Designing Volatility into Lead Precursors

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Volatility is a critical property of ALD precursors, but there is no reliable method to predict it. This was recently highlighted in our research when we discovered that bis[lead(II) *N,N'*-di-*tert*-butyl-1,1-dimethylsilanediamide] [(**4Pb**)$_2$] had good volatility (112 °C/1 Torr) despite being dimeric in the solid and vapor phases. Oligomerization usually decreases volatility, so we attempted to cleave the dimer to improve volatility by increasing steric bulk, adducting the monomer with a Lewis base, and by installing a pendant tertiary amine onto the ligand itself. None of these strategies produced a more volatile complex than (**4Pb**)$_2$. Indeed, even the monomeric complex lead(II) *N,N'*-bis(1-(dimethylamino)-2-methylpropan-2-yl)-1,1-dimethylsilanediamide (**5Pb**) had slightly lower volatility (118 °C/1 Torr). These counter-intuitive results led us to investigate the origins of high volatility with density functional theory (DFT) and experimentally with thermogravimetric analysis (TGA). In this talk, we will introduce and discuss our efforts to combine theoretical and experimental methods to predict precursor volatility.

Since volatility is governed by intermolecular interactions, which in turn are determined by the molecular electrostatic potential (ESP), we modeled vapor pressure against the statistical properties of the ESP (e.g., polar surface area, total variance). To fit our models, we obtained a consistent set of experimental vapor pressures for several known and novel lead precursors: the novel (**4Pb**)$_2$ and **5Pb** were compared to the recently reported acyclic lead(II) bis[bis(trimethylsilyl)amide] (Pb(btsa)$_2$, 127 °C/1 Torr) and the cyclic lead(II) *rac-N,N'*-di-*tert*-butyl-2,3-diamidobutane (**1Pb**, 94 °C/1 Torr), as well as more classical precursors (e.g., Pb(tmhd)$_2$, 166 °C/1 Torr). For the theoretical calculations, we developed an efficient and reliable DFT methodology (ωB97X-D3(BJ)//revPBE) which was benchmarked against high-level ab initio coupled-cluster calculations (DLPNO-CCSD). Statistical analysis revealed strong correlations between vapor pressure and 3 factors: the total variance ($\sigma_{\pm}^2$, $R^2 = 0.987$), the absolute polar surface area (A, $R^2 = 0.983$), and the standard deviation ($\prod$, $R^2 = 0.970$) of the ESP. This computation framework helped explain how dimerization improves the volatility of (**4Pb**)$_2$ compared to monomeric **5Pb**, as well as proposing new lead precursors with better volatility. This talk will als discuss how general this approach is for qualitative precursor design considerations, as well as critically evaluate the limitations of this approach, and outline the path toward a quantitative methodology to predict volatility.

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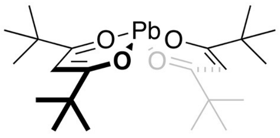
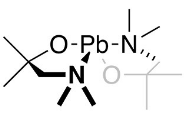
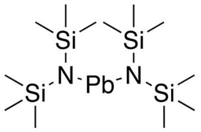
Known Lead ALD Precursors



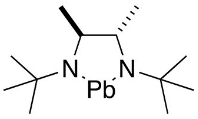
$Pb(tmhd)_2$



$Pb(dmamp)_2$

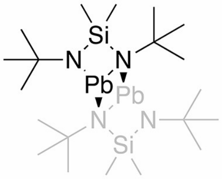


$Pb(btsa)_2$

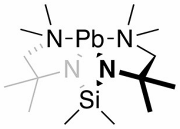


1Pb

New Precursors!



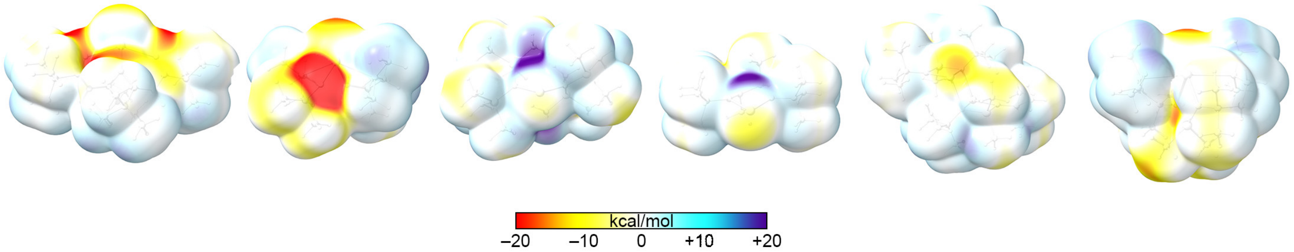
(4Pb)$_2$



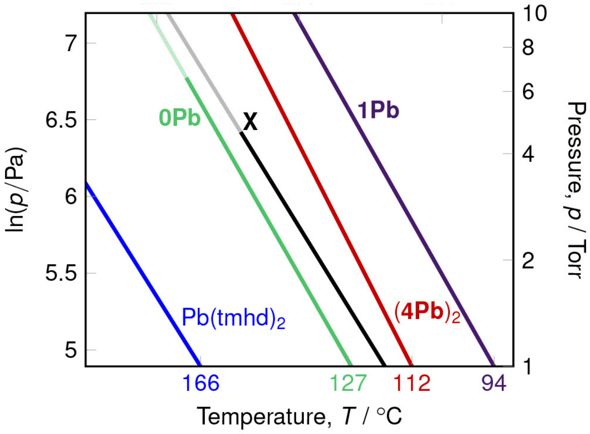
5Pb

DFT

Electrostatic Potential (ESP) Surfaces



Experimental Thermal Analysis



Predictive Vapor Pressure Model