Title
Small Molecule Activation and Coordination Chemistry of Bismuth, f-Element, and Alkaline Earth Complexes

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Small Molecule Activation and Coordination Chemistry of Bismuth, f-Element, and Alkaline Earth Complexes

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

By

Douglas R. Kindra

Dissertation Committee:
Professor William J. Evans, Chair
Professor Andrew S. Borovik
Professor Alan F. Heyduk

2014
Dedication

This dissertation is dedicated to my loving wife Lindsay, who encouraged me to pursue my goals with enthusiasm, as long as I was home from lab by midnight.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF COMPOUNDS</td>
<td>xii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>xiv</td>
</tr>
<tr>
<td>CURRICULUM VITAE</td>
<td>svi</td>
</tr>
<tr>
<td>ABSTRACT OF DISSERTATION</td>
<td>xviii</td>
</tr>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 1: Synthesis and Structure of Bis- and Tris-Benzyl Bismuth</td>
<td>17</td>
</tr>
<tr>
<td>Complexes</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 2: Insertion of CO$_2$ and COS into Bi–C Bonds: Reactivity of a</td>
<td>27</td>
</tr>
<tr>
<td>Bismuth NCN Pincer Complex of an Oxyaryl Dianionic Ligand, [2,6-</td>
<td></td>
</tr>
<tr>
<td>(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Bi(C$_6$H$_2$Bu$_2$O)</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 3: Bismuth-Based Cyclic Synthesis of 3,5-Di-</td>
<td>66</td>
</tr>
<tr>
<td>tert-butyl-4-hydroxybenzoic Acid via the Oxyarylcarboxy Dianion,</td>
<td></td>
</tr>
<tr>
<td>(O$_2$CC$_6$H$_2$Bu$_2$O)$^{2-}$</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 4: Nitric Oxide Insertion Reactivity with the Bismuth–Carbon</td>
<td>80</td>
</tr>
<tr>
<td>Bond: Formation of the Oximate Anion, [ON=(C$_6$H$_2$Bu$_2$O)]$^{1-}$,</td>
<td></td>
</tr>
<tr>
<td>from the Oxyaryl Dianion, (C$_6$H$_2$Bu$_2$O)$^{2-}$</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 5: Bismuth in Tri- and Polydentate Nitrogen Coordination</td>
<td>100</td>
</tr>
<tr>
<td>Environments with H–Bond Acceptors: Isolation of an Empty Cavity Metal</td>
<td></td>
</tr>
<tr>
<td>Complex and a Polymetallic Cluster</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 6: Facile Transfer of the Dianionic Oxyarylcarboxy Ligand, \([O_2C(C_6H_2'Bu_2-3,5-O-4)]^{2-}\), from Bismuth to Uranium: Isolation and Characterization of \((C_5Me_5)_2U(Cl)[O_2C(C_6H_2'Bu_2-3-5-OH-4)]\)

CHAPTER 7: Magnetic Susceptibility of Uranium Complexes

CHAPTER 8: Samarium Metallocene Chemistry in Carbon Dioxide Activation and Reductive Carbon-Carbon Coupling

APPENDIX A: Synthesis, Characterization, and Reduction Chemistry of Alkaline Earth Metallocenes

APPENDIX B: Room Temperature and Low Temperature Magnetic Data of \(U^{3+}, U^{4+}\) and \(U^{5+}\) ions.
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 0.1</td>
<td>ORTEP representation of [2,6-(Me₂NCH₂)₂C₆H₅]BiCl₂ showing the ψ-octahedral geometry often times seen in B³⁺ complexes.</td>
</tr>
<tr>
<td>Figure 0.2</td>
<td>Bond distances of the oxyaryl dianionic ligand of compound 1 and the monoanionic phenyl ligand of [1-H][BPh₄].</td>
</tr>
<tr>
<td>Figure 1.1</td>
<td>ORTEP representation of Ar′Bi(η¹-CH₂Ph)₂, Bn-2, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only a dashed line is drawn between Bi1 and N1 because the distance is 3.058(4) Å.</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>ORTEP representation of Bi(η¹-CH₂Ph)₃, Bn-3, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity.</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>ORTEP representation of Ar′Bi[O₂C(C₆H₅)₂Bu₂-3-5-O-4]-κ²O,O′], 2, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>ORTEP representation of Ar′Bi[OSC(C₆H₅)₂Bu₂-3-5-O-4]-κ²O,S], 3, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Bond distances in the oxyaryl, oxyarylcarboxy, and oxyarylthiocarboxy dianionic ligands of compounds 1, 2, and 3 and the normal bond lengths of the closely related monoanionic hydroxyaryl ligand in [1-H][BPh₄].</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>ORTEP representation of {Ar′Bi[O₂C(C₆H₅)₂Bu₂-3-5-OH-4]-κ²O,O′}]BF₄, [2-H][BF₄], with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.</td>
</tr>
</tbody>
</table>
Figure 2.5  Bond distances in the oxyaryl and oxyarylcarboxy dianionic ligands of compounds 1 and 2 compared to the normal bond lengths of the closely related monoanionic carboxylate ligand in [2-H][BF₄].

Figure 2.6  From left to right, HOMO of compounds 1, 2 and 3. All orbitals are drawn with a contour value of 0.05.

Figure 2.7  ORTEP representation of [Ar′Bi(C₆H₂Bu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 2.8  ORTEP representation of Ar′Bi(CN)(C₆H₂Bu₂-3,5-OSiMe₃-4), 7, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 2.9  ORTEP representation of Ar′Bi(N₃)₂, 9, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 3.1  ¹H NMR spectrum of compound 2 and 1 equiv of [Et₃NH][Cl] in acetonitrile-d₃ showing evidence for the proposed intermediate Ar′Bi(Cl)[O₂C(C₆H₂Bu₂-3,5-OH-4)].

Figure 3.2  ORTEP representation of both linkage isomers of Ar′Bi[O₂C(C₆H₂Bu₂-3,5-OH-4)]₂, 11, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 4.1  ORTEP representation of [Ar′Bi(ONC₆H₂-3,5-′Bu₂-4-O)]₂(μ-O), 13, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The two bismuth centers are bound by a bridging oxygen (O1).

Figure 4.2  ORTEP representation of Ar′Bi(ONC₆H₂-3,5-′Bu₂-4-O)₂, 14, with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.
Figure 4.3 ORTEP representation of (Ph₃CS)(Ar')Bi(ONC₆H₂-3,5-Bu₂-4-O), 15, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 4.4 Bond distances in the oximate ligands of compounds 13, 14, and 15 compared to the dianionic oxyaryl and oxyarylcarboxy ligands in 1 and 2, respectively. Compounds containing two oximate ligands (13 and 14) list both distances for each bond.

Figure 4.5 UV-vis of compound 13 in THF (black), DCM (red), Et₂O (green), MeCN (blue) and toluene (orange). In only THF and MeCN is the second absorption at ca. 600 nm present.

Figure 5.1 ORTEP representation of Bi[MST], 16, drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Figure 5.2 (A) Voltammogram of Bi[MST], 16 (B) voltammogram of Al[MST] control. All CV performed in DMSO vs ferrocene/ferrocenium with 0.1 M of [Bu₄N][PF₆].

Figure 5.3 ORTEP representation of Bi₅Na₂O₅[TSB]₅, 17, drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. The coordination environment for Bi2, Bi3, Bi4, and Bi5 are shown.

Figure 5.4 Coordination environment for Bi1 in compound 17, and surrounding bismuth and sodium metal centers.

Figure 6.1 ORTEP representation of (C₅Me₅)₂U(Cl)[O₂C(C₆H₂Bu₂-3-5-OH-4)], 18, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 7.1 Histogram of the uranium magnetic moments for monometallic complexes of the three common oxidation states with U³⁺, U⁴⁺, and U⁵⁺ in black, grey, and white, respectively. Histogram bin widths are 0.20 μB.
Figure 7.2 Room temperature magnetic moments of monometallic $^{3+}$ (top, green), $^{4+}$ (middle, orange), and $^{5+}$ (bottom, blue) complexes in $\mu_B$. Histogram bin widths of 0.20, y-axis are not to scale.

Figure 7.3 Low temperature (1.8 – 5 K) magnetic moments ($\mu_B$) of monometallic $^{3+}$ (top, green), $^{4+}$ (middle, orange), and $^{5+}$ (bottom, blue) complexes in $\mu_B$. Histogram bin widths of 0.20, y-axis are not to scale.

