Theor Chem Acc (2014) 133:1416
DOI 10.1007/s00214-013-1416-y

REGULAR ARTICLE

Copper(I) carbene hydride complexes acting both as reducing agent and precursor for Cu ALD: a study through density functional theory

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Received: 3 October 2013 / Accepted: 24 October 2013 / Published online: 14 November 2013
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Abstract We propose dual functional copper complexes that may act both as reducing agents and as Cu sources for prospective Cu atomic layer deposition. The example here is a CuH carbene complex, which can donate the H^- anion to another Cu precursor forming neutral by-products and metallic Cu(0). We compute that such a reaction is thermodynamically possible because the Cu–H bond is weaker than that of Cu–C (from the carbene). Most other neutral ligands such as PPh_3 and BEt_3 show opposite order of bond strengths. We also find that substitution in the carbene by electronegative groups reduces the Cu–H bond strength. This further facilitates the donation of H^- to the surface. The most promising copper carbene precursor is computed to be 1,3-diphenyl-4,5-imidazolidinedithione copper hydride (S-NHC)–CuH.

Keywords ALD · Carbene hydride · DFT · Cu

1 Introduction

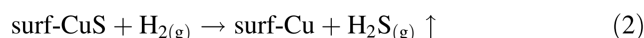
The atomic layer deposition (ALD) of copper is a challenge to the scientific community due to the need for conformal thin films of Cu in the electronics industry, where it is used as an interconnect material. A decrease in thickness of the Cu seed layer will permit further decrease in the size of the electronic devices. However, the formation of copper islands rather than a uniform layer during ALD is preventing such scaling of the seed layer. This problem has been highlighted by the International Technology Roadmap for Semiconductors as a key target [1].

The usual approach to Cu ALD is to try reducing agents such as hydrogen [2–5], alcohols [6] or hydrazine [7] along with Cu precursors known for chemical vapor deposition (CVD). Problems remain with the island formation and the impurities that come into the system from the reducing agents. In 2009, Lee et al. [8] proposed the use of an organometallic reagent $ZnEt_2$ as the reducing agent. But a subsequent study by Vidjayacoumar et al. [9, 10] showed that there is Zn contamination in the system. We have studied this transmetallation reaction mechanism using density functional theory (DFT) [11]. We suggest that metals close to Cu in the electrochemical series, such as Zn, have a high chance of co-deposition along with copper. Thus, the use of an organometallic reagent as a reducing agent is limited by the choice of the metal.

Hydrogen (H_2) can be viewed formally as a proton donor and hydride donor and so can be used in various different ways for copper formation. First, it can be used to protonate the ligand (L) that is attached to the copper center and simultaneously reduce copper to metallic form.

$$CuL_{2(g)} + H_{2(g)} \rightarrow Cu_{(s)} + 2HL_{(g)} \quad (1)$$

Alternatively, if there is a sulfide or nitride covered surface, it can combine to form H_2S or NH_3, respectively, leaving elemental Cu on the surface.



$$\text{surf-CuS} + H_{2(g)} \rightarrow \text{surf-Cu} + H_2S_{(g)} \uparrow \quad (2)$$

There have been similar attempts to convert other copper binary compounds such as Cu_3N [12] into copper metal by using molecular hydrogen. However, in order to crack the H–H bond, energy in excess of 400 kJ/mol is

Published as part of a special collection of articles focusing on chemical vapor deposition and atomic layer deposition.

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required [13]. Providing this as thermal energy means a high deposition temperature, which has been considered responsible for copper agglomeration. As an alternative, H plasma has often been used for the reduction [14]. However, the narrow and deep interconnect features where the Cu is to be coated increase the probability of re-formation of a H_2 molecule rather than a reactive H radical. Thus, a thermal ALD technique is being targeted for deposition of Cu in these applications.

If a new hydride source can be found with the following criteria, then it can be regarded as a good alternative to molecular hydrogen.

- *Weakly bound hydride*: Hydride should be easily donated by the compound without needing high thermal energy to break the bond.
- *Exothermic reaction*: The overall ALD reaction between the reagents producing Cu(0) should be exothermic in nature.
- *Precursors adsorb readily*: The precursors that are used in the ALD reaction should have strong adsorption onto the growing copper surface.
- *By-products desorb readily*: By-products that remain adsorbed onto the surface may lead to impurities. Thus, by-products that can be easily desorbed should be favored.
- *Free of foreign metals*: Metals that are close to copper in the electrochemical surface have a high chance of co-deposition along with copper. Thus, a non-copper organometallic reducing agent should be avoided even if it has other desirable properties.
- *Commercially available chemical*: Being easily available in the market and cheap would be an added advantage.
- *Volatile and stable during delivery*: The hydride source should be volatile at low temperature and stable during delivery into the reactor in the gas phase.

Ritala et al. [15] have proposed in 2004 a technique to deposit Al_2O_3 with two Al compounds AlR_3 and $Al(OR)_3$. The use of only Al in the two reagents helps to reduce the changes in impurity and improve the quality of deposition. In this paper, our main target is to achieve a similar deposition technique for Cu metal from two Cu precursors.

Recently, Cu carbenes have been considered as a new family of precursor compounds [16, 17]. A carbene is a neutral molecule containing carbon with two bonds and two unshared electrons, i.e., R_2C: Carbenes are thus strong Lewis bases and candidates as neutral ligands in metal complexes. The first persistent carbene was prepared by Wanzlick's group in 1970s. They formed imidazole-2-ylidene carbene by the deprotonation of an imidazolium salt. It was believed that these imidazole-based carbenes, with a $4n + 2$ π-electron ring system, should be more stable than the 4,5-dihydro analogs, due to Hückel-type aromaticity. The carbene molecule is not isolated, but obtained as a coordination compound with, e.g., mercury, copper and isothiocyanate [18–20]. Copper carbene complexes have a number of uses in organic chemistry. For instance, a copper carbene complex with Cl has been widely studied for possible use in alkylation, allylation and reduction in organic chemistry [21–23]. A copper(I) carbene OH complex has been used for C–H bond activation [24]. Copper(I) hydride complexes such as $CuH(PPh_3)$ are known to be mild reducing agents [25] and intermediates during catalysis reactions.

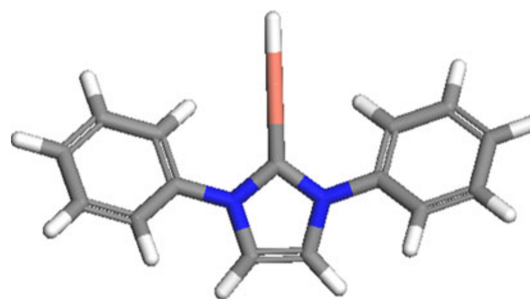


Fig. 1 The *N*-heterocyclic-Cu hydride 1,3-diphenyl-imidazolin-2-ylidene (NHC) copper hydride. *Color* code: *brown* copper, *white* hydrogen, *blue* nitrogen, *gray* carbon

In this work, we are proposing a modified 1,3-diphenyl-imidazolin-2-ylidene copper hydride complex that has been synthesized by Mankad et al. [26], as a suitable hydride donor and as a source of Cu (as seen in Fig. 1). Donation of hydride as a reducing agent broadens the chemistry of its use as the resulting proton can bond with various anionic ligands from other copper precursors and form neutral by-products that can be readily purged out of the system. Related *N*-heterocyclic copper hexamethyldisilazides $(NHC)Cu(Si(NMe)_2)_2$ have been studied by Coyle et al. [27]. In this work, we use DFT to examine the potential of the copper carbene hydride complex to be used for Cu ALD.

2 Methods

To evaluate certain aspects such as the reaction energies, the adsorption of the precursors and desorption of the by-products of the copper carbene complexes, we have used DFT as implemented in the TURBOMOLE code version 6.4 [28]. As a level of calculation, we have taken the Perdew–Burke–Ernzerhof (PBE) [29] functional, which is suitable for organometallic systems and an all electron double zeta with polarization basis set SV(P) [30]. Selected geometries were re-optimized with triple zeta TZVPP basis set [31, 32] and PBE+D3 dispersion corrected functional

[33], first separately and then together to check the effect on reaction energies (Sect. 3.3). Unconstrained geometry optimization was carried out on all systems. The Cu_{55} cluster of C_{3v} geometry developed by Larsson et al. [34] has been chosen as a model for the Cu(111) surface during growth. All the Cu complexes studied are closed shell. In order to check the adsorption of the molecules at the edges, a few calculation using larger molecules such as the copper precursors has been carried out at the edges.

To calculate reaction energies for Cu ALD, we require the total energy per Cu atom of bulk copper metal. However, TURBOMOLE is limited to gas-phase atoms or clusters. We therefore correct the computed energy of a gas-phase $Cu_{(g)}$ atom using the adhesion energy computed for bulk $Cu_{(s)}$ with the periodic code VASP [35]. In these calculations, the energy cutoff is 300 eV, an $8 \times 8 \times 8$ Monkhorst-Pack k-point mesh is used and the functional (PBE) is the same as for the gas-phase cluster calculations. Nevertheless, there may still be basis set or functional dependence in the calculations of $Cu_{(g)}$, and the resulting reaction energies should be interpreted as rough estimates.

The entropy of the molecules (both precursors and by-products) has also been calculated in the gas phase from vibrational analysis using TURBOMOLE [36]. $\Delta G_{ad} = \Delta E_{ad} - T\Delta S_{ad}$ denotes the free energy needed by the molecules to be adsorbed onto the surface. The entropy has been calculated at $T = 120$ °C as this is a typical target temperature for Cu ALD. It is assumed that the entropy of the molecules adsorbed onto the bare copper surface is primarily vibrational entropy and that is roughly constant. This is because, after being adsorbed onto the surface, the molecule loses its translational and rotational degrees of freedom. These are therefore the major contributions to ΔS_{ad}.

3 Results and discussion: evaluation of the copper carbene as a new precursor and reducing agent

We use the criteria in Sect. 1 to evaluate the copper carbene complexes as new alternative sources of both hydride and copper.

3.1 Weakly bound hydride source

We seek a Cu–H bond that is sufficiently weak to break during ALD, but stable during delivery.

Therefore, using quantum chemical calculations, we have explored bond energies in the copper carbene complexes via Eqs. 3 and 4. Equation 3 shows the homolytic dissociation of the complex to form XCu and neutral H (X = ligand) while Eq. 4 refers to homolytic dissociation of the same into CuH and X. In reality of course, these bond dissociation energies may be modified by adsorption and by the presence of co-reagents. We have taken neutral ligands such as PPh_3 and BF_3 to understand the chemistry of bond breaking.

Table 1 Homolytic bond dissociation energy for copper ligand complexes XCuH according to Eqs. 3 and 4 with the copper-ligating atom bond length shown as Cu–X

Ligand (X)	Cu–X (Å)	ΔE (kJ/mol)	
		Equation 3	Equation 4
PPh_3	2.21	216.3	169.8
$P(OEt)_3$	2.19	228.5	167.3
BEt_3	2.13	165.2	106.6
BF_3	2.20	139.6	57.9
N-heterocyclic carbene (NHC)	1.91	231.1	241.5
Sulfur substituted *N*-heterocyclic carbene (S-NHC)	1.90	200.1	247.0
Methyl substituted *N*-heterocyclic carbene (CH_3-NHC)	1.90	248.8	239.6
Oxosubstituted *N*-heterocyclic carbene (O-NHC)	1.89	269.1	281.0
Chlorosubstituted *N*-heterocyclic carbene (Cl-NHC)	1.90	231.3	236.2

$$\mathrm{XCuH} \rightarrow \mathrm{XCu} + \mathrm{H} \quad (3)$$

$$\mathrm{XCuH} \rightarrow \mathrm{CuH} + \mathrm{X} \quad (4)$$

The computed ΔE values for these reactions at $T = 0$ K are presented in Table 1 along with the bond length of Cu to the ligating atom in the ligand. The Cu–H bond length remains almost constant (1.5 Å) in all the cases regardless of ΔE for Eq. 3.

From Table 1, we can see that the P- and B-based ligands give complexes with stronger Cu–H bonding (Eq. 3) than Cu–X (Eq. 4), assuming that there is no chemical effect at the surface that changes the energetics of Cu–H versus Cu–X dissociation. We find that the NHC complex (Fig. 1) shows a difference between ΔE values of <12 kJ/mol. However, when we substitute two hydrogen atoms at 4,5 positions on the heterocycle with sulfur atoms as in Fig. 2, the difference is around 47 kJ/mol. This substituted ligand in the compound is called 1,3-diphenyl-4,5-imidazolidinedithione copper hydride (S-NHC)CuH. This lower bond strength for Cu–H compared to Cu–X enables the Cu–H bond to break first and liberate a H radical (homolytic fission) or anion (heterolytic fission), which can act as the electron donor to the Cu centers. The difference in ΔE is very little if we substitute with other electron-withdrawing groups (–I inductive effect) such as Cl^-. If we substitute with positive inductive effect (electron donating) groups such as $-CH_3$, then the energy

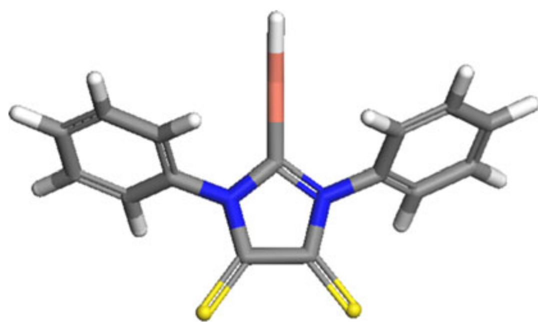


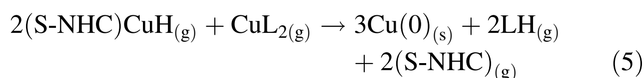
Fig. 2 (S-NHC)CuH showing S substituted for H at 4 and 5 positions. *Color* code: *brown* copper, *white* hydrogen, *blue* nitrogen, *gray* carbon, *yellow* sulfur

difference is reversed. We conclude that an electron-withdrawing group on the heterocycle is favorable for making the hydride accessible.

3.2 Exothermic reaction energy

The next metric that we computed to assess the suitability of the copper carbene, both as a precursor and also as a reducing agent, is the reaction energy of the proposed ALD reaction. Deposition of copper from the single source copper carbene might be possible via a CVD-type reaction at elevated temperatures rather than ALD. However, our interest is in ALD and so at least two reagents are necessary.

One ALD reaction in which we propose using the carbene as a reducing agent is as follows:



$$2(\text{S-NHC})\text{CuH}_{(g)} + \text{CuL}_{2(g)} \rightarrow 3\text{Cu}(0)_{(s)} + 2\text{LH}_{(g)} + 2(\text{S-NHC})_{(g)} \quad (5)$$

Here, L is the ligand from the second precursor.

In (S-NHC)CuH, the S-NHC is a spectator ligand that does not have any specific role. The H has the dual role of delivering electrons to Cu(I)/Cu(II) and also bonding with the ligand L in order to form a neutral by-product. The second copper precursor $\text{CuL}_{2(g)}$ has the dual role of delivering the copper atom and also providing ligands to saturate the surface and later bond with the H from the copper carbene complex. The ligand (L) can be dmap (diphenylamine-2-propoxide), acac (acetylacetonate) or any other commonly used ligand [11].

The two ligands studied here differ in the π conjugation (present in the acac ligand) and also in the electronegativity of the ligating atom. Both the precursors have exothermic reaction energies of similar magnitude for Eq. 5. For the dmap precursor, the computed reaction energy is −22 kJ/mol, and for the acac precursor, it is −28 kJ/mol at $T = 0$ K. This shows that the reaction is feasible for different copper precursors, with only a weak dependence on the precursor used. However, the exact magnitude of the exothermicity is probably dependent on the method used.

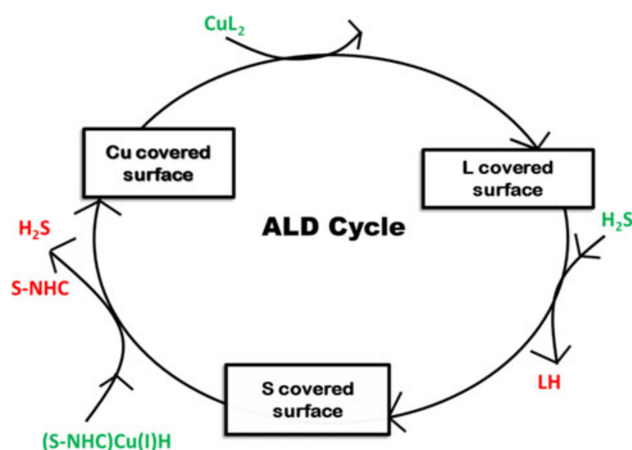
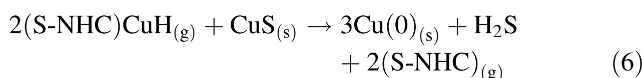


