Inorg. Chem. **2005**, *44*, 1728–1735

Inorganic Chemistry
Article

Synthesis and Characterization of Copper(I) Amidinates as Precursors for Atomic Layer Deposition (ALD) of Copper Metal

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Received October 27, 2004

A series of copper(I) amidinates of the general type $[(R'NC(R)NR'')Cu]_2$ (R' and $R'' =$ *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl; $R =$ methyl, *n*-butyl) have been synthesized and characterized. These compounds are planar dimers, bridged by nearly linear N–Cu–N bonds. Their properties (volatility, low melting point, high thermal stability, and self-limited surface reactivity) are well-suited for atomic layer deposition (ALD) of copper metal films that are pure, highly conductive, conformal, and strongly adherent to substrates.

Introduction

Atomic layer deposition (ALD) is a method currently used for making highly conformal thin films in computer chips, displays, magnetic devices for information storage, and optical communication systems.[1,2] ALD processes have been investigated intensively in recent years, particularly for metal oxides,[3] metal nitrides, and pure metals.[4] Metal amidinates have been found to be suitable as precursors for the ALD of transition metals and metal oxides.[5] Certain amidinates of Ti, V, Mn, Fe, Co, Ni, Cu, and La have the required volatility, high thermal stability, and high reactivity required for successful use in ALD.[6]

Copper is replacing aluminum as the interconnect metal in microelectronics because of its relatively low resistivity and excellent electromigration properties. Much attention has focused on the deposition of copper in increasingly narrow trenches.[7,8] Because of their excellent step coverage, conformality, and high aspect ratio, thin films made by ALD might be able to satisfy the future requirements in microelectronics metallization.[9] ALD has been demonstrated to make barrier layers such as WN,[10] Co adhesion layers,[11] and thin copper films as seed layers for subsequent electrochemical deposition of copper.[5]

Despite the promising properties of ALD films, a lack of suitable copper precursors has hindered the use of ALD for copper metallization or other applications. All of the copper compounds previously proposed as precursors (summarized in Table 1) have one or more shortcomings. Copper halides, such as copper(I) chloride, Cu_3Cl_3, can be reduced with molecular hydrogen,[12] but their high vaporization and deposition temperatures (around 400 °C) resulted in agglomerated, discontinuous copper films. Also, the hydrochloric acid byproduct from this process can etch substrates and corrode deposition equipment. ALD of copper from copper(II) 2,2,6,6-tetramethylheptanedionate, $Cu(thd)_2$, succeeded only on platinum/palladium substrates.[13,14] Fluorination of β-diketonates [e.g., copper(II) hexafluoroacetyl-

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10.1021/ic048492u CCC: $30.25

Table 1. Melting Points and Vapor Pressures of Various Copper Precursors Used in ALD of Copper

copper precursor	melting point (°C)	vapor pressure/ temperature (Torr/°C)	ref(s)
Cu_3Cl_3	430	−	12
$Cu(thd)_2$	198 (dec)	−	13, 14
$Cu(hfac)_2.xH_2O$	130−134	0.25/60	16, 17
$[Cu(^iPr\text{-}Me\text{-}amd)]_2$, **3**	147	0.05/70	5, 6
$[Cu(^sBu\text{-}Me\text{-}amd)]_2$, **9**	77	0.1/85	this work
$[Cu(^nPr\text{-}Me\text{-}amd)]_2$, **1**	65	0.05/55	this work

acetonate, $Cu(hfac)_2$] increases their volatility;[15] ALD of copper was demonstrated with $Cu(hfac)_2$ using formaldehyde as a reducing agent.[16,17] However, fluorine impurities in these copper films cause poor adhesion to substrates such as tantalum and reliability problems in microelectronic devices. Copper(I) *N*,*N*′-diisopropylacetamidinate, $[Cu(^iPr\text{-}amd)]_2$, contains no halogens, and is volatile, thermally stable, and reactive to molecular hydrogen at low temperatures (<200 °C).[5]

All of these copper precursors previously used for ALD have melting points above the sublimation temperatures typically used for operating ALD processes. Thus, their solid sublimation rates are generally nonreproducible, because they depend on the particle size, which changes during the sublimation process. The purification and handling of solid precursors is also inconvenient. One of the advantages of copper(I) amidinates is that one can vary the six pendant alkyl groups to adjust the properties of the precursors. In this paper, we report a family of 11 previously unknown copper(I) amidinate compounds with various different pendant alkyl groups. These new amidinato copper precursors provide at least four benefits compared with other types of ALD precursors: Many of these amidinate complexes have lower melting points, such as copper(I) *N*,*N*′-di-*sec*-butylacetamidinate ($[Cu(^sBu\text{-}Me\text{-}amd)]_2$, **9**) and copper(I) *N*,*N*′-di-*n*-propylacetamidinate ($[Cu(^nPr\text{-}Me\text{-}amd)]_2$, **1**). These compounds (melting points around 60−80 °C) evaporate from their thermally stable liquid states (around 100 °C), thereby providing very reproducible sources of vapor for ALD. Their second advantage is that the deposition temperatures are lower (around 180 °C) than has been achieved by any of the previous precursors, providing smoother film morphology because less agglomeration occurs at lower temperatures. A third advantage is that the copper films are pure [impurities below the detection limit of Rutherford backscattering spectroscopy (RBS), <1 atom %]; thus low electrical resistivity can be achieved. Finally, unlike copper halides, the byproduct vapors do not corrode substrates or deposition equipment and do not cause poor adhesion of the films.

Experimental Section

General Considerations. All reactions and manipulations were done under a pure N_2 atmosphere using either standard Schlenk techniques or a glovebox. Ether, tetrahydrofuran (THF), acetonitrile, and hexanes were purified by being passed through a drying column and a deoxygenating column using an Innovative Technology solvent purification system. Solvents were then stored over 4-Å molecular sieves. Alkylamines (RNH_2, R = *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, diethyl) were distilled from sodium or KOH prior to use. Methyllithium, butyllithium, valeronitrile, 1,3-diisopropylcarbodiimide, 1,3-di-*tert*-butylcarbodiimide, *N*-bromosuccinimide (NBS), *tert*-butyl isothiocyanate, and CuCl were purchased and used as received from Aldrich Chemical Co. *sec*-Butyl isothiocyanate was used as received from Alfa Aesar Co. Dichloromethane was used as received from EMD Chemicals Inc.