Figure 7.4 Examples of $\mu_B$ versus temperature plots for a series of related ($^{\text{AdArO}})_{3}\text{tacn}$ complexes from Meyer and co-workers: (A) $^{3+}$ complexes [((t-Bu$^{\text{ArO}})_{3}\text{tacn})U], (1)], [((^{\text{AdArO}})_{3}\text{tacn})U], (1-Ad)] and [((t-Bu$^{\text{ArO}})_{3}\text{tacn})U(NCCMe$_{3}$)], (4); (B) $^{4+}$ complexes [((^{\text{AdArO}})_{3}\text{tacn})U(N$_{3}$)], (U(IV)-N3), [((^{\text{AdArO}})_{3}\text{tacn})U(Cl)], (U(IV)-Cl), [((^{\text{AdArO}})_{3}\text{tacn})U(Br)], (U(IV)-Br), and [((^{\text{AdArO}})_{3}\text{tacn})U(I)], (U(IV)-I); (C) the $^{5+}$ complex [((^{\text{AdArO}})_{3}\text{tacn})U(NSi(CH$_{3}$)$_{3}$)]. Reprinted with permission from *Chemical Communications* 2006, 1353.

Figure 8.1 ORTEP representation of [(C$_{5}$Me$_{5}$)$_{2}$Sm(THF)$_{2}$(μ-$\kappa^{1}$-$\kappa^{2}$-CO$_{3}$)], 20, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 8.2 ORTEP representation of [(C$_{5}$Me$_{5}$)$_{2}$Sm(C$_{5}$H$_{5}$N)$_{2}$(μ-$\eta^{1}$-$\eta^{2}$-C$_{10}$H$_{8}$N$_{2}$)], 21, drawn at 50% probability level. Hydrogen atoms and co-crystallized solvent molecules omitted for clarity.

Figure 8.3 ORTEP representation of [(C$_{5}$Me$_{5}$)$_{2}$Sm][(μ-$\eta^{2}$-$\eta^{2}$-BuC$_{4}$Bu), 22, drawn at 25% probability level. Hydrogen atoms are omitted for clarity.

Figure A.1 X-band EPR spectra of a 5:1 THF:Et$_{2}$O solution of 25-Ba at a) 293 K and b) 77 K.

Figure A.2 UV-vis spectra of 25-Ba in THF showing decomposition over 2 hours. A new spectra was collected every 15 min.

Figure A.3 X-band EPR spectra of a 5:1 THF:Et$_{2}$O solution of the dark green/yellow reaction mixture from Scheme 1 at a) 293 K and b) 77 K.
### List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 0.1</strong></td>
<td>Abundance of metals in Earth’s crust, and their cost. All listed prices are for 99.5 to 99.99% anhydrous metal powders, except for Hg. Prices determined from Sigma-Aldrich (<a href="http://www.sigmaaldrich.com">http://www.sigmaaldrich.com</a>) on November 2014.</td>
<td>2</td>
</tr>
<tr>
<td><strong>Table 1.1</strong></td>
<td>X-ray data collection parameters for Ar′Bi(CH&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;2&lt;/sub&gt;, Bn-2, and Bi(CH&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;3&lt;/sub&gt;, Bn-3.</td>
<td>24</td>
</tr>
<tr>
<td><strong>Table 2.1</strong></td>
<td>Comparison of Bi–C and Bi–N distances involving the Ar′ ancillary ligand.</td>
<td>32</td>
</tr>
<tr>
<td><strong>Table 2.2</strong></td>
<td>X-ray Data Collection Parameters for [2,6-(Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]Bi[O&lt;sub&gt;2&lt;/sub&gt;CrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-O-4-κ&lt;sup&gt;2&lt;/sup&gt;O,O′], 2, [2,6-(Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]Bi[OSC(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-O-4-κ&lt;sup&gt;2&lt;/sup&gt;O,S], 3, and {Ar′Bi[O&lt;sub&gt;2&lt;/sub&gt;C(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OH-4-κ&lt;sup&gt;2&lt;/sup&gt;O,O′)]}[BF&lt;sub&gt;4&lt;/sub&gt;], [2-H][BF&lt;sub&gt;4&lt;/sub&gt;].</td>
<td>61</td>
</tr>
<tr>
<td><strong>Table 2.3</strong></td>
<td>X-ray Data Collection Parameters for {[2,6-(Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]Bi(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OSiMe&lt;sub&gt;3&lt;/sub&gt;-4)}, 6, [2,6-(Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]Bi(CN)(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OSiMe&lt;sub&gt;3&lt;/sub&gt;-4), 7, and [2,6-(Me&lt;sub&gt;2&lt;/sub&gt;NCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;]Bi(N&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;, 9.</td>
<td>62</td>
</tr>
<tr>
<td><strong>Table 2.4</strong></td>
<td>Selected Bond lengths (Å) and angles (°) for compounds Ar′Bi(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;tBu&lt;sub&gt;2&lt;/sub&gt;-3,5-O-4), 1, Ar′Bi[O&lt;sub&gt;2&lt;/sub&gt;C(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-O-4-κ&lt;sup&gt;2&lt;/sup&gt;O,O′], 2, Ar′Bi[OSC(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-O-4-κ&lt;sup&gt;2&lt;/sup&gt;O,S], 3, [Ar′Bi(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OH-4)][BPh&lt;sub&gt;4&lt;/sub&gt;], [1-H][BPh&lt;sub&gt;4&lt;/sub&gt;].</td>
<td>63</td>
</tr>
<tr>
<td><strong>Table 2.5</strong></td>
<td>Selected Bond lengths (Å) and angles (°) for compounds {Ar′Bi[O&lt;sub&gt;2&lt;/sub&gt;C(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OH-4-κ&lt;sup&gt;2&lt;/sup&gt;O,O′)]}[BF&lt;sub&gt;4&lt;/sub&gt;], [2-H][BF&lt;sub&gt;4&lt;/sub&gt;], [Ar′Bi(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OSiMe&lt;sub&gt;3&lt;/sub&gt;-4)][CF&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;], 6, Ar′Bi(CN)(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OSiMe&lt;sub&gt;3&lt;/sub&gt;-4), 7, and Ar′Bi(N&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;, 9.</td>
<td>63</td>
</tr>
<tr>
<td><strong>Table 3.1</strong></td>
<td>X-ray Data Collection Parameters for 11.</td>
<td>78</td>
</tr>
<tr>
<td><strong>Table 3.2</strong></td>
<td>Selected Bond lengths (Å) and angles (°) for compounds Ar′Bi(O&lt;sub&gt;2&lt;/sub&gt;C(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;′Bu&lt;sub&gt;2&lt;/sub&gt;-3,5-OH-4)[2-H][BF&lt;sub&gt;4&lt;/sub&gt;].</td>
<td>78</td>
</tr>
</tbody>
</table>
**Table 4.1** X-ray data collection parameters for $[\text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O})]_2(\mu-\text{O}), \ 13$, $\text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O})_2$, 14, and $(\text{Ph}_3\text{CS})(\text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O}), \ 15.$

**Table 4.2** Selected Bond lengths (Å) and angles (°) for compounds $\text{Ar}'\text{Bi}(\text{C}_6\text{H}_2\text{Bu}_2-3,5'-\text{O}-4), \ 1$, $[\text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O})]_2(\mu-\text{O}), \ 13$, $\text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O})_2$, 14, and $(\text{Ph}_3\text{CS})(\text{Ar}')\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O}), \ 15.$

**Table 4.3** Selected Bond lengths (Å) and angles (°) for compounds $(\text{Ph}_3\text{CS})(\text{Ar}')\text{Bi}(\text{ONC}_6\text{H}_2-3,5'-\text{Bu}_2-4'-\text{O}), \ 15.$

**Table 5.1** X-ray data collection parameters for $\text{Bi}[\text{MST}], \ 16$, and $\text{Bi}_5\text{Na}_2\text{O}_5[\text{TST}], \ 17.$

**Table 6.1** X-ray Data Collection Parameters for $(\text{C}_5\text{Me}_5)_2\text{U}(\text{Cl})[\text{O}_2\text{C}(\text{C}_6\text{H}_2'\text{Bu}_2-3-5'-\text{OH}-4)], \ 18.$

**Table 6.2** Selected Bond lengths (Å) and angles (°) for compounds $(\text{C}_5\text{Me}_5)_2\text{U}(\text{Cl})[\text{O}_2\text{C}(\text{C}_6\text{H}_2'\text{Bu}_2-3-5'-\text{OH}-4)], \ 18$ compared to $2$ and $[2-\text{H}][\text{BF}_4].$

**Table 7.1** Statistical analysis of all monometallic uranium complexes reported for room temperature and low temperature (1.8 – 5 K).

