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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 ([(η⁵-C₅H₄R)Cu(CN₄Bu)] 2b: R = H; 3b: R = Me; 4b: R = Et; 5b: R = iPr) 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 H₂ 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 [(η⁵-C₅H₅)Cu(CNᵢPr)] (2a) and the tert-butyl isocyanide complex [(η⁵-C₅H₅)Cu(CNᵢBu)] (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 [(η⁵-C₅H₅)Cu(CNᵢBu)] (2b), [(η⁵-MeC₅H₄)Cu(CNᵢBu)] (3b), [(η⁵-EtC₅H₄)Cu(CNᵢBu)]
(4b) and [(η⁵-iPrC₅H₄)Cu(CN’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 films\(^1\) 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 Pt(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 \textit{in-situ} to form nascent Cu metal,\textsuperscript{31,4} but as CVD precursors their application has been limited.\textsuperscript{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,\textsuperscript{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 = 2\(e^-\) donor ligand) which compete most effectively, in terms of stability and volatility, with \(\beta\)-diketonate copper systems as CVD precursors.\textsuperscript{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≡C-Cu-L], derivatives.\textsuperscript{2d,7}

The cyclopentadienyl copper phosphine adduct [Cp-Cu-P\textsubscript{Et} \textsubscript{3}] was first described by Wilkinson \textit{ca.} 1956,\textsuperscript{8} but it wasn’t until the 1980-90s that this and related complexes were developed as MOCVD precursors.\textsuperscript{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 \(\beta\)-diketonate copper systems.\textsuperscript{2d,7}
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**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 carbene and ylide 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, [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. 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. 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.\textsuperscript{27} Since then it has been used as a precursor for copper metal deposition,\textsuperscript{10,28} a vinyl polymerization catalyst\textsuperscript{29} and a number of derivatives have been reported.\textsuperscript{28a-c}

As an extension of our continuing interest in the development of precursors for copper thin film formation,\textsuperscript{30} we describe here the synthesis of a range of substituted cyclopentadienyl copper alkyl and aryl isocyanide complexes of the general form $[(\eta^5-\text{C}_5\text{H}_4\text{R'})\text{Cu}($CN\text{R''})]$ (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.

\begin{center}
\textbf{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)
\end{center}

\textbf{Results and Discussion}

The formation of the cyclopentadienyl copper(I) tert-butyl isocyanide complex (2b) was originally reported in 1971,\textsuperscript{27} from the reaction of Cu\textsubscript{2}O 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 $^{1}$H and $^{13}$C NMR spectroscopy, with $^{1}$H 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 CN 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 e: 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 [CuX(PR₃)] that their structure in the solid state depends not only on the complex itself but also on the solvent used for growing the crystal. 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 [ClCu(CNAr)_2]. 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 Cᵢ symmetry and contain Cu···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 [Cu(1)-Cl(1) = 2.4796(5) Å; Cu(1)-Cl(1A) = 2.3641(5) Å], a feature which has been noted previously within related complexes. The Cu-C bond lengths [Cu(1)-C(11) = 1.896(2) Å, Cu(1)-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 [(η⁵-C₅)Cu(CNR)] complexes is that the steric 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-iPr) in stoichiometric ratios results in the formation of the η⁵-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,³¹α along with the para-fluorinated and nitrated derivatives [(η⁵-C₅H₃)CuCNC₆H₄F] and [(η⁵-C₅H₅)CuCNC₆H₄NO₂],³⁴ with excess isocyanide ligand, to form 6-aminofulvene-2-aldimine complexes.³¹β 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 ºC 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 [(η^5-Cp)Cu(CNPr)], 2b [(η^5-Cp)Cu(CN′Bu)], 2c [(η^5-Cp)Cu(CNCy)], 2d [(η^5-Cp)Cu(CNPh)], 2e [(η^5-Cp)Cu(CNXYl)] and 2f [(η^5-Cp)Cu(CNMes)] were prepared. In all cases the ^1H NMR and ^13C NMR spectra of these systems (2a-f) show a singlet resonance associated with the {Cp} moiety: ^1H NMR; δ = 5.89 – 5.96 ppm respectively (integrating to five H atoms), ^13C NMR; between δ = 94.62 – 94.83 ppm. The ^1H and ^13C 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 ^14N coupling, the CN resonances are not observed in the ^13C 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 η⁵-fashion and the isocyanide ligand by the carbon atom in a κ¹ coordination mode. If we consider the {C₅H₅} ligands as occupying a single coordination site, the individual copper geometries are almost linear with Cp centroid-Cu-C angles between 168.69-176.15°. 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.