Physical Measurements. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 spectrometer. Elemental analysis was performed by Desert Analytics Laboratory, Tucson, AZ. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Netzsch STA 449C instrument in nitrogen atmosphere inside a drybox. The measurements were done in open aluminum crucibles with 10−20 mg of sample; the temperature ramp rate was 10 K/min. Melting points were measured in sealed capillaries using a Mel-Temp II apparatus and are compared with the results from TGA/DSC. Molecular weight determinations by the freezing point depression method in solution were done by dissolving 0.3−0.4 g of compound in 3.0−4.0 g of recrystallized *p*-xylene. The temperature was recorded electronically from a thermocouple every 10 s for at least 2 min, and the measurements were repeated at least three times to ensure reproducibility. Vapor pressures were estimated using a thermocouple pressure gauge during sublimation or distillation of purified compounds. In the case of compound **9**, the vapor pressure was also corroborated by transport measurements of a known mass from a source bubbler.

Synthesis of Symmetric Amidine Ligands. *N*,*N*′-Dialkylacetamidines were synthesized as illustrated in Scheme 1, in a manner similar to that reported in the literature.[18] A solution of 50:50:1 mole ratio of alkylamine/acetonitrile/$La(CF_3SO_3)_3$ was refluxed for 18 h at around 80 °C under nitrogen atmosphere. The unreacted starting materials (mainly acetonitrile) were then removed under partial vacuum at room temperature. The byproduct 2,4,6-trimethyl-1,3,5-triazine [$C_6N_3H_9$, white crystals, melting point 55 °C, ^1H NMR (C_6D_6, 23 °C, 500 MHz) 2.37 (s)] was removed from the reaction mixture by sublimation at 40 °C at around 0.18 Torr. The colorless liquid amidine was then isolated in 50−80% yield by distilling the remaining liquid at approximately 90 °C and 0.06−0.18 Torr. The *N*,*N*′-dialkylvaleroamidines were prepared similarly to the *N*,*N*′-dialkylacetamidines, except that the original solution was refluxed for a longer time (3 days) to increase the yield.

Preparation of Symmetric Copper(I) Amidinate Compounds. For symmetric compounds (those having the same alkyl group on all nitrogens), the free symmetric amidines were synthesized by the above procedure and then deprotonated with methyllithium. The resulting lithium amidinates were then reacted with copper chloride.

Copper(I) *N*,*N*′-Di-*n*-propylacetamidinate $[Cu(^nPr\text{-}Me\text{-}amd)]_2$ (1). 1,3-Di-*n*-propylacetamidine was synthesized by lanthanide-catalyzed reaction of acetonitrile and propylamine with a yield of 60%, according to Scheme 1. A solution of methyllithium (1.6 M in Et_2O, 12.5 mL, 0.02 mol) was added dropwise by syringe into a solution of 1,3-di-*n*-propylacetamidine in 30 mL of Et_2O at −30 °C. The solution was stirred for 2 h at room temperature. The resulting solution was then transferred to a copper monochloride

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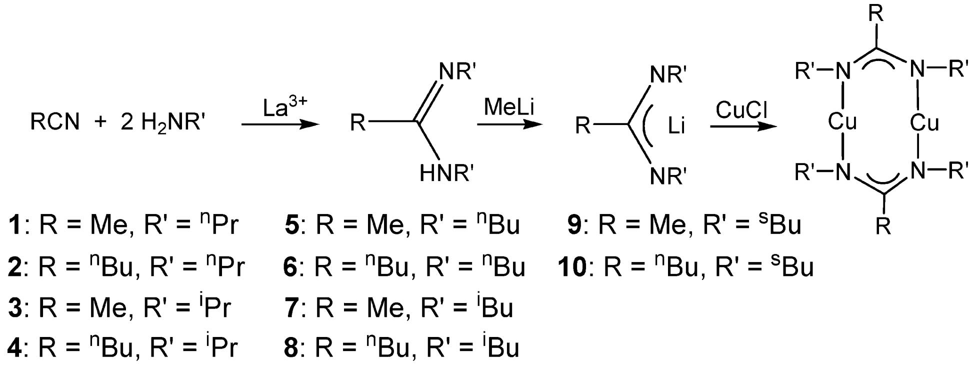
Scheme 1. Synthesis of Symmetric Amidines and the Corresponding Symmetric Copper(I) Amidinate Compounds



1: R = Me, R' = ^{n}Pr **5**: R = Me, R' = ^{n}Bu **9**: R = Me, R' = ^{s}Bu
2: R = ^{n}Bu, R' = ^{n}Pr **6**: R = ^{n}Bu, R' = ^{n}Bu **10**: R = ^{n}Bu, R' = ^{s}Bu
3: R = Me, R' = ^{i}Pr **7**: R = Me, R' = ^{i}Bu
4: R = ^{n}Bu, R' = ^{i}Pr **8**: R = ^{n}Bu, R' = ^{i}Bu

(1.98 g, 0.02 mol) solution in 30 mL of Et_2O. The solution was stirred for 18 h under nitrogen atmosphere. The solvent was removed under reduced pressure, and the resulting solid was extracted with hexanes (30 mL). The hexane extract was filtered through a glass frit to afford a pale yellow solution. A saturated solution was formed by removing part of the hexane under reduced pressure. The saturated solution was cooled to −30 °C and afforded colorless crystals (3.62 g, 83%). Pure white compound was obtained through sublimation at 50 °C (0.05 mmHg). mp: 65 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.06 (t, 4H), 1.70 (sextet, 4H), 1.60 (s, 3H), 0.96 (t, 6H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 173.6, 53.2, 27.49, 13.98, 12.05. Anal. Calcd for $C_{16}H_{34}N_4Cu_2$: C, 46.92; H, 8.37; N, 13.68. Found: C, 46.70; H, 8.20; N, 14.02.