**Table 8.1** X-ray Data Collection Parameters for $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\kappa^1:\kappa^2-\text{CO}_3), \ 20$, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{H}_5\text{N})]_2(\mu-\text{C}_{10}\text{H}_8\text{N}_2), \ 21$, and $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu-\eta^2:\eta^2-\text{Bu}_4\text{C}_4\text{Bu}), \ 22.$

**Table 8.2** Selected Bond lengths (Å) and angles (°) for compounds $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})]_2(\mu-\kappa^1:\kappa^2-\text{CO}_3), \ 20$, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{H}_5\text{N})]_2(\mu-\text{C}_{10}\text{H}_8\text{N}_2), \ 21$, and $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu-\eta^2:\eta^2-\text{Bu}_4\text{C}_4\text{Bu}), \ 22$ compared to known compounds $(\text{C}_5\text{Me}_5)_2\text{Sm}$ and $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu-\text{O}), \ 19.$
Table B.1  Room temperature (RT) and low temperature (LT) magnetic moments ($\mu_B$) of monometallic uranium complexes in various formal oxidation states, $U^{n+}$, and formal coordination numbers (CN) determined by various methods (E = Evans Method; F = Faraday Method; G = Gouy Balance; S = SQUID; V = VSM). Values determined from graphs of $\chi T$ or $\mu$ vs. temperature are denoted with a † superscript.

Table B.2  Room temperature (RT) and low temperature (LT) magnetic moments ($\mu_B$) of bimetallic uranium complexes in various formal oxidation states, $U^{n+}$, and formal coordination number (CN) determined by various methods (E = Evans Method; F = Faraday Method; G = Gouy Balance; S = SQUID; V = VSM). Values determined from graphs of $\chi T$ or $\mu$ vs. temperature are denoted with a † superscript. Values reported without specifying if per uranium metal or per formula unit are denoted with a § superscript.
## List of Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar′Bi(C₆H₂′Bu₂-3,5-O-4)</td>
<td>1</td>
</tr>
<tr>
<td>[Ar′Bi(C₆H₂′Bu₂-3,5-OH-4)][BPh₄]</td>
<td>1-H][BPh₄]</td>
</tr>
<tr>
<td>Ar′Bi(CH₂Ph)₂</td>
<td>Bn-2</td>
</tr>
<tr>
<td>Bi(CH₂Ph)₃</td>
<td>Bn-3</td>
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<td>Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-O-4)-κ²O,O′]</td>
<td>2</td>
</tr>
<tr>
<td>Ar′Bi[O₂¹³C(C₆H₂′Bu₂-3-5-O-4)-κ²O,O′]</td>
<td>2-¹³C</td>
</tr>
<tr>
<td>Ar′Bi[OSC(C₆H₂′Bu₂-3-5-O-4)-κ²O,S]</td>
<td>3</td>
</tr>
<tr>
<td>{Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-OH-4)-κ²O,O′]}[BPh₄]</td>
<td>2-H][BPh₄]</td>
</tr>
<tr>
<td>{Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-OH-4)-κ²O,O′]}[BF₄]</td>
<td>2-H][BF₄]</td>
</tr>
<tr>
<td>Ar′BiCl(C₆H₂′Bu₂-3,5-OsiMe₃-4)</td>
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<tr>
<td>Ar′BiCl(C₆H₂′Bu₂-3,5-OsiPh₃-4)</td>
<td>5</td>
</tr>
<tr>
<td>[Ar′Bi(C₆H₂′Bu₂-3,5-OsiMe₃-4)][CF₃SO₃]</td>
<td>6</td>
</tr>
<tr>
<td>Ar′Bi(CN)(C₆H₂′Bu₂-3,5-OsiMe₃-4)</td>
<td>7</td>
</tr>
<tr>
<td>Ar′Bi(CN)₂</td>
<td>8</td>
</tr>
<tr>
<td>Ar′Bi(N₃)₂</td>
<td>9</td>
</tr>
<tr>
<td>3,5-di-tert-butyl-4-hydroxybenzoic acid</td>
<td>10</td>
</tr>
<tr>
<td>dipotassium 3,5-di-tert-butyl-4-oxidobenzoate</td>
<td>K₂-10</td>
</tr>
<tr>
<td>Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-OH-4)]₂</td>
<td>11</td>
</tr>
<tr>
<td>3,5-di-tert-butyl-4-(trimethylsilyloxy)benzoate</td>
<td>12</td>
</tr>
<tr>
<td>[Ar′Bi(ONC₆H₂-3,5-′Bu₂-4-O)]₂(μ-O)</td>
<td>13</td>
</tr>
<tr>
<td>Ar′Bi(ONC₆H₂-3,5-′Bu₂-4-O)₂</td>
<td>14</td>
</tr>
</tbody>
</table>
(Ph₃CS)(Ar')Bi(ONC₆H₂-3,5-′Bu₂-4-O)  
Bi[MST]  
Bi₅Na₂O₅[TSB]₅  
(C₅Me₅)₂U[O₂C(C₆H₂′Bu₂-3-5-OH-4)]  
[(C₅Me₅)₂Sm]₂(μ-O)  
[(C₅Me₅)₂Sm(THF)]₂(μ-κ¹;κ²-CO₃)  
[(C₅Me₅)₂Sm(THF)]₂(μ-κ¹;κ²-13CO₃)  
[(C₅Me₅)₂Sm(C₅H₅N)]₂(μ-C₁₀H₈N₂)  
[(C₅Me₅)₂Sm](μ-η²:η²-BuC₄Bu)  
(C₅H₄SiMe₃)₂Ba  23-Ba  
(C₅H₄SiMe₃)₂Ca  23-Ca  
[(C₅H₄SiMe₃)₃Ba][K(crypt)]  24-Ba  
[(C₅H₄SiMe₃)₃Ca][K(crypt)]  24-Ca  
[(C₅H₄SiMe₃)₃Ba][K(crypt)]₂  25-Ba  
[(C₅H₄SiMe₃)₃Ca][K(crypt)]₂  25-Ca  
[C₅H₃(SiMe₃)₂]₂Ba  26  
{[(C₅H₃(SiMe₃)₂)₃Ba][K(crypt)]}  27  
[(C₅H₄SiMe₃)₃Ba][K(18-C-6)]  28
Acknowledgments

I would like to first thank my graduate advisor, Professor William J. Evans. When I first came to University of California, Irvine I was unsure what chemistry I wanted to pursue, and found myself pulled toward each of the three inorganic groups. However, after sitting in on my first Evans’ Lab group meeting, I was captivated by the chemistry. It is fortuitous that my first meeting featured Dr. Ian Casley presenting his bismuth chemistry, forever ensnaring my interest with that rarely studied metal. Now that my Ph.D. is complete I know I made the right decision on what chemistry to pursue. Bill has provided me with nothing but the best guidance, support, and patience during every day of my Ph.D.

I also would like to thank Professors Andrew S. Borovik and Alan F. Heyduk who have participated in my defense committees. Andy and Alan have both given incredible guidance and assistance from the very beginning to the very end of my time at UCI. I have learned much about their specific specialties in inorganic chemistry and broader chemistry knowledge in general. I also was fortunate enough to be welcomed with open arms to the Borovik lab for collaboration, where I was able to expand my knowledge to new chemistry.

I was privileged enough to spend much of my time in the Evans’ lab with first rate post doc’s, namely Dr. Ian Casely, Dr. Ming Fang, and Dr. Joy Farnaby. Each post doc shared their deep knowledge in chemistry with me whenever prompted, and never hesitated to drop what they were doing and help me in the lab. I want to especially thank Ian who was the first to introduce me to bismuth chemistry and, over just a few weeks, cram everything he knew into my head. Ian is still the only other bismuth chemist from the lab and happily discusses bismuth via email despite it being 4 years later and him 5,000 miles away. To him I owe extra thanks.
I want to also thank Dr. Joe Ziller for helping extensively with X-ray crystallography. Joe, and assistants Ryan Zarkesh and Jordan Corbey, were always willing to help with mounting the small crystals my bismuth compounds would typically produce, which took great skill and patience. Joe and Jordan also helped in teaching me the basics of X-ray crystallography and structure solving. Without Joe’s hard work and patience much of my Ph. D. wouldn’t be possible.

I also want to thank my wonderful wife, Lindsay, for her constant love and support during my Ph.D. Her enthusiastic encouragement, along with her own chemistry expertise, was an invaluable asset and any success without her would not have been possible.

