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

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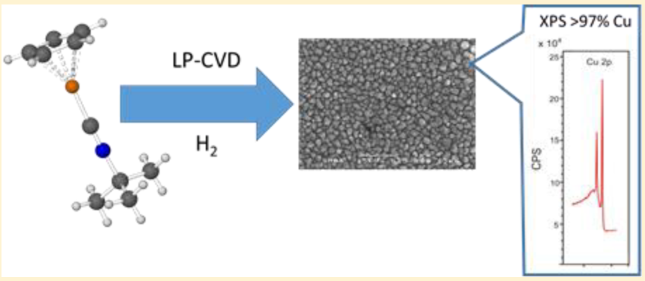
S *Supporting Information*

ABSTRACT: We report here the synthesis and characterization of a family of copper(I) metal precursors based around cyclopentadienyl and isocyanide ligands. The molecular structures of several cyclopentadienylcopper(I) isocyanide complexes have been unambiguously determined by single-crystal X-ray diffraction analysis. Thermogravimetric analysis of the complexes highlighted the isopropyl isocyanide complex $[(\eta^5\text{-}C_5H_5)Cu(CN^iPr)]$ (**2a**) and the *tert*-butyl isocyanide complex $[(\eta^5\text{-}C_5H_5)Cu(CN^tBu)]$ (**2b**) as possible copper metal chemical vapor deposition (CVD) precursors. Further modification of the precursors with variation of the substituents on the cyclopentadienyl ligand system (varying between H, Me, Et, and ^{i}Pr) has allowed the affect that 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 **2b**, $[(\eta^5\text{-}MeC_5H_4)Cu(CN^tBu)]$ (**3b**), $[(\eta^5\text{-}EtC_5H_4)Cu(CN^tBu)]$ (**4b**), and $[(\eta^5\text{-}{}^iPrC_5H_4)Cu(CN^tBu)]$ (**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 a H_2 atmosphere. Analysis of the thin films deposited onto both silicon and gold substrates at substrate temperatures of 180 and 300 °C by scanning electron microscopy and atomic force microscopy reveals temperature-dependent growth features: Films grown at 300 °C are continuous and pinhole-free, whereas films grown at 180 °C consist of highly crystalline nanoparticles. In contrast, deposition onto platinum substrates at 180 °C shows a high degree of surface coverage with the formation of high-density, continuous, and pinhole-free thin films. Powder X-ray diffraction and X-ray photoelectron spectroscopy (XPS) both show the films to be high-purity metallic copper.



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 because of the numerous potential applications in which these materials can be exploited.[2d,e,3a,b] As the size downscaling of microelectronics continues, the use of copper as an interconnect material in integrated circuitry has increased.[2c,e,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 (although inferior to that of 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, are of interest.

In principle, copper(0) compounds would be the most desirable precursors; ligand dissociation would produce atomized metal, and any such process should lead to the formation of high-purity films, as is the case for the CVD of platinum

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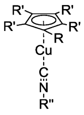
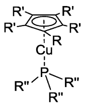
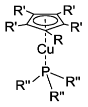
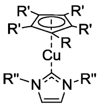
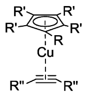
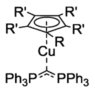
Chart 1. Stable Copper(I) Cyclopentadienyl Complexes[10−25]

Complex	R	R'	R''	Ref
	H	H	^{t}Bu	10
	H	H	Ph	11
	Me	H	^{t}Bu	10
	tBu	H	^{t}Bu	10
	CF_3	H	^{t}Bu	10
	Me	Me	^{t}Bu	10
	H	H	Me	12
	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
	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	*c*-$[CMe_2CH_2]_2S$	24
	H	H	-	25
	H	Me	-	25

metal from $Pt(PF_3)_4$.[5] To date, no such homoleptic copper(0) complexes are known.

This leaves copper(I) and copper(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,d] have been used extensively for the CVD of copper, the inherent instability of organometallic Cu^{II} d^9 species means that, to date, copper(II) organometallic species are unknown. As was already noted, the inherent instability in copper(II) organometallics has been utilized by groups working on the development of ALD processes in which copper(II) organometallics are formed in situ to form nascent copper 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) that 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≡C−Cu−L]) derivatives.[2d,7]

The cyclopentadienylcopper phosphine adduct [$CpCu(PEt_3)$] was first described by Piper and Wilkinson around 1956,[8] but it was not until the 1980s−1990s that this and related complexes were developed as metal−organic CVD (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]

To date, only the phosphine adduct [$CpCu(PEt_3)$] is commercially available and has been studied as a CVD precursor. The remaining N-heterocyclic carbene[23] and ylide[25] adducts have not been investigated as potential precursors thus far.

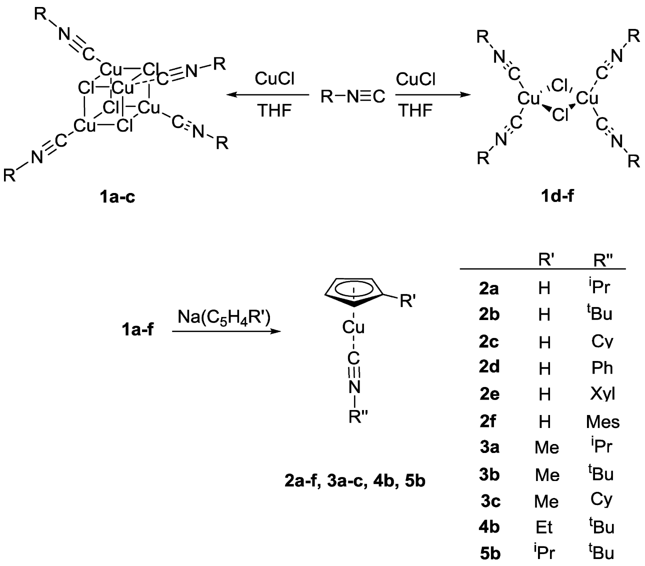
However, to mass produce copper thin films, laboratory methods must be scalable for commercial production. While the thermal behavior of [$CpCu(PEt_3)$] and the MOCVD process of copper deposition from it are well established,[9b,c,26] [$CpCu(PR_3)$] systems are not considered by industry to be good copper sources for commercial CVD processing because of a high degree of contamination of the copper thin films.[9n,o,q,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,d,7] Consequently, new precursors that are preferably halogen-free and contain as few heteroatoms as possible have been sought. Foremost among these compounds is cyclopentadienylcopper *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 catalyst[29] 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 cyclopentadienylcopper alkyl and aryl isocyanide complexes of the general form [$(\eta^5\text{-}C_5H_4R')Cu(CNR'')$] (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.

■ RESULTS AND DISCUSSION

Formation of the cyclopentadienylcopper(I) *tert*-butyl isocyanide complex **2b** was originally reported in 1971[27] from the reaction of Cu_2O with excess freshly distilled cyclopentadiene (which also acts as a solvent) in the presence of *tert*-butyl

Scheme 1. Synthetic Procedure for the Synthesis of Copper(I) Chloride Isocyanide Adducts (1a−1f) and Cyclopentadienylcopper(I) Isocyanide Adducts (2a−2f, 3a−3c, 4b, and 5b)



	R'	R''
2a	H	^{i}Pr
2b	H	^{t}Bu
2c	H	Cy
2d	H	Ph
2e	H	Xyl
2f	H	Mes
3a	Me	^{i}Pr
3b	Me	^{t}Bu
3c	Me	Cy
4b	Et	^{t}Bu
5b	^{i}Pr	^{t}Bu

isocyanide to afford the desired complex, which can be recrystallized to afford pure product. Despite this synthetically unpretentious strategy, its utility is limited because the use of methyl-, ethyl-, and other alkyl-substituted cyclopentadienyl systems is 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 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 tetrahydrofuran (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 carbon atoms; 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 the 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 (XRD) was used to unequivocally determine the molecular structure of the adducts.

The direct reaction of copper chloride with the alkyl isocyanides **a**−**c** (**a**, isopropyl isocyanide; **b**, *tert*-butyl isocyanide; **c**, cyclohexyl isocyanide) results in the formation of colorless crystalline materials in moderate-to-high yields (56−89%), which were identified by elemental analysis as the 1:1 adducts (**1a**−**1c**)[10,31a,b] 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(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**−**1c** could be isolated in moderate yields, crystals suitable for single-crystal XRD analysis were not obtained.

In contrast, the 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 that by elemental analysis are consistent with the form [ClCu(CNAr)$_2$].[31c,f] Amendment of the reaction stoichiometries allowed isolation of the bis(isocyanide) adducts (**1d**−**1f**) in high yield (73−88%) as colorless crystalline products. In all cases, crystals suitable for single-crystal XRD analysis were obtained. Figure 1 shows the molecular structure of complex **1e**, which crystallizes in the $P\bar{1}$ space group with half of a molecule of the complex in the asymmetric unit cell. Complexes **1d**−**1f** 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.