Copper(I) *N,N'*-Di-*n*-propyl-2-butylamidinate [Cu(^{n}Pr-Bu-amd)]$_2$ (2). This compound was obtained in a fashion similar to [Cu(^{n}Pr-Me-AMD)]$_2$, **1**. 1,3-Di-*n*-propyl-2-butylamidine was prepared according to Scheme 1, similarly to 1,3-di-*n*-propylacetamidine, in 58% yield. Treatment of (^{n}Pr-butylamidinato)lithium [obtained from ^{n}Pr-butylamidine (3.68 g, 0.02 mol) and a 1.6 M solution of methyllithium in diethyl ether (12.5 mL, 0.02 mol)] with CuCl (1.98 g, 0.02 mol) in ether solution (30 mL). Crystallization afforded colorless crystals (3.75 g, 76%). An analytical sample was obtained by distillation at 75 °C (0.05 mmHg). mp: 60 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.19 (t, 4H), 2.26 (t, 2H), 1.77 (m, 4H), 1.49 (m, 2H), 1.26 (m, 2H), 0.98 (t, 6H), 0.84 (t, 3H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 186.5, 176.7, 52.4, 29.7, 28.0, 27.5, 23.4, 14.0, 12.0. Anal. Calcd for $C_{22}H_{46}N_4Cu_2$: C, 53.52; H, 9.39; N, 11.35. Found: C, 53.13; H, 9.07; N, 11.18.

All compounds **3**−**10** were obtained in the same way as [Cu(^{n}Pr-Me-amd)]$_2$, **1** unless described otherwise.

Copper *N,N'*-Di-isopropylacetamidinate [Cu(^{i}Pr-Me-amd)]$_2$ (3): Colorless crystals (70%). Sublimation: 70 °C, 0.05 mmHg. mp: 147 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 1.16 (d, 12H), 1.65 (s, 3H), 3.40 (m, 2H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 170.1, 48.8, 27.2, 13.6. Anal. Calcd for $C_{16}H_{34}N_4Cu_2$: C, 46.92; H, 8.37; N, 13.68. Found: C, 46.80; H, 8.29; N, 13.35.

Copper *N,N'*-Di-isopropyl-2-butylamidinate [Cu(^{i}Pr-Bu-amd)]$_2$ (4): Colorless crystals (74%). Sublimation: 75 °C, 0.04 mmHg. mp: 97 °C.^{1}H NMR (C_6D_6, 25 °C, ppm): 3.19 (t, 4H), 2.26 (t, 2H), 1.77 (m, 4H), 1.49 (m, 2H), 1.26 (m, 2H), 0.98 (t, 6H), 0.84 (t, 3H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 186.5, 176.7, 52.4, 29.7, 28.0, 27.5, 23.4, 14.0, 12.0. Anal. Calcd for $C_{22}H_{46}N_4Cu_2$: C, 53.52; H, 9.39; N, 11.35. Found: C, 55.80; H, 9.33; N, 12.06.

Copper *N,N'*-Di-*n*-butylacetamidinate [Cu(^{n}Bu-Me-amd)]$_2$ (5): Dark brown crystals (84%). Distillation: 70 °C, 0.1 mmHg. mp: 65 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.12 (t, 4H), 1.69 (m, 4H), 1.63 (s, 3H), 1.44 (m, 4H), 0.93 (t, 6H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 173.5, 51.0, 36.9, 21.0, 14.4, 14.0. Anal. Calcd for $C_{20}H_{42}N_4Cu_2$: C, 51.59; H, 9.09; N, 12.03. Found: C, 51.81; H, 8.82; N, 12.28.

Copper *N,N'*-Di-*n*-butyl-2-butylamidinate [Cu(^{n}Bu-Bu-amd)]$_2$ (6): Yellow viscous supercooled liquid at room temperature. After being quenched in liquid nitrogen, it remained as a solid glass at room temperature. It decomposed at 190 °C, 0.1 mmHg. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.25 (t, 4H), 2.28 (m, 2H), 1.77 (m, 4H), 1.46 (m, 6H, overlapping signals), 1.28 (m, 2H), 0.94 (t, 6H), 0.86 (t, 3H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 176.5, 50.2, 37.4, 29.7, 27.5, 23.4, 20.9, 14.5, 14.0. Anal. Calcd for $C_{26}H_{54}N_4Cu_2$: C, 56.80; H, 9.90; N, 10.19. Found: C, 56.72; H, 9.69; N, 9.97.

Copper *N,N'*-Di-isobutylacetamidinate [Cu(^{i}Bu-Me-amd)]$_2$ (7): Colorless crystals (94%). Sublimation: 90 °C, 0.2 mmHg. mp: 114 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 2.98 (d, 4H), 1.94 (m, 2H), 1.62 (s, 3H), 1.02 (d, 12H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 173.7, 59.63, 32.71, 21.1, 14.4. Anal. Calcd for $C_{20}H_{42}N_4Cu_2$: C, 51.59; H, 9.09; N, 12.03. Found: C, 51.66; H, 8.82; N, 12.09.

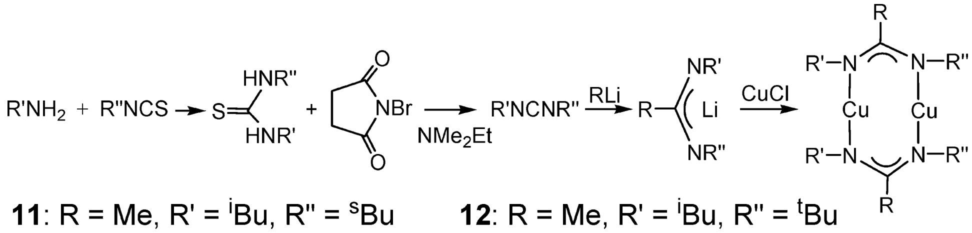
Copper *N,N'*-di-isobutyl-2-butylamidinate [Cu(^{i}Bu-Bu-amd)]$_2$ (8): Pale yellow crystals (81%). mp: 111 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.10 (d, 4H), 2.49 (m, 2H), 2.05 (m, 2H), 1.50 (m, 2H), 1.27 (m, 2H), 1.05 (d, 12H), 0.841 (t, 3H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 176.9, 58.9, 33.2, 29.6, 27.6, 23.4, 21.1, 14.0. Anal. Calcd for $C_{26}H_{54}N_4Cu_2$: C, 56.80; H, 9.90; N, 10.19. Found: C, 56.60; H, 10.08; N, 10.09.

