The Role of Ligand Displacement in Sm(II)-HMPA Based Reductions

Edamana Prasad,\textsuperscript{a} Brian W. Knettle,\textsuperscript{b} and Robert A. Flowers, II*\textsuperscript{a}

\textsuperscript{a}Department of Chemistry, Lehigh University, Bethlehem PA 18015, USA

\textsuperscript{b}Department of Chemistry and Biochemistry, Texas Tech University, Box 41061, Lubbock, TX 79409-1061, USA

Supporting Information

List of Contents

| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 1 equ. HMPA+ 2-butanone system | S3 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 1 equ. HMPA+ 1-iodobutane system | S3 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 2 equ. HMPA+ 2-butanone system | S4 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 2 equ. HMPA+ 1-iodobutane system | S4 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 6 equ. HMPA+ 2-butanone system | S5 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 6 equ. HMPA+ 1-iodobutane system | S5 |
| Stopped Flow decay trace for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 10 equ. HMPA+ 1-iodobutane system | S6 |
| Plot of k vs equivalents of HMPA in [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] /2-butanone system | S6 |
| Erying plot for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 10 equ. HMPA+ 2-butanone system | S7 |
| Erying plot for [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 10 equ. HMPA+ 1-iodobutane system | S7 |
| Rate order determination with respect to 1-iodobutane in [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 1 equ. HMPA+ 1-iodobutane system | S8 |
| Rate order determination with respect to 1-iodobutane in [Sm\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}] + 2 equ. HMPA+ 1-iodobutane system | S8 |
Rate order determination with respect to 1-iodobutane in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 6 equ. HMPA+ 1-iodobutane system 

Rate order determination with respect to 1-iodobutane in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 10 equ. HMPA+ 1-iodobutane system 

Rate order determination with respect to 2-butanone in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 1 equ. HMPA+ 2-butanone system 

Rate order determination with respect to 2-butanone in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 2 equ. HMPA+ 2-butanone system 

Rate order determination with respect to 2-butanone in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 6 equ. HMPA+ 2-butanone system 

Rate order determination with respect to 2-butanone in 
[Sm{N(SiMe$_3$)$_2$)$_2$] + 10 equ. HMPA+ 2-butanone system 

Calibration curve for VPO experiment 

Molecular Weight determination data by VPO experiment 

ITC experimental data
**Figure S1**: Stopped Flow decay trace for [Sm\{N(SiMe$_3$)$_2$\}]$_2$ (0.02M) in presence of HMPA (1 equivalent to the concentration of Sm (II) species) and 2-butanone (0.20 M) in THF at 25 °C.

**Figure S2**: Stopped Flow decay trace for [Sm\{N(SiMe$_3$)$_2$\}]$_2$ (0.02M) in presence of HMPA (1 equivalent to the concentration of Sm (II) species) and 1-iodobutane (0.20 M) in THF at 25 °C.
Figure S3: Stopped Flow decay trace for $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ (0.02M) in presence of HMPA (2 equivalent to the concentration of Sm (II) species) and 2-butanone (0.20 M) in THF at 25 $^\circ$C.

Figure S4: Stopped Flow decay trace for $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ (0.02M) in presence of HMPA (2 equivalent to the concentration of Sm (II) species) and 1-iodobutane (0.20 M) in THF at 25 $^\circ$C.
Figure S5: Stopped Flow decay trace for $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ (0.02M) in presence of HMPA (6 equivalent to the concentration of Sm (II) species) and 2-butanone (0.20 M) in THF at 25 °C.

Figure S6: Stopped Flow decay trace for $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ (0.02M) in presence of HMPA (6 equivalent to the concentration of Sm (II) species) and 1-iodobutane (0.20 M) in THF at 25 °C.
Figure S7: Stopped Flow decay trace for $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ (0.02M) in presence of HMPA (10 equivalent to the concentration of Sm (II) species) and 1-iodobutane (0.20 M) in THF at 25 °C.

Figure S8: A plot of rate constant vs equivalents of HMPA for the reduction of 2-butanone by $[\text{Sm}\{\text{N(SiMe}_3\}_2\}]$ in THF at 25 °C.
Figure S9: Erying plot for [Sm{N(SiMe$_3$)$_2$}] + 10 equ. HMPA+ 2-butanone system in THF.