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It is also noteworthy that complexes 2a-d and 2f are scarce examples of structurally characterized Cu-Cp systems with the general form [(η^5-C_5H_5)Cu-L] (L = 2e- donor ligand).

Figure 3: Thermogravimetric analysis traces of 2a-f from 30 to 500 °C. Experiments were run under N_2 (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.

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§ 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\textsuperscript{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 \textsuperscript{1}H NMR spectra for the complexes 3-5b each contain an unresolvable multiplet resonance between \(\delta = 5.70 - 5.73\) ppm for the \(\text{C}_5\text{H}_4\)-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 \{\(\text{\eta}^5\)-\(\text{C}_5\text{H}_4\)-R\} rings in the \textsuperscript{13}C NMR spectra. Analysis of the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra for these complexes show very little change in the resonances associated with the \textsuperscript{tBu}NC ligand, compared to both 1b and 2b. As with complexes 2a-f, the CN resonances are not observed in the \textsuperscript{13}C 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 (\textit{t}ert-butyl isocyanide) complexes 3b and 4b (50% probability ellipsoids).
Table 3: Selected bond lengths and angles for 2a-d and 2f.

<table>
<thead>
<tr>
<th></th>
<th>3b</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-C(11)</td>
<td>1.810(2) Å</td>
<td>1.809(2) Å</td>
</tr>
<tr>
<td>Cu(1)-Cp&lt;sub&gt;cent&lt;/sub&gt;</td>
<td>1.850(4) Å</td>
<td>1.845(5) Å</td>
</tr>
<tr>
<td>Cp&lt;sub&gt;cent&lt;/sub&gt;-Cu(1)-C(11)</td>
<td>169.86(17) °</td>
<td>175.87(16) °</td>
</tr>
<tr>
<td>Cu(1)-C(11)-N(1)</td>
<td>175.74(16) °</td>
<td>178.1(2) °</td>
</tr>
</tbody>
</table>

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<sub>cent</sub>-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.

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

‡ 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’Bu 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’Bu) occurs initially to form {CuCp} species. 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.\textsuperscript{3m,3n}

For \textbf{4b} and \textbf{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 \textbf{2-5b} using a previously reported method and apparatus.\textsuperscript{36} Details of these analyses are supplied in the supporting information. The results of the vapor pressure measurements of \textbf{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 \textbf{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).\textsuperscript{37}

\textbf{Figure 6:} Vapor pressure measurements of \textbf{2-5b}.
Table 5: Vapor pressure data for the copper metal precursors 2-5b. Data are fitted to log $P$ (mTorr) = A−(1000·B)/(T/K). Error margins are established by a linear regression method and given at the 95% confidence interval.

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

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 ethylcyclopentadienyl (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 \{C_5H_5\}.

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.

<table>
<thead>
<tr>
<th>CVD parameters</th>
<th>2a</th>
<th>2b</th>
<th>2a</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Temperature (°C)</td>
<td>180</td>
<td>180</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Operating pressure (Torr)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>(H_2)</td>
<td>(H_2)</td>
<td>(H_2)</td>
<td>(H_2)</td>
</tr>
<tr>
<td>Carrier flow rate (L min(^{-1}))</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Bubbler flow rate (L min(^{-1}))</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Temp. of bubbler (°C)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Temp. of gas lines (°C)</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Deposition duration (mins)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>
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 as 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 ºC 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 ºC failed to provide films with sufficient coverage for analysis, and have not been discussed here; at intermediate temperatures between 180-300 ºC LP-CVD copper films were discontinuous and comparable to those grown at 180 ºC. Only at 300 ºC, and above, were continuous pinhole free films observed.

