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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Volatile and Thermally Stable Mid to Late Transition Metal Complexes Containing α-Imino Alkoxide Ligands, a New Strongly Reducing Coreagent, and Thermal Atomic Layer Deposition of Ni, Co, Fe, and Cr Metal Films

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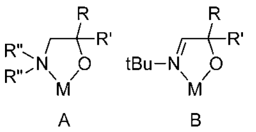
Supporting Information

ABSTRACT: Treatment of MCl_2 (M = Cu, Ni, Co, Fe, Mn, Cr) with 2 equiv of α-imino alkoxide salts K(RR′COCNtBu) (R = Me, tBu; R′ = iPr, tBu) afforded $M(RR'COCNtBu)_2$ or $[Mn(RR'COCNtBu)_2]_2$ in 9−75% yields. These complexes combine volatility and high thermal stability and have useful atomic layer deposition (ALD) precursor properties. Solution reactions between Ni, Co, and Mn complexes showed that $BH_3(NHMe_2)$ can reduce all to metal powders. ALD growth of Ni, Co, Fe, and Cr films is demonstrated. Mn film growth may be possible, but the films oxidize completely upon exposure to air.

There is considerable interest in the growth of metallic first row transition metal thin films by atomic layer deposition (ALD), in view of their applications in microelectronics and other devices.[1] ALD of these metals requires precursors that combine volatility, thermal stability at the deposition temperature, and high reactivity toward a second reagent to afford the metallic film.[2] Moreover, the films need to be grown at <200 °C, to avoid agglomeration of the metal atoms and resultant rough films.[1] For transition metals, thermal ALD is preferred over plasma ALD, to avoid loss of conformal growth in high aspect ratio features in the latter.[1] While several low temperature (<200 °C) thermal ALD processes have been reported for Cu,[3] analogous growth of the other first row transition metals remains scantly documented.[4] Alloy films, such as Cu/Mn for fabrication of ultrathin, conformal Mn−Si−O Cu diffusion barriers,[5] require Cu, Mn, and other precursors with similar chemistry and deposition temperatures, as well as a common coreagent that can reduce all metal precursors equally well ($E°$ Cu(II) = 0.3419 V; Mn(II) = −1.185 V[6]). Such precursors do not currently exist.[1] Cu[7] and Ni[8] complexes containing β-amino alkoxide ligands (Chart 1A) are widely used precursors for the growth of Cu and Ni films by ALD and chemical vapor deposition (CVD).[3,9] However, volatile β-amino alkoxide complexes are unknown for the other first row transition metals, presumably because these ligands cannot saturate the coordination spheres of the larger metal(II) ions. Moreover, there is a lack of volatile, strong reducing agents that can transform first row transition metal(II) ions to the metals at low temperatures.[1]

Chart 1. β-Amino Alkoxide (A) and α-Imino Alkoxide (B) Ligands



Herein, we describe the synthesis, structure, volatility, and thermal stability of a series of Cu(II), Ni(II), Co(II), Fe(II), Mn(II), and Cr(II) complexes that contain α-imino alkoxide ligands (Chart 1B). These complexes exhibit good volatilities, high thermal stabilities, and high reactivities toward reducing agents and, thus, have excellent properties for use as ALD precursors. Additionally, we demonstrate that $BH_3(NHMe_2)$ is a reducing coreagent in the ALD growth of Ni, Co, Fe, and Cr films from the α-imino alkoxide precursors. The present work therefore demonstrates a general new class of ALD precursors as well as a strong reducing agent that can be used for the ALD growth of metal films from metal ions with negative $E°$ values.