Figure S10: Erying plot for [Sm{N(SiMe$_3$)$_2$}] + 10 equ. HMPA+ 1-iodobutane system in THF.
**Figure S11**: A plot of \( \log k_{\text{obs}} \) vs \( \log [1\text{-iodobutane}] \) in Sm\{N(SiMe}_3\}_2 \] + 1 equ. HMPA+ 1-iodobutane system

\[ \text{slope} = 0.92 \pm 0.01 \]
\[ R^2 = 0.9997 \]

**Figure S12**: A plot of \( \log k_{\text{obs}} \) vs \( \log [1\text{-iodobutane}] \) in Sm\{N(SiMe}_3\}_2 \] + 2 equ. HMPA+ 1-iodobutane system

\[ \text{slope} = 1.00 \pm 0.03 \]
\[ R^2 = 0.9982 \]
slope = 0.90 ± 0.01
$R^2 = 0.9996$

**Figure S13**: A plot of log $k_{obs.}$ vs log [1-iodobutane] in Sm{N(SiMe$_3$)$_2$)$_2$} + 6 equ. HMPA+ 1-iodobutane system

slope = 0.80 ± 0.1
$R^2 = 0.9916$

**Figure S14**: A plot of log $k_{obs.}$ vs log [1-iodobutane] in Sm{N(SiMe$_3$)$_2$)$_2$} + 10 equ. HMPA+ 1-iodobutane system
**Figure S15**: A plot of log $k_{\text{obs.}}$ vs log [2-butanone] in Sm\{N(SiMe$_3$)$_2$\}$_2$ + 1 equ. HMPA+ 2-butanone

**Figure S16**: A plot of log $k_{\text{obs.}}$ vs log [2-butanone] in Sm\{N(SiMe$_3$)$_2$\}$_2$ + 2 equ. HMPA+ 2-butanone
**Figure S17:** A plot of log \( k_{\text{obs}} \) vs log [2-butanone] in Sm\{N(SiMe\(_3\))\(_2\)\} \( + 6 \) equ. HMPA + 2-butanone

slope = 1.21 ± 0.12
\( R^2 = 0.9902 \)

**Figure S18:** A plot of log \( k_{\text{obs}} \) vs log [2-butanone] in Sm\{N(SiMe\(_3\))\(_2\)\} \( + 10 \) equ. HMPA + 2-butanone

slope = 1.2 ± 0.10
\( R^2 = 0.9920 \)
Figure S19: A plot of VPO molality vs actual molality of biphenyl solutions in THF. R² = 0.999.

Table S1: The calculated Molecular weights and VPO generated molecular weights of [Sm{N(SiMe₃)₂}₂] and [Sm{N(SiMe₃)₂}₂]-HMPA combinations

<table>
<thead>
<tr>
<th>System</th>
<th>Molecular weight Calculated</th>
<th>VPO generated Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sm{N(SiMe₃)₂}₂]</td>
<td>471.13</td>
<td>479.36±24</td>
</tr>
<tr>
<td>[Sm{N(SiMe₃)₂}₂].1 HMPA</td>
<td>650.33</td>
<td>641.3±33</td>
</tr>
<tr>
<td>[Sm{N(SiMe₃)₂}₂].2 HMPA</td>
<td>829.53</td>
<td>447.86±44</td>
</tr>
</tbody>
</table>

Average MW of [Sm{N(SiMe₃)₂}₂].1HMPA+ HMPA = 414.77
Isothermal Titration Calorimetry

HMPA and [Sm{N(SiMe$_3$)$_2$}$_2$] solutions were prepared in distilled degassed THF. Calorimetric studies were carried out in a MicroCal Omega isothermal titration calorimeter at room temperature. The [Sm{N(SiMe$_3$)$_2$}$_2$] solution was placed in the 1.4 µL titration cell and the HMPA solution was loaded into a 250 µL calorimetric syringe. The instrument was modified with the appropriate inert seals and equipped with a small port capable of keeping a static inert gas (Ar) atmosphere over the sample. These instrumental changes allow for calorimetric analysis of air-sensitive compounds in organic solvents. A 50-55 injection matrix was employed with each 5 µL injection lasting a duration of 10 seconds. A three minute interval was allotted between each injection of HMPA into [Sm{N(SiMe$_3$)$_2$}$_2$].

Figure S20: ITC trace from titration of HMPA into the Sm{N[Si(CH$_3$)$_3$]$_2$}$_2$ complex in THF.