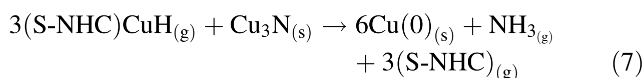
Fig. 3 Flowchart showing the three-step ALD cycle for the deposition of Cu with the intermediate formation of CuS layer. *L* ligand and *S* sulfide

Cu can also be deposited by a three-step ALD process. A thin layer of CuS or else Cu_3N can be deposited in the first two ALD steps. The sulfide or the nitride layer can then be reduced by (S-NHC)CuH in the third step, resulting in the deposition of $Cu_{(s)}$. ALD of CuS [37] is known in the literature, and deposition of Cu with Cu_3N has also been tried before [12]. The different steps are shown in Fig. 3.

For the reduction in copper sulfide, the probable reactions are presented in Eq. 6 and those for copper nitride are presented in Eq. 7. If H_2S or NH_3 are used as the co-reagents to generate CuS or Cu_3N respectively from CuL_2, then the ALD reaction energies for these three-step processes are identical to those of the two-step ones (Eq. 5).



$$2(\text{S-NHC})\text{CuH}_{(g)} + \text{CuS}_{(s)} \rightarrow 3\text{Cu}(0)_{(s)} + \text{H}_2\text{S} + 2(\text{S-NHC})_{(g)} \quad (6)$$



$$3(\text{S-NHC})\text{CuH}_{(g)} + \text{Cu}_3\text{N}_{(s)} \rightarrow 6\text{Cu}(0)_{(s)} + \text{NH}_{3_{(g)}} + 3(\text{S-NHC})_{(g)} \quad (7)$$

3.3 Precursors should adsorb and by-products should desorb readily

It is a criterion for successful ALD that the reactants adsorb but the by-products desorb from the surface, even at low temperatures. Therefore, another metric is the free energy of adsorption onto or desorption from the bare copper surface, modeled by a Cu(111) facet on a 55-atom Cu cluster. There is molecular adsorption for all the compounds listed in Table 2. NH_3,H_2S, acacH and dmapH show physisorption on the bare copper surface. However, there are significant differences in the Δ*G* values due to the

Table 2 Energy of adsorption of the molecules onto a Cu(111) model surface computed by SV(P)/PBE

Molecules	ΔE_{ad}	$T\Delta S_{ad}$	ΔG_{ad}^{120}
(S-NHC)CuH	−518.4	638.2	119.8
(NHC)CuH	−296.6	677.6	381.0
$Cu(acac)_2$	−258.4	179.2	−79.2
$Cu(dmap)_2$	−249.0	184.0	−64.9
NH_3	−47.1	95.8	48.7
H_2S	−43.8	47.7	3.8
S-NHC	−253.0	608.4	355.4
NHC	−182.1	648.4	460.3
acacH	−91.5	339.8	248.3
dmapH	−102.1	497.4	395.3

Negative energy shows that adsorption of the molecule is favorable. The entropy contribution of the molecules has been calculated at $T = 120$ °C. The energies are in kJ/mol