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Curriculum Vitae

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- AGS Travel Grant, University of California, Irvine 2014.
Abstract of the Dissertation

Small Molecule Activation and Coordination Chemistry of Bismuth, f-Element, and Alkaline Earth Complexes

By

Douglas R. Kindra

Doctor of Philosophy in Chemistry

University of California, Irvine, 2014

Professor William J. Evans, Chair

This dissertation describes the synthesis, characterization, and reactivity of unique organometallic compounds of bismuth, samarium, uranium, and barium metal in efforts to expand the fundamental knowledge of their coordination and redox chemistry, particularly with respect to small molecule activation. This dissertation research involves the investigation of the NCN pincer ligand supported bismuth complex, Ar′BiCl₂, to form bismuth benzyl, aryloxyde, and dianionic ligand complexes, as well as studies of the reduction chemistry of (C₅Me₅)₂Sm(THF)₅ in support of density functional theory research, along with projects with uranium and barium metallocenes.

Chapter 1 describes the synthesis, characterization, and structure of the first two bismuth-benzyl compounds, namely Ar′Bi(η¹-C₅H₄Ph)₂ and Bi(η¹-C₅H₄Ph)₃, synthesized by reaction of the analogous chloride salts with the Grignard reagent MgCl(CH₂Ph).

Chapter 2 describes the reactivity of the unique oxyaryl bismuth compound Ar′Bi(C₅H₅Bu₂-3,5-O-4), containing the unusual dianionic oxyaryl ligand (C₅H₅Bu₂-3,5-O-4)²⁻. The first examples of carbon dioxide and carbonyl sulfide insertions into a bismuth-carbon bond are reported along with formal 1,5-addition of R₃SiX (R = Me, Ph; X = Cl, CN, N₃) reagents to...
this complex. Chapter 3 further expands this chemistry by coupling the facile carbon dioxide insertion with protonation or silylation to functionalize CO\textsubscript{2} to generate 3,5-di-\textit{tert}-butyl-4-hydroxybenzoic acid or 3,5-di-\textit{tert}-butyl-4-(trimethylsilyloxy)benzoate, respectively, in a cyclic process. This is a rare example of bismuth small molecule functionalization.

Chapter 4 describes the reactivity of \textit{Ar}'\textsuperscript{2+}\textit{Bi}(C\textsubscript{6}H\textsubscript{2}'Bu\textsubscript{2}-3,5-O-4) with nitric oxide (NO) gas and the NO delivery reagent Ph\textsubscript{3}CSNO. The first examples of NO insertion into a bismuth-carbon bond are reported with three spectroscopically and crystallographically characterized complexes. In each case, the monoanionic oximate [ON=(C\textsubscript{6}H\textsubscript{2}'Bu\textsubscript{2}O)]\textsuperscript{1-} is generated by formal oxidation of the dianionic ligand and concomitant reduction of nitric oxide to (NO)\textsuperscript{1-}.

Chapter 5 describes the reactivity of bismuth with the tripodal ligands N,N',N''-[2,2',2''-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) ([MST]\textsuperscript{3-}) along with the analogous tridentate bipodal ligand N,N'((methylazanediyl)bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) ([TSB]\textsuperscript{2-}). Synthesis and crystallographic characterization of Bi[MST] and the polymetallic bismuth cluster, Bi\textsubscript{5}Na\textsubscript{2}O\textsubscript{5}[TSB], are reported.

Chapter 6 describes the ligand transfer chemistry of Ar'\textit{Bi}[O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}'Bu\textsubscript{2}-3,5-O-4)-κ\textsuperscript{2}O,O'], with the dianionic ligand [O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}'Bu\textsubscript{2}-3,5-O-4)]\textsuperscript{2-}, with oxophilic metal compounds, namely (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}UCl\textsubscript{2}, SmI\textsubscript{2}(THF)\textsubscript{2}, and (C\textsubscript{3}H\textsubscript{5})\textsubscript{2}TiCl\textsubscript{2}. Successful ligand transfer was accomplished and the product, (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}UCl[O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}'Bu\textsubscript{2}-3,5-OH-4)-κ\textsuperscript{2}O,O'] was structurally and spectroscopically characterized. Chapter 7 explores the magnetic properties of uranium complexes in detail. Over 500 literature examples from the last 50 years are compiled and examined to find trends dependent on metal oxidation state and ligand identity.

Chapter 8 describes the reaction chemistry of the samarium oxide [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm]\textsubscript{2}(μ-O) with CO\textsubscript{2} to test DFT rationales for the formation of the oxalate [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm]\textsubscript{2}(μ-η\textsuperscript{2}:η\textsuperscript{2}-O\textsubscript{2}CCO\textsubscript{2})
from $(\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_x$ with CO$_2$. Analogously, the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm(THF)}_x$ with pyridine and 1-hexyne in support of DFT work on the affects of ligand donation strength on Sm$^{2+}$ reactivity and carbon-carbon coupling of alkynes is reported.

Appendix A describes the exploration of the reduction chemistry of the alkaline earth metallocenes $\text{Cp}_2\text{M}$ and $[\text{Cp}_3\text{M}[\text{K(chelate)}]]$ ($\text{M} = \text{Ba, Ca}$; $\text{Cp} = \text{C}_5\text{H}_4\text{SiMe}_3, \text{C}_5\text{H}_3(\text{SiMe}_3)_2$; chelate = 18-crown-6, 2.2.2.-cryptand) in efforts to isolate monovalent alkaline earth species. Spectroscopic analysis of the reduced barium species along with initial reactivity is reported.
Introduction

Bismuth is a rare example of a sixth period heavy metal that it is non-toxic.$^{1-3}$ Although it is surrounded in the periodic table by metals such as mercury, thallium, lead, and polonium, bismuth finds use in oral medicines such as Pepto-Bismol.$^3$ In addition to a variety of medical applications, bismuth is a component of ammoxidation catalysts, where it is thought to be involved in C–H activation of propene,$^4$ and in polymerization catalysis.$^2$ Although bismuth chemistry is dominated by the Bi$^{3+}$ oxidation state,$^5$ a wide range of formal oxidation states are accessible to this metal, namely Bi(V), Bi(III), Bi(0), and Bi(−1). Despite this demonstrated chemistry, the organometallic and coordination chemistry of bismuth is scarcely studied compared to that of the transition and f-block metals. This lack of study is possibly due to the fact that bismuth makes weak bonds to most ligands as is typical of sixth period elements.$^6,7$ However, as this thesis will demonstrate, bismuth has the potential to provide new types of organometallic chemistry and small molecule reactivity.

Properties of Bismuth

Bismuth is the group 15 heavy metal with atomic number 83. Bismuth-209, the only naturally occurring isotope of bismuth, was considered the heaviest non-radioactive nuclide until 2003. In that year, it was found that Bi-209 is formally radioactive by alpha emission.$^8$ The reported half-life of $1.9(2)\times10^{19}$ years is a billion times longer than the age of the universe. Synthetic bismuth isotopes, namely Bi-212 and Bi-213, have been used as alpha emitters for cancer therapy.$^9$
Bismuth is found in the ores bismite (Bi$_2$O$_3$) and bismuthinite (Bi$_2$S$_3$).\textsuperscript{10} Despite an abundance of 85 ppb in Earth’s crust,\textsuperscript{11} similar to silver (70 ppb), the cost of bismuth is significantly less than that of the precious metals (Ru, Rh, Pd, Pt, and Au) used extensively in academic and industrial chemistry, Table 0.1.\textsuperscript{12}

**Table 0.1.** Abundance of metals in Earth’s crust\textsuperscript{11} and their cost. All listed prices are for 99.5 to 99.99\% anhydrous metal powders, except for Hg. Prices determined from Sigma-Aldrich (http://www.sigmaaldrich.com) on November 2014.

