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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(SMe3)3)2 with ZnX2 (X = Cl, Br, I) in tetrahydrofuran at 23 °C afforded [Zn(Si(SMe3)3)X(THF)]2 in 83-99% yields. X-ray crystal structures revealed dimeric structures with ZnX2 cores. Thermogravimetric analyses of [Zn(Si(SMe3)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(SMe3)3)X(THF)]2 between 210 and 250 °C afforded Zn metal in 97-99% yields; Si(SMe3)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(SiR3)3/MX2 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. 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. In many future devices, transition metal and other metal films will need to be grown by ALD to meet performance requirements. 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, 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. By contrast, most other metal ions have negative E° values and are much more difficult to reduce to the metals. As such, the thermal ALD growth of these metals is difficult and remains poorly developed. H2 has been the most commonly used reducing co-reagent to date in ALD, but many metal ions have low reactivities toward H2 at desired ALD growth temperatures of ≤ 200 °C. We recently reported that BH3(NHMe2) serves as a powerful reducing co-reagent for Ni(II), Co(II), Fe(II), Cr(II), and possibly Mn(II) α-imino alkoxyd precursors in the ALD growth of these metals at ≤ 200 °C. However, these processes required a Ru substrate to decompose the BH3(NHMe2) 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 ≥ 200 °C by thermal decomposition of bis(allyl)zinc. Thermal decomposition of ZnBr2 to Zn metal occurs below 127 °C on many surfaces. Additionally, use of ZnBr2 as a reducing agent in ALD growth with Cu(OCHMeCH2NHMe2)2 affords Cu-Zn alloys at ≥ 120 °C through parasitic thermal decomposition of ZnBr2 to Zn metal. However, no ALD processes for Zn metal have been reported, due to a lack of appropriate chemical precursors.

Recently, the ALD growth of Sn thin films was demonstrated using SbCl3 and Sb(SiEt3)3. This process proceeds by elimination of SbCl3, and is a totally new approach for the ALD of element films, in this case a nonmetal. 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 H2 and highly reactive hydride reagents. Within this context, we describe a series of reactions that occur upon treatment of bis(hypersilyl)zinc, Zn(Si(SMe3)3)2(X = Cl, Br, I) ultimately to afford Zn metal and Si(SMe3)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 Zn2+ ion (E° = -0.76 eV) is significantly more negative than that of the Sn2+ ion (E° = 0.12 eV), implying that silyl halide reductive eliminations may provide general access to many electropositive metals.

Zn(Si(SMe3)3)2 was prepared according to a literature procedure, and was treated with one equivalent of ZnX2 (X = Cl, Br, I) in THF (Scheme 1). No color changes or precipitation occurred upon mixing at ambient temperature or refluxing for 2 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. The H and 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.$^3$ 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 2.10(3) Å, respectively.

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

\[
\text{Zn(Si(SiMe$_3$)$_3$)$_2$} + \text{ZnX}_2 \xrightarrow{\text{THF, 23 °C}} \text{Zn(Si(SiMe$_3$)$_3$)}
\]

1. X = Cl, 99%
2. X = Br, 83%
3. X = I, 99%

Thermolysis:
- 200-250 °C
- 1 THF
- 270 °C
- 2 THF
- 96-99%

**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), 2.5382(6), Zn-Si2: 2.352(1), Zn-O: 2.10(3), Zn-Br: 81.16(2), Zn-Si2: 12.53(2), Zn-Br: 127.0(3), Zn-Si-O: 96.88(9), Zn-O: 94.56(9).

The DFT calculations revealed that formation of THF adducts from [Zn(Si(SiMe$_3$)$_3$)$_2$Cl] 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 ($\Delta E = -68.4$ kJ/mol-Zn neglecting entropy), consistent with the isolation of 1-3. However, the trimer [Zn(Si(SiMe$_3$)$_3$)Cl(THF)$_2$] 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 (2.39(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$_3$)$_3$. 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$_3$)$_2$Cl 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 2.5 kJ/mol-Zn toward reductive elimination of Si(SiMe$_3$)$_2$Cl and formation of Zn metal. Since entropy has been neglected, this energy difference (-22.5 to 2.5 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) (+46.4 to -45.9 kJ/mol-Zn) and trimer [Zn(Si(SiMe$_3$)$_3$)Cl(THF)$_2$] (+20.9 to -2.5 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(SiMe3)3)2 + ZnCl2 → 2 Zn + 2 Si(SiMe3)2Cl 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 Sn from SnCl4 and Sn(SiEt3)2 predict a favorable ΔE value of -140 kJ/mol-Sn. This is the highest occupied molecular orbital of Zn(Si(SiMe3)3)2, which 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(SiMe3)3)2]Cl4 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(Si-Si) bonding orbitals in Sn(SiEt3)2.

This work has several implications for the growth of metal containing films by CVD and ALD using M(SiR3)2Cl which are thermally at about 350 °C, and thus has excellent ALD pretreatment. In this present work may lead to a Zn metal ALD process. In this work several implications for the growth of metal

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.
Treatment of Zn(Si(SiMe\textsubscript{3})\textsubscript{3})\textsubscript{2} with ZnX\textsubscript{2} (X = Cl, Br, I) in tetrahydrofuran at 23 °C afforded the halide-bridged dimers [Zn(Si(SiMe\textsubscript{3})\textsubscript{3})X(THF)]\textsubscript{2} in 83-99% yields. Bulk thermolyses of [Zn(Si(SiMe\textsubscript{3})\textsubscript{3})X(THF)]\textsubscript{2} afforded Zn metal in 97-99% yields and Si(SiMe\textsubscript{3})\textsubscript{3}X in 91-94% yields. Similar reductive eliminations are likely to be general for M(SiR\textsubscript{3})\textsubscript{n}/MX\textsubscript{n} pairs, where M is an electropositive element, and may lead to new metal film growth processes for chemical vapor deposition and atomic layer deposition.