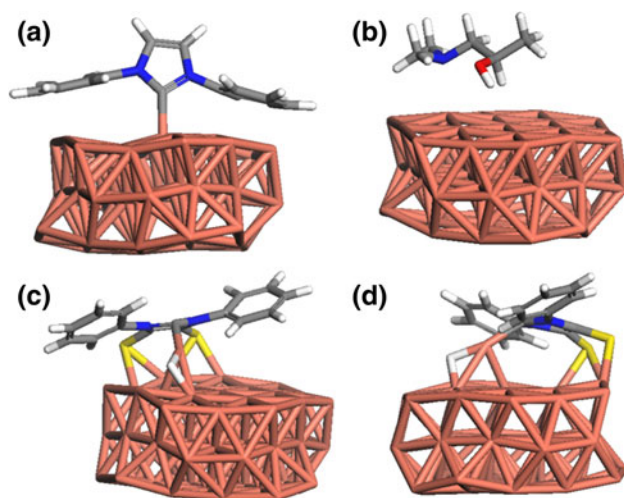


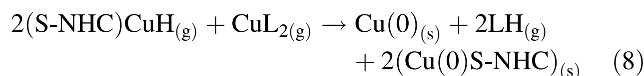
Fig. 4 **a** NHC carbene chemisorbed onto the bare copper surface via C. **b** dmapH protonated ligand physisorbed onto the surface. **c** (S-NHC)CuH adsorbed onto the surface via Cu and S. **d** is the same as **c** from a different viewpoint. *Color* code: *brown* copper, *white* hydrogen, *blue* nitrogen, *gray* carbon, *yellow* sulfur

entropy factor. As shown in Table 2, we find that $\Delta G > 0$ at $T = 120$ °C for all reactants (except the CuL_2 precursors) and by-products, indicating that desorption is always favored. The (S-NHC)CuH precursor adsorbs strongly onto the copper surface through bonds between the under coordinated Cu surface and the S atoms.

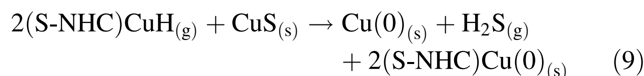
We can see that the (S-NHC)CuH compound adsorbs more strongly than the corresponding compound without any sulfur substitution Fig. 4c, d. Thus, the sulfur containing compound will be a better choice as a precursor. The by-products S-NHC and NHC are computed to desorb readily, as evidenced by the positive values of their adsorption free energy. The adsorption energies for the two carbene precursors were checked by optimization at the SV(P)/PBE+D3 level of calculation at first. This gives ΔE_{ad} of −573.7 kJ/mol for (S-NHC)CuH and −311.6 kJ/mol for (NHC)CuH, 4–10 % greater than the uncorrected PBE values in Table 2. At TZVPP/PBE+D3 level of calculation, we obtain ΔE_{ad} of −592.6 kJ/mol for (S-NHC)CuH and −320.6 kJ/mol for (NHC)CuH, 14–8 % greater than the SV(P)/PBE values in Table 2. The (S-NHC)CuH has larger change in ΔE_{ad} compared to the non-sulfated precursor. This indicates slight under-bonding with the smaller basis and without dispersion. The computational cost of the larger basis precludes us from applying it to all the other adsorption energies.

The by-product NH_3 has low adsorption energy and hence can be easily desorbed. However, H_2S has a free energy of adsorption approximately equal to zero and therefore is less likely to desorb. Free protonated ligands such as acacH and dmapH also have poor adsorption energies and hence can be readily desorbed. Testing the adsorption of the molecules near the edge of the cluster with the larger precursor molecules, we find that the adsorption energy increases by around 30 kJ/mol as the larger adsorbate wraps around the cluster edge.

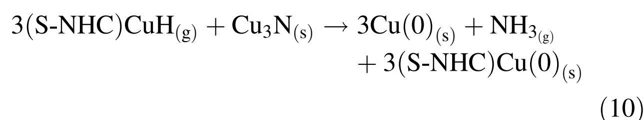
There can be a competing reaction to Eq. 5 where the carbene does not desorb from the surface but stays attached to the copper atom. This is described in Eq. (8). However, our calculations show that desorption of free carbenes is highly favored (Table 2). We therefore suggest that the Eq. 8 is unlikely. Likewise, competing reactions for the 3-step ALD Eqs. (9, 10) in which (S-NHC)Cu adducts persist is possible.



$$2(\text{S-NHC})\text{CuH}_{(g)} + \text{CuL}_{2(g)} \rightarrow \text{Cu}(0)_{(s)} + 2\text{LH}_{(g)} + 2(\text{Cu}(0)\text{S-NHC})_{(s)} \quad (8)$$



$$2(\text{S-NHC})\text{CuH}_{(g)} + \text{CuS}_{(s)} \rightarrow \text{Cu}(0)_{(s)} + \text{H}_2\text{S}_{(g)} + 2(\text{S-NHC})\text{Cu}(0)_{(s)} \quad (9)$$



$$3(\text{S-NHC})\text{CuH}_{(g)} + \text{Cu}_3\text{N}_{(s)} \rightarrow 3\text{Cu}(0)_{(s)} + \text{NH}_{3_{(g)}} + 3(\text{S-NHC})\text{Cu}(0)_{(s)} \quad (10)$$