SEM analysis of films deposited onto Au/Si at 300 ºC show the films to be continuous and comprise of uniformly granular shaped particles (Fig. 8) of approximately 200 mn thickness. While films deposited onto Si at 300 ºC 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 ($I_s = 284eV$) and oxygen ($I_s = 532eV$) on the surface. The Cu LMM auger ionization energy, which is a clearer indicator of copper oxidation state, indicates the presence of Cu$_2$O 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$_2$O 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 °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, even in the presence of H$_2$ 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 °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

<table>
<thead>
<tr>
<th>Substrate (Temp. °C)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Si (300)</td>
<td>60.39</td>
</tr>
<tr>
<td>Au/Si (300)</td>
<td>74.33</td>
</tr>
<tr>
<td>Pt/Si (180)</td>
<td>54.66</td>
</tr>
</tbody>
</table>
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, 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). 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 (Cu$_{50}$Pt$_{50}$). 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](image.png)

**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 case the complexes display linear pogo-stick like geometries in the solid state.

Comparison of the complexes 3-5b [(η⁵-R'C₅H₅)Cu(CN₃Bu)] (3b: R = Me, 4b: R = Et, 5b = iPr) 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 iPrNC, tBuNC and CyNC were bought from commercial sources and used without further purification. The salts NaCp, NaMeCp, NaEtCp and NaPrCp 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 spectrsocopy (XPS) measurements were performed on a Kratos Axis Ultra-DLD photoelectron spectrometer, utilizing monochromatic Al Kα 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 \( \mu \text{m} \) apparatus 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, (\( \text{K} \alpha \) wavelength = 1.5406 Å) at the University of Bath.

**Synthesis of \([\text{ClCu(CN}^\text{Pr})]_4 \)(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, \( ^3 \text{PrNC} \) (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 \([\text{ClCu(CN}^\text{Pr})]_4 \) as pale yellow crystals (7.46 g, 89 %). \( ^1 \text{H NMR (CDCl}_3, \text{300.22 MHz)} \delta: 1.38 (d, \text{CH(C}_3\text{H}_3)_2, 6H, J = 6.64 \text{ Hz}), 6.64 (\text{sept, CH(C}_3\text{H}_3)_2, 1H, J = 6.64 \text{ Hz}). \) \( ^{13} \text{C}\{^1 \text{H}\} \text{ NMR (CDCl}_3, \text{75.50 MHz)} \delta: 22.59 (\text{CH(C}_3\text{H}_3)_2), 47.33 (t, \text{CH(C}_3\text{H}_3)_2, J = 5.50 \text{ Hz}), 136.60 (t, \text{CN, J} = 15.29 \text{ Hz}) \) Anal. Calc for \( \text{C}_{16}\text{H}_{28}\text{Cl}_4\text{Cu}_4\text{N}_4: \text{C}, 28.58, \text{H}, 4.20, \text{N}, 8.33, \text{found: C, 31.59, H, 4.70, N, 7.61\%}. \)

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

\([\text{ClCu(CN}^\text{Bu})]_4 \) was synthesized in an analogous manner to \([\text{ClCu(CN}^\text{Pr})]_4 \) using 4.26g (43.0 mmol) of CuCl and 4.84 ml (43.0 mmol) of \( ^3 \text{BuNC} \) to yield \([\text{ClCu(CN}^\text{Bu})]_4 \) as colorless crystals (5.58 g, 71 %). \( ^1 \text{H NMR (CDCl}_3, \text{300.22 MHz)} \delta: 1.46 (s, \text{C(CH}_3)_3, 9H). \) \( ^{13} \text{C}\{^1 \text{H}\} \text{ NMR (CDCl}_3, \text{75.50 MHz)} \delta: 30.05 (\text{C(CH}_3)_3), 56.50 (\text{C(CH}_3)_3), 134.62 (t, \text{CN, J} = 15.75 \text{ Hz}) \) Anal. Calc for \( \text{C}_{20}\text{H}_{36}\text{Cl}_4\text{Cu}_4\text{N}_4: \text{C, 32.97, H, 4.98, N, 7.69, found: C, 33.40, H, 5.03, N, 7.73\%}. \)
Synthesis of [ClCu(CNCy)]₄ (1c).