Copper *N,N'*-Di-*sec*-butylacetamidinate [Cu(^{s}Bu-Me-amd)]$_2$ (9): Colorless crystals (90%). Vapor pressure: 85 °C, 0.1 mmHg (by thermocouple vacuum gauge during distillation); 95 °C, 0.23 mmHg (by mass loss from a bubbler). mp: 77 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.16 (m, 2H), 1.71 (d, 3H), 1.69 (m, 2H), 1.52 (m, 2H), 1.19 (dd, 6H), 0.94 (m, 6H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 170.8, 55.0, 34.7, 25.2, 14.5, 11.6. (Note: equilibrium or isomerization.) Anal. Calcd for $C_{20}H_{42}N_4Cu_2$: C, 51.59; H, 9.09; N, 12.03. Found: C, 51.66; H, 8.82; N, 12.09.

Copper *N,N'*-Di-*sec*-butyl-2-butylamidinate [Cu(^{s}Bu-Bu-amd)]$_2$ (10): Colorless crystals (14% after several recrystallizations). Sublimation: 60 °C, 0.01 mmHg. mp: 71 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.25 (m, 2H), 2.28 (t, 2H), 1.73 (m, 2H), 1.54 (dm, 4H), 1.28 (m, 2H), 1.26, (dd, 6H), 0.98 (dt, 6H), 0.88 (dt, 3H).^{13}C NMR (C_6D_6, 25 °C, ppm): 174.3, 54.5, 34.9, 30.7, 28.0, 25.9, 23.4, 14.1, 11.9. Anal. Calcd for $C_{26}H_{54}N_4Cu_2$: C, 56.80; H, 9.90; N, 10.19. Found: C, 56.96; H, 9.65; N, 9.92.

Synthesis of Asymmetric Carbodiimides and Copper Amidinates. As illustrated in Scheme 2, a thiourea solution was made by the addition of 1.46 g (0.02 mol) of isobutylamine dissolved in 20 mL of dichloromethane to 2.30 g (0.02 mol) of *sec*-butyl isothiocyanate (for compound **11**) or *tert*-butyl isothiocyanate (for compound **12**) in 200 mL of dichloromethane at room temperature; then 4.40 g (0.06 mol) of *N,N*-dimethylethylamine was added to

Scheme 2. Synthesis of Unsymmetric Carbodiimides and the Corresponding Unsymmetric Copper(I) Amidinate Compounds



11: R = Me, R' = ^{i}Bu, R" = ^{s}Bu **12**: R = Me, R' = ^{i}Bu, R" = ^{t}Bu

the solution, which had been cooled to −30 °C.[19] *N*-Bromosuccinimide (NBS; 3.54 g, 0.02 mol) was dissolved in 100 mL of dichloromethane and stirred for 12 h to promote dissolution. Then the NBS solution was added slowly to the thiourea/NMe_2Et solution.[20] Undissolved NBS was washed into the reaction vessel using minimal additional CH_2Cl_2. The mixture solution turned orange after being stirred overnight. The pale yellowish powder precipitate (sulfur) was filtered off and the volatiles were removed from the filtrate under partial pressure. The carbodiimide was isolated by distillation of the remaining liquid.

The following two asymmetric copper amidinates were synthesized according to Scheme 2, using asymmetric carbodiimides prepared as described above. Methyllithium (1.6 M in Et_2O, 6.25 mL, 0.02 mol) was added to a solution of the carbodiimide (3.76 g, 0.02 mol) in 30 mL of diethyl ether. The resulting solution of lithium amidinate was added to CuCl (1.98 g, 0.02 mol) in 30 mL of ether solution, and the product was isolated as described above for **1**.

Copper *N*-Isopropyl-*N′*-*sec*-butylacetamidinate [Cu(^{i}Pr-Me-^{s}Bu-amd)]$_2$ (11): Pale yellow crystals (80%). Sublimation: 72 °C, 0.05 mmHg. mp: 86 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.46 (m, 2H), 3.15 (m, 2H), 1.70 (s, 3H), 1.69 (m, 4H), 1.52 (m, 4H), 1.20 (m, 18H, overlapping signals), 0.93 (dt, 6H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 170.5, 55.0, 48.9, 34.6, 27.3, 25.3, 14.1, 11.8. Anal. Calcd for $C_{18}H_{38}N_4Cu_2$: C, 49.40; H, 8.75; N, 12.80. Found: C, 49.42; H, 8.52; N, 12.61.

Copper *N*-Isopropyl-*N′*-*tert*-butylacetamidinate [Cu(^{i}Pr-Me-$_t$Bu-amd)]$_2$ (12): Dark brown crystals (70%). Sublimation: 75 °C, 0.05 mmHg. mp: 121 °C. ^{1}H NMR (C_6D_6, 25 °C, ppm): 3.43 (m, 2H), 1.89 (s, 3H), 1.39 (ds, 18H), 1.20 (dd, 12H). ^{13}C NMR (C_6D_6, 25 °C, ppm): 172.1, 53.8, 48.4, 34.1, 33.9, 27.1, 26.8, 18.0, 17.9. Anal. Calcd for $C_{18}H_{38}N_4Cu_2$: C, 49.40; H, 8.75; N, 12.80. Found: C, 49.68; H, 8.62; N, 12.64.

X-ray Structure Determination. The crystal structure of [Cu(^{s}Bu-Me-amd)]$_2$, **9**, was found by X-ray crystallography. Crystals were grown by sublimation at 75 °C under vacuum. Diffraction data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 193 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using Ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.76 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software, which corrects for Lorenz polarization and decay. Absorption corrections were applied using SADABS supplied by Sheldrick. The structures were solved by the direct method using the SHELXS-97 program and refined by least-squares method on F^2 by SHELXL-97, incorporated in SHELXTL-PC V 6.10.

The structure was solved in the space group *C*2/*c* (No. 15). All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The ligand was modeled as 50% disordered at the chiral carbons. The crystal used for the diffraction study showed no decomposition during data collection. The drawing was done at 50% ellipsoids.

NMR Studies of Thermal Stability. Decomposition rates of four of these copper amidinates were determined in deuterated benzene solution. Each of the four compounds [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**; [Cu(^{i}Pr-^{n}Bu-amd)$_2$]$_2$, **4**; [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**; and [Cu-(^{s}Bu-^{n}Bu-amd)$_2$]$_2$, **10**, was dissolved in C_6D_6 NMR solvent. These solutions were sealed in thick-walled glass NMR tubes and heated to 190 °C in an oven. Periodically, the tubes were removed from the oven and their proton NMR spectra recorded. The intensity of the relatively isolated peak near chemical shift $\delta = 3.25$ ppm was recorded relative to the proton impurity peak ($\delta = 7.15$) in the C_6D_6 solvent taken as a reference.

Results and Discussion

Synthesis and Structures. All Cu(I) amidinate compounds listed in Table 2 below were synthesized by the metathesis reactions of anhydrous CuCl with the corresponding equivalents of lithium amidinates (*N*,*N′*-dialkylacetamidinate or *N*,*N′*-dialkylvaleroamidinate) in diethyl ether at ambient temperature to afford the final products, according to reaction 1.

$$2\mathrm{CuCl} + 2\mathrm{Li(R'NC(R)NR'')} \rightarrow [\mathrm{Cu(R'NC(R)NR'')}]_2 + 2\mathrm{LiCl} \quad (1)$$

The overall process is illustrated in Schemes 1 and 2. Symmetric amidinates ($R' = R''$) were formed by Scheme 1, in which the lithium amidinate is formed by first coupling two amines with a nitrile to form an amidine that is subsequently deprotonated with an alkyllithium. Unsymmetric amidines (R′ not the same as R″) were synthesized by Scheme 2, in which an unsymmetric lithium amidinate is made by first coupling an amine and an isothiocyanate to form a thiourea, followed by sulfur removal with *N*-bromosuccinimide and treatment of the resulting carbodiimide with an alkyllithium. Scheme 1 has the advantage of avoiding the highly toxic carbodiimide intermediate used in Scheme 2. Scheme 1 fails, however, for tertiary amines such as *tert*-butylamine, because the coupling reaction becomes too slow.

All of the compounds are easily soluble in hexane. They were purified by crystallization of the crude materials from hexane at −30 °C and by sublimation. All of the pure compounds are colorless or light yellow crystalline solids

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Table 2. Properties of Amidinato Cu(I) Compounds 1-12

compd	melting point (°C)	vapor pressure/ temperature (Torr/°C)	yield (%)	color	residue after TGA (%)	half-life[a] (days)
[Cu(^{n}Pr-Me-amd)$_2$]$_2$, **1**	65	0.05/50	83	white	9.7	
[Cu(^{n}Pr-^{n}Bu-amd)$_2$]$_2$, **2**	60	0.05/75	76	white	31.9	
[Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**[5,6]	147	0.05/70	70	white	2.8	45
[Cu(^{i}Pr-^{n}Bu-amd)$_2$]$_2$, **4**	97	0.04/75	74	white	11.7	20
[Cu(^{n}Bu-Me-amd)$_2$]$_2$, **5**	65	0.1/70	84	dark brown	32.3	
[Cu(^{n}Bu-^{n}Bu-amd)$_2$]$_2$, **6**	38	0.1/190	−	yellow	22.0	
[Cu(^{i}Bu-Me-amd)$_2$]$_2$, **7**	114	0.2/90	84	white	5.4	
[Cu(^{i}Bu-^{n}Bu-amd)$_2$]$_2$, **8**	111	−	81	pale yellow	18.3	
[Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**	77	0.1/85	90	white	0.7	33
[Cu(^{s}Bu-^{n}Bu-amd)$_2$]$_2$, **10**	71	0.01/60	−	white	3.5	21
[Cu(^{i}Pr-Me-^{s}Bu-amd)$_2$]$_2$, **11**	86	0.05/72	80	pale yellow	17.4	
[Cu(^{i}Pr-Me-^{t}Bu-amd)$_2$]$_2$, **12**	121	0.05/75	70	dark brown	14.2	

[a] Measured at 190 °C in C_6D_6 solution.

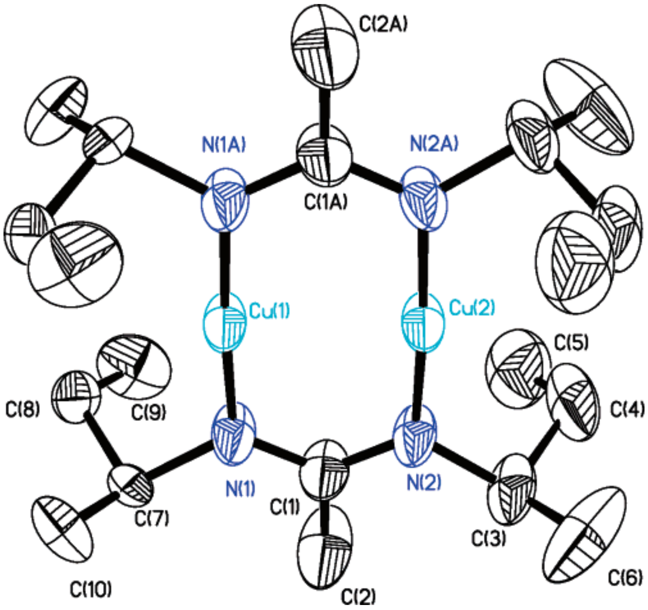

Figure 1. Structure of [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, showing 50% probability ellipsoids and partial atom-labeling schemes. Atoms labeled A are related to other atoms by an inversion center.

Table 3. Crystal Data and Data Collection Parameters for [Cu(^{s}Bu-Me-amd)$_2$]$_2$, 9

empirical formula	$C_{20}H_{42}Cu_2N_4$	
formula weight	465.66	
temperature	193(2) K	
wavelength	0.71073 Å	
crystal system	monoclinic	
space group	*C*2/*c*	
unit cell dimensions		
	$a = 18.884(2)$ Å	$\alpha = 90°$
	$b = 10.950(2)$ Å	$\beta = 115.842(4)°$
	$c = 12.9230(19)$ Å	$\gamma = 90°$
volume	2405.1(7) Å^3	
Z	4	
density (calcd)	1.286 Mg/m^3	
absorption coefficient	1.779 mm^{-1}	
θ range for data collection	2.21 to 28.26°.	
completeness to $\theta = 28.26°$	99.8%	
GOF on F^2	1.046	
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0302	wR2 = 0.0700
R indices (all data)	R1 = 0.0497	wR2 = 0.0762
largest diff peak and hole	0.300 and −0.574 e.Å^{-3}	

Table 4. Bond Distances (Å) and Angles (deg) for [Cu(^{s}Bu-Me-amd)$_2$]$_2$, 9

Cu−N[a]	1.877(2)
Cu−Cu	2.4031(6)
N−C[a,b]	1.326(3)
N−C[a]	1.505(15)
N−Cu−N[a]	176.62(10)
N−C−N[b]	119.62(17)

[a] Mean value. [b] Amidinate backbone.

except [Cu(^{n}Bu-^{n}Bu-amd)]$_2$, **6**, which is waxy and becomes a glass at room temperature after being quenched in liquid nitrogen. Dark impurities were not successfully removed from compounds **5** and **12**.

The structures of two of these copper complexes were found to be dimeric by X-ray crystal structure determinations ([Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**; [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**[6]). Melting point depression of *p*-xylene solutions showed that [Cu(^{n}Pr-Me-amd)$_2$]$_2$, **1**, is a dimer and confirmed that [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, remains dimeric in solution [complexity 2.0(2)]. Other copper compounds were found to be dimers in the vapor phase by mass spectroscopy: [Cu(^{n}Pr-Me-amd)$_2$]$_2$, **1**; [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**; [Cu(^{n}Bu-Me-amd)$_2$]$_2$, **5**; [Cu(^{i}Bu-Me-amd)$_2$]$_2$, **7**; [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**; [Cu(^{s}Bu-Bu-amd)$_2$]$_2$, **10**. The physical properties are summarized in Table 2.

The X-ray structure of [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, is shown in Figure 1 and selected metric data are collected in Tables 3 and 4. Its structure was disordered at the chiral centers in the *sec*-butyl groups on the ligand, but only one configuration is shown in Figure 1 for clarity. Acetamidinate ligands bridge copper atoms in a μ, η^1:η^1 fashion, which is similar to the structure of [Cu(I) (*N*,*N′*-diisopropylacetamidinate)]$_2$.[6] The average distance of Cu−N is 1.877(2) Å, and this distance is similar to that obtained for the analogous compounds **3** and [Cu(p-tolyl-amd)]$_2$.[21] The distance between copper atoms is 2.4031(6) Å,[22] which might be short enough to indicate some bonding interaction between the Cu−Cu atoms. On the other hand, the N−Cu−N bonds are nearly linear with an average angle of 176.62(10)°, suggesting little or no bonding between the copper atoms. The dihedral angle for N−Cu−Cu−N is 178.96(8)°, almost planar with imposed centrosymmetry.

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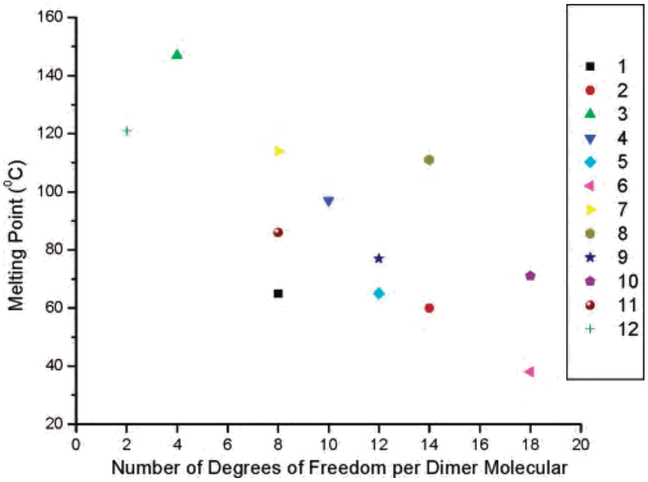

Figure 2. Melting points plotted as a function of the number of disruptive degrees of freedom of the alkyl groups (see text).

Melting Points. Melting points, listed in Table 2, are below 100 °C for most of the new compounds. Compound **6**, having all *n*-butyl groups, has the lowest melting point, whereas compound **3** (isopropyl and methyl) has the highest. Although there is no rigorous theory of melting points that can be applied to these compounds, it seems reasonable that the large number of conformations accessible to *n*-butyl groups would hinder crystallization of compounds and lower their melting points. The various alkyl groups can be ranked in terms of the number of accessible configurations by counting the number of single bonds about which nearly free rotation can take place. In this scheme for counting the degrees of freedom, we ignore a single bond that only rotates a methyl group around its 3-fold axis, because the resulting changes in energy might not be sufficient to disrupt crystallization. Similarly, rotating a whole *tert*-butyl group might not have much influence on crystal packing, so we do not count this rotation as an effective degree of freedom. The *sec*-butyl group introduces an additional degree of disorder because of its chiral carbon; thus we increase its degrees of freedom from 2 (if we counted only its disruptive single bonds) to 3. This somewhat arbitrary increase in degrees of freedom for *sec*-butyl might seem excessive, but the two enantiomers cannot interconvert at normal temperatures; in contrast, the rotations about single bonds can readily adjust to the conditions within the crystals, thereby reducing the disorder that they might produce. In summary, we estimated the effective number of disruptive degrees of freedom for the alkyl groups as follows: methyl = 0, *tert*-butyl = 0, isopropyl = 1, *n*-propyl = 2, isobutyl = 2, *sec*-butyl = 3, *n*-butyl = 3. Then the total number of disruptive degrees of freedom was calculated for the six alkyl groups on each of the compounds. In Figure 2, we plot the melting points as a function of this total number of disruptive degrees of freedom. A reasonable qualitative correlation is shown between these quantities, although there is certainly a degree of scatter. One conclusion that we can draw from these trends is that reduction of melting points can be achieved most readily by synthesizing compounds having more *sec*-butyl and *n*-butyl substitutents.

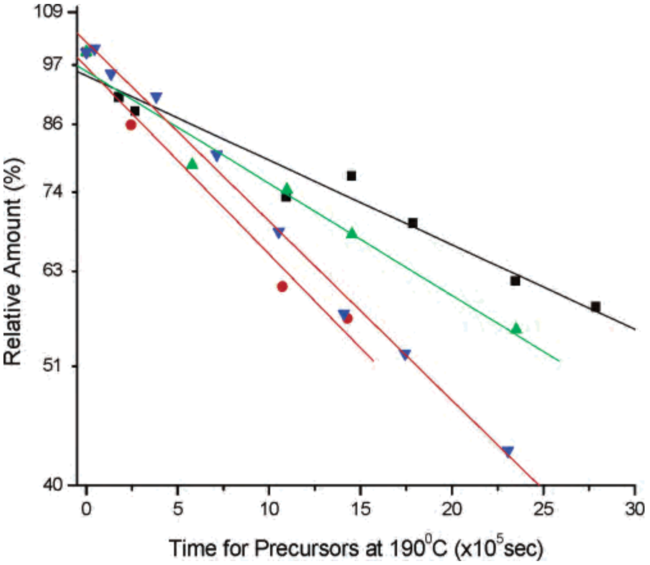

Figure 3. NMR decomposition study of four compounds at 190 °C. The lines represent the best fits to a first-order decomposition rate law with the following rate constants: (■) [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**, rate = 1.8 × 10^{-7} s^{-1}; (●) [Cu(^{i}Pr-^{n}Bu-amd)$_2$]$_2$, **4**, rate = 4.0 × 10^{-7} s^{-1}; (▲) [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, pyramids, rate = 2.4 × 10^{-7} s^{-1}; (▼) [Cu(^{s}Bu-^{n}Bu-amd)$_2$]$_2$, **10**, rate = 3.8 × 10^{-7} s^{-1}.

Stability of the Compounds. All of the compounds listed in Table 2 are much more stable in air than other first-row transition metal amidinates, such as those of Ti, V, Mn, Fe, Co, and Ni.[6] Over a period of days, ambient air does cause gradual darkening, presumably by oxidation to copper(II) compounds. The compounds were synthesized with exclusion of ambient air to avoid this oxidation and because the intermediate lithium amidinates are very moisture-sensitive.

Initial NMR decomposition measurements showed that compounds [Cu(^{i}Pr-Me-amd)]$_2$, **3**; [Cu(^{i}Pr-^{n}Bu-amd)]$_2$, **4**; [Cu(^{s}Bu-Me-amd)]$_2$, **9**; and [Cu(^{s}Bu-^{n}Bu-amd)]$_2$, **10**, showed very little decomposition after the NMR tubes containing these compounds had been kept for 1 week at 175 °C. Thus the oven temperature was raised to 190 °C to induce thermal decomposition at a more readily measurable rate. Figure 3 shows the relative intensity of the peak (C) as a function of time t (×10^5 s), where the vertical axis is on a logarithmic scale. We found approximately linear relationships between ln(C) and t at 190 °C, indicating that the decomposition is a first-order reaction. The first-order rate constants for decomposition were extracted from the slope as $k_d = 1.8 \times 10^{-7}$ s^{-1} for [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**; 4.0 × 10^{-7} s^{-1} for [Cu(^{i}Pr-^{n}Bu-amd)$_2$]$_2$, **4**; 2.4 × 10^{-7} s^{-1} for [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**; and 3.8 × 10^{-7} s^{-1} for [Cu(^{s}Bu-^{n}Bu-amd)$_2$]$_2$, **10**, corresponding to the half-lives around 1 month (see Table 2). These NMR results show that these compounds are very stable even at 190 °C, which is a typical substrate temperature for ALD of copper using these precursors. Although the vacuum environment of these precursors during ALD is different from the solvent environment in the NMR tubes, the NMR results suggest that these copper amidinates should not thermally decompose during the short time (seconds) that they are inside the deposition chamber during an ALD cycle. These results also demonstrate that the compounds are completely stable at typical vaporization temperatures of around 100 °C.

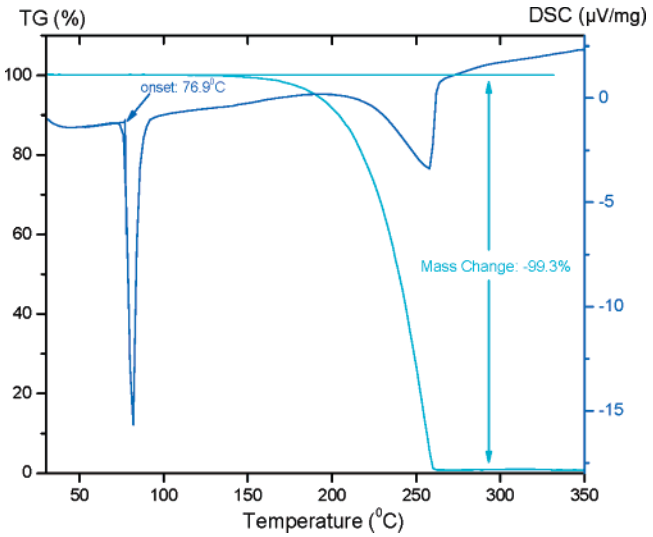

Figure 4. TGA/DSC data for [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**. The experiment was done at N_2 carrier gas (~50 sccm). The ramp rate for TGA/DSC is 10 K/min.