We can also use the data in Table 2 to assess the viability of the proposed two-step (Eq. 5) and three-step (Eqs. 6, 7) ALD process. A two-step process without intermediate formation of the binary compound might be a better choice because the protonated ligands (LH) desorb more readily from the surface than NH_3 and H_2S. A three-step process might therefore increase the chances of impurities.

To summarize this section, we see that the proposed new precursors (S-NHC)CuH adsorb strongly and the by-

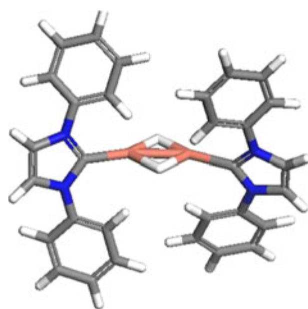


Fig. 5 *N*-heterocyclic-Cu hydride dimer. *Color* code: *brown* copper, *white* hydrogen, *blue* nitrogen, *gray* carbon. The computed dihedral angle between C–Cu–Cu–C where the C is from the ligated carbene molecule is 16°

products desorb readily, thus fulfilling an important requirement for a good ALD reaction to take place.

3.4 Free of foreign metals

There is no foreign metal present in the proposed system, and hence, there is no chance of any impurity coming from the co-deposition of another metal as happens for the reaction with $ZnEt_2$ [8]. C, N and O impurities are expected from the possible thermal decomposition of the ligands.

3.5 Synthesizable and commercially available

Although copper carbene compounds have not been functionalized yet with S in this way, a Pd carbene has been functionalized at 4, 5 carbons with ester groups by Hara et al. [38].

3.6 Volatile and stable during delivery

Since the –I electron-withdrawing (inductive effect) substituted copper compounds have not been synthesized yet, we cannot comment about stability during delivery. However, (NHC)CuH complexes have a tendency to be in dimer form as mentioned by Mankad et al. [26]. The probable dimer structure optimized with DFT is presented in Fig. 5. The dimer is computed to be nearly isoenergetic with a pair of monomers (dimerization costs $\Delta E = +5$ kJ/mol). However, the monomer structure is favored by entropy. Coyle et al. [19] mention in their work that the copper carbene compounds synthesized by them show low volatility in thermogravimetric analysis (TGA).

4 Conclusion

As new precursors for Cu ALD, we propose *N*-heterocyclic copper carbene hydrides, substituted with –I (electron-withdrawing inductive) groups. An example is 4,5 imidazolidinedithione-*N*-heterocyclic copper carbene (S-NHC)CuH. Due to the weak bond between copper and hydrogen in (S-NHC)CuH, the hydride anion is readily available as a reducing agent. A second Cu precursor is needed as co-reagent to complete the ALD cycle. Thus, low-temperature ALD can perhaps be carried out, and the problem of islanding can perhaps be alleviated in this manner. As the computed ALD reaction energies are exothermic for our test cases, we can conclude that the proposed ALD reactions are feasible.

When using an organometallic reagent as a reducing agent, there is always the danger of reduction in the metal center, which may lead to unwanted co-deposition of that metal. Here, we propose a Cu-based reducing agent, so that co-deposition is desirable. We find that such co-deposition of copper from the copper carbene complex is always favored. We can also see that the reactant adsorbs more readily to the surface than the corresponding by-products, such as the protonated acac ligand. This indicates that the by-products can be desorbed from the surface in a clean ALD process. A current disadvantage of the process is that the proposed precursor is not commercially available.

Thus, we propose a S substituted copper(I) carbene hydride functioning both as a reducing agent and as a copper source for the ALD of copper metal.

Acknowledgments We are grateful to Science Foundation Ireland (SFI) for funding under the project ALDesign http://www.tyndall.ie/aldesign Grant Number 09.IN1.I2628 and to Prof. Chuck Winter of Wayne State University for useful discussions.

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