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance</th>
<th>Element</th>
<th>Cost (per 100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>4.32%</td>
<td>Fe</td>
<td>$ 26</td>
</tr>
<tr>
<td>Ti</td>
<td>4010 ppm</td>
<td>Ni</td>
<td>$ 30</td>
</tr>
<tr>
<td>Ce</td>
<td>60 ppm</td>
<td>Hg</td>
<td>$ 30</td>
</tr>
<tr>
<td>Ni</td>
<td>56 ppm</td>
<td>Bi</td>
<td>$ 51</td>
</tr>
<tr>
<td>Cu</td>
<td>25 ppm</td>
<td>Co</td>
<td>$ 84</td>
</tr>
<tr>
<td>Co</td>
<td>24 ppm</td>
<td>Cu</td>
<td>$ 105</td>
</tr>
<tr>
<td>Pb</td>
<td>14.8 ppm</td>
<td>Pb</td>
<td>$ 163</td>
</tr>
<tr>
<td>Tl</td>
<td>520 ppb</td>
<td>Tl</td>
<td>$ 209</td>
</tr>
<tr>
<td>Lu</td>
<td>350 ppb</td>
<td>Ti</td>
<td>$ 364</td>
</tr>
<tr>
<td>Bi</td>
<td>85 ppb</td>
<td>Ag</td>
<td>$ 382</td>
</tr>
<tr>
<td>Ag</td>
<td>70 ppb</td>
<td>Ce</td>
<td>$2,650</td>
</tr>
<tr>
<td>Hg</td>
<td>40 ppb</td>
<td>Pt</td>
<td>$ 15,540</td>
</tr>
<tr>
<td>Au</td>
<td>2.5 ppb</td>
<td>Lu</td>
<td>$ 20,750</td>
</tr>
<tr>
<td>Pt</td>
<td>0.4 ppb</td>
<td>Au</td>
<td>$ 32,350</td>
</tr>
<tr>
<td>Rh</td>
<td>0.06 ppb</td>
<td>Rh</td>
<td>$ 47,150</td>
</tr>
</tbody>
</table>

Bi$^{3+}$ has a 6 coordinate ionic radius of 117 pm\textsuperscript{13} that is very similar to the 6 coordinate ionic radius of La$^{3+}$ at 117.2 pm.\textsuperscript{13} In spite of this similarity in size and common oxidation state, M$^{3+}$, the Lewis acidity of the two metals differs significantly. The electronegativity of bismuth is 2.02 on the Pauling Scale,\textsuperscript{14} which is significantly less electropositive than the lanthanides that
range from 1.1 (La) to 1.27 (Lu). The Van der Waals\textsuperscript{15} and covalent radii\textsuperscript{15} of bismuth, 240 and 148 pm, respectively, are also not similar to those of lanthanum, 229 and 207 pm. For these reasons, the coordination chemistry of bismuth has significant differences from that of its similarly sized f-element analogs (see below for more details).\textsuperscript{16}

The chemistry of bismuth is dominated by a single oxidation state, namely Bi(III).\textsuperscript{1,5} The next most common oxidation state, Bi(V), is a strong oxidant:\textsuperscript{17,18} the Bi(V) / Bi(III) reduction potential is +1.59 V (vs NHE).\textsuperscript{19} Although the coordination chemistry of Bi(V) is largely unexplored,\textsuperscript{5} Bi(V) salts have found use in organic transformations.\textsuperscript{17,20,21}

Other, more exotic, oxidation states of bismuth include Bi(I), Bi(0), and Bi(−1). The first reported examples of Bi(I), the halogen salts formulated as BiX (X = Cl, Br, I),\textsuperscript{22-24} were later determined by X-ray crystallography to be best described as complicated (Bi\textsubscript{9})\textsuperscript{5+} clusters with the stoichiometry of Bi\textsubscript{6}X\textsubscript{7}.\textsuperscript{25,26} More low valent bismuth complexes have been reported, Scheme 0.1, in dimeric structures with bismuth-bismuth single\textsuperscript{27-29} and double bonds,\textsuperscript{30} along with cyclic complexes.\textsuperscript{31} However, only one structurally characterized monomeric Bi(I) complex, the dark blue 2,6-bis[N-(2′,6′-dimethylphenyl)ketimino]phenyl bismuth, has thus far been reported.\textsuperscript{32}
Bismuth has also been observed in the formal oxidation states of Bi(0) and Bi(−1). Examples of Bi(0) include [Bi$_2$Fe$_3$(CO)$_9$] and [Bi$_2$(Mn(CO)$_2$C$_5$H$_4$CH$_3$)$_3$] while the formal −1 oxidation state is found in the samarium metallocene [(C$_5$Me$_5$)$_2$Sm](µ-$η^2$:$η^2$-Bi$_2$). This complex, analogous to the bridging nitrogen complex, [(C$_5$Me$_5$)$_2$Sm](µ-$η^2$:$η^2$-N$_2$), features a bridging (Bi=Bi)$^{2-}$ moiety.

In some cases, low valent bismuth oxidation states are invoked as reaction intermediates. For example, the oxidative addition of PhEEPh (E = S, Se, Te) by the in situ generated bismuth(I), “[o,o-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$]Bi”, forms [o,o-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$]Bi(EPh)$_2$.

### The Chemistry of Bismuth

The organometallic and coordination chemistry of bismuth has been reported in literature for over 100 years, including one early report describing the explosive reaction between...
perchloric acid and bismuth-containing alloys.\textsuperscript{39} Despite this long history, the growth of bismuth coordination and organometallic chemistry has been slow. Bismuth organometallic complexes frequently have one or more sp\textsuperscript{2} carbon bound ligands,\textsuperscript{5} ranging from simple aryl ligands,\textsuperscript{40-57} such as the homoleptic compounds Ph\textsubscript{3}Bi and Ph\textsubscript{5}Bi,\textsuperscript{58-60} to aryl ligands with appended nitrogen pincer arms,\textsuperscript{16,61-86} such as 2,6-(Me\textsubscript{2}NCH\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3} (Ar'), and many other aryl based ligands.\textsuperscript{40,87-95} The bismuth-aryl bonds in these complexes are robust and unreactive under most conditions and make these aryl groups excellent ancillary ligands for bismuth. Other bismuth–carbon bonds are significantly less common,\textsuperscript{5} but there are examples of Bi–C(sp\textsuperscript{1})\textsuperscript{49,70,96} and Bi–C(sp\textsuperscript{3})\textsuperscript{97-99} complexes in the literature.

Cyclopentadienyl (C\textsubscript{5}H\textsubscript{5})\textsuperscript{1−}, phosphine (PR\textsubscript{3}), and N-heterocyclic carbene (NHC) ligands, common ligands of transition metal chemistry, have not yet found significant use with bismuth. Cyclopentadienyl complexes of bismuth,\textsuperscript{100,101} Scheme 0.2, often bind with hapticity less than the common $\eta^5$, even in compounds with the least sterically demanding (C\textsubscript{5}H\textsubscript{5})\textsuperscript{1−} ligand.\textsuperscript{100} Bismuth half-sandwich complexes containing only one cyclopentadienyl ligand typically show $\eta^3$ and $\eta^5$ hapticity,\textsuperscript{5,102-104} but are prone to making clusters. Currently, there is only one reported metallocene sandwich compound of bismuth with two parallel $\eta^5$-cyclopentadienyl ligands, [(\(\eta^5\)-\textsuperscript{t}Bu\textsubscript{3}C\textsubscript{5}H\textsubscript{2})\textsubscript{2}Bi]\textsuperscript{+},\textsuperscript{5,105} despite the fact that this bonding motif is ubiquitous for transition metals.
Scheme 0.2. Cyclopentadienyl compounds of bismuth showing (from left to right): \((\eta^1\text{-C}_5\text{H}_5)_3\text{Bi}\), \((\eta^3\text{-C}_5\text{Me}_5)\text{BiBr}_2\), and \([(\eta^5\text{-Bu}_3\text{C}_5\text{H}_2)_2\text{Bi}]^+\). 

Other potentially polyhapto ligands such as allyl, \([\text{CH}_2\text{C(R)CH}_2]^-\), and benzyl, \((\text{CH}_2\text{Ph})^-\), also bind \(\eta^1\) even in complexes in which the bismuth metal centers are coordinatively unsaturated. Phosphine ligands have only seen limited use with bismuth, with only two molecular examples: \([\text{Bi}\{2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_3\text{S}\}_3\}\) and \([(\text{Ph}_3\text{P})_2\text{BiPh}_2][\text{PF}_6]\). Scheme 0.3. The reactions of simple bismuth salts, \(\text{BiX}_3\) (\(\text{X} = \text{Cl}, \text{Br}, \text{I}\)), with phosphines are very sensitive to

Scheme 0.3. Molecular phosphine compounds of bismuth: \([\text{Bi}\{2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_3\text{S}\}_3\]\ and \([(\text{Ph}_3\text{P})_2\text{BiPh}_2][\text{PF}_6]\).
reaction conditions\textsuperscript{110} and produce a number of oligomeric structures,\textsuperscript{111-115} in some cases with the starting phosphine being oxidized to the corresponding phosphine oxide, presumably through reaction with molecular dioxygen.\textsuperscript{110} NMR spectroscopic studies are consistent with weak bonding of the neutral ligands and rapid ligand exchange in solution.\textsuperscript{110} Finally, NHC ligands have been rarely explored with bismuth: the only NHC-bismuth complex found in literature, (Dipp\textsubscript{2}NHC)BiCl\textsubscript{3}, was reported in 2014.\textsuperscript{116}