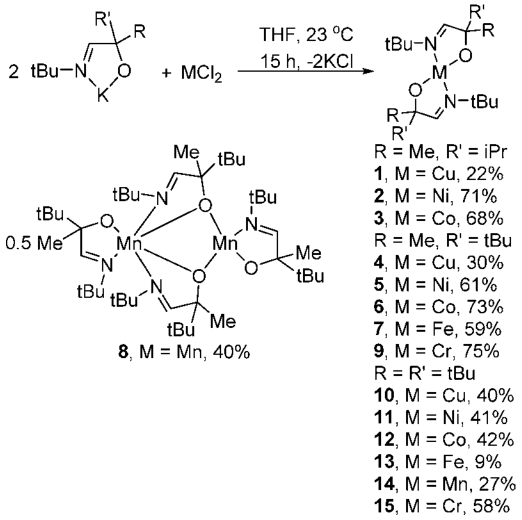
The α-imino alcohols were prepared as described in the Supporting Information.[10] Treatment of the alcohols with KH in tetrahydrofuran, followed by addition of anhydrous MCl_2, afforded **1**−**15** after workup by sublimation (Scheme 1). These complexes were characterized by spectral and analytical methods and by X-ray crystallography.[10] The Ni complexes **2**, **5**, and **11** are diamagnetic, and the ^1H NMR spectrum of **11** showed the expected two singlets in a 2:1 ratio for the ligand tBu groups. The ^1H NMR spectra of **2** and **5**, by contrast, revealed sets of resonances for two diastereomers in 1:1 ratios, due to the presence of a chiral center in each ligand. The remaining complexes are paramagnetic and exhibited very broad resonances in their ^1H NMR spectra. Solid state and solution magnetic moment data suggested that **1**, **4**, **9**, **10**, and **15** are square planar in both media, which was corroborated by X-ray structural data for **1**, **10**, and **15**. Magnetic data showed that **3**, **7**, **13**, and **14** are tetrahedral in the solid state and in solution, which fit the crystal structures of **3** and **14**. Magnetic data suggest that **6** and **12** are square planar in the solid state, but are tetrahedral in solution.

Among **1**−**9**, only low resolution X-ray crystal structures could be obtained for **1**−**3** and **8**, due to the diastereomeric

Received: July 10, 2013
Published: August 15, 2013

dx.doi.org/10.1021/ja407014w | *J. Am. Chem. Soc.* 2013, 135, 12588−12591

Scheme 1. Synthesis of 1−15



mixtures and difficulty in growing single crystals. However, high quality X-ray crystal structures of **10−12**, **14**, and **15** were determined.[10] A low resolution X-ray crystal structure of **8** showed a dimer with the atom connectivity shown in Scheme 1. A representative X-ray crystal structure of **14** is shown in Figure 1. Complex **14** has distorted tetrahedral geometry, with κ^2-coordination of the α-imino alkoxide ligands. The Mn−O and Mn−N bond lengths are 1.963(1) and 1.967(1) Å and 2.205(1) and 2.216(1) Å, respectively. The intraligand O−Mn−N angles are 79.30(4)° and 79.68(4)°, while the corresponding interligand angles are 121.00(4)° and 115.02(5)°. The O−Mn−O and N−Mn−N angles are 139.12(5)° and 131.18(5)°, respectively. Within the MnC_2NO ligand cores, the C−N, C−C, and C−O bond lengths are 1.263(2) and 1.267(2), 1.517(2), and 1.382(2) and 1.390(2) Å, respectively. These values are consistent with C−N double bonds as well as C−C and C−O single bonds.

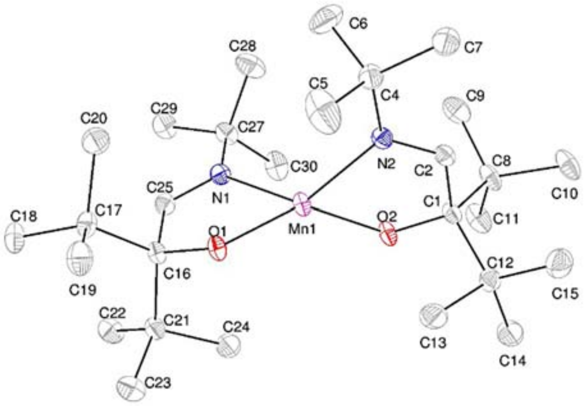


Figure 1. Perspective views of **14** with thermal ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): Mn−N1 2.216(1), Mn−N2 2.205(1), Mn−O1 1.967(1), Mn−O2 1.963(1), C1−O2 1.382(2), C1−C2 1.517(2), C2−N2 1.267(2), N1−Mn−N2 131.18(5), N1−Mn−O1 79.68(4), N1−Mn−O2 115.02(5), N2−Mn−O2 79.30(4), O1−Mn−O2 139.12(5).

The suitability of **1−15** for use as CVD and ALD precursors was assessed by preparative sublimation experiments, decomposition point measurements, and thermogravimetric analysis (TGA).[10] Table 1 lists selected data for the "optimum" precursors **2**, **3**, and **7−9**. These complexes sublime on ~0.5 g scales in ~3 h with <5% nonvolatile residues between 90 and 160 °C at 0.05 Torr (Table 1). The sublimation temperature of **8** is higher than those of **2**, **3**, **7**, and **9** because of its dimeric structure. The decomposition temperatures of **2**, **3**, and **7−9** range from 216 to 259 °C, which should permit self-limited ALD growth at <200 °C. For comparison, monomeric **14** sublimes at 130 °C/0.05 Torr, but undergoes thermal decomposition at 200 °C. Accordingly, **8** has more useful properties, in spite of its dimeric structure. Cu complexes **1**, **4**, and **10** are less volatile than $Cu(dmap)_2$ (dmap = 2-dimethylamino-1-propoxide), have similar decomposition temperatures to $Cu(dmap)_2$, and pose no advantage over $Cu(dmap)_2$ for use in ALD.[3,7]

Table 1. Selected Volatility and Thermal Stability Data

compd	sublimation temp (°C)	melting point (°C)	decomposition point (°C)
2	90	127	216
3	90	98	234
7	85	114	246
8	160	223	259
9	115	175	230

Previous reports have shown that solution reactions between metal precursors and reducing agents are useful in screening precursor pairs for transition metal ALD processes.[3,11] Therefore, **2**, **3**, and **8** were treated with anhydrous hydrazine or $BH_3(NHMe_2)$ in tetrahydrofuran at 23 °C. Metallic black powders were observed with both reducing agents with **2** and **3** in <0.25 h. These precipitates stuck to the magnetic stir bar, and powder X-ray diffraction spectra indicated crystalline Ni and Co. Treatment of **8** with $BH_3(NHMe_2)$ resulted in a black powder only upon reflux, and no precipitates were observed with hydrazine.

Encouraged by the solution reactivity results, film depositions with **2**, **3**, and **7−9** and $BH_3(NHMe_2)$ were carried out. Growth conditions, scanning electron micrographs, and X-ray photoelectron spectroscopy (XPS) data of the Ni, Co, Fe, Mn, and Cr films are contained in the Supporting Information.[10] Self-limiting behavior was observed for **2**, **3**, and **7−9**,[10] with growth rates of about 0.09 (Ni), 0.07 (Co), 0.07 (Fe), 0.10 (Mn), and 0.08 (Cr) Å/cycle at temperatures of 180 (Ni, Co, Fe, Cr) or 225 °C (Mn). Film growth was observed only on Ru (5 nm)/SiO_2 (100 nm)/Si substrates, and only after application of a nucleation process that entailed 50 cycles comprising 20 s pulses of **2**, **3**, **7**, **8**, or **9**, 1 s pulses of $BH_3(NHMe_2)$, and purge times of 5 and 10 s after the metal and $BH_3(NHMe_2)$ pulses, respectively.[10] XPS confirmed deposition of metallic Ni, Co, Fe, and Cr, but films derived from **8** revealed MnO_x, which likely arises from postdeposition oxidation of Mn upon exposure to air.[12] A complete ALD study was carried out on Cr films, using **9** and $BH_3(NHMe_2)$.[10] Saturative growth occurred at 180 °C with pulse lengths of ≥4.0 s for **9** and ≥1.0 s for $BH_3(NHMe_2)$. As shown in Figure 2, an ALD window was observed between 170 and 185 °C, with a growth rate of 0.08 Å/cycle in this range. A plot of thickness versus number of cycles revealed linear growth up to 1000 cycles, but the film thickness plateaued at >1000 cycles.[10] Ni, Co, and Mn films grown with >1000 cycles were also the same thicknesses as those grown with 1000 cycles. The origins of this effect are not clear, but it is

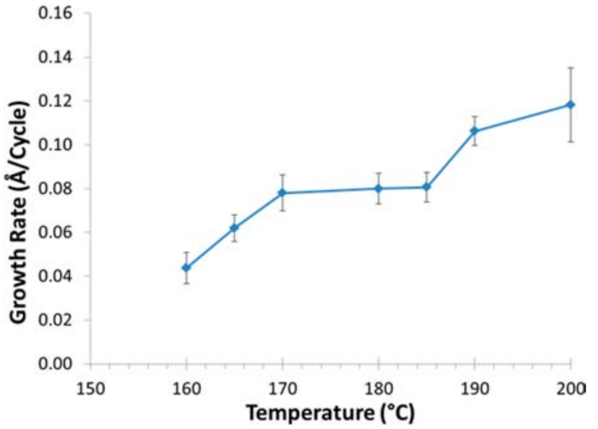


Figure 2. ALD window plot for growth of Cr films from **9** and $BH_3(NHMe_2)$.

possible that the Ru substrate plays a catalytic role in activating $BH_3(NHMe_2)$ until the growing metal layer blocks all of the Ru sites.[13] XPS spectra of an as-deposited Cr film grown at 170 °C showed Cr 2p binding energies consistent with Cr_2O_3, but Ar ion sputtering for 60−90 s led to Cr 2p binding energies that match Cr metal. Hence, the surfaces of the Cr films are oxidized upon exposure to air, consistent with the easily oxidized nature of Cr metal and other first row transition metals, particularly in nanoscale form.[12] AFM images of films grown at 170 and 180 °C had rms surface roughnesses of 0.37−0.59 nm, indicating smooth surfaces.

We have documented a new series of first row transition metal(II) α-imino alkoxide complexes with useful ALD precursor properties and have demonstrated the thermal ALD growth of Ni, Co, Fe, and Cr films using $BH_3(NHMe_2)$ as the coreagent. Cr films have not been previously grown by ALD. Thermal ALD growth of Ni, Co, and Fe films was claimed using the amidinate precursors $M(RNCMeNR)_2$ (R = iPr or tBu) and H_2 at 250 °C.[4a] While the growth rates in these processes (0.04−0.12 Å/cycle) were similar to those reported herein, the 250 °C deposition temperature is well above the decomposition point of $Ni(iPrNCMeNiPr)_2$ (180 °C[14]) and the Co and Fe precursors.[1] Hence, these processes are almost certainly strongly enhanced by precursor decomposition (CVD-like growth). A process comprising (2-*tert*-butylallyl)cobalt tricarbonyl and 1,1-dimethylhydrazine claimed the growth of Co metal films at a substrate temperature of 140 °C,[4c] although the basic ALD growth parameters of this process were not reported. In the present study, the high reactivity of $BH_3(NHMe_2)$ toward **2**, **3**, **7**, and **9** permits self-limited film growth at <200 °C. These attributes should enable many new applications of ALD-grown first row transition metal films.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, analytical and spectroscopic data for **1**−**15**, X-ray crystallographic data for **10**−**12**, **14**, and **15** in CIF format, and film deposition and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Semiconductor Research Corporation. Scott B. Clendenning of Intel Corporation is acknowledged for helpful discussions.

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