Comparison of compounds **3** and **9** (methyl) with **4** and **10** (*n*-butyl) shows that *n*-butyl groups are less stable than methyl groups on the amidinate ligand. This approximate doubling of the decomposition rate might be due to additional pathways for β-hydrogen elimination from the *n*-butyl groups of **4** and **10**. A compound with *sec*-butyl groups (**9**) showed better stability than a similar compound with *n*-butyl groups (**5**), which was difficult to purify because of decomposition. Thus *sec*-butyl groups are the best choice for compounds combining low melting points with high thermal stability.

The NMR spectra also showed formation of unsaturated hydrocarbon decomposition products, although assigning all of the new peaks is difficult because of their relatively low intensities. One major decomposition product was identified from the NMR spectra as a dimer of two amidinate ligands joined by a nitrogen–nitrogen bond.[23] Copper metal mirrors were also deposited on the inside walls of the NMR tubes after the long thermal decomposition runs. Taken together, these two byproducts indicate the presence of a reductive elimination pathway for the thermal decomposition of these compounds.

Vaporization of the Compounds. Table 2 lists the TGA/DSC data (melting point, sublimation temperature, residual mass) for most of these copper compounds. Most of the copper amidinates left little residue after thermal evaporation. Figure 4 gives the TGA/DSC graphs for **9**; the Supporting Information contains TGA/DSC curves for compounds **1**, **6**–**8**, **10**, and **12**. Figure 4 shows the TGA curve for complex [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, which left very little residual mass (0.7%), showing that negligible decomposition happened during its melting and evaporation. The DSC curves have only endothermic peaks due to the melting and evaporation of the compounds, confirming their thermal stabilities. Many of the compounds have similar vapor pressures, except that the ones with *n*-butyl or *tert*-butyl substituents tended to have lower vapor pressures.

Isothermal TGA runs with precursor **9** showed that, at 100 °C, its liquid vaporizes at a rate of 4.1×10^{-4} mg cm^{-2} s^{-1}, which is sufficiently high to replenish the vapor needed for an ALD cycle within a typical cycle time of a few seconds.

Investigation of These Copper Compounds as ALD Precursors. To satisfy the requirements of ALD, the precursors must be sufficiently volatile, thermally stable, and highly reactive to the surface produced by a complementary ALD reactant. Lim et al.[5,6] successfully used [Cu(^{i}Pr-Me-amd)$_2$]$_2$, **3**, as a precursor to make Cu films, using molecular hydrogen as the complementary reactant. However, the melting point of **3** (147 °C) is higher than the typical temperatures (~100 °C) used for its vaporization, so the precursor **3** remains in the solid state as it sublimes into the vapor. Thus the rate of vaporization of **3** depends on its surface area, which is not reproducible from run to run.

Many of the copper(I) compounds listed in Table 3 have much lower melting points (60–80 °C) and vapor pressures similar to that of **3**. Thus we can easily keep these new precursors in the liquid phase while vaporizing them, which makes the vapor delivery more reproducible than sublimation from solid sources. As an example, we tried the two compounds [Cu(^{n}Pr-Me-amd)$_2$]$_2$, **1**, and Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, for the ALD of copper. Keeping the precursor reservoir at 95 °C, we obtained ALD Cu films from both of these precursors at rates up to 1 Å per cycle. The nitrogen and carbon impurities are below the detection levels of RBS (<1 atom %), showing that the ligands were completely removed during the ALD process. The byproducts of these reactions (most probably hydrogenated amidine ligands) are not corrosive toward the reactor chamber and substrates, providing a further advantage over copper halide precursors. More detailed ALD results will be reported elsewhere.

Conclusions. Most of the copper(I) amidinates listed in Table 2 are suitable as ALD precursors. Bis(copper(I) *N,N′*-di-*sec*-butylacetamidinate) [Cu(^{s}Bu-Me-amd)$_2$]$_2$, **9**, has a particularly useful combination of sufficiently low melting point and excellent thermal stability. These new compounds provide several advantages over traditional precursors, such as copper halides and β-diketonates. The copper(I) amidinates are sufficiently volatile, low melting, thermally stable, highly reactive, and noncorrosive. The weak intermolecular attraction between the hydrocarbon outer parts of the complexes contributes to their high volatility. The high thermal stability is due to the chelating effects from the amidinate ligands that connect the dimer together. The copper–nitrogen bond is weaker than the copper–oxygen bond, which leads to higher reactivity compared to copper β-diketonates. We obtained ALD copper films from precursor **9** at 160 °C, a much lower temperature than those required for CuCl (400 °C) and Cu(hfac)$_2$·H_2O (230–300 °C). Finally, these ALD copper films show strong adhesion to cobalt films as substrates, so that robust microelectronic interconnections can be based on ALD copper seed layers from these new precursors.[24]

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(23) Full characterization of the amidine ligand dimer will be reported by Huazhi Li and Roy G. Gordon.

(24) de Rouffignac, P.; Li, Z.; Gordon, R. G. *Electrochem. Solid State Lett.* **2004**, *7*, G306.

Acknowledgment. We thank Dr. Xinjian Lei of Schumacher Chemical Company for the TGA/DSC analyses and Dr. Richard Staples for X-ray structure analysis. We appreciate helpful discussions with Dr. Booyong Lim. This work was supported in part by the National Science Foundation (Grant ECS-0354213)

Supporting Information Available: TGA and DSC curves for compounds **1**, **6**−**8**, **10**, and **12**. X-ray crystallographic file in CIF format for the structure determination of compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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