Despite being a large metal (vide supra), trivalent bismuth complexes are often sterically unencumbered. Unlike the f-block metals, which depend on sterically demanding ligands to protect the reactive metal center,\textsuperscript{117} stable bismuth complexes often have open coordination sites.\textsuperscript{5} These geometries are designated with a “ψ”. For example, [2,6-(Me\textsubscript{2}NCH\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]BiCl\textsubscript{2}\textsuperscript{64} has a ψ-octahedral geometry, with one of the octahedral sites vacant, Figure 0.1. In some cases this can be attributed to the stereochemically active 6s lone pair which can occupy a coordination

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure01.png}
\caption{ORTEP\textsuperscript{118} representation of [2,6-(Me\textsubscript{2}NCH\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}]BiCl\textsubscript{2}\textsuperscript{64} showing the ψ-octahedral geometry often times seen in B\textsuperscript{3+} complexes.}
\end{figure}
site about the bismuth metal center. However, it is difficult to predict when the 6s lone pair will be stereochemically active or not,\(^1\) and other factors may contribute to the unusual geometry. This inert pair effect\(^{119}\) inhibits oxidation of Bi\(^{3+}\) to Bi\(^{5+}\) as the 6s electrons are less likely to participate in bonding interactions due to their radial contraction and energetic stabilization.\(^{119}\) Chemical oxidation of Bi(III) to Bi(V) is uncommon, even with strong oxidizing agents, though oxidation has been reported by the “Cl\(_2\)” delivery reagent SO\(_2\)Cl\(_2\).\(^{120,121}\)

**Reactivity with the [2,6-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)]Bi\(^{2+}\) System**

Initial work began with organometallic bismuth in hopes of expanding bismuth chemistry to small molecule activation, specifically with the oxygen containing small molecules: CO\(_2\), CO, NO and H\(_2\)O. The tendency of bismuth to make weak bonds with oxygen\(^{1,5}\) suggested that catalysis could be possible with oxygen-containing substrates since cleavage of the M–O bond would be facile. This is a process that can be difficult for the oxophilic transition and f-element metals.

Aryl ligands with neutral nitrogen pincer arms have afforded exceptional bismuth synthons for further study. These ligand systems take advantage of the excellent stability of bismuth sp\(^2\)-carbon bonds. The NCN pincer ligand [2,6-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)]\(^{1-}\) (Ar')\(^{16,61-69}\) provides two pincer arms which can coordinate to the bismuth metal center when needed, but dissociate to allow further reactivity when necessary. This monoanionic ligand has provided a satisfactory ligand environment for the synthesis of the corresponding halogen salts, Ar'BiX\(_2\) (X = Cl, Br, I),\(^{64}\) and other simple complexes.\(^{65,67}\) The X-ray structure of these compounds shows monomeric complexes in the case of the halogen salts (Ar'BiX\(_2\)) but oligomeric structures in the
case of Ar′Bi(SO₄), Ar′Bi(NO₃) and Ar′Bi(CO₃). This suggests that the Ar′ ligand environment can be sterically demanding enough to discourage cluster and oligomer formation.

Initial work on the coordination chemistry of Ar′ bismuth compounds was undertaken, Scheme 0.4, by Dr. Ian Casely, along with reactivity of Ar′BiCl₂ with aryloxides, Scheme 0.5.⁶²

\[
\begin{align*}
\text{Ar′Bi(allyl)} & \rightarrow \text{MgCl(allyl)} & \text{K(O′Bu)} & \rightarrow \text{Ar′Bi(O′Bu)} \\
\text{Ar′₂BiCl} & \rightarrow \text{NaBPh₄} & \rightarrow \text{Ar′₂Bi(OAr)} \\
\text{[Ar′₂Bi][BPh₄]} & \rightarrow \text{R} & \rightarrow \text{Ar′₂Bi(OAr} &\text{R}) \\
\text{[Ar′₂Bi][OAr} \text{Bu]} & \end{align*}
\]

\[\text{Ar′} = 2,6-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3, \quad \text{R} = \text{Me, iPr}\]

**Scheme 0.4.** Coordination chemistry and reactivity of the Ar′₂Bi⁺ system.⁶²

The reaction of Ar′BiCl₂ with the potassium salts of 2,6-dimethylphenol and 2,6-di-isopropylphenol, Scheme 0.5, produced the expected bismuth bis(aryloxides), Ar′Bi(OAr)₂. However, when a more sterically demanding aryloxide was used, namely potassium 2,6-di-tert-butylphenolate, an entirely different product was identified, Scheme 0.5. Formed by facile C–H
Scheme 0.5. Reaction of Ar’BiCl₂ with the potassium salt of different phenols, namely 2,6-di-methylphenol, 2,6-di-isopropylphenol, and 2,6-di-tert-butylphenol.⁶²

Bond activation, the bright orange compound, Ar’Bi(C₆H₅′Bu₂-3,5-O-4), 1, features only a single phenolate moiety bound through the para-carbon. Based on spectroscopic, crystallographic, and theoretical studies,⁶² this complex is best described as a complex of trivalent bismuth with a single bond to an oxyaryl dianionic ligand, Scheme 0.6a, rather than a bismuth(II) diradical (Scheme 0.6b) or a metallaquinone (Scheme 0.6c) with a bismuth-carbon double bond.

\[
\begin{align*}
\text{Ar’Bi} & \quad \text{Ar’Bi} & \quad \text{Ar’Bi} \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} & \quad \text{Bu} \\
\text{Bu} & \quad \text{Bu} & \quad \text{Bu}
\end{align*}
\]

\(\text{Ar’} = \text{2,6-(Me₂NCH₂)₂C₆H₃}\)

Scheme 0.6. The different formulations of compound 1 and the oxyaryl dianionic ligand.

The electronic structure of the oxyaryl dianionic ligand can be described by two resonance forms, one with a phenolate-like structure where anionic charge is localized on the oxygen and the aryl ring has normal aromatic character, and one with a quinone-like structure where anionic charge is localized on the para-carbon and the aryl ring has quinoidal character,
Scheme 0.7. This is supported by the X-ray crystal data that shows distances for the C–C ring and C–O bonds that are intermediate between single and double bonds, Figure 0.2.

\[
\begin{align*}
\text{Ar'}\text{Bi} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\quad \quad 1 \\
\text{Phenolate Form} \\
\text{Quinoidal Form}
\end{align*}
\]

\[
\text{Ar'} = 2,6-\text{(Me}_2\text{NCH}_2\text{)}\text{C}_6\text{H}_3
\]

Scheme 0.7. Resonance structures of the oxyaryl dianionic ligand \((\text{C}_6\text{H}_2\text{Bu}_2-3,5-\text{O}-4)^{2-}\).

**Figure 0.2.** Bond distances of the oxyaryl dianionic ligand of compound 1 and the monoanionic phenyl ligand of \([1-\text{H}][\text{BPh}_4]\).

This formulation is further supported by synthesis and characterization of an analogous compound, \([\text{Ar'}\text{Bi}(\text{C}_6\text{H}_2\text{Bu}_2-3,5-\text{OH}-4)][\text{BPh}_4]\, [1-\text{H}][\text{BPh}_4]\, which has the same connectivity and geometry as compound 1, but with the dianionic oxyaryl ligand protonated to form a monoanionic phenyl ligand. Examination of the X-ray data, Figure 0.2, shows normal distances for the C–C ring and C–O bonds in \([1-\text{H}][\text{BPh}_4]\). The bismuth–carbon bond is only 0.03 Å longer than that in 1, Figure 0.2, which is consistent with the formulation in Scheme 0.6a that has no bismuth–carbon double bond.
Given the proposed resonance structures of the oxyaryl dianionic ligand in compound 1, Scheme 0.7, reactivity at the oxygen and para-carbon are possible. The reactivity of this species is the topic of Chapters 2, 3, and 4.