[ClCu(CNCy)]₄ was synthesized in an analogous manner to [ClCu(CNPr)] 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), C₅N 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, [ClCu(CNXyl)]₂ and [ClCu(CNMes)]₂ were all synthesized in an analogous fashion. The synthesis of [ClCu(CNPh)]₂ is given as an example.

Synthesis of [ClCu(CNPh)]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 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 (1e).

[ClCu(CNXyl)]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 (C₆H₅), 150.62 (broad
multiplet, $\text{CN}$). Anal. Calc for $C_{36}H_{30}Cl_2Cu_2N_4$: 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 %). $^1$H NMR (CDCl$_3$, 300.22 MHz) $\delta$: 2.27 (s, $\text{para-CC}_H_3$, 12H), 2.37 (s, $\text{ortho-CC}_H_3$, 24H), 6.88 (s, $\text{meta-CH}_2$, 8H). $^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$, 75.50 MHz) $\delta$: 18.68 ($\text{ortho-C}_C_H_3$), 21.24 ($\text{para-C}_C_H_3$), 123.78, 128.63, 135.25, 139.84 ($C_6H_2$), 148.21 (m, $\text{CN}$). Anal. Calc for $C_{40}H_{44}Cl_2Cu_2N_4$: C, 49.18, H, 4.54, N, 5.74, found: C, 49.09, H, 4.54, N, 5.71%.

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

$[\text{ClCu}(\text{CN}^{t}\text{Pr})]_4$ (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 °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 $[(\text{Cp})\text{Cu}(\text{CN}^{t}\text{Pr})]$ as pale yellow crystals (1.24 g, 52 %, mp. 73 °C).$^1$H NMR (CDCl$_3$, 300.22 MHz) $\delta$: 1.35 (dt, $\text{CH}(\text{C}_H_3)_2$, 6H, $J = 6.60$, $J = 2.39$), 3.81 (m, $\text{CH}(\text{CH}_3)_2$, 1H), 5.89 (s, $C_5H_5$, 5H). $^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$, 75.50 MHz) $\delta$: 22.78 (CH$(\text{CH}_3)_2$), 47.84 (CH$(\text{CH}_3)_2$), 94.62 ($C_5H_5$), No $\text{CN}$ carbon observed. Anal. Calc for $C_9H_{12}Cu_1N_1$: C, 54.67, H, 6.12, N, 7.08, found: C, 54.60, H, 5.95, N, 7.13%. 
Synthesis of [(Cp)Cu(CN'Bu)] (2b).

[(Cp)Cu(CN'Bu)] was synthesized in an analogous fashion to 2a, using, [ClCu(CN'Bu)]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'Bu)] 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(C₃H₃)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, C₅H₅, 5H), 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). CN carbon not observed. Anal. Calc for C₁₂H₁₆Cu₁₁N₁: C, 56.61, H, 6.78, N, 5.89; found: C, 56.78, 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, C₅H₅CH₃, 3H), 3.81 (septet of triplets, CH(CH₃)₂, 1H, J = 1.75
Hz, J = 6.56 Hz), 5.70 (m, C₅H₄CH₃, 5H). $^{13}$C {$^1$H} NMR (CDCl₃, 75.50 MHz) δ: 14.44 (C₅H₄CH₃), 22.76 (CH(CH₃)₂), 47.79 (CH(CH₃)₂), 92.15, 95.38, 109.90 (C₅H₄CH₃), No CN carbon observed. The complex was too unstable to characterize by elemental analysis.

Synthesis of [(MeCp)Cu(CN'Bu)] (3b).

[(MeCp)Cu(CN'Bu)] was synthesized in an analogous fashion to 2a, using 7.29 g (10 mmol) of [ClCu(CN'Bu)]₄ and 4.12 g (40 mmol) sodium methyl-cyclopentadienide. Sublimation (1 x 10⁻¹ torr, 70 °C) of the crude product afforded [(MeCp)Cu(CN'Bu)] as off-yellow crystals (7.96 g, 88 %). $^1$H NMR (CDCl₃, 300.22 MHz) δ: 1.42 (t, C(CH₃)₃, 9H, J = 2.13 Hz); 2.24 (s, C₅H₄CH₃, 3H); 5.70 (m, C₅H₄CH₃, 5H). $^{13}$C {$^1$H} NMR (CDCl₃, 75.50 MHz) δ: 14.44 (C₅H₄CH₃), 30.09 (C(CH₃)₃), 56.65 (C(CH₃)₃); 92.17, 95.38, 109.86 (C₅H₄CH₃). CN carbon not observed. Anal. Calc for C₁₂H₁₉CuN: 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 methycyclopentadienyl (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).$^1$H NMR (CDCl₃, 300.22 MHz) δ:1.38 (m, C(CH₃)₂, 4H), 1.68 (m, C(CH₃)₂, 4H), 1.87 (m, C₅H₄CH₃, 4H). $^{13}$C {$^1$H} NMR (CDCl₃, 75.50 MHz) δ: 14.44 (C₅H₄CH₃), 22.75, 24.70, 32.02 (C(CH₃)₂), 53.60 (m, C₅H₄CH₃), 1C, 92.14, 95.41, 109.95 (C₅H₄CH₃). No CN carbon observed. The complex was too unstable to characterize by elemental analysis.

Synthesis of [EtCpCu(CN'Bu)] (4b).

[(EtCp)Cu(CN'Bu)] was synthesized in an analogous fashion to 2a, using [ClCu(CN'Bu)]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 \([\text{EtCp}Cu(\text{CN}t\text{Bu})]\) as colorless crystals (1.20 g, 73%). Sublimation (1 x 10^{-1} torr, 70 °C) was also used to produce pure materials.  

\(^1\)H NMR (CDCl\(_3\), 300.22 MHz) δ: 1.21 (t, C\(_5\)H\(_4\)CH\(_2\)C\(_5\)H\(_4\), 3H, J\(^3\) = 7.56 Hz); 1.43 (s, C(CH\(_3\))\(_3\), 9H) 2.54 (q, C\(_5\)H\(_4\)CH\(_2\)CH\(_2\)C\(_5\)H\(_4\), 2H, J\(^3\) = 7.56 Hz); 5.72 (m, C\(_5\)H\(_4\)CH\(_2\)CH\(_3\), 4H).  

\(^{13}\)C{\(^1\)H} NMR (CDCl\(_3\), 75.50 MHz) δ: 17.87 (C\(_5\)H\(_4\)CH\(_2\)C\(_5\)H\(_4\); 22.18 (C\(_5\)H\(_4\)C\(_5\)H\(_4\)CH\(_3\)); 30.29 (C(C\(_5\)H\(_3\))\(_3\)); 56.92 (C(CH\(_3\))\(_3\)); 92.02, 93.84, 118.58 (C\(_5\)H\(_4\)CH\(_2\)CH\(_3\)). CN carbon not observed. Anal. Calc for C\(_{13}\)H\(_{21}\)CuN: C, 60.23, H, 7.59, N, 5.86, found: C, 60.14, H, 7.34, N, 5.91%.