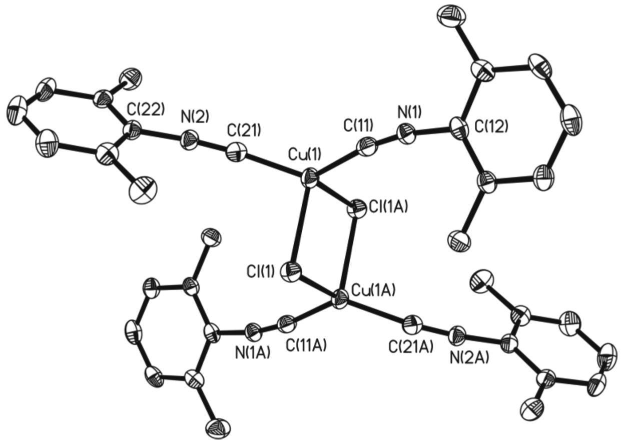


Figure 1. Molecular structure of the copper(I) chloride bis(xylylisocyanide) dimer **1e** showing the labeling scheme used in the text. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are at the 30% probability level. Symmetry operation: 1 − *x*, 1 − *y*, −*z*.

In the solid state, complex **1e** forms a halogen-bridged complex, with two isocyanide ligands completing *pseudo*tetrahedral coordination of the copper atoms. The dimers **1d**−**1f** all have an imposed crystallographic C_i symmetry and contain Cu···Cu units separated by distances between approximately 3.20 and 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 that has been noted previously within related complexes.[31c,f] 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 complexes **1d** and **1f** are included in the Supporting Information and need no further comment here.

Synthesis of Cyclopentadienylcopper(I) Isocyanide Adducts. An attractive feature of the [(η^5-Cp)Cu(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

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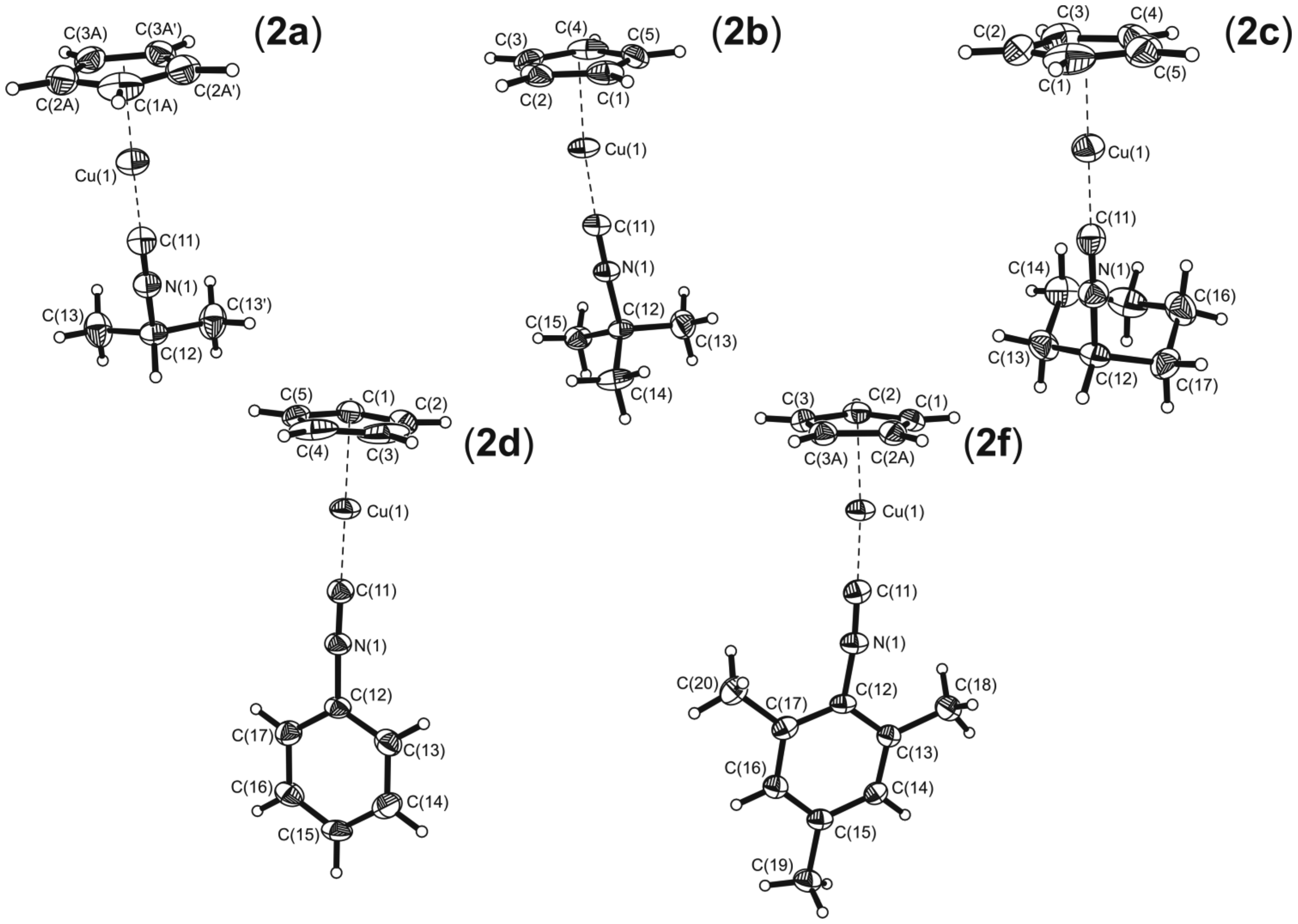


Figure 2. Diagram showing the molecular structures of complexes **2a**–**2d** and **2f** (50% probability ellipsoids). Symmetry transformations used to generate equivalent atoms: in **2a**, x, $-y + {}^{3}/_{2}$, z; in **2f**, $-x + {}^{1}/_{2}$, y, z.

Table 1. Selected Bond Lengths and Angles for 2a–2d and 2f

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

precursor for copper CVD (or ALD). It has been previously suggested that the size of the ligands (especially Cp ligands) associated with particular precursors can play an important role in determining its suitability.[33]

Reaction of the copper(I) chloride isocyanide adducts with either sodium cyclopentadienide (NaCp), sodium methylcyclopentadienide (NaCpMe), sodium ethylcyclopentadienide (NaCpEt), or sodium isopropylcyclopentadienide (NaCp^{i}Pr) in stoichiometric ratios results in formation of the η^5-cyclopentadienylcopper 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 [(η^5-C_5H_5)$CuCNC_6H_4F$] and [(η^5-C_5H_5)$CuCNC_6H_4NO_2$],[34] with excess isocyanide ligand, to form 6-aminofulvene-2-aldimine complexes.[31b] Reduced reaction times (<2 h) between sodium cyclopentadienide and the isocyanide adducts **1d**–**1f** limits the formation of these complexes, and selective crystallization from a hexane solution at −28 °C allows complexes **2d**–**2f** 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(CN^{i}Pr)], **2b** [(η^5-Cp)Cu(CN^{t}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 ^{1}H and ^{13}C NMR spectra of these systems (**2a**–**2f**) show a singlet resonance associated with the Cp moiety: ^{1}H NMR, δ 5.89–5.96 respectively (integrating to five hydrogen atoms); ^{13}C NMR, between δ 94.62 and 94.83.

The ^{1}H and ^{13}C NMR spectral resonances associated with the isocyanide groups show no significant change upon substitution of Cl for Cp. Unfortunately, because of the fast relaxation time of quaternary carbon atoms and ^{14}N coupling, the CN resonances are not observed in the ^{13}C NMR spectra.

Crystalline materials suitable for single-crystal XRD experiments were isolated for **2a**−**2d** and **2f**. In the solid state, **2a**−**2d** and **2f** form discrete monomers with one-legged piano-stool (pogo stick)-type geometries (Figure 2). In all cases, the central copper atom of the complexes is bound to the C_5H_5 ligands in a η^5 fashion and the isocyanide ligand by the carbon atom in a κ^1-coordination mode. If we consider the C_5H_5 ligands as occupying a single coordination site, the individual copper geometries are almost linear, with $Cp_{centroid}$−Cu−C angles between 168.69 and 176.15°. This variance in the 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**−**2d** and **2f** (Table 1) are in good agreement with other Cp and substituted CpCu complexes, reflecting an apparent indifference to the nature of the isocyanide.

It is also worth noting that complexes **2a**−**2d** and **2f** are scarce examples of structurally characterized CuCp systems with the general form $[(\eta^5\text{-}C_5H_5)CuL]$ (L = 2e$^-$ donor ligand).

Thermogravimetric analyses (TGA) of complexes **2a**−**2f** are shown in Figure 3. Of the compounds analyzed, only **2a**, **2b**, and **2f** were found to produce stable residues below 500 °C. Compounds **2a** and **2b** 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** and **2b** have single-step decomposition pathways, **2c**−**2f** display multistep decomposition pathways. For complexes **2c**−**2e**, 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.