**Uranium, Samarium, and Barium Metallocene Chemistry**

In addition to the bismuth chemistry reported in Chapters 1 – 6, studies of f-element and alkaline earth metallocene chemistry are described in Chapters 6 – 8 and Appendix A. A more detailed introduction to these projects can be found at the beginning of the relevant chapters. In Chapter 8, experimental studies of decamethylsamarocene, (C₅Me₅)₂Sm, involving carbon dioxide activation and carbon–carbon coupling are reported to evaluate predictions of density functional theory (DFT) calculations. Chapter 6 and 7 reports the reaction of uranium compounds with organobismuth complexes to study ligand transfer, along with a review of the magnetic properties of uranium complexes. Finally, in Appendix A, synthesis, characterization, and reduction chemistry of alkaline earth analogs of the Ln²⁺ system [(C₅H₄SiMe₃)Ln][K(crypt)] was described.
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Chapter 1

Synthesis and Structure of Bis- and Tris-Benzyl Bismuth Complexes

INTRODUCTION

Although organobismuth complexes have been in the literature for over 100 years,\textsuperscript{1-3} the number of crystallographically characterized homoleptic, BiR\textsubscript{3}, complexes is small in this underdeveloped area of organometallic chemistry. In contrast to triphenylbismuth, which is a frequently-used and stable homoleptic organobismuth complex that was first crystallographically characterized in 1942,\textsuperscript{4,5} structures of only a few other homoleptic species have been reported. The structure of Bi(CH(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3}\textsuperscript{6} was reported in 1983 and Bi(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{3}\textsuperscript{7} was described in 2005, but the methylallyl complex, Bi(CH\textsubscript{2}(CMe)CH\textsubscript{2})\textsubscript{3}\textsuperscript{8} was only reported in 2012 and BiMe\textsubscript{3}\textsuperscript{9} and Bi(iPr)\textsubscript{3}\textsuperscript{9} in 2013.\textsuperscript{10}

Surprisingly, examination of the literature showed that the tris(benzyl) complex, Bi(CH\textsubscript{2}Ph)\textsubscript{3}\textsuperscript{11,12} originally reported in 1957 had never been crystallographically characterized. This is the only example of a bismuth-benzyl compound in the literature, despite the fact that benzyl is a special type of alkyl group that can coordinate in a variety of ways to metals, Scheme 1.1.\textsuperscript{13-15} To determine how bismuth benzyl complexes compared structurally to BiPh\textsubscript{3} and
Bi(allyl)$_3$ complexes, the reactions of a benzyl Grignard reagent with bismuth chlorides were explored. The reaction with the NCN pincer aryl ligated complex, Ar′BiCl$_2$ [Ar′ = 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], was studied first because this ancillary Ar′ ligand has proven useful in isolating many new types of complexes. The homoleptic complex, Bi(CH$_2$Ph)$_3$, was synthesized for crystallographic studies and the results are reported here.

RESULTS AND DISCUSSION

A colorless THF solution of Ar′BiCl$_2$ reacts with two equiv of the benzyl Grignard reagent, (PhCH$_2$)MgCl, to rapidly form a yellow solution. $^1$H NMR spectroscopy indicated that a single product had formed with a 1:2 ratio of Ar′ to benzyl resonances. Single crystals suitable for X-ray crystallography were grown from a concentrated solution of hexane at −30 °C and the product was identified as Ar′Bi($\eta^1$-CH$_2$Ph)$_2$, Bn-2, eq 1.1, Figure 1.1. $^1$H NMR spectroscopy
in acetonitrile shows a single resonance for the nitrogen bound methyl protons and a pair of doublets for the methylene protons of the chelated arms of Ar'. The spectrum of 1 is invariant between 343 K and 238 K. This suggests that both pincer arms in solution are equivalent on the NMR time scale.

![Diagram](image)

**Figure 1.1.** ORTEP representation of Ar'Bi(η^1-CH₂Ph)₂, Bn-2, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only a dashed line is drawn between Bi1 and N1 because the distance is 3.058(4) Å.

The X-ray crystal structure of Bn-2 shows asymmetric bonding of the NCN pincer ligand to the bismuth metal center in the solid state in contrast to the data in solution. The 2.287(4) Å
Bi1–C1 distance is typical for Ar′BiX₂ compounds,¹⁶,¹⁷,¹⁹-²⁵ but the two Bi–N distances, 3.058(4) Å (Bi1–N1) and 4.940(4) Å (Bi1–N2), are quite different and much longer than the 2.561(3) and 2.570(4) Å analogs in the precursor, Ar′BiCl₂.²⁰ The 3.058(4) Å Bi1–N1 distance is within the 3.9 Å sum of the van der Waals radii and is in the range of distances in some bismuth Ar′ species.¹⁶,¹⁸,²⁷ However, the Bi1–N2 distance indicates that this nitrogen pincer arm is not coordinated. This is similar to the structure of [Ar′₂Bi]₂(O₂) which has two of the four pincer arms 4.9 Å away from the bismuth metal center.²²

Each benzyl ligand in Bn-2 is coordinated in an η¹-bonding mode with Bi–C–C(ipso) bond angles of 105.0(3)° and 107.9(3)°.¹³ The 2.299(4) and 2.340(4) Å Bi–C(benzyl) bond lengths are in the range observed for Bi–C(alkyl) single bonds: 2.23(2)-2.29(2) Å, BiMe₃;⁹ 2.200(9)-2.267(7) Å, Bi(iPr)₃;⁹ 2.2739(9) Å, Bi(CH₂SiMe)₃;⁷ 2.306(13)-2.347(13) Å, Bi[CH(SiMe₃)₂]₃;⁶ 2.309(16) – 2.324(16) Å, in the allyl complex, Bi[CH₂(CMe)CH₂]₃;⁸ The distances in Bn-2 are also consistent with other main group metal benzyl bonds, e.g. Ph₃Pb(CH₂Ph),²⁸ Sb(CH₂Ph)₃,²⁹ and Al(CH₂Ph)₃·Et₂O,³⁰ at 2.242(7), 2.175(3), and 1.986(6) Å, respectively, when the difference in metal size is taken into account.³¹ The bismuth metal center in Bn-2 sits out of the plane formed by the three bonding carbons by 1.137 Å, similar to Bi(CH₂SiMe)₃ (1.217 Å),⁷ which leaves an open coordination site directly above the metal centers as is typical in bismuth complexes.²⁶-⁹ The closest Bi···Bi distance in the structure is 7.27 Å, a distance much longer than the Bi···Bi 3.899(1) and 4.318(1) Å distances found in BiMe₃.⁹

The structure and bonding motif of bismuth benzyl compounds was further explored with the synthesis of Bi(CH₂Ph)₃, Bn-3.¹¹,¹² A single set of benzyl resonances was observed by ¹H
NMR spectroscopy, consistent with that observed in compound \textbf{Bn-2}. Single crystals suitable for X-ray crystallography were grown from a concentrated hexane solution at $-30$ °C, Figure 1.2.

\textbf{Figure 1.2.} ORTEP representation of Bi($\eta^1$-CH$_2$Ph)$_3$, \textbf{Bn-3}, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

Complex \textbf{Bn-3} also has all the benzyl ligands in an $\eta^1$-coordination mode with 109.2(2)$^\circ$, 109.6(2)$^\circ$, and 110.8(2)$^\circ$ Bi–C–C(ipso) angles. The 2.289(4), 2.291(4), and 2.295(4) Å Bi–C(benzyl) distances in \textbf{Bn-3} are similar to the analogous bond distances in \textbf{1} and the homoleptic BiR$_3$ complexes cited above. These Bi–C(benzyl) distances are longer than the 2.224(4) Å Bi–C(Ph) bonds of BiPh$_3$. The bismuth center in \textbf{Bn-3} is even further out of the plane of the three coordinating carbon atoms, 1.241 Å, than in \textbf{Bn-2}, which again provides a large open space in the coordination sphere. The nearest Bi····Bi distance is 5.63 Å.

The structure of \textbf{Bn-3} is reminiscent of the previously reported Bi(CH$_2$(CMe)CH)$_3$ complex which features only $\eta^1$ bonding to each of the three allyl ligands. The Bi–C bonds of \textbf{Bn-3} are about 0.02 Å shorter than that in Bi(CH$_2$(CMe)CH)$_3$. The bismuth metal center in the
bismuth allyl complex is out of the plane of the three coordinating carbon atoms by 1.247 Å, which is very similar to that in Bn-3.

The stability of the homoleptic bismuth allyl complexes, namely tris(allyl)bismuth and tris(methylallyl)bismuth, is quite limited, with the compounds being temperature, light, air, and vacuum sensitive.\(^8\) In contrast, earlier studies have shown that although Bi(CH\(_2\)Ph)\(_3\) is air sensitive,\(^12\) it has a melting point of 65 °C\(^{11}\) and begins to decompose thermally at 110 °C.\(^{12}\) Compound 1 shows no evidence of decomposition from prolonged exposure to light or vacuum. Further, no decomposition is observable after months of storage at room temperature or after over 24 hours at 80 °C in acetonitrile. Compound 1 has a melting point of 40 – 45 °C.

CONCLUSION

In summary, both homoleptic and heteroleptic benzyl complexes of bismuth can be synthesized and crystallographically characterized. Like allyl\(^8,^{19}\) and cyclopentadienyl\(^{32,33}\) bismuth complexes, the benzyl group is observed to coordinate only in an \(\eta^1\)-coordination mode even though there is ample open space for further coordination. This is consistent with the fact that bismuth is not very electropositive and can have a stereochemically active lone pair.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use.
\(^1\)H NMR spectra were recorded on Bruker DR400 and GN500 and CRYO500 MHz spectrometers (\(^{13}\)C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FT-IR system. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. Benzylmagnesium chloride (1.5 M solution in THF, Sigma-Aldrich) and BiCl\(_3\) (99.99%, Aldrich) were used as received. Ar′BiCl\(_2\)^18 and Bi(CH\(_2\)Ph)\(_3\)^30 were synthesized as reported in literature.

**Ar′Bi(CH\(_2\)Ph)\(_2\), Bn-2.** A THF solution of (PhCH\(_2\))MgCl (1.5 M, 0.40 mL, 0.77 mmol) was added to a stirred white suspension of Ar′BiCl\(_2\) (170 mg, 0.38 mmol) in THF (6 mL) resulting in a light yellow solution. After stirring overnight, the solvent was removed under reduced pressure and the crude product was stirred in hexane (10 mL) for 1 h. Off-white solids were separated from a yellow supernatant by centrifugation. Drying of the soluble fraction yielded Bn-2 (177 mg, 79%) as a yellow tacky solid. Recrystallization out of acetonitrile gave 1 as a light yellow microcrystalline solid (mp = 40–45 °C). X-ray quality crystals were grown from a saturated hexane solution at −30 °C. \(^1\)H NMR (500 MHz, acetonitrile-\(d_3\), 343 K): \(\delta\) 7.43 [d, 2H, \(m\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.27 [t, 1H, \(p\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.18 [m, 4H, \(o\)-(CH\(_2\)C\(_6\)H\(_5\))], 6.90 [t, 2H, \(o\)-(CH\(_2\)C\(_6\)H\(_3\))], 3.50 [s, 4H, (C\(_H_2\)Ph)], 3.48 [d, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 3.23 [d, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 2.16 [s, 12H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)]. \(^1\)H NMR (500 MHz, acetonitrile-\(d_3\), 298 K): \(\delta\) 7.42 [d, 2H, \(m\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.25 [t, 1H, \(p\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.16 [m, 4H, \(o\)-(CH\(_2\)C\(_6\)H\(_5\))], 6.88 [t, 2H, \(o\)-(CH\(_2\)C\(_6\)H\(_3\))], 6.84 [d, 4H, \(m\)-(CH\(_2\)C\(_6\)H\(_5\))], 3.51 [d, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 3.45 [s, 4H, (CH\(_2\)Ph)], 3.14 [d, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 2.13 [s, 12H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)]. \(^1\)H NMR (500 MHz, acetonitrile-\(d_3\), 238 K): \(\delta\) 7.40 [d, 2H, \(m\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.25 [t, 1H, \(p\)-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.15 [m, 4H, \(o\)-(CH\(_2\)C\(_6\)H\(_5\))], 6.86 [t, 2H, \(o\)-
(CH$_2$C$_6$H$_5$), 6.79 [d, 4H, m-(CH$_2$C$_6$H$_5$)], 3.51 [d, 2H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 3.40 [s, 4H, (CH$_2$Ph)], 3.02 [d, 2H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 2.10 [s, 12H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$]. $^{13}$C NMR (125 MHz, acetonitrile-$d_3$): δ 148.9, 144.4, 143.2, 130.2, 128.4, 125.5, 125.0, 118.3 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$ and (CH$_2$C$_6$H$_5$)], 69.3 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 45.2 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 37.6 [(CH$_2$C$_6$H$_5$)]. IR: 3029m, 2889m, 2871m, 2799w, 1650m, 1453s, 1359s, 1206w, 1174w, 1032m, 1002m, 841s, 744s, 699s cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{33}$BiN$_2$: C, 53.61; H, 5.71; N, 4.81. Found: C, 53.90; H, 5.58; N, 4.47.

**X-ray Crystallographic Data.** Crystallographic information for complexes Bn-2 and Bn-3 is summarized in Table 1.1.

**Table 1.1.** X-ray data collection parameters for Ar′Bi(CH$_2$Ph)$_2$, Bn-2, and Bi(CH$_2$Ph)$_3$, Bn-3.

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<th>Bn-2</th>
<th>Bn-3</th>
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<td>C$<em>{26}$H$</em>{33}$BiN$_2$</td>
<td>C$<em>{21}$H$</em>{21}$Bi</td>
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<td>P$_2_1_2_1$</td>
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<td>9.8001(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.7269(5)</td>
<td>10.5018(6)</td>
</tr>
<tr>
<td>c (Å)</td>
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<td>16.8532(9)</td>
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<td>90</td>
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<td>90</td>
</tr>
<tr>
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<td>90</td>
</tr>
<tr>
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<td>1734.51(16)</td>
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<tr>
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<td>4</td>
</tr>
<tr>
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<td>1.847</td>
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<td>R1$^a$ [I &gt; 2.0σ(I)]</td>
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<td>0.0142</td>
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<tr>
<td>wR2$^a$ (all data)</td>
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<td>0.0307</td>
</tr>
</tbody>
</table>

$^a$ Definitions: R1 = Σ||F$_o$|−|F$_c$|| / Σ|F$_o$|, wR2 = [Σ[w(F$_o^2$−F$_c^2$)$^2$] / Σ[w(F$_o^2$)$^2$]]$^{1/2}$
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Chapter 2

Insertion of CO$_2$ and COS into Bi–C Bonds: Reactivity of a Bismuth NCN Pincer Complex of an Oxyaryl Dianionic Ligand, [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Bi(C$_6$H$_2$'Bu$_2$O)

INTRODUCTION†

Recent studies of the chemistry of bismuth stabilized by the NCN phenyl pincer ligand, 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$, Ar', have revealed that a new type of ligand, a dianionic oxyaryl species, (C$_6$H$_2$'Bu$_2$-3,5-O-4)$^{2-}$, can be created when sterically bulky aryloxide ligands react with Ar'BiCl$_2$, eq 2.1. In contrast to reactions with smaller aryloxide anions that make the three ligand complexes Ar'Bi(OC$_6$H$_3$R$_2$)$_2$ (R = Me, 'Pr), Ar'BiCl$_2$ reacts with KOC$_6$H$_2$'Bu$_2$-2,6 to form a product with only two ligands, Ar'Bi(C$_6$H$_2$'Bu$_2$-3,5-O-4), 1. This reaction involves C–H bond activation and formation of HOC$_6$H$_3$'Bu$_2$-2,6 as a byproduct.

NMR and IR spectroscopy, crystallographic studies, and DFT calculations indicate that complex 1 is a Bi$^{3+}$ complex with an oxyaryl dianionic ligand that has ring C–C and C–O distances consistent with considerable quinoidal character. This complex is best described by

† Portions of this chapter have been published: Kindra, D. R.; Casely, I. J.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. *J. Am. Chem. Soc.*, 2013, 135, 7777.
structure A, Scheme 2.1, rather than as a Bi\(^{2+}\) complex of a radical, structure B, or a complex with a Bi=C(aryl) double bond, structure C.

![Chemical structures](image)

**Scheme 2.1.** Possible Bonding Arrangements for 1, the Bismuth NCN Pincer Complex of the Oxyaryl Dianionic Ligand (C\(_6\)H\(_2\)tBu\(_2\)-3,5-O-4)\(^{2-}\)

The reaction chemistry of this unusual oxyaryl dianionic ligand complex is described in this Chapter. Complex 1 reacts with CO\(_2\) and COS to provide the first examples of insertion of these small molecule substrates into a Bi–C bond. These reactions generate two new dianionic ligands with quinoidal characteristics. Reactions of silyl halides and pseudohalides are also reported in which Me\(_3\)Si–X formally adds over five bonds to the bismuth and oxygen components of complex 1.

**RESULTS**

**CO\(_2\) and COS Insertion Reactivity of 1.** The red oxyaryl complex, Ar’Bi(C\(_6\)H\(_2\)tBu\(_2\)-3,5-O-4), 1, reacts within 1 h with carbon dioxide in acetonitrile to form a yellow product that can be recrystallized from acetonitrile and identified by X-ray crystallography as the oxyarylcarboxy complex Ar’Bi[O\(_2\)C(C\(_6\)H\(_2\)tBu\(_2\)-3,5-O-4)-\(\kappa^2\)O,O’], 2, Figure 2.1, eq 2.2. Complex 1 reacts similarly with carbonyl sulfide (COS) to form the oxyarylthiocarboxy complex Ar’Bi[OSC(C\(_6\)H\(_2\)tBu\(_2\)-3,5-O-4)-\(\kappa^2\)O,S], 3, Figure 2.2. Complexes 2 and 3 were also
characterized by NMR and IR spectroscopy and elemental analysