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Reductive Elimination of Hypersilyl Halides from Zinc(II) Complexes. Implications for Electropositive Metal Thin Film Growth

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Supporting Information Placeholder

ABSTRACT: Treatment of $Zn(Si(SiMe_3)_3)_2$ with ZnX_2 (X = Cl, Br, I) in tetrahydrofuran at 23 °C afforded $[Zn(Si(SiMe_3)_3)X\text{-}(THF)]_2$ in 83-99% yields. X-ray crystal structures revealed dimeric structures with Zn_2X_2 cores. Thermogravimetric analyses of $[Zn(Si(SiMe_3)_3)X(THF)]_2$ demonstrated loss of coordinated THF between 50-155 °C, and then single step weight losses between 200 and 275 °C. The nonvolatile residue was Zn metal in all cases. Bulk thermolyses of $[Zn(Si(SiMe_3)_3)X\text{-}(THF)]_2$ between 210 and 250 °C afforded Zn metal in 97-99% yields, $Si(SiMe_3)_3X$ in 91-94% yields, and THF in 81-98% yields. Density functional theory calculations confirmed that Zn formation becomes energetically favorable upon THF loss. Similar reactions are likely to be general for $M(SiR_3)_n/MX_n$ pairs, and may lead to new metal film growth processes for chemical vapor deposition and atomic layer deposition.

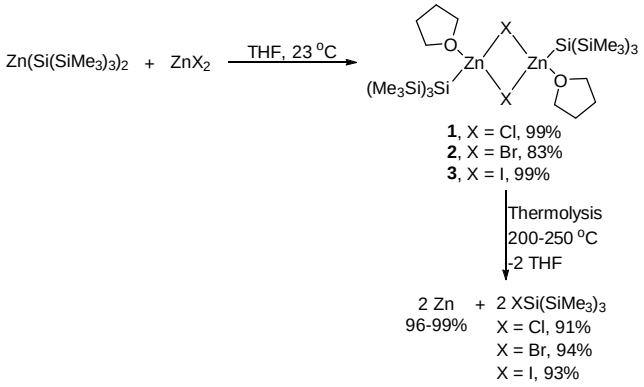
Thin films of metals have many important applications in microelectronics and magnetic devices.[1] Atomic layer deposition (ALD) is a film growth technique that provides conformal coverage of nanoscale features and sub-nm control over film thicknesses, due to its self-limited growth mechanism.[2] In many future devices, transition metal and other metal films will need to be grown by ALD to meet performance requirements.[1-3] Such ALD growth requires a rapid, complementary reaction between a metal precursor and a reducing co-reagent to afford the metal. Considerable progress has been made on the ALD growth of metallic Cu and noble metal films,[1-3] due largely to the positive electrochemical potentials (E°) of ions of these metals and attendant ease of reduction to the metals with a range of reagents.[1-3] By contrast, most other metal ions have negative E° values and are much more difficult to reduce to the metals.[1] As such, the thermal ALD growth of these metals is difficult and remains poorly developed.[1] H_2 has been the most commonly used reducing co-reagent to date in ALD,[1,4] but many metal ions have low reactivities toward H_2 at desired ALD growth temperatures of ≤ 200 °C.[1] We recently reported that $BH_3(NHMe_2)$ serves as a powerful reducing co-reagent for Ni(II), Co(II), Fe(II), Cr(II), and possibly Mn(II) α-imino alkoxide precursors in the ALD growth of these metals at ≤ 200 °C.[5] However, these processes required a Ru substrate to decompose the $BH_3(NHMe_2)$ to more reactive reducing species, and the growth stopped once the film covered the Ru surface. Elemental Zn films have been grown by chemical vapor deposition (CVD) at ≥150 °C by thermal decomposition of bis(allyl)zinc.[6] Thermal decomposition of $ZnEt_2$ to Zn metal occurs below 127 °C on many surfaces.[7] Additionally, use of $ZnEt_2$ as a reducing agent in ALD growth with $Cu(OCHMeCH_2NMe_2)_2$ affords Cu-Zn alloys at ≥ 120 °C through parasitic thermal decomposition of $ZnEt_2$ to Zn metal.[8] However, no ALD processes for Zn metal have been reported, due to a lack of appropriate chemical precursors.