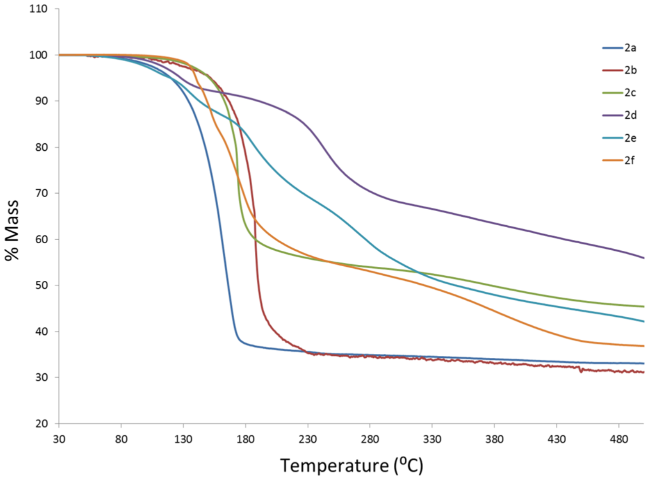


Figure 3. TGA traces of **2a**−**2f** from 30 to 500 °C. Experiments were run under N_2 (50 mL/min) at a ramp rate of 20 °C/min.

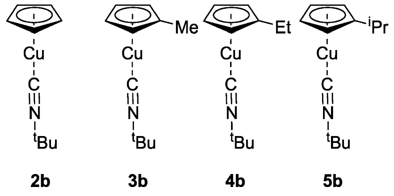
In an effort to ascertain the effect of derivatization of the cyclopentadienyl moiety on features such as the stability, volatility, and decomposition, a series of complexes were produced (Chart 2) in which the isocyanide moiety was kept the same (i.e., CN^{t}Bu) and the substituent group on the cyclopentadienyl group was modified.

Table 2. Expected % Residue, % Nonvolatile Residue, and Onset of Volatilisation/Decomposition Temperature for 2a−2f

precursor	expected % for Cu	% nonvolatile residue (temp, °C)	onset temp (°C)[a]
2a	32.1	36.0 (200)	100
2b	30.0	34.8 (280)	121
2c	26.7	45.4 (500)[b]	119
2d	27.4	55.9 (500)[b]	98
2e	24.5	42.2 (500)[b]	82
2f	23.2	36.8 (500)	125

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

Chart 2



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 ^{1}H NMR spectra for complexes **3**−**5b** each contains an unresolvable multiplet resonance between δ 5.70 and 5.73 for the C_5H_4−R hydrogen protons, which correlate to resonances between δ 91.69 and 92.17, 92.62 and 95.38, and 109.86 and 124.42, for the three equivalent carbon atoms in the $\eta^5\text{-}C_5H_4$−R rings in the ^{13}C NMR spectra. Analysis of the ^{1}H and ^{13}C NMR spectra for these complexes shows very little change in the resonances associated with the ^{t}BuNC ligand, compared to both **1b** and **2b**. As with complexes **2a**−**2f**, the CN resonances are not observed in the ^{13}C NMR spectra.

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

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 the reactivity of the complexes as the Cp substituent changes as HCp < MeCp < EtCp < ^{i}PrCp, 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.

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 and 114 °C, followed by a further mass loss of 44.5% (down to 21.7%) between 130 and 218 °C (Table 4). With a residual mass of 21.7% at 218 °C

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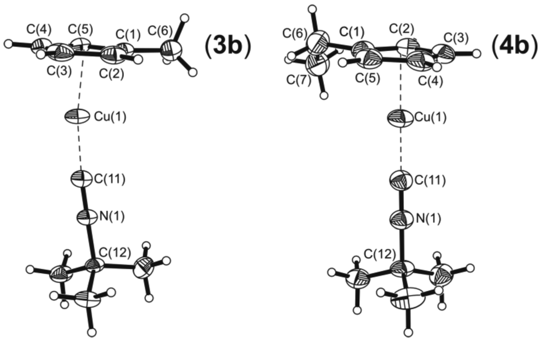

Figure 4. Diagram showing the molecular structures of the methyl- and ethylcyclopentadienylcopper (*tert*-butyl isocyanide) complexes **3b** and **4b** (50% probability ellipsoids).

Table 3. Selected Bond Lengths and Angles for 2a−2d and 2f

	3b	4b
Cu(1)−C(11) (Å)	1.810(2)	1.809(2)
Cu(1)−Cp_{cent} (Å)	1.850(4)	1.845(5)
Cp_{cent}−Cu(1)−C(11) (deg)	169.86(17)	175.87(16)
Cu(1)−C(11)−N(1) (deg)	175.74(16)	178.1(2)

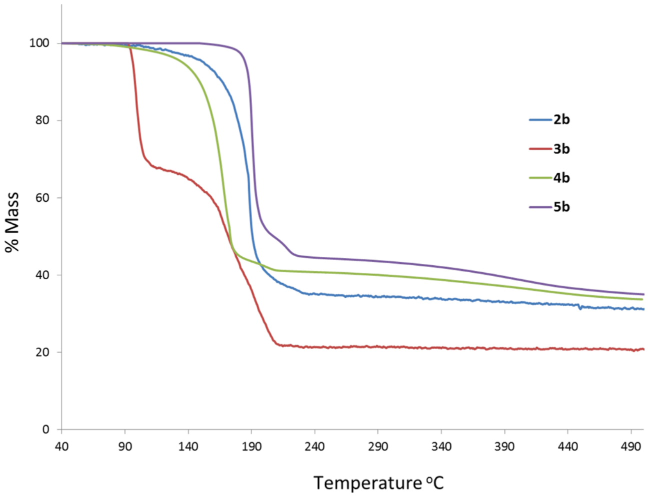

Figure 5. TGA traces of **2**−**5b** from 40 to 500 °C. Experiments were run under N_2 (50 mL/min) at a ramp rate of 20 °C/min.

(which is lower than the expected residual mass for pure copper), complex **2b** appears to possess a small degree of volatility.

Despite a clear two-step decomposition process for **3b**, assignment of each thermal event (CpMe vs CN^tBu loss) has not been possible because of the volatility of this complex, making assignment of the thermal events problematic. However, work by others has suggested that 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 copper(I) silylamide precursors work most efficiently at elevated temperatures (>170 °C) in order to provide sufficient energy to break the Cu−carbene bond, or in our case the Cu−isocyanide bond, to form surface-chemisorbed copper(I) species, which then react with a hydrogen coreagent.[3m,n]

Table 4. Expected % Residue, % Nonvolatile Residue, and Onset of Volatilization/Decomposition Temperature for 2−5b

precursor	expected % for Cu	% nonvolatile residue (temp, °C)	onset temp (°C)[a]	mp/ sublimation point
2b	30.0	34.8 (280)	121	95 °C/40 °C, 0.1 Torr
3b	28.1	21.7 (218)	107	dec/70 °C, 0.1 Torr
4b	26.5	33.6 (500)[b]	90	dec/80 °C, 0.1 Torr
5b	25.0	34.9 (500)[b]	171	dec/80 °C, 0.1 Torr

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

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 SI. 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 parameter B (Table 5).[37]

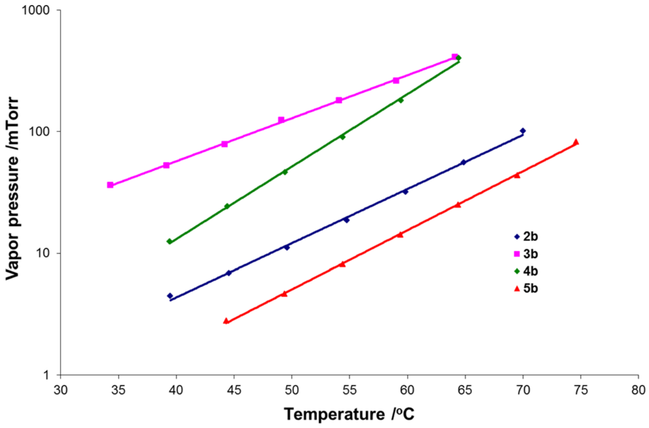

Figure 6. Vapor-pressure measurements of **2**−**5b**.

As can be seen from the calculated vapor pressures of complexes **2**−**5b** at 60 °C, shown in Table 5, the order of volatility is **3b** > **4b** ≫ **2b** > **5b**, which is attributed to the difference in the Cp substituent such that the order of volatility can be viewed as MeCp > EtCp > HCp > ^{i}PrCp; in fact, a 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 and 150 mTorr, respectively) shows **3b** and **4b** to be more volatile at these operating temperatures.[35,38]

Despite the significant effects of 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 upon standing at room temperature

Table 5. Vapor-Pressure Data for the Copper Metal Precursors 2−5b[a]

precursor	A	$B \times 10^{-3}$	ΔH_{sub} (kJ/mol)	temp range of measurement (°C)	calcd vapor pressure at 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

[a] Data are fitted to $\log P\,(\text{mTorr}) = A - 1000B/(T/\text{K})$. Error margins are established by a linear regression method and given at the 95% confidence interval.

over a period of weeks, producing a black microcrystalline powder identified as copper metal. More significantly, attempts to synthesize the corresponding methyl and ethylcyclopentadienyl (isopropyl isocyanide) copper(I) complexes (**3a** and **4a**) and the methyl-cyclopentadienyl (cyclohexyl 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 that inhibited full characterization of the products by elemental analysis and TGA. However, single crystals suitable for XRD analysis of both **3a** and **3c** were obtained and the molecular structures (which are included in the SI) determined, which show features that match those of the complexes already described.

The reduced stability of the methylcyclopentadienyl derivatives **3a**−**3c** 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 production of the cyclopentadienyl and methylcyclopentadienyl copper derivatives **2a**, **2b**, **3a**, and **3b** on multigram scales for deposition studies. However, attempts to upscale the production of systems **3a** and **3b** 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.

Copper was initially deposited onto silicon (400) wafers using complexes **2a** and **2b** at low pressure (40 Torr) using a cold-walled Electrogas CVD apparatus. However, because copper has been shown to adhere poorly to silicon, gold on silicon was also investigated as a suitable substrate. Copper metal was deposited on both substrates at both 180 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 H_2 as the carrier gas at a flow rate of 0.3 L/min. Typically, H_2 is used a reductant for copper precursors because 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; for this reason, the subsequent discussion is limited to films deposited using **2b**.

Table 6. General Physical Parameters for the LP-CVD of Complex 2a and 2b

CVD parameters	2a	2b	2a	2b
substrate temp (°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)	0.3	0.3	0.3	0.3
bubbler flow rate (L/ min)	0.3	0.3	0.3	0.3
temp of the bubbler (°C)	60	60	60	60
temp of the gas lines (°C)	75	75	75	75
deposition duration (min)	60	60	60	60

Films deposited at 180 °C for both precursors appeared silvery-blue in color and discontinuous to the naked eye, a feature that is confirmed by scanning electron microscopy (SEM) analysis of the films (Figure 7), which reveals the presence of single crystals of copper metal between 400 nm and 1 μm in length, dispersed over the surface of the substrates.

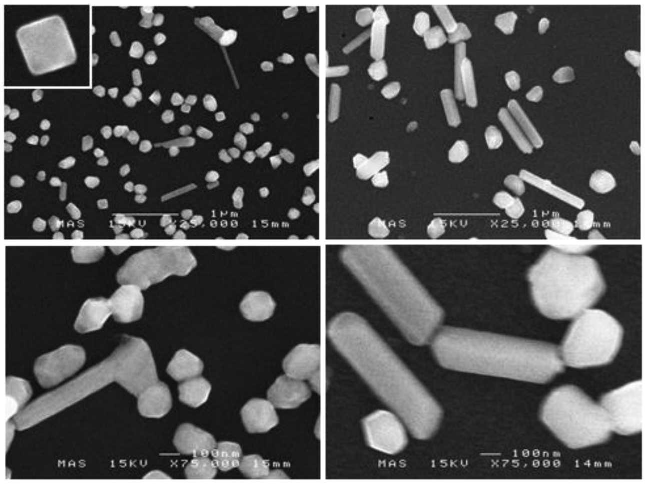

Figure 7. Micrographs of copper films deposited on gold/silicon (left) and silicon (right) at a substrate temperature of 180 °C.

In stark contrast, those films deposited at 300 °C possessed a metallic luster and appeared continuous on both silicon and gold/silicon 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 and 300 °C, low-pressure CVD (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 gold/silicon at 300 °C shows the films to be continuous and comprised of uniformly granular-shaped particles (Figure 8) of approximately 200 mn thickness. While films deposited onto silicon at 300 °C were somewhat similar, larger particles of material on the film were also present (Figure 8), likely to be a result of the thermal mobility of copper, leading to particle agglomeration.[30a]

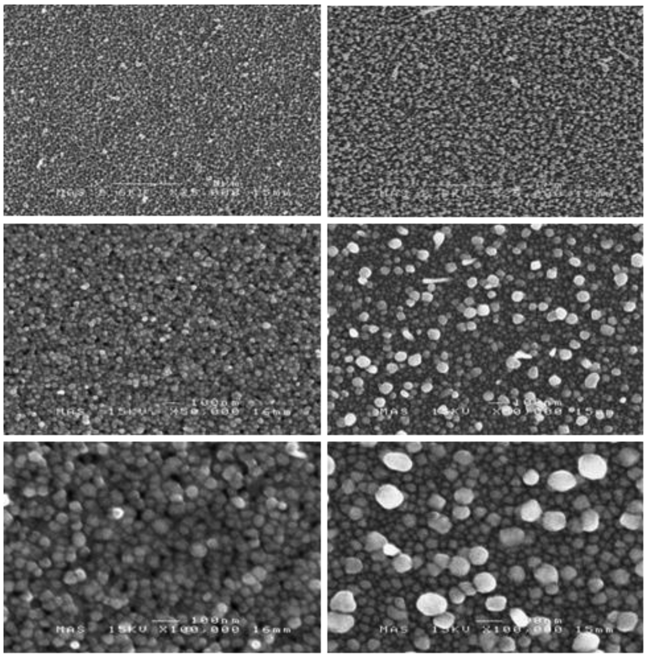

Figure 8. Micrographs of copper films deposited on gold/silicon (left) and silicon (right) at a substrate temperature of 300 °C.

Energy-dispersive X-ray (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.

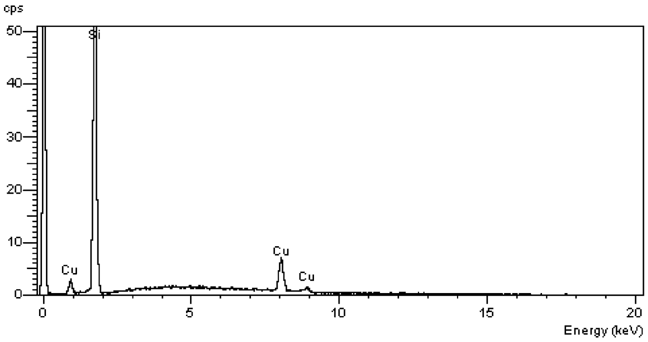

Figure 9. Typical EDX plot of copper films grown on a silicon (400) wafer from **2a**.

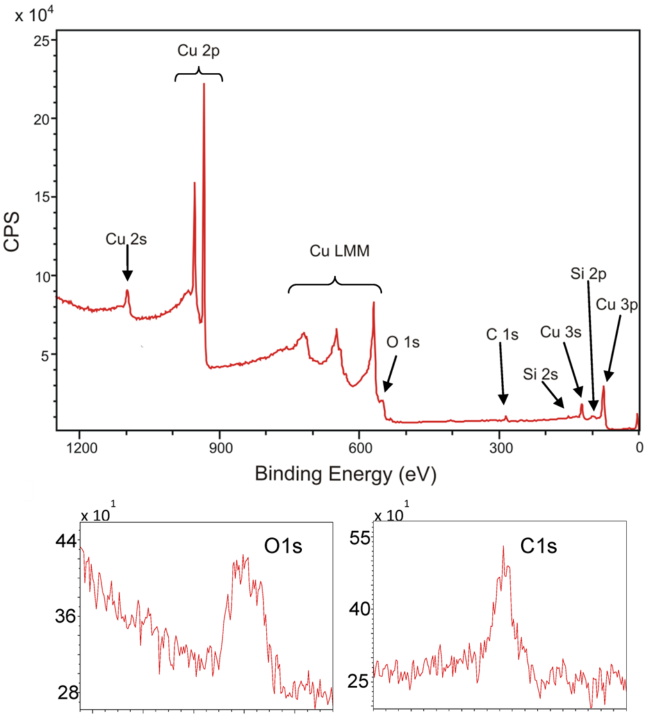

Figure 10. XPS profile of a film deposited at a substrate temperature of 300 °C on silicon. Magnified regions for oxygen (left) and carbon (right) are also shown.

Table 7. Elemental Analysis for Etched Copper Films Deposited from 2b

	atom %					
substrate (temp, °C)	copper	oxygen	carbon	gold	silicon	platinum
silicon (300)	60.39	3.08	21.51		14.01	
gold/silicon (300)	74.33	1.81	14.43	9.42		
platinum/silicon (180)	54.66	0.33	1.15			43.86

X-ray photoelectron spectrsocopy (XPS) analysis of the as-deposited films revealed the presence of significant peaks associated with C 1s (284 eV) and O 1s (532 eV) on the surface. The Cu LMM auger ionization energy, which is a clearer indicator of the copper oxidation state,[39] indicates the presence of Cu_2O on the surface [570.72 eV (gold/silicon) and 570.77 eV (silicon)] 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 (gold/silicon) and 567.7 eV (silicon)], 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 4 min argon etch, as a function of the 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 atom %), but significant carbon contamination still remains (14.4–21.5%), which can arise from decomposition of the cyclopentadienyl ligand,[9b,o] even in the presence of H_2,[40] when relatively high deposition temperatures are needed to induce precursor decomposition.

However, if background elements (silicon and gold) are removed from elemental analysis, we find that the films produced are of moderately high purity (71 and 82 atom % of copper, respectively) although still with a significant degree of carbon inclusion. XPS data for films deposited onto silicon and gold/silicon from complexes **2a** and **2b** at 180 °C are not reported because of the inability to obtain reliable measurements as a consequence of the significantly reduced surface coverage and larger particle size.

