Synthesis and Structural Elucidation of Solvent-Free and Solvated Lithium Dimethyl(HMDS) zincates

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Computational Details

The geometry of the molecules was optimized using Gaussian 03.[1] Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed, utilising the 6-31g* basis set.[2] The resultant optimised geometries were subject to a frequency analysis and the refined by further density functional theory (DFT) calculations[3] using the B3LYP functionals[45] and the 6-311G** basis set.[67] The geometrical structural features from the DFT calculations are reported here while the total energy value from the DFT calculation is adjusted by including the zero-point energy abstracted from the HF calculation modified by the factor 0.91.

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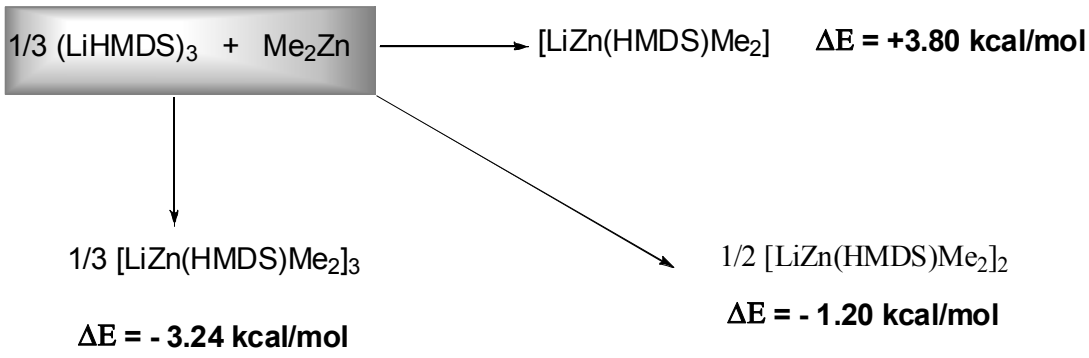


$1/3\ (LiTMP)_3 + Me_2Zn + PMDETA$

↓

$[(\kappa^3\text{-PMDETA})Li(\mu Me)(Me)Zn(HMDS)]$ $\Delta E = -13.64$ kcal/mol

$1/3\ (LiTMP)_3 + Me_2Zn + PMDETA$

↓

$[(\kappa^1\text{-PMDETA})Li(\mu HMDS)(Me)Zn(Me)]$ $\Delta E = -8.35$ kcal/mol

$1/3\ (LiTMP)_3 + Me_2Zn$

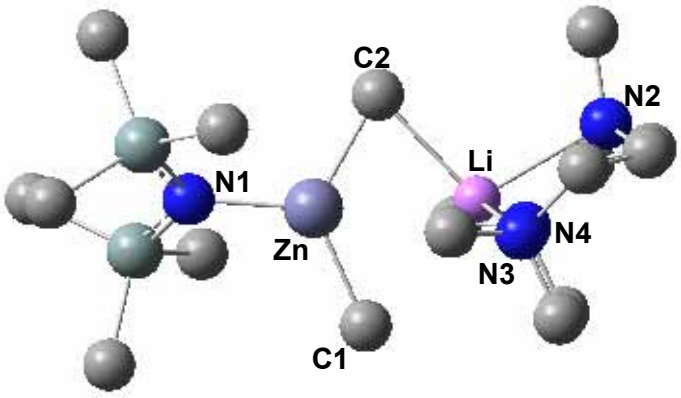
↓

$[Li(\mu Me)(Me)Zn(HMDS)]$ $\Delta E = +3.80$ kcal/mol

$1/3\ (LiTMP)_3 + Me_2Zn$

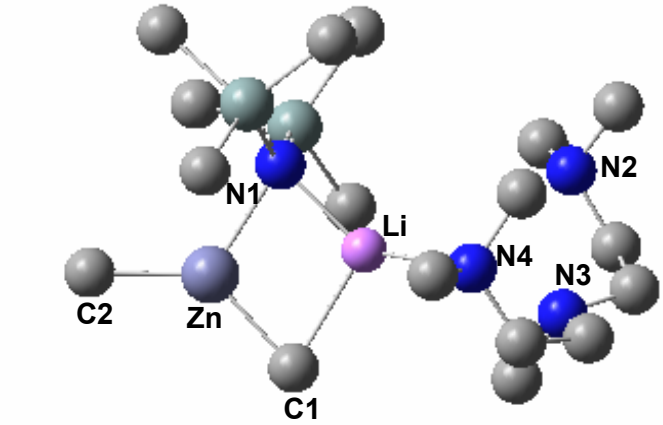
↓

$[Li(\mu HMDS)(Me)Zn(Me)]$ $\Delta E = +17.81$ kcal/mol



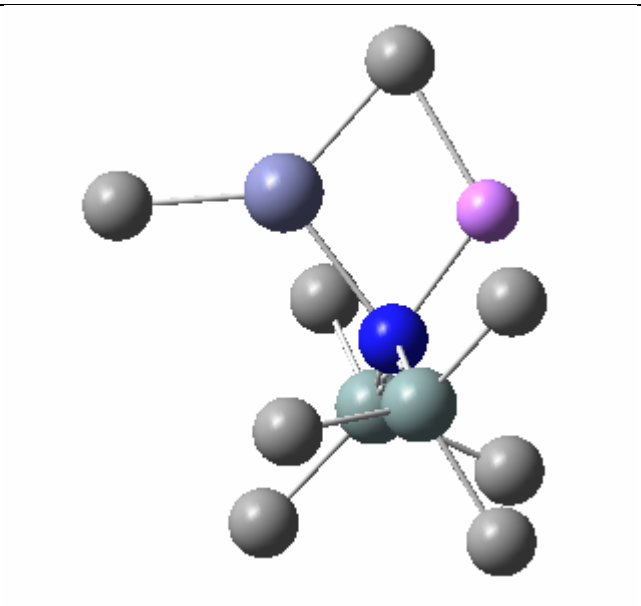
Principal Bond Lengths (Å)

Li – N (outer)	**2.251, 2.256**
Li – N (inner)	**2.362**
Li – C (Me)	**2.271, 2.671**
Zn – C (Me)	**2.067, 2.042**
Zn – N	**1.975**
N – Si	**1.719, 1.720**



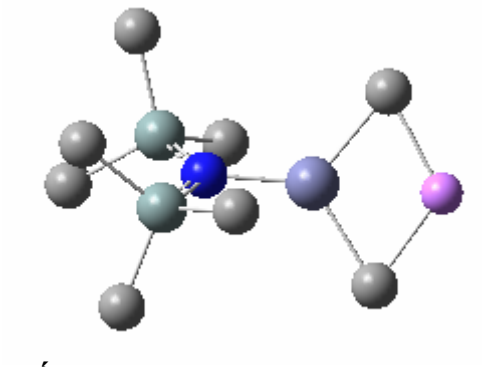
Principal Bond Lengths (Å)

Li – N (outer)	**2.130, 5.035**
Li – N (inner)	**3.711**
Li – C (Me)	**2.569**
Li – N	**1.978**
Zn – C (Me)	**1.981, 2.057**
Zn – N	**2.143**
N – Si	**1.740, 1.743**



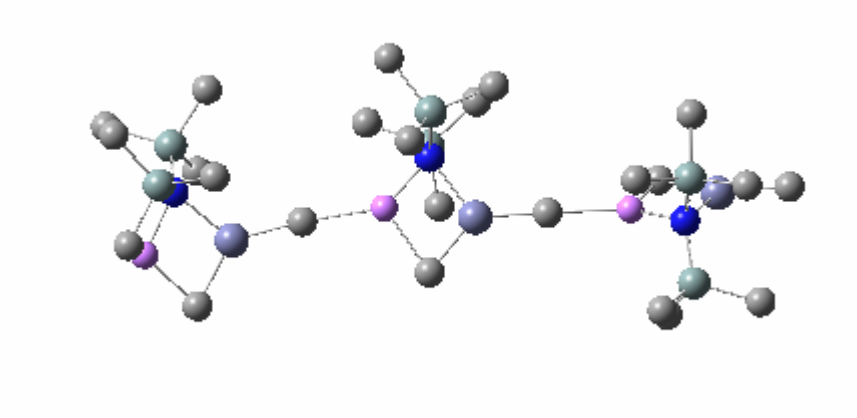
Principal Bond Lengths (Å)

Li – C (Me)	**2.060**
Li – N	**1.896**
Zn – C (Me)	**1.970, 2.084**
Zn – N	**2.164**
N – Si	**1.734, 1.741**
Li – C (hmds)	**2.542**



Principal Bond Lengths (Å)

Li – C (Me)	**2.033, 2.033**
Zn – C (Me)	**2.120, 2.120**
Zn – N	**1.912**
N – Si	**1.728, 1.728**



Principal Bond Lengths of Central (Li μ-HMDS, μ-Me ZnMe) portion(Å)

Li – C (Me terminal)	**2.274, 2.275**
Li – C (Me bridge)	**2.197**
Li – N	**1.952**
Zn – C (Me)	**1.999, 2.050**
Zn – N	**2.107**
N – Si	**1.742, 1.743**
Li – C (hmds)	**2.992**