Recently, the ALD growth of Sb thin films was demonstrated using $SbCl_3$ and $Sb(SiEt_3)_3$.[9] This process proceeds by elimination of $SiEt_3Cl$, and is a totally new approach for the ALD of element films, in this case a nonmetal.[9] Related reactions could represent powerful methodologies for the ALD growth of *metallic* first row transition and electropositive metal films, and could avoid potential problems associated with H_2 and highly reactive hydride reagents.[1,5] Within this context, we describe a series of reactions that occur upon treatment of bis(hypersilyl)zinc, $Zn(Si(SiMe_3)_3)_2$,[11] with ZnX_2 (X = Cl, Br, I) ultimately to afford Zn metal and $Si(SiMe_3)_3X$. These results demonstrate that reductive eliminations of silyl halides from Zn(II) centers are facile, thus suggesting new, potentially general chemistry for the growth of metal films. Significantly, the electrochemical potential of the Zn^{2+} ion (E° = -0.7618 V[10]) is significantly more negative than that of the Sb^{3+} ion (E° = 0.152 V[10]), implying that silyl halide reductive eliminations may provide general access to many electropositive metals.

$Zn(Si(SiMe_3)_3)_2$ was prepared according to a literature procedure,[11a] and was treated with one equivalent of ZnX_2 (X = Cl, Br, I) in THF (Scheme 1). No color changes or precipitation occurred upon mixing at ambient temperature or refluxing for 18 h. Analysis of these reaction mixtures after stirring at 23 °C for 3 h indicated the formation of the products **1-3**, as outlined in Scheme 1. Complexes **1-3** were isolated by crystallization, and were characterized by spectral and analytical data, and by X-ray crystallography.[12] The ^1H and $^{13}C\{^1H\}$ NMR

spectra revealed the expected resonances for the $Si(SiMe_3)_3$ and THF ligands, and the former resonances were shifted from those of $Zn(Si(SiMe_3)_3)_2$. Complex **1** was previously reported using a different synthetic method.[13] Complexes **1-3** have similar dimeric structures, with one $Si(SiMe_3)_3$ and one THF ligand per Zn ion and two halide ions that bridge between the Zn ions. The $Si(SiMe_3)_3$ groups are anti to each other within the dimers, to avoid steric crowding. Figure 1 shows a perspective view of **2**. The Zn-Br, Zn-Si, and Zn-O bond lengths are 2.5030(6) and 2.5382(6), 2.352(1), and 2.101(3) Å, respectively.

Scheme 1. Synthesis and thermolysis of **1-3**



Thermogravimetric analyses (TGA) of **1-3** were carried out to understand their solid state decompositions. The THF ligands are labile and their loss was observed starting at 50 °C and was complete by 155 °C. Then, single step weight losses occurred between 200 and 275 °C to afford 11.67, 6.02, and 3.84% weight residues for **1-3**, respectively. The percentages of Zn in **1-3** are 15.55, 14.06, and 12.77%, respectively. The lower observed residues, compared to those predicted by the percent zinc in **1-3**, may originate from partial sublimation of **1-3** or the THF-free products thereof.

Encouraged by the TGA data, we next explored solid state thermolyses of **1-3**.[12] Pressure tubes fitted with Teflon stoppers were charged with ~0.4 mmol each of **1-3** and hexamethylbenzene as an internal standard. These tubes were then heated at 210 (**1**), 225 (**2**), and 250 °C (**3**) for 4 hours. During the thermolyses, the white solids gradually transformed to granular gray solids and colorless liquids condensed at the cool area near the Teflon stoppers. Workup entailed extraction of the flask contents with benzene-d_6, decanting the extracts, and vacuum drying of the gray powders. X-ray powder diffraction revealed the gray powders to be Zn metal, with isolated yields of 96-99%.[12] ^1H and $^{13}C\{^1H\}$ NMR spectra of the extracts showed that the soluble products were $Si(Si(CH_3)_3)_3X$ and THF, based upon comparison with the NMR data of authentic samples.[12] The yields of $Si(Si(CH_3)_3)_3X$ and THF were 91-94% and 81-98%, respectively.

Density functional theory (DFT) calculations using VASP[14] and TURBOMOLE[15] were used to predict the structures of intermediates and quantify the changes in bonding, as detailed in the Supporting Information.[12] The gas phase compounds $[Zn(Si(SiMe_3)_3)Cl]_n$ increase in stability upon oligomerization, with n = 4 predicted to be the most stable (ΔE = -49.1 kJ/mol-Zn relative to $ZnCl_2$ and $Zn(Si(SiMe_3)_3)_2$). The tetramer is predicted to contain a cubic Zn_4Cl_4 core. The X-ray crystal structure of $[Zn(Si(tBu)_3)Br]_4$ has been reported,[16] and exists with a cubic Zn_4Br_4 core, thus supporting the DFT calculations of $[Zn(Si(SiMe_3)_3)Cl]_4$. However, it is not clear if the tetramer is accessible after THF loss in the current experiments. Thermolysis of solid **2** at 111 °C/0.05 Torr for 24 hours in a drying tube afforded a THF-free complex of the apparent formula $[Zn(Si(SiMe_3)_3)Br]_x$,[12] however, X-ray quality crystals could not be obtained despite multiple attempts and the compound was not pursued further.

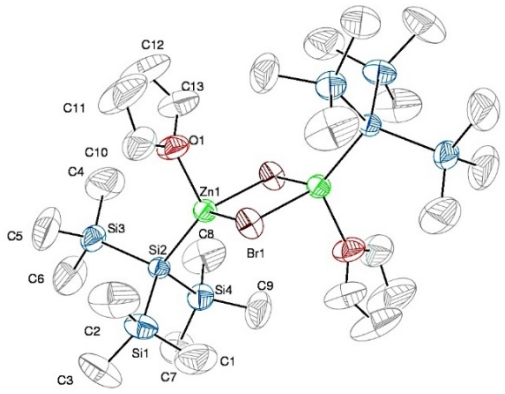


Figure 1. Perspective views of **2** with thermal ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): Zn-Br 2.5030(6), Zn-Br' 2.5382(6), Zn-Si2 2.352(1), Zn-O1 2.101(3), Zn-Br-Zn' 81.16(2), Br-Zn-Br' 93.84(2), Br-Zn-Si2 124.52(3), Br-Zn-Br' 121.70(3), Br-Zn-O 96.88(9), Br'-Zn-O 94.56(9).

The DFT calculations revealed that formation of THF adducts from $[Zn(Si(SiMe_3)_3)Cl]_n$ is thermodynamically favorable for n = **1-3**. For formation from $ZnCl_2$, $Zn(Si(SiMe_3)_3)_2$, and THF, the dimer $[Zn(Si(SiMe_3)_3)Cl(THF)]_2$ is computed to be the most stable (ΔE = -68.4 kJ/mol-Zn neglecting entropy), consistent with the isolation of **1-3**. However, the trimer $[Zn(Si(SiMe_3)_3)Cl(THF)]_3$ is predicted to be only <2 kJ/mol less stable than the dimer. The calculated Zn-Cl (2.40-2.43 Å) and Zn-Si (2.39 Å) distances in the dimer are within 2% of those observed in the X-ray crystal structure of **1** (2.391(2), 2.347(2) Å), which is within the accuracy of DFT.

We next used DFT to predict the thermodynamic stabilities of various Zn complexes toward elimination of $Si(SiMe_3)_3X$. Consistent with the high stabilities of **1-3** documented above, the THF-coordinated dimer **1** is thermodynamically stable by +22 kJ/mol-Zn at 0 K with respect to reductive elimination of $Si(SiMe_3)_3Cl$ and production of Zn metal. However, loss of the THF ligands causes the resulting THF-free $[Zn(Si(SiMe_3)_3)Cl]_2$ to become metastable by -12.5 kJ/mol-Zn toward reductive elimination of $Si(SiMe_3)_3Cl$ and formation of Zn metal. Since entropy has been neglected, this energy difference (+22→-12.5 kJ/mol) reflects metastable bonding within the complex. Similar switches to metastability upon loss of the THF ligands are computed for the monomer $Zn(Si(SiMe_3)_3)Cl(THF)$ (+14.4→ -45.9 kJ/mol-Zn) and trimer $[Zn(Si(SiMe_3)_3)Cl(THF)]_3$ (+20.9→-12.5 kJ/mol-Zn). The metastability toward reductive elimination is likely due to lower coordination numbers at Zn upon THF loss. These observations are consistent with experiment, since the TGA data reveal that THF loss from **1-3** occurs prior to decomposition. By contrast, reductive elimination from the tetramer $[Zn(Si(SiMe_3)_3)Cl]_4$ is not favored, apparently since each Zn ion is four coordinate and thus coordinatively saturated, ,

although the small energy cost (ΔE = +2.9 kJ/mol-Zn) can probably be overcome at elevated temperatures.

The overall reaction $Zn(Si(SiMe_3)_3)_2 + ZnCl_2 \rightarrow 2\ Zn + 2\ Si(SiMe_3)_3Cl$ is computed by DFT to show ΔE = -46 kJ/mol-Zn and ΔG = -52 kJ/mol-Zn at T = 100 °C, indicating that it is a thermodynamically viable route to the ALD of Zn. This prediction is consistent with the observed decompositions of **1-3** upon thermolysis. For reference, analogous DFT calculations of the ALD reaction for the deposition of Sb from $SbCl_3$ and $Sb(SiEt_3)_3$[9] predict a favorable ΔE value of -140 kJ/mol-Sb.[12] The highest occupied molecular orbital of $Zn(Si(SiMe_3)_3)_2$ is found to be Si-Zn-Si σ-bonding and this is the ultimate source of the electrons that reduce the Zn ion to metallic form. The $[Zn(Si(SiMe_3)_3)Cl]_n$ clusters also show 2n electrons in high-lying σ(Zn-Si) orbitals that become available for reduction of Zn when the Zn-Si bond is broken. At the same time, the ligating Si atoms of the hypersilyl groups become oxidized. The DFT calculations reveal a similar role for σ(Sb-Si) bonding orbitals in $Sb(SiEt_3)_3$.

This work has several implications for the growth of metal films by CVD and ALD using silyl halide elimination reactions. Most importantly, reductive elimination of $Si(SiMe_3)_3X$ is predicted to be energetically favorable for the Zn(II) ion, although no prediction about kinetics can be made without knowledge of a reaction pathway in solution or during ALD. The formation of Zn metal from **1-3** demonstrates favorable reactions at 210-250 °C. The metastable unsolvated adducts $[ZnSi(SiMe_3)_3Cl]_n$ are representative of structures that might form on the growing surface in a potential film growth process using $ZnCl_2$ and $Zn(Si(SiMe_3)_3)_2$, which implies that the present work may lead to a Zn metal ALD process. In this vein, $Zn(Si(SiMe_3)_3)_2$ sublimes at 110 °C/0.05 Torr, decomposes thermally at about 350 °C, and thus has excellent ALD precursor properties.[12] Virtually all ALD processes for Zn-containing films use $ZnEt_2$ as a precursor,[17] and our calculations predict ΔE = -103 kJ/mol-Zn for the reaction $Zn(Si(SiMe_3)_3)_2 + ZnEt_2 \rightarrow 2Zn + 2Si(SiMe_3)_3Et$.[12] This is even more exothermic than the formation of Zn metal from $ZnCl_2$ and $Zn(Si(SiMe_3)_3)_2$, and may be a promising ALD approach if the depositions proceed at or below the thermal decomposition temperature of $ZnEt_2$ (~130 °C).[7,8] The favorable energetics with $ZnEt_2$ suggest that precursors other than metal halides can likely be used. However, more volatile and thermally stable Zn precursors need to be developed. Finally, Zn is an excellent model for first row transition metals, since its metal radius is about the same as V and Cr, the E° value of the Zn(II) ion (E° = -0.74 V[10]) lies between those of Fe(II) (E° = -0.44 V[10]) and Cr(II) (E° = -0.94 V[10]), and the coordination chemistry of Zn(II) is similar to first row transition metal(II) ions. Analogous reactions of $M(SiR_3)_n$[18] and MX_n are likely to afford metals and should be similarly exothermic, which may lead to new growth processes for metal films upon appropriate precursor development.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, analytical and spectroscopic data for **1-3**, X-ray crystallographic data for **1-3** in CIF format, and details of the DFT calculations. 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 interests.

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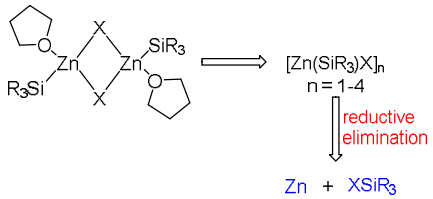
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