In an attempt to reduce the carbon content within the deposited films, platinum substrates [platinum-coated silicon (400) wafers], which are 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** and **2b** at deposition temperatures of 180 °C. Platinum 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 copper(I) to copper metal (Figure 11).

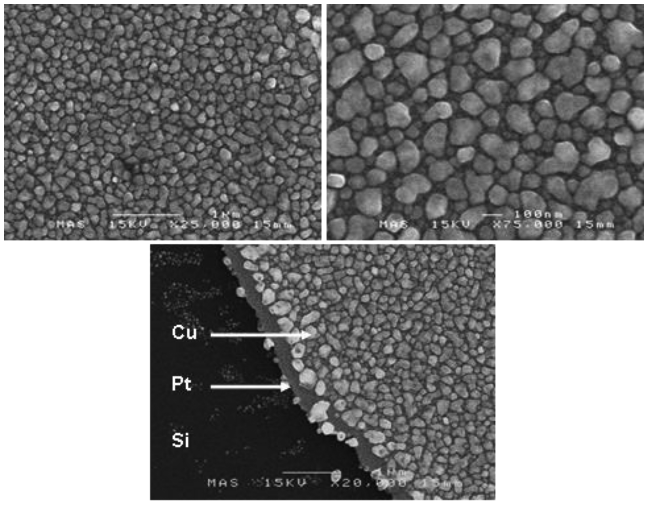

Figure 11. (Top) Electron micrographs of the copper thin films deposited onto a platinum/silicon wafer at 180 °C using complex **2a**. (Bottom) Micrograph showing the successive layers of silicon, platinum, and copper metal.

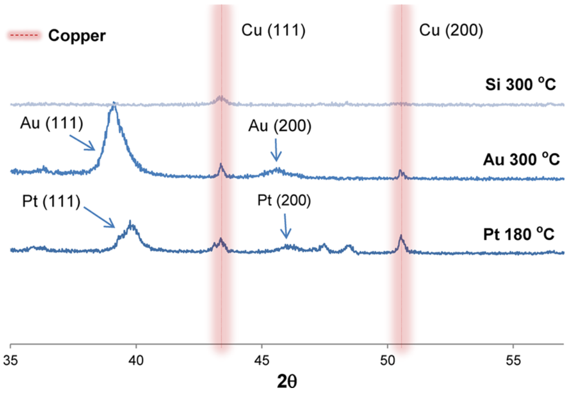

Figure 12. XRD pattern of continuous copper films deposited onto silicon (300 °C), gold/silicon (300 °C), and platinum/silicon (300 °C) substrates.

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

Analysis of the films by SEM indeed shows the films deposited onto platinum/silicon to be continuous and approximately 200 nm thick, consisting of layers of microcrystals of copper of approximately 100 μm diameter that cover the entirety of the platinum/silicon substrate.

Subsequent analysis of the films, using XPS (see ESI), shows the presence of Cu_2O 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 that 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] The removal of underlying platinum from the analysis suggests that copper thin films with ca. 97% purity are being formed.

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

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

Evaluation of the Precursor Properties and Thin Films. The copper(I) cyclopentadienyl complexes containing aryl-substituted isocyanide ligands, **2d**–**2f**, 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**–**2c** showed significantly more promise, with both the isopropyl (**2a**) and *tert*-butyl (**2b**) derivatives displaying a single thermal decomposition event with residual masses close to that expected for a copper-only residue. As part of the study, the molecular structures of complexes **2a**–**2d** and **2f** were unambiguously determined in single-crystal XRD studies, and in all cases, the complexes display linear pogo-stick-like geometries in the solid state.

A comparison of complexes **3**–**5b** $[(\eta^5\text{-R}'C_5H_4)\text{Cu}(\text{CN}^t\text{Bu})]$, where R = Me (**3b**), Et (**4b**), ^{i}Pr (**5b**), and the parent unsubstituted complex shows that, despite their isostructural nature, there are significant changes in the stability and volatility of the complexes. TGA shows that for all of 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 of these properties against the commercially available precursors cyclopentadienyl(triethylphosphine)copper(I) and CupraSelect, the lifetimes of **3b** and **4b** were low, with the products decomposing to copper metal upon standing at room temperature.

Subsequent CVD experiments therefore focused on the use of complexes **2a** and **2b**. Thin films were deposited onto silicon and gold substrates at 180 and 300 °C, under a reduced-pressure H_2 atmosphere. Films deposited onto silicon and gold 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 atom % of copper, respectively), as shown by XPS. Contrastingly, films deposited onto platinum 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 platinum substrates at low temperatures (<200

°C). Studies into the utility of complexes **2a** and **2b** 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 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 ^{i}PrNC, ^{t}BuNC, and CyNC were bought from commercial sources and used without further purification. The salts NaCp, NaMeCp, NaEtCp, and Na^{i}PrCp were all prepared according to a modified literature procedure.[43]

Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz FT-NMR spectrometer as saturated solutions in $CDCl_3$; chemical shifts are quoted in units of parts per million, relative to Me_4Si (^{1}H and ^{13}C); coupling constants are in hertz.

TGA of the complexes was performed at SAFC Hitech, Bromborough, U.K., using a Shimadzu TGA-51 thermogravimetric analyzer. Data points were collected every second at a ramp rate of 20 °C/min in a flowing (50 mL/min) N_2 stream.

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 predetermined 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 apperature in place to focus on the center of the etch pit.

Field-emission SEM 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 diffractometer, using a copper-anode X-ray source (Kα wavelength = 1.5406 Å) at the University of Bath.

*Synthesis of [ClCu(CN^{i}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 tube, followed by THF (50 mL) to give a yellow slurry. To this was added via syringe ^{i}PrNC (4.55 mL, 50.0 mmol). The reaction mixture was left to stir for 30 min, 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 **1a** as pale-yellow crystals (7.46 g, 89%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.38 (d, CH(CH_3)$_2$, 6H, J = 6.64 Hz), 6.64 (sept, CH(CH$_3$)$_2$, 1H, J = 6.64 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 22.59 (CH(CH_3)$_2$), 47.33 (t, CH(CH$_3$)$_2$, J = 5.50 Hz), 136.60 (t, CN, J = 15.29 Hz) Anal. Calcd for $C_{16}H_{28}Cl_4Cu_4N_4$: C, 28.58; H, 4.20; N, 8.33. Found: C, 31.59; H, 4.70; N, 7.61.

*Synthesis of [ClCu(CN^{t}Bu)]$_4$ (**1b**).* **1b** was synthesized in a manner analogous to that of **1a** using 4.26 g (43.0 mmol) of CuCl and 4.84 mL (43.0 mmol) of ^{t}BuNC to yield **1b** as colorless crystals (5.58 g, 71%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.46 (s, C(CH_3)$_3$, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 30.05 (C(CH$_3$)$_3$), 56.50 (C(CH$_3$)$_3$), 134.62 (t, CN, J = 15.75 Hz). Anal. Calcd for $C_{20}H_{36}Cl_4Cu_4N_4$: 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**).* **1c** was synthesized in a manner analogous to that of **1a** using 1.98 g (20.0 mmol) of CuCl and 2.49 mL (20.0 mmol) of CyNC to yield **1c** as colorless crystals (2.35 g, 56%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.42 (br m, CH_2, 16H), 1.71 (br m, CH_2, 16H), 1.89 (br m, CH_2, 8H), 3.72 (br m, CH, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 22.71, 24.70, 31.92 (CH$_2$), 53.39 (t, CH, J = 5.61 Hz), CN carbon not observed. Anal. Calcd for $C_{28}H_{44}Cl_4Cu_4N_4$: C, 40.39; H, 5.32; N, 6.72. Found: C, 41.43; H, 5.12; N, 6.76.

Complexes **1d**−**1f** 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 tube, followed by THF (25 mL) to give a yellow slurry. To this was added via syringe PhNC (2.06 g, 20.0 mmol). The reaction mixture was left to stir for 30 min, 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 **1d** as colorless crystals (2.69 g, 88%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 7.44 (br m, CH, 20H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 126.13, 126.46, 129.51, 130.08 (C_6H$_5$), 145.50 (m, CN). Anal. Calcd for $C_{28}H_{20}Cl_2Cu_2N_4$: 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**).* **1e** was synthesized using 1.13 g (11.4 mmol) of CuCl and 3.00 g of XylNC (22.8 mmol) to yield the product as colorless crystals (3.02 g, 73%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 2.42 (s, o-CCH_3, 24H), 7.08 (m, m-CH, 8H), 7.20 (m, p-CH, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 18.62 (o-CCH$_3$), 125.81, 127.75, 129.28, 135.23 (C_6H$_3$), 150.62 (br m, CN). Anal. Calcd 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 [ClCu(MesNC)$_2$]$_2$ (**1f**).* **1f** 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): δ 2.27 (s, p-CCH_3, 12H), 2.37 (s, o-CCH_3, 24H), 6.88 (s, m-CH, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 18.68 (o-CCH$_3$), 21.24 (p-CCH$_3$), 123.78, 128.63, 135.25, 139.84 (C_6H$_2$), 148.21 (m, CN). Anal. Calcd 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 [CpCu(CN^{i}Pr)] (**2a**).* **1a** (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 h, 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 min, and the volatiles were 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 **2a** as pale-yellow crystals (1.24 g, 52%, mp 73 °C).^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.35 (dt, CH(CH_3)$_2$, 6H, J = 6.60 and 2.39 Hz), 3.81 (m, CH(CH$_3$)$_2$, 1H), 5.89 (s, C_5H_5, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 22.78 (CH(CH$_3$)$_2$), 47.84 (CH(CH$_3$)$_2$), 94.62 (C_5H$_5$), CN carbon not observed. Anal. Calcd 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 [CpCu(CN^{t}Bu)] (**2b**).* **2b** was synthesized in a fashion analogous to that of **2a** using **1b** (14.57 g, 20 mmol) and sodium cyclopentadienide (7.05 g, 80.0 mmol). The dried crude product was further purified by sublimation (1×10^{-1} Torr, 40−50 °C) to afford **2b** as off-white crystals (15.25 g, 90%, mp 95 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.41 (s, C(CH_3)$_3$, 9H), 5.90 (s, C_5H_5, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 30.13 (C(CH$_3$)$_3$), 56.96 (C(CH$_3$)$_3$), 94.70 (C_5H$_5$), CN carbon not observed. Anal. Calcd for $C_{11}H_{17}CuN$: C, 56.86; H, 6.69; N, 6.64. Found: C, 56.70; H, 6.68; N, 6.57.

*Synthesis of [CpCu(CNCy)] (**2c**).* **2c** was synthesized in a fashion analogous to that of **2a** using **1c** (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 **2c** as white crystals (0.70 g, 37%, mp 118 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.36 (m, CH_2, 4H), 1.65 (m, CH_2, 4H), 1.84 (m, CH_2, 2H), 3.63 (m, CH, 1H), 5.93 (s, C_5H_5, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.50 MHz): δ 22.75, 24.72, 31.10 (CH$_2$), 53.72 (t, CH, J = 6.43 Hz), 94.64 (C_5H$_5$), CN carbon not observed. Anal. Calcd for $C_{12}H_{16}Cu_1N_1$: C, 60.61; H, 6.78; N, 5.89. Found: C, 60.78; H, 6.67; N, 5.97.

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*Synthesis of [MeCpCu(CN^{i}Pr)] (**3a**).* **3a** was synthesized in a fashion analogous to that of **2a** using **1a** (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 **3a** as white crystals (1.14 g, 67%, mp 46 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.36 (doublets of triplets, $CH(CH_3)_2$, 6H, J = 6.56 and 2.3 Hz), 2.24 (s, $C_5H_4CH_3$, 3H), 3.81 (septet of triplets, $CH(CH_3)_2$, 1H, J = 1.75 and 6.56 Hz), 5.70 (m, $C_5H_4CH_3$, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 14.44 ($C_5H_4CH_3$), 22.76 ($CH(CH_3)_2$), 47.79 ($CH(CH_3)_2$), 92.15, 95.38, 109.90 ($C_5H_4CH_3$), CN carbon not observed. The complex was too unstable to characterize by elemental analysis.

*Synthesis of [MeCpCu(CN^{t}Bu)] (**3b**).* **3b** was synthesized in a fashion analogous to that of **2a** using 7.29 g (10 mmol) of **1b** and 4.12 g (40 mmol) of sodium methylcyclopentadienide. Sublimation (1 × 10^{-1} Torr, 70 °C) of the crude product afforded **3b** as off-yellow crystals (7.96 g, 88%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.42 (t, $C(CH_3)_3$, 9H, J = 2.13 Hz), 2.24 (s, $C_5H_4CH_3$, 3H), 5.70 (m, $C_5H_4CH_3$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 14.44 ($C_5H_4CH_3$), 30.09 ($C(CH_3)_3$), 56.65 ($C(CH_3)_3$), 92.17, 95.38, 109.86 ($C_5H_4CH_3$), CN carbon not observed. Anal. Calcd 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**).* **3c** was synthesized in a fashion analogous to that of **2a** using **1c** (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 **3c** as colorless crystals (0.40 g, 40%, mp 111 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.38 (m, CH_2, 4H), 1.68 (m, CH_2, 4H), 1.87 (m, CH_2, 2H), 2.24 (s, $C_5H_4CH_3$, 3H), 3.64 (m, CH, 1H), 5.71 (m, $C_5H_4CH_3$, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 14.46 ($C_5H_4CH_3$), 22.75, 24.70, 32.02 (CH_2), 53.60 (m, CH, 1C), 92.14, 95.41, 109.95 ($C_5H_5CH_3$), CN carbon not observed. The complex was too unstable to characterize by elemental analysis.

*Synthesis of [EtCpCu(CN^{t}Bu)] (**4b**).* **4b** was synthesized in a fashion analogous to that of **2a** using **1b** (1.25 g, 1.72 mmol) and sodium ethycyclopentadienide (1.03 M in THF, 7.8 mL, 8.00 mmol). The crude product that was purified by recrystallization (hexane) to afford **4b** as colorless crystals (1.20 g, 73%). Sublimation (1 × 10^{-1} Torr, 70 °C) was also used to produce pure materials. ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.21 (t, $C_5H_4CH_2CH_3$, 3H, J^3 = 7.56 Hz), 1.43 (s, $C(CH_3)_3$, 9H), 2.54 (q, $C_5H_4CH_2CH_3$, 2H, J^3 = 7.56 Hz), 5.72 (m, $C_5H_4CH_2CH_3$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 17.87 ($C_5H_4CH_2CH_3$), 22.18 ($C_5H_4CH_2CH_3$), 30.29 ($C(CH_3)_3$), 56.92 ($C(CH_3)_3$), 92.02, 93.84, 118.58 ($C_5H_4CH_2CH_3$), CN carbon not observed. Anal. Calcd 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 [(^{i}PrCp)Cu(CN^{t}Bu)] (**5b**).* **5b** was synthesized in a fashion analogous to that of **2a** using **1b** (0.51 g, 2.00 mmol) and sodium isopropylcyclopentadienide (1.05 M in THF, 8.86 mL, 9.30 mmol). The crude product was purified by recrystallization (hexane) followed by sublimation (1 × 10^{-1} Torr, 80 °C) to afford **5b** as colorless crystals (1.42 g, 70%). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 1.23 (m, $C_5H_4CH(CH_3)_2$, 6H), 1.42 (s, $C(CH_3)_3$, 9H), 2.85 (sept, $C_5H_4CH(CH_3)_2$, 1H, J^3 = 6.80 Hz), 5.73 (m, $C_5H_4CH(CH_3)_2$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 25.77, 27.69 ($C_5H_4CH(CH_3)_2$), 30.27 ($C(CH_3)_3$), 56.84 ($C(CH_3)_3$), 91.69, 92.62, 124.42 ($C_5H_4CH(CH_3)_2$), CN carbon not observed. Anal. Calcd for $C_{13}H_{20}CuN$: C, 61.61; H, 7.94; N, 5.52. Found: C, 61.49; H, 7.72; N, 5.57.

*Synthesis of [CpCu(CNPh)] (**3d**).* **1d** (3.66 g, 6.00 mmol) and sodium cyclopentadienyl (1.06 g, 12.0 mmol) were added to separate dry Schlenk tubes under inert atmospheres of argon. THF (15 mL) was added to each, and the sodium cyclopentadienyl solution was transferred into the **1d** solution via cannula. The mixture was then left to stir for 16 h. 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 min, and the volatiles were 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 the removal of volatiles in vacuo. This resulted in a dark-yellow crude solid, which was purified by recrystallization (hexane) to afford **3d** as yellow crystals (0.990 g, 35%, mp 76 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 5.95, (s, C_5H_5, 5H), 7.45−7.28 (m, C_6H_5, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 94.82 (C_5H_5), 121.74, 126.43, 129.61, 129.82 (C_6H_5), CN carbon not observed. Anal. Calcd for $C_{12}H_{10}Cu_1N_1$: C, 62.19; H, 4.35; N, 6.04. Found: C, 67.76; H, 5.56; N, 5.38.

*Synthesis of [CpCu(XylNC)] (**3e**).* **3e** was synthesized in a fashion analogous to that of **3d** using **1e** (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 **3e** as off-white crystals (0.215 g, 30%, mp 132 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 2.35 (s, o-CCH_3, 6H), 5.96 (s, C_5H_5, 5H), 7.08 (m, m-CH, 2H), 7.20 (m, p-CH, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 18.75 (CCH_3), 94.83 (C_5H_5), 127.98, 129.36, 135.49 (C_6H_5), CN carbon not observed. The complex was too unstable to characterize by elemental analysis.

*Synthesis of [CpCu(CNMes)] (**3f**).* **3f** was synthesized in a fashion analogous to that of **3d** using **1f** (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 **3f** as off-white crystals (0.72 g, 59%, mp 140 °C). ^{1}H NMR ($CDCl_3$, 300.22 MHz): δ 2.27 (s, p-CCH_3, 3H), 2.38 (s, o-CCH_3, 6H), 5.96, (s, C_5H_5, 5H), 6.88 (s, m-CH, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.50 MHz): δ 18.59 (o-CCH_3), 21.23 (p-CCH_3), 94.81 (C_5H_5), 128.24, 135.13, 139.52 (C_6H_2, 6C), CN carbon not observed. Anal. Calcd for $C_{15}H_{16}Cu_1N_1$: 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 in the SI. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo Kα radiation (λ = 0.71073 Å). Structure solution and refinements were performed using *SHELX86*[44] and *SHELX97*[45] software, respectively. Corrections for absorption were made in all cases. For all complexes, hydrogen atoms were included at calculated positions. Data for complexes **1d**−**1f**, **2a**−**2d**. **2f**, **3a**−**3c**, and **4b** have been deposited with the Cambridge Structural Database as CCDC 1050605−1050616.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures of **1d** and **1f**, vapor pressure measurements of **2b**, **3b**, **4b**, and **5b**, EDX plots, XPS profiles, and crystallographic data for **1d**−**1f**, **2a**−**2d**, **3a**−**3c**, and **4b**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00448.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Gordon, P. G.; Kurek, A.; Barry, S. T. *ECS J. Solid State Sci. Technol.* **2015**, *4*, N3188−N3197.

(2) (a) Creighton, J. R.; Parmeter, J. E. *Crit. Rev. Solid State Mater. Sci.* **1993**, *18*, 175−238. (b) Hampdensmith, M. J.; Kodas, T. T. *Polyhedron* **1995**, *14*, 699−732. (c) Norman, J. A. T. *J. Phys. IV* **2001**, *11*, Pr3/497−Pr493/503. (d) Rickerby, J.; Steinke, J. H. G. *Chem. Rev.*

2002, *102*, 1525−1549. (e) Luo, B.; Gladfelter, W. L. *Chem. Vap. Deposition* **2009**, 320−356. (f) Grodzicki, A.; Lakomska, I.; Piszczek, P.; Szymanska, I.; Szlyk, E. *Coord. Chem. Rev.* **2005**, *249*, 2232−2258.

(3) (a) Lim, B. S.; Rahtu, A.; Gordon, R. G. *Nat. Mater.* **2003**, *2*, 749−754. (b) Mane, A. U.; Shivashankar, S. A. *Mater. Sci. Semicond. Process.* **2004**, *7*, 343−347. (c) Li, Z.; Barry, S. T.; Gordon, R. G. *Inorg. Chem.* **2005**, *44*, 1728−1735. (d) Park, K.-H.; Marshall, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 9330−9331. (e) Li, Z.; Gordon, R. G. *Chem. Vap. Deposition* **2006**, *12*, 435−441. (f) Li, Z.; Rahtu, A.; Gordon, R. G. *J. Electrochem. Soc.* **2006**, *153*, C787−C794. (g) Park, K.-H.; Bradley, A. Z.; Thompson, J. S.; Marshall, W. J. *Inorg. Chem.* **2006**, *45*, 8480−8482. (h) Ma, Q.; Guo, H.-S.; Gordon, R. G.; Zaera, F. *Chem. Mater.* **2010**, *22*, 352−359. (i) Vidjayacoumar, B.; Emslie, D. J. H.; Clendenning, S. B.; Blackwell, J. M.; Britten, J. F.; Rheingold, A. *Chem. Mater.* **2010**, *22*, 4844−4853. (j) Ma, Q.; Guo, H.; Gordon, R. G.; Zaera, F. *Chem. Mater.* **2011**, *23*, 3325−3334. (k) Dey, G.; Elliott, S. D. *J. Phys. Chem. A* **2012**, *116*, 8893−8901. (l) Huo, J.; Solanki, R.; McAndrew, J. *J. Mater. Res.* **2002**, *17*, 2394−2398. (m) Hagen, D. J.; Povey, I. M.; Rushworth, S.; Wrench, J. S.; Keeney, L.; Schmidt, M.; Petkov, N.; Barry, S. T.; Coyle, J. P.; Pemble, M. E. *J. Mater. Chem., C* **2014**, *2*, 9205−9214. (n) Coyle, J. P.; Dey, G.; Sirianni, E. R.; Kemell, M. L.; Yap, G. P. A.; Ritala, M.; Leskela, M.; Elliott, S. D.; Barry, S. T. *Chem. Mater.* **2013**, *25*, 1132−1138.

(4) (a) Lee, B. H.; Hwang, J. K.; Nam, J. W.; Lee, S. U.; Kim, J. T.; Koo, S. M.; Baunemann, A.; Fischer, R. A.; Sung, M. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4536−4539. (b) Emslie, D. J. H.; Chadha, P.; Price, J. S. *Coord. Chem. Rev.* **2013**, *257*, 3282−3296. (c) Vidjayacoumar, B.; Emslie, D. J. H.; Blackwell, J. M.; Clendenning, S. B.; Britten, J. F. *Chem. Mater.* **2010**, *22*, 4854−4866.

(5) (a) Rand, M. J. *J. Electrochem. Soc.* **1973**, *120*, 686−693. (b) Xue, Z. L.; Thridandam, H.; Kaesz, H. D.; Hicks, R. F. *Chem. Mater.* **1992**, *4*, 162−166. (c) Hierso, J. C.; Feurer, R.; Kalck, P. *Coord. Chem. Rev.* **1998**, *178*, 1811−1834. (d) Thurier, C.; Doppelt, P. *Coord. Chem. Rev.* **2008**, *252*, 155−169.

(6) (a) Dollimore, D. In *Handbook of Copper Compounds and Applications*; Richardson, H. W., Ed.; CRC Press: Toronto, 1997; pp 231−264. (b) Lang, H.; Jakob, A.; Milde, B. *Organometallics* **2012**, *31*, 7661−7693.

(7) Kodas, T. T.; Hampden-Smith, M. J. *The Chemistry of Metal CVD*; VCH: Cambridge, U.K., 1994.

(8) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104−124. (b) Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *2*, 32−37.

(9) (a) Prud'hme, N.; Duguet, T.; Samelor, D.; Senocq, F.; Vahlas, C. *Appl. Surf. Sci.* **2013**, *283*, 788−793. (b) Turgambaeva, A. E.; Prud'homme, N.; Krisyuk, V. V.; Vahlas, C. *Chem. Vap. Deposition* **2012**, *18*, 209−214. (c) Senocq, F.; Turgambaeva, A.; Prud'homme, N.; Patil, U.; Krisyuk, V. V.; Samelor, D.; Gleizes, A.; Vahlas, C. *Surf. Coat. Technol.* **2007**, *201*, 9131−9134. (d) Shirakata, S.; Yudate, S.; Terasako, T.; Isomura, S. *Jpn. J. Appl. Phys., Part 2* **1998**, *37*, L1033−L1035. (e) Shirakata, S.; Tamura, K.; Isomura, S. *Jpn. J. Appl. Phys., Part 2* **1996**, *35*, L531−L534. (f) Shirakata, S.; Morita, K.; Isomura, S. *Jpn. J. Appl. Phys., Part 2* **1994**, *33*, L739−L742. (g) Kondoh, E.; Kawano, Y.; Takeyasu, N.; Ohta, T. *J. Electrochem. Soc.* **1994**, *141*, 3494−3499. (h) Chichibu, S.; Sudo, R.; Yoshida, N.; Harada, Y.; Uchida, M.; Matsumoto, S.; Highuchi, H. *Jpn. J. Appl. Phys., Part 2* **1994**, *33*, L286−L289. (i) Honda, T.; Otoma, H.; Hara, K.; Yoshino, J.; Kukimoto, H. *Jpn. J. Appl. Phys., Part 2* **1993**, *32*, L560−L562. (j) Chichibu, S.; Yoshida, N.; Sudo, R.; Uchida, M.; Harada, Y.; Matsumoto, S.; Higuchi, H. *Proc. Electrochem. Soc.* **1993**, *93−25*, 216−224. (k) Kumar, R.; Fronczek, F. R.; Maverick, A. W.; Lai, W. G.; Griffin, G. L. *Chem. Mater.* **1992**, *4*, 577−582. (l) Houlding, V. H.; Maxwell, H., Jr.; Crochiere, S. M.; Farrington, D. L.; Rai, R. S.; Tartaglia, J. M. *Mater. Res. Soc. Symp. Proc.* **1992**, *260*, 119−124. (m) Chichibu, S.; Yoshida, N.; Higuchi, H.; Matsumoto, S. *Jpn. J. Appl. Phys., Part 2* **1992**, *31*, L1778−L1780. (n) Gross, M. E. *J. Electrochem. Soc.* **1991**, *138*, 2422−2426. (o) Beach, D. B.; LeGoues, F. K.; Hu, C. K. *Chem. Mater.* **1990**, *2*, 216−219. (p) Beach, D. B.; Kane, W. F.; Legoues, F. K.; Knors, C. J. *Mater. Res. Soc. Symp. Proc.* **1990**, *181*, 73−77. (q) Dupuy, C. G.; Beach, D. B.; Hurst, J. E., Jr.; Jasinski, J. M. *Chem. Mater.* **1989**, *1*, 16−18. (r) Hara, K.; Shinozawa, T.; Yoshino, J.; Kukimoto, H. *J. Cryst. Growth* **1988**, *93*, 771−775. (s) Hara, K.; Kojima, T.; Kukimoto, H. *Jpn. J. Appl. Phys., Part 2* **1987**, *26*, L1107−L1109.