**Synthesis of [(iPrCp)Cu(CNtBu)] (5b).**

[(iPrCp)Cu(CNtBu)] was synthesized in an analogous fashion to 2a, using [ClCu(CNtBu)]\(_4\) (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(CNtBu)] as colorless crystals (1.42 g, 70%). \(^1\)H NMR (CDCl\(_3\), 300.22 MHz) δ: 1.23 (m, C\(_5\)H\(_4\)CH(C\(_5\)H\(_3\))\(_2\), 6H), 1.42 (s, C(CH\(_3\))\(_3\), 9H), 2.85 (sept, C\(_5\)H\(_4\)CH(CH\(_3\))\(_2\), 1H, J\(^3\) = 6.80 Hz), 5.73 (m, C\(_5\)H\(_4\)CH(CH\(_3\))\(_2\), 4H). \(^{13}\)C{\(^1\)H} NMR (CDCl\(_3\), 75.50 MHz) δ: 25.77, 27.69 (C\(_5\)H\(_4\)CH(CH\(_3\))\(_2\); 30.27 (C(CH\(_3\))\(_3\)); 56.84 (C(CH\(_3\))\(_3\)); 91.69, 92.62, 124.42 (C\(_5\)H\(_4\)CH(CH\(_3\))\(_2\)). CN carbon not observed. Anal. Calc for C\(_{13}\)H\(_{20}\)CuN: C, 61.23, H, 7.59, N, 5.86, 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\textsuperscript{®} to remove any insoluble materials, followed by removal of the volatiles \textit{in vacuo}. This resulted in a dark yellow crude solid that was purified by recrystallization (hexane) to afford [(CpCu(PhNC))] as yellow crystals (0.990 g, 35 \%, mp. 76 °C). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300.22 MHz) δ: 5.95, (s, C\textsubscript{5}H\textsubscript{5}, 5H), 7.45-7.28 (m, C\textsubscript{6}H\textsubscript{5}, 5H). \textsuperscript{13}C\{-\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 75.50 MHz) δ: 94.82 (C\textsubscript{5}H\textsubscript{5}), 121.74, 126.43, 129.61, 129.82 (C\textsubscript{6}H\textsubscript{5}). No CN carbon observed. Anal. Calc for C\textsubscript{12}H\textsubscript{10}CuN\textsubscript{1}: C, 62.19, H, 4.35, N, 6.04, found: C, 67.76, H, 5.56, N, 5.38%.

\textbf{Synthesis of [(Cp)Cu(XylNC)] (3e).}

[(Cp)Cu(CNXyl)] was synthesized in an analogous fashion to 3d using [ClCu(CNXyl)\textsubscript{2}]\textsubscript{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). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300.22 MHz) δ: 2.35 (s, \textit{ortho}-CC\textsubscript{6}H\textsubscript{3}, 6H), 5.96 (s, C\textsubscript{5}H\textsubscript{5}, 5H), 7.08 (m, \textit{meta}-CH\textsubscript{2}, 2H), 7.20 (m, \textit{para}-CH\textsubscript{3}, 1H). \textsuperscript{13}C\{-\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 75.50 MHz) δ: 18.75 (\textit{ortho}-CC\textsubscript{6}H\textsubscript{3}), 94.83 (C\textsubscript{5}H\textsubscript{5}), 127.98, 129.36, 135.49 (C\textsubscript{6}H\textsubscript{5}). No CN carbon observed. The complex was too unstable to characterize by elemental analysis.

\textbf{Synthesis of [(Cp)Cu(CNMes)] (3f).}

[(Cp)Cu(CNMes)] was synthesized in an analogous fashion to 3d using [ClCu(CNMes)\textsubscript{2}]\textsubscript{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). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300.22 MHz) δ: 2.27 (s, \textit{para}-CC\textsubscript{6}H\textsubscript{3}, 3H), 2.38 (s, \textit{ortho}-CC\textsubscript{6}H\textsubscript{3}, 6H), 5.96, (s, C\textsubscript{5}H\textsubscript{5}, 5H), 6.88 (s, \textit{meta}-CH\textsubscript{2}, 2H). \textsuperscript{13}C\{-\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 75.50 MHz) δ: 18.59 (\textit{ortho}-CC\textsubscript{6}H\textsubscript{3}),
21.23 (para-C\textsubscript{2}H\textsubscript{3}) 94.81 (C\textsubscript{3}H\textsubscript{5}), 128.24, 135.13, 139.52 (C\textsubscript{6}H\textsubscript{2}, 6C), No C\textsubscript{N} carbon observed.

Anal. Calc for C\textsubscript{15}H\textsubscript{16}Cu\textsubscript{1}N\textsubscript{1}: 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\textsubscript{\alpha} radiation (\(\lambda = 0.71073\) Å). Structure solution and refinements were performed using SHELX86\textsuperscript{44} and SHELX97\textsuperscript{45} 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](http://pubs.acs.org).
References