Pt coated Si (400) wafers (Pt/Si)), which are also considered to be oxide free, show a high affinity for copper and are typically employed as both strong adhesion and diffusion barrier materials in microelectronics,⁴⁰ were investigated using **2a-b** at deposition temperatures of 180 °C. Pt is also employed as a hydrogenation catalyst and as such shows a high affinity to hydrogen and the production of chemisorbed hydrogen, which we believe is important in the reduction of Cu(I) to Cu metal.

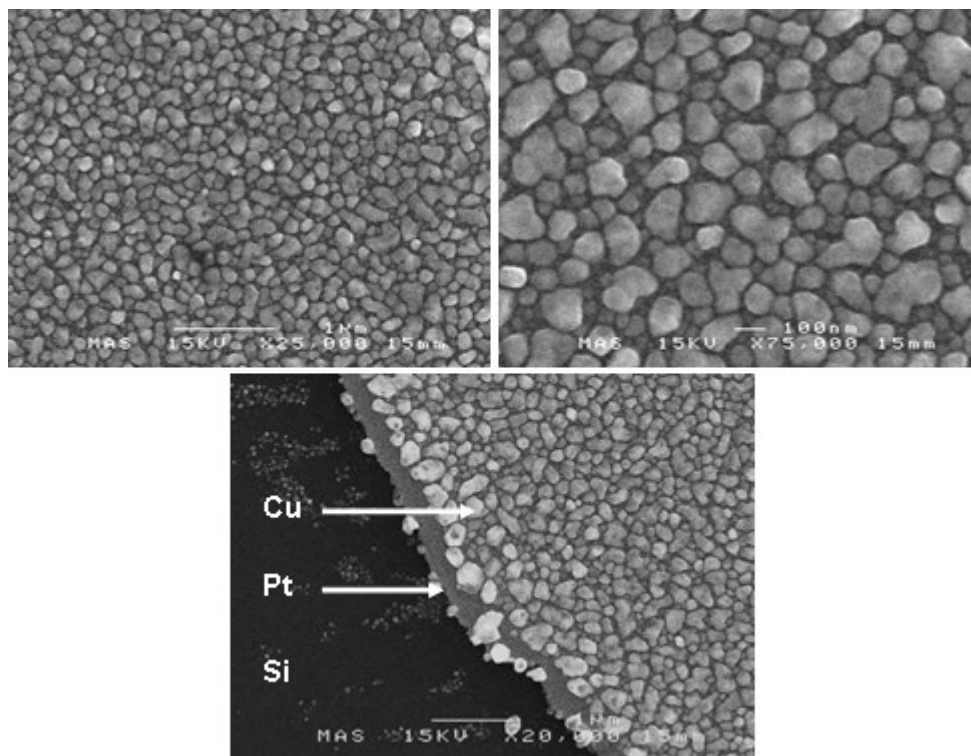


Figure 11: (Top) Electron micrographs of the copper thin films deposited onto a Pt coated Silicon wafer (Pt/Si) at 180 °C using complex **2a**. (Bottom) A micrograph showing the successive layers of silicon, platinum and copper metal.

Using identical protocols to those outlined in Table 6, copper metal was successfully deposited at 180 °C onto Pt/Si, using both **2a** and **2b**; to the naked eye the films displayed a significant metallic luster and appeared pin hole free. EDX (ESI) clearly shows the presence of Cu with no evidence from the EDX of underlying Pt substrate suggesting a hole-free coverage.

Analysis of the films by SEM indeed show the films deposited onto Pt/Si to be continuous and approximately 200nm thick, consisting of layers of microcrystals of copper of approx. 100 μm in diameter which cover the entirety of the Pt/Si substrate.

Subsequent analysis of the films, using XPS (see ESI), shows the presence of Cu₂O on the surface of the deposited materials as indicated by the Cu LMM auger ionization (570.62 eV) and a significant reduction in the carbon content of the film (Table 7); As before, etching of the sample indicates oxygen contamination is localized to the surface of the sample, as indicated by the change in the Cu LMM ionization to that associated with copper metal (567.76 eV).³⁹ Removal of underlying Pt from the analysis suggests that thin copper films with ca. 97% purity are being formed.

It should also be noted that growth of Cu on Pt substrates can result in a partial incorporation of Pt into the growing Cu layer, forming a bilayer alloy at the interface ($\text{Cu}_{50}\text{Pt}_{50}$).⁴¹ However, given an approximate thickness of 200 nm, we see no evidence of this bilayer material in the XPS data.

Powder X-ray diffraction (XRD) analysis (Figure 12) revealed the films to be crystalline showing a reflection at $2\theta = 43.3^\circ$ (highlighted red, Figure 12), which corresponds to the Cu(111) Miller plane and at $2\theta = 50.5^\circ$ which corresponds to the Cu(200) Miller plane; both of which are associated with fcc copper metal. All other reflections are associated with the respective substrates.

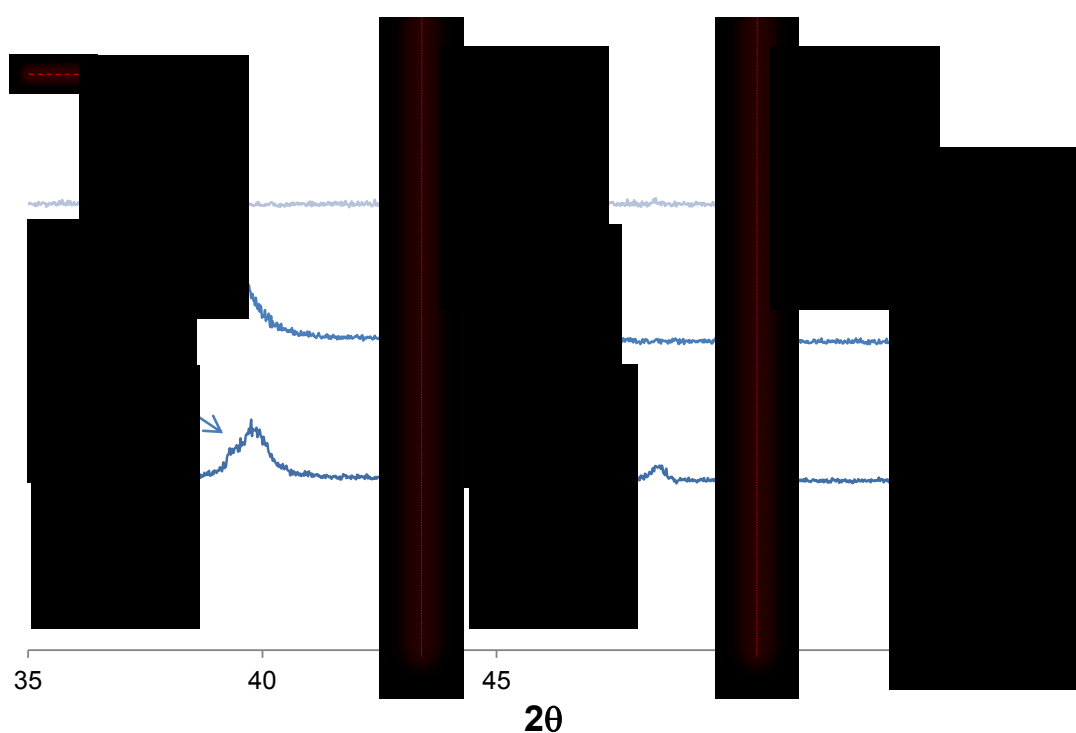


Figure 12: The XRD pattern of continuous copper films deposited onto Si (300 °C), Au/Si (300 °C) and Pt/Si (300 °C) substrates.

Evaluation of Precursor Properties and Thin Films

The copper(I) Cp-complexes, containing aryl substituted isocyanide ligands, **2d-f**, proved to be less than suitable as prospective CVD precursors, with TGA traces showing high residual masses and incomplete decomposition over a wide temperature range (80-500 °C). In contrast, the alkyl

isocyanide derivatives **2a-c** showed significantly more promise with both the isopropyl (**2a**) and tert-butyl derivative (**2b**) displaying a single thermal decomposition event with residual masses close to those expected for a copper only residue. As part of the study the molecular structures of the complexes **2a-d** and **2f** were unambiguously determined in single crystal X-ray diffraction studies and in all cases the complexes display linear pogo-stick like geometries in the solid state.

Comparison of the complexes **3-5b** [$(\eta^5\text{-R}'\text{C}_5\text{H}_4)\text{Cu}(\text{CN}^t\text{Bu})$] (**3b**: R = Me, **4b**: R = Et, **5b** = *i*Pr) and against the parent unsubstituted complex shows that, despite their isostructural natures, there are significant changes in the stability and volatility of the complexes. TGA analysis shows that for all the complexes thermal decomposition results in uncomplicated mass loss processes with residues close to those expected for copper metal. Surprisingly however, the methyl substituted derivative **3b** shows the presence of a two step decomposition process. While our specific interest here is the growth of metal thin films by CVD, complex **3b** may also be useful in the ALD growth of metal thin films by virtue of what appears to be a thermally controlled stepwise decomposition process. The prospective precursors **2-5b** show the order of volatility to be **3b**>**4b**>>**2b**>**5b** as calculated by vapor pressures.

Despite a favorable comparison to these properties against the commercially available precursors Cyclopentadienyl(triethylphosphine)copper(I) and CupraSelect™, the life time of **3b** and **4b**, was low with the products decomposing on standing at room temperature to copper metal.

Subsequent CVD experiments therefore focused on the use of complexes **2a** and **2b**. Thin films were deposited onto Si and Au substrates at 180 °C and 300 °C, under a reduced pressure H₂ atmosphere. Films deposited onto Si and Au substrates at 180 °C were found to consist of a regular array of copper metal nanoclusters (rods), the size of which appears to be dependent on the deposition temperature and is likely to be dependent on the deposition time also. In contrast, at high temperatures films were found to be continuous and of moderately high purity (71 and 82 at.% of Cu respectively) as shown by XPS. Contrastingly, films deposited onto Pt substrates at 180 °C were found to be continuous, with *ca.* 97% purity and with significantly less carbon and oxygen

contamination. Significantly, complex **2b** represents a precursor capable of depositing continuous copper metal films onto Pt substrates at low temperatures (<200 °C). Studies into the utility of complexes **2a-b** in Plasma enhanced-ALD of copper thin films are presently underway and will be reported separately.

Experimental Section

General Procedures:

All reactions were carried out under an inert atmosphere, and in the absence of light, using standard Schlenk techniques. Solvents were dried over activated alumina columns using an Innovative Technology solvent purification system (SPS) and degassed under an argon atmosphere. All other reagents were purchased from commercial sources.

The aryl isocyanides PhNC, MesNC and XylNC were prepared using a literature procedure.⁴² The alkyl isocyanides ^tPrNC, ^tBuNC and CyNC were bought from commercial sources and used without further purification. The salts NaCp, NaMeCp, NaEtCp and Na^tPrCp were all prepared according to a modified literature procedure.⁴³

Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, UK. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz FT-NMR spectrometer, as saturated solutions in CDCl₃; chemical shifts are quoted in units of ppm, relative to Me₄Si (¹H, ¹³C); coupling constants are in Hz.

Thermogravimetric analysis (TGA) of the complexes was performed at SAFC Hitech, Bromborough, UK, using a Shimadzu TGA-51 Thermogravimetric Analyzer. Data points were collected every second at a ramp rate of 20 °C min⁻¹ in a flowing (50 mL min⁻¹) N₂ stream.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra-DLD photoelectron spectrometer, utilizing monochromatic Al K α radiation (photon energy 1486.6 eV), at the University of Cardiff. Spectra were calibrated to the C(2p) peak. Samples were sputtered for a pre-determined set time over a 4 mm wide area using 4 kV argon ions using a minibeam I ion

source. Spectra were collected at pass energies of 80 and 160 eV for high resolution and survey scans respectively, with the 100 μm aperture in place to focus on the centre of the etch pit.

FESEM analysis of the films was undertaken on a JEOL JSM-6480LV scanning electron microscope with EDX capability.

Powder XRD of the films was performed on a Bruker D8 Powder Diffract meter, using a Cu anode X-ray source, ($K\alpha$ wavelength = 1.5406 \AA) at the University of Bath.

Synthesis of $[\text{ClCu}(\text{CN}^i\text{Pr})_4]$ (**1a**).