(10) Kruck, T.; Terfloth, C. *Chem. Ber.* **1993**, *126*, 1101−1106.

(11) Johnson, A. L.; Willcocks, A. M.; Raithby, P. R.; Warren, M. R.; Kingsley, A. J.; Odedra, R. *Dalton Trans.* **2009**, 922−924.

(12) Werner, H.; Otto, H.; Ngokhac, T.; Burschka, C. *J. Organomet. Chem.* **1984**, *262*, 123−136.

(13) (a) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 5114. (b) Tsuda, T.; Saegusa, T.; Hashimoto, T. *J. Am. Chem. Soc.* **1972**, *94*, 658−659.

(14) Ogorodnikova, N. A.; Kravtsov, D. N. *Polyhedron* **1985**, *4*, 311−316.

(15) Kumar, R.; Fronczek, F. R.; Maverick, A. W.; Lai, W. G.; Griffin, G. L. *Chem. Mater.* **1992**, *4*, 577−582.

(16) Tang, J. A.; Ellis, B. D.; Warren, T. H.; Hanna, J. V.; Macdonald, C. L. B.; Schurko, R. W. *J. Am. Chem. Soc.* **2007**, *129*, 13049−13065.

(17) Hanusa, T. P.; Ulibarri, T. A.; Evans, W. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 1036−1038.

(18) Beach, D. B.; Kane, W. F.; Legoues, F. K.; Knors, C. J. *Mater. Res. Soc. Symp. Proc.* **1990**, *181*, 73−77.

(19) Tacke, M.; Teuber, R. *J. Mol. Struct.* **1997**, *408*, 507−512.

(20) Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325−5329.

(21) Lettko, L.; Rausch, M. D. *Organometallics* **2000**, *19*, 4060−4065.

(22) Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Priester, R. D.; Pittman, C. U. *J. Am. Chem. Soc.* **1982**, *104*, 884−886.

(23) Ren, H. P.; Zhao, X.; Xu, S. S.; Song, H. B.; Wang, B. Q. *J. Organomet. Chem.* **2006**, *691*, 4109−4113.

(24) (a) Olbrich, F.; Schmidt, G.; Weiss, E.; Behrens, U. *J. Organomet. Chem.* **1993**, *456*, 299−303. (b) Olbrich, F.; Behrens, U.; Groger, G.; Weiss, E. *J. Organomet. Chem.* **1993**, *448*, C10−C12.

(25) Zybill, C.; Muller, G. *Organometallics* **1987**, *6*, 2489−2494.

(26) Turgambaeva, A. E.; Krisyuk, V. V.; Prud'homme, N.; Vahlas, C. *ECS Trans.* **2009**, *25*, 1301−1308.

(27) Saegusa, T.; Ito, Y.; Tomita, S. *J. Am. Chem. Soc.* **1971**, *93*, 5656−5661.

(28) (a) Gräfe, A.; Heinen, R.; Klein, F.; Kruck, T.; Scherer, M.; Schober, M. *Appl. Surf. Sci.* **1995**, *91*, 187−191. (b) Blessmann, D.; Gräfe, A.; Heinen, R.; Jansen, F.; Kruck, T.; Terfloth, C. *Mater. Sci. Eng., B* **1993**, *17*, 104−107. (c) Blessmann, D.; Gräfe, A.; Heinen, R.; Jansen, F.; Kruck, T.; Terfloth, C. *Mater. Sci. Eng., B* **1993**, *33*, 104−107. (d) Artaud-Gillet, M. C.; Duchemin, S.; Odedra, R.; Orsal, G.; Rega, N.; Rushworth, S.; Siebentritt, S. *J. Cryst. Growth* **2003**, *248*, 163−168. (e) Hermes, S.; Schroeder, F.; Amirjalayer, S.; Schmid, R.; Fischer, R. A. *J. Mater. Chem.* **2006**, *16*, 2464−2472. (f) Mueller, M.; Hermes, S.; Kaehler, K.; van den Berg, M. W. E.; Muhler, M.; Fischer, R. A. *Chem. Mater.* **2008**, *20*, 4576−4587. (g) Mueller, M.; Lebedev, O. I.; Fischer, R. A. *J. Mater. Chem.* **2008**, *18*, 5274−5281. (h) Xue, C.; Papadimitriou, D.; Raptis, Y. S.; Esser, N.; Richter, W.; Siebentritt, S.; Lux-Steiner, M. C. *J. Appl. Phys.* **2003**, *94*, 4341−4347.

(29) Saegusa, T.; Horiguchi, S.; Tsuda, T. *Macromolecules* **1975**, *8*, 112−114.

(30) (a) Willcocks, A. M.; Pugh, T.; Hamilton, J. A.; Johnson, A. L.; Richards, S. P.; Kingsley, A. J. *Dalton Trans.* **2013**, *42*, 5554−5565. (b) Willcocks, A. M.; Robinson, T. P.; Roche, C.; Pugh, T.; Richards, S. P.; Kingsley, A. J.; Lowe, J. P.; Johnson, A. L. *Inorg. Chem.* **2012**, *51*, 246−257.

(31) (a) Bowmaker, G. A.; Hanna, J. V.; Hahn, F. E.; Lipton, A. S.; Oldham, C. E.; Skelton, B. W.; Smith, M. E.; White, A. H. *Dalton Trans.* **2008**, 1710−1720. (b) Willcocks, A. M.; Gilbank, A.; Richards, S. P.; Brayshaw, S. K.; Kingsley, A. J.; Odedra, R.; Johnson, A. L. *Inorg. Chem.* **2011**, *50*, 937−948. (c) Benouazzane, M.; Coco, S.; Espinet, P.; Barbera, J. *Inorg. Chem.* **2002**, *41*, 5754−5759. (d) Johnson, A. L.; Willcocks, A. M.; Raithby, P. R.; Warren, M. R.; Kingsley, A. J.; Odedra, R. *Dalton Trans.* **2009**, 922−924. (e) Liu, M.; Reiser, O. *Org.

Lett. **2011**, *13*, 1102−1105. (f) Toth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1988**, 1599−1605.

(32) Peng, R.; Li, M.; Li, D. *Coord. Chem. Rev.* **2010**, *254*, 1−18.

(33) Putkonen, M.; Niinistö, L. *Top. Organomet. Chem.* **2005**, *9*, 125−145.

(34) Willcocks, A. M.; Johnson, A. L.; Raithby, P. R.; Schiffers, S.; Warren, J. E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2011**, *67*, M215−M217.

(35) Senocq, E.; Turgambaeva, A.; Prud'hmme, N.; Patil, U.; Krisyuk, V. V.; Samelor, D.; Gleizes, A.; Vahlas, C. *Surf. Coat. Technol.* **2007**, *201*, 9131−9134.

(36) (a) Rushworth, S. A.; Smith, L. M.; Kingsley, A. J.; Odedra, R.; Nickson, R.; Hughes, P. *Microelectron. Reliab.* **2005**, *45*, 1000−1002. (b) Knisley, T. J.; Saly, M. J.; Heeg, M. J.; Roberts, J. L.; Winter, C. H. *Organometallics* **2011**, *30*, 5010−5017. (c) Fulem, M.; Růžička, K.; Růžička, V.; Hulicius, E.; Šimeček, T.; Melichar, K.; Pangrác, J.; Rushworth, S. A.; Smith, L. M. *J. Cryst. Growth* **2003**, *248*, 99−107.

(37) van Mol, A. M. B.; Driessen, J. P. A. M.; Linden, J. L.; de Croon, M. H. J. M.; Spee, C. I. M. A.; Schouten, J. C. *Chem. Vap. Deposition* **2001**, *7*, 101−104.

(38) See http://www.airproducts.com/~/media/downloads/c/cupraselect-cutmvs/data-sheets/en-cutmvs-datasheet.pdf.

(39) Waechtler, T.; Ding, S. F.; Hofmann, L.; Mothes, R.; Xie, Q.; Oswald, S.; Detavernier, C.; Schulz, S. E.; Qu, X. P.; Lang, H.; Gessner, T. *Microelectron. Eng.* **2011**, *88*, 684−689.

(40) Martensson, P.; Carlsson, J. O. *J. Electrochem. Soc.* **1998**, *145*, 2926−2931.

(41) (a) Tsay, J. S.; Mangen, T.; Wandelt, K. *Thin Solid Films* **2001**, *397*, 152−156. (b) Holst, B.; Nohlen, M.; Wandelt, K.; Allison, W. *Surf. Sci.* **1997**, *377*, 891−894.

(42) Tanabiki, M.; Tsuchiya, K.; Kumanomido, Y.; Matsubara, K.; Motoyama, Y.; Nagashima, H. *Organometallics* **2004**, *23*, 3976−3981.

(43) Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2003**, *22*, 877−878.

(44) Sheldrick, G. M. *SHELX-86, Computer Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

(45) (a) Sheldrick, G. M. *SHELX-97, Computer Program for Crystal Structure Refinement*; Univerity of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

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