Under an inert atmosphere of argon gas, copper(I) chloride (4.95 g, 50.0 mmol) was placed in a dry Schlenk, followed by THF (50 ml) to give a yellow slurry. To this, $^i\text{PrNC}$ (4.55 ml, 50.0 mmol) was added via syringe. The reaction mixture was left to stir for 30 minutes, followed by cannula filtration to remove unreacted copper(I) chloride. The volatiles were removed *in vacuo* and the resulting off-yellow crude product was purified by recrystallization from THF to afford $[\text{ClCu}(\text{CN}^i\text{Pr})_4]$ as pale yellow crystals (7.46 g, 89 %). ^1H NMR (CDCl_3 , 300.22 MHz) δ : 1.38 (d, $\text{CH}(\underline{\text{C}}\text{H}_3)_2$, 6H, $J = 6.64$ Hz), 6.64 (sept, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$, 1H, $J = 6.64$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.50 MHz) δ : 22.59 ($\text{CH}(\underline{\text{C}}\text{H}_3)_2$), 47.33 (t, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$, $J = 5.50$ Hz), 136.60 (t, $\underline{\text{C}}\text{N}$, $J = 15.29$ Hz) Anal. Calc for $\text{C}_{16}\text{H}_{28}\text{Cl}_4\text{Cu}_4\text{N}_4$: C, 28.58, H, 4.20, N, 8.33, found: C, 31.59, H, 4.70, N, 7.61%.

Synthesis of $[\text{ClCu}(\text{CN}^t\text{Bu})_4]$ (**1b**).

$[\text{ClCu}(\text{CN}^t\text{Bu})_4]$ was synthesized in an analogous manner to $[\text{ClCu}(\text{CN}^i\text{Pr})_4]$ using 4.26g (43.0 mmol) of CuCl and 4.84 ml (43.0 mmol) of $^t\text{BuNC}$ to yield $[\text{ClCu}(\text{CN}^t\text{Bu})_4]$ as colorless crystals (5.58 g, 71 %). ^1H NMR (CDCl_3 , 300.22 MHz) δ : 1.46 (s, $\text{C}(\underline{\text{C}}\text{H}_3)_3$, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.50 MHz) δ : 30.05 ($\text{C}(\underline{\text{C}}\text{H}_3)_3$), 56.50 ($\underline{\text{C}}(\text{CH}_3)_3$), 134.62 (t, $\underline{\text{C}}\text{N}$, $J = 15.75$ Hz). Anal. Calc for $\text{C}_{20}\text{H}_{36}\text{Cl}_4\text{Cu}_4\text{N}_4$: C, 32.97, H, 4.98, N, 7.69, found: C, 33.40, H, 5.03, N, 7.73%.

Synthesis of [ClCu(CNCy)]₄ (1c).

[ClCu(CNCy)]₄ was synthesized in an analogous manner to [ClCu(CN^{*i*}Pr)] using 1.98g (20.0 mmol) of CuCl and 2.49 ml (20.0 mmol) of CyNC to yield [ClCu(CNCy)]₄ as colorless crystals (2.35 g, 56 %). ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.42 (br m, CH₂, 16H), 1.71 (br m, CH₂, 16H), 1.89 (br m, CH₂, 8H), 3.72 (br m, CH, 4H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 22.71, 24.70, 31.92 (CH₂), 53.39 (t, CH, J = 5.61 Hz), CN carbon not observed. Anal. Calc for C₂₈H₄₄Cl₄Cu₄N₄: C, 40.39, H, 5.32, N, 6.72, found: C, 41.43, H, 5.12, N, 6.76%.

The complexes [ClCu(CNPh)₂]₂, [ClCu(CNXyl)₂]₂ and [ClCu(CNMes)₂]₂ were all synthesized in an analogous fashion. The synthesis of [ClCu(CNPh)₂]₂ is given as an example.

Synthesis of [ClCu(CNPh)₂]₂ (1d).

Under an inert atmosphere of argon gas, copper(I) chloride (0.990 g, 10.0 mmol) was placed in a dry Schlenk, followed by THF (25 ml) to give a yellow slurry. To this, PhNC (2.06 g, 20.0 mmol) was added via syringe. The reaction mixture was left to stir for 30 minutes, followed by cannula filtration to remove unreacted copper(I) chloride. The volatiles were removed *in vacuo* and the resulting off-white crude product was purified by recrystallization from THF to afford [ClCu(CNPh)₂]₂ as colorless crystals (2.69 g, 88 %). ¹H NMR (CDCl₃, 300.22 MHz) δ: 7.44 (br m, CH, 20H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 126.13, 126.46, 129.51, 130.08, (C₆H₅), 145.50 (m, CN). Anal. Calc for C₂₈H₂₀Cl₂Cu₂N₄: C, 55.09, H, 3.30, N, 9.18, found: C, 54.82, H, 3.28, N, 9.17%.

Synthesis of [ClCu(CNXyl)₂]₂ (1e).

[ClCu(CNXyl)₂]₂ was synthesized using 1.13 g (11.4 mmol) of CuCl and 3.00g of XylNC (22.8 mmol) to yield the product as colorless crystals (3.02 g, 73 %). ¹H NMR (CDCl₃, 300.22 MHz) δ: 2.42 (s, *ortho*-CCH₃, 24H), 7.08 (m, *meta*-CH, 8H), 7.20 (m, *para*-CH, 4H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 18.62 (*ortho*-CCH₃), 125.81, 127.75, 129.28, 135.23 (C₆H₃), 150.62 (broad

multiplet, $\underline{\text{CN}}$). Anal. Calc for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{Cu}_2\text{N}_4$: C, 59.83, H, 5.02, N, 7.75, found: C, 59.73, H, 5.00, N, 7.67%.

Synthesis of $[\text{ClCu}(\text{MesNC})]$ (1f).

$[\text{ClCu}(\text{CNMes})_2]_2$ was synthesized using 2.47 g (25.0 mmol) of CuCl and 7.26 ml of MesNC (50.0 mmol) to yield the product as colorless crystals (7.20 g, 74 %). ^1H NMR (CDCl_3 , 300.22 MHz) δ : 2.27 (s, *para*- CCH_3 , 12H), 2.37 (s, *ortho*- CCH_3 , 24H), 6.88 (s, *meta*- CH , 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.50 MHz) δ : 18.68 (*ortho*- CCH_3), 21.24 (*para*- CCH_3), 123.78, 128.63, 135.25, 139.84 (C_6H_2), 148.21 (m, $\underline{\text{CN}}$). Anal. Calc for $\text{C}_{40}\text{H}_{44}\text{Cl}_2\text{Cu}_2\text{N}_4$: C, 49.18, H, 4.54, N, 5.74, found: C, 49.09, H, 4.54, N, 5.71%.

Synthesis of $[(\text{Cp})\text{Cu}(\text{CN}^i\text{Pr})]$ (2a).

$[\text{ClCu}(\text{CN}^i\text{Pr})]_4$ (2.02 g, 3.00 mmol) was added to a dry Schlenk tube under an inert atmosphere of argon, followed by THF (80 ml). The solution was then cooled ($-78\text{ }^\circ\text{C}$) and sodium cyclopentadienide (1.06 g, 12.0 mmol) in 40 ml of THF was added. The mixture was left to stir for 16 hours and after this time the volatiles were removed under reduced pressure. Hexane (20 ml) was added to the resultant residue, which was left to stir for 15 minutes and the volatiles then removed under reduced pressure. The process was repeated on two further occasions to remove any residual THF. Further hexane (80 ml) was added and the slurry was filtered through Celite[®] to remove any insoluble materials, followed by removal of the volatiles *in vacuo*. The crude product was purified by recrystallization (hexane) to afford $[(\text{Cp})\text{Cu}(\text{CN}^i\text{Pr})]$ as pale yellow crystals (1.24 g, 52 %, mp. $73\text{ }^\circ\text{C}$). ^1H NMR (CDCl_3 , 300.22 MHz) δ : 1.35 (dt, $\text{CH}(\underline{\text{C}}\text{H}_3)_2$, 6H, $J = 6.60$, $J = 2.39$), 3.81 (m, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$, 1H), 5.89 (s, C_5H_5 , 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.50 MHz) δ : 22.78 ($\text{CH}(\underline{\text{C}}\text{H}_3)_2$), 47.84 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 94.62 ($\underline{\text{C}}_5\text{H}_5$), No $\underline{\text{CN}}$ carbon observed. Anal. Calc for $\text{C}_9\text{H}_{12}\text{Cu}_1\text{N}_1$: C, 54.67, H, 6.12, N, 7.08, found: C, 54.60, H, 5.95, N, 7.13%.

Synthesis of [(Cp)Cu(CN^tBu)] (2b).

[(Cp)Cu(CN^tBu)] was synthesized in an analogous fashion to **2a**, using [ClCu(CN^tBu)]₄ (14.57 g, 20 mmol) and sodium cyclopentadienide (7.05 g, 80.0 mmol). The dried crude product was further purified by sublimation (1 x 10⁻¹ torr, 40-50 °C) to afford [CpCu(CN^tBu)] as off-white crystals (mp. 95 °C) (15.25 g, 90 %). ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.41 (s, C(CH₃)₃, 9H); 5.90 (s, C₅H₅, 5H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 30.13 (C(CH₃)₃); 56.96 (C(CH₃)₃); 94.70 (C₅H₅). CN carbon not observed. Anal. Calc for C₁₁H₁₇CuN: C, 56.86, H, 6.69, N, 6.64%, found: C, 56.70, H, 6.68, N, 6.57%.

Synthesis of [CpCu(CNCy)] (2c).

[CpCu(CNCy)] was synthesized in an analogous fashion to **2a**, using [ClCu(CNCy)]₄ (1.67 g, 2.00 mmol) and sodium cyclopentadienide (0.70 g, 8.00 mmol). The dark brown crude product was purified by recrystallization (hexane) to afford [CpCu(CNCy)] as white crystals (0.70 g, 37 %, mp. 118 °C). ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.36 (m, CH₂, 4H), 1.65 (m, CH₂, 4H), 1.84 (m, CH₂, 2H), 3.63 (m, CH, 1H), 5.93 (s, C₅H₅, 5H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 22.75, 24.72, 31.10 (CH₂), 53.72 (t, CH, J = 6.43 Hz), 94.64 (C₅H₅), No CN carbon observed. Anal. Calc for C₁₂H₁₆CuN: C, 60.61, H, 6.78, N, 5.89, found: C, 60.78, H, 6.67, N, 5.97%.

Synthesis of [(MeCp)Cu(CNⁱPr)] (3a).

[(MeCp)Cu(CNⁱPr)] was synthesized in an analogous fashion to **2a** using [ClCu(CNⁱPr)]₄ (1.34 g, 2.00 mmol) and sodium methyl cyclopentadienide (0.82 g, 8.00 mmol). The dark brown crude product was purified by recrystallization (hexane) to afford [(MeCp)Cu(CNⁱPr)] as white crystals (1.14 g, 67 %, mp. 46 °C). ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.36 (doublets of triplets, CH(CH₃)₂, 6H, J = 6.56 Hz, J = 2.3 Hz), 2.24 (s, C₅H₄CH₃, 3H), 3.81 (septet of triplets, CH(CH₃)₂, 1H, J = 1.75

Hz, $J = 6.56$ Hz), 5.70 (m, $C_5H_4CH_3$, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz) δ : 14.44 ($C_5H_4\text{C}H_3$), 22.76 ($CH(\text{C}H_3)_2$), 47.79 ($\text{C}H(\text{C}H_3)_2$), 92.15, 95.38, 109.90 ($C_5H_4CH_3$), No $\text{C}N$ carbon observed. The complex was too unstable to characterize by elemental analysis.

Synthesis of [(MeCp)Cu(CN^tBu)] (3b).

[(MeCp)Cu(CN^tBu)] was synthesized in an analogous fashion to **2a**, using 7.29 g (10 mmol) of $[ClCu(CN^tBu)]_4$ and 4.12 g (40 mmol) sodium methyl-cyclopentadienide. Sublimation (1×10^{-1} torr, 70 °C) of the crude product afforded [(MeCp)Cu(CN^tBu)] as off-yellow crystals (7.96 g, 88 %). 1H NMR ($CDCl_3$, 300.22 MHz) δ : 1.42 (t, $C(\text{C}H_3)_3$, 9H, $J = 2.13$ Hz); 2.24 (s, $C_5H_4\text{C}H_3$, 3H); 5.70 (m, $C_5H_4CH_3$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz) δ : 14.44 ($C_5H_4\text{C}H_3$); 30.09 ($C(\text{C}H_3)_3$); 56.65 ($\text{C}(\text{C}H_3)_3$); 92.17, 95.38, 109.86 ($C_5H_4CH_3$). $\text{C}N$ carbon not observed. Anal. Calc for $C_{12}H_{19}CuN$: C, 58.65, H, 7.14, N, 6.22%, found: C, 58.00, H, 7.14, N, 6.32%.

Synthesis of [MeCpCu(CNCy)] (3c).

[(MeCp)Cu(CNCy)] was synthesized in an analogous fashion to **2a** using $[ClCu(CNCy)]_4$ (0.83 g, 1 mmol) and sodium methylcyclopentadienyl (0.35 g, 4 mmol). The crude dark brown solid was purified by recrystallization (hexane) to afford [(MeCp)Cu(CNCy)] as colorless crystals (0.40 g, 40 %, mp. 111 °C). 1H NMR ($CDCl_3$, 300.22 MHz) δ : 1.38 (m, $\text{C}H_2$, 4H), 1.68 (m, $\text{C}H_2$, 4H), 1.87 (m, $\text{C}H_2$, 2H), 2.24 (s, $C_5H_4\text{C}H_3$, 3H), 3.64 (m, $\text{C}H$, 1H), 5.71 (m, $C_5H_4CH_3$, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz) δ : 14.46 ($C_5H_4\text{C}H_3$), 22.75, 24.70, 32.02 ($\text{C}H_2$), 53.60 (m, $\text{C}H$, 1C), 92.14, 95.41, 109.95 ($C_5H_5CH_3$), No $\text{C}N$ carbon observed. The complex was too unstable to characterize by elemental analysis.

Synthesis of [EtCpCu(CN^tBu)] (4b).

[(EtCp)Cu(CN^tBu)] was synthesized in an analogous fashion to **2a**, using $[ClCu(CN^tBu)]_4$ (1.25 g, 1.72 mmol) and sodium ethyl-cyclopentadienide (1.03 M in THF, 7.8 ml, 8.00 mmol). The crude

product that was purified by recrystallization (hexane) to afford [(EtCp)Cu(CN^tBu)] as colorless crystals (1.20 g, 73 %). Sublimation (1 x 10⁻¹ torr, 70 °C) was also used to produce pure materials. ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.21 (t, C₅H₄CH₂CH₃, 3H, J³ = 7.56 Hz); 1.43 (s, C(CH₃)₃, 9H) 2.54 (q, C₅H₄CH₂CH₃, 2H, J³ = 7.56 Hz); 5.72 (m, C₅H₄CH₂CH₃, 4H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 17.87 (C₅H₄CH₂CH₃); 22.18 (C₅H₄CH₂CH₃); 30.29 (C(CH₃)₃); 56.92 (C(CH₃)₃); 92.02, 93.84, 118.58 (C₅H₄CH₂CH₃). CN carbon not observed. Anal. Calc for C₁₃H₂₁CuN: C, 60.23, H, 7.59, N, 5.86, found: C, 60.14, H, 7.34, N, 5.91%.

Synthesis of [(ⁱPrCp)Cu(CN^tBu)] (5b).

[(ⁱPrCp)Cu(CN^tBu)] was synthesized in an analogous fashion to **2a**, using [ClCu(CN^tBu)]₄ (0.51 g, 2.00 mmol) and sodium isopropyl cyclopentadienide (1.05 M in THF, 8.86 ml, 9.30 mmol) added. The crude product was purified by recrystallization (hexane) followed by sublimation (1 x 10⁻¹ torr, 80 °C) to afford [(ⁱPrCp)Cu(CN^tBu)] as colorless crystals (1.42 g, 70 %). ¹H NMR (CDCl₃, 300.22 MHz) δ: 1.23 (m, C₅H₄CH(CH₃)₂, 6H), 1.42 (s, C(CH₃)₃, 9H), 2.85 (sept, C₅H₄CH(CH₃)₂, 1H, J³ = 6.80 Hz), 5.73 (m, C₅H₄CH(CH₃)₂, 4H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 25.77, 27.69 (C₅H₄CH(CH₃)₂); 30.27 (C(CH₃)₃); 56.84 (C(CH₃)₃); 91.69, 92.62, 124.42 (C₅H₄CH(CH₃)₂). CN carbon not observed. Anal. Calc for C₁₃H₂₀CuN: C, 61.61, H, 7.94, N, 5.52, found C, 61.49, H, 7.72, N, 5.57%.

Synthesis of [(Cp)Cu(CNPh)] (3d).

[ClCu(CNPh)]₂ (3.66 g, 6.00 mmol) and sodium cyclopentadienyl (1.06 g, 12.0 mmol) were added to separate dry Schlenks under inert atmospheres of argon. THF (15 ml) was added to each, and the sodium cyclopentadienyl solution was transferred into the [ClCu(CNPh)]₂ solution via cannula. The mixture was then left to stir for 16 hours. The volatiles were removed under reduced pressure and dry hexane (20 ml) was added to the resultant residue. This was left to stir for 15 minutes and the

volatiles then removed under reduced pressure. The process was repeated on two further occasions to remove any residual THF. Further hexane (20 ml) was added and the slurry was filtered through Celite[®] to remove any insoluble materials, followed by removal of the volatiles *in vacuo*. This resulted in a dark yellow crude solid that was purified by recrystallization (hexane) to afford [(Cp)Cu(PhNC)] as yellow crystals (0.990 g, 35 %, mp. 76 °C). ¹H NMR (CDCl₃, 300.22 MHz) δ: 5.95, (s, C₅H₅, 5H), 7.45-7.28 (m, C₆H₅, 5H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 94.82 (C₅H₅), 121.74, 126.43, 129.61, 129.82 (C₆H₅). No CN carbon observed. Anal. Calc for C₁₂H₁₀Cu₁N₁: C, 62.19, H, 4.35, N, 6.04, found: C, 67.76, H, 5.56, N, 5.38%.

Synthesis of [(Cp)Cu(XylNC)] (3e).

[(Cp)Cu(CNXyl)] was synthesized in an analogous fashion to **3d** using [ClCu(CNXyl)₂]₂ (1.00 g, 1.38 mmol) and sodium cyclopentadienyl (0.243 g, 2.76 mmol). The crude solid that was purified by recrystallization (hexane) to afford [(Cp)Cu(CNXyl)] as off-white crystals (0.215 g, 30 %, mp. 132 °C). ¹H NMR (CDCl₃, 300.22 MHz) δ: 2.35 (s, *ortho*-CCH₃, 6H), 5.96 (s, C₅H₅, 5H), 7.08 (m, *meta*-CH, 2H), 7.20 (m, *para*-CH, 1H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 18.75 (CCH₃), 94.83 (C₅H₅), 127.98, 129.36, 135.49 (C₆H₅), No CN carbon observed. The complex was too unstable to characterize by elemental analysis

Synthesis of [(Cp)Cu(CNMes)] (3f).

[(Cp)Cu(CNMes)] was synthesized in an analogous fashion to **3d** using [ClCu(CNMes)₂]₂ (1.67 g, 2.15 mmol) and sodium cyclopentadienyl (0.379 g, 4.30 mmol). The crude solid was purified by recrystallization (hexane) to afford [(Cp)Cu(CNMes)] as off-white crystals (0.72 g, 59 %, mp. 140 °C). ¹H NMR (CDCl₃, 300.22 MHz) δ: 2.27 (s, *para*-CCH₃, 3H), 2.38 (s, *ortho*-CCH₃, 6H), 5.96, (s, C₅H₅, 5H), 6.88 (s, *meta*-CH, 2H). ¹³C{¹H} NMR (CDCl₃, 75.50 MHz) δ: 18.59 (*ortho*-CCH₃),

21.23 (*para*-CCH₃) 94.81 (C₅H₅), 128.24, 135.13, 139.52 (C₆H₂, 6C), No CN carbon observed.

Anal. Calc for C₁₅H₁₆Cu₁N₁: C, 65.79, H, 5.89, N, 5.11, found: C, 65.06, H, 5.89, N, 5.34%.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table S1 of the electronic supplementary information for this manuscript. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K α radiation ($\lambda = 0.71073$ Å). Structure solution and refinements were performed using SHELX86⁴⁴ and SHELX97⁴⁵ software, respectively. Corrections for absorption were made in all cases. For all complexes, hydrogen atoms were included at calculated positions. Data for the complexes **1d-f**, **2a-d**, **2f**, **3a-c**, and **4b** have been deposited with the Cambridge Structural Database with CCDC reference numbers 1050605-1050616.

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Supporting Information Available: The X-ray crystallographic files in CIF format are available free of charge *via* the internet at <http://pubs.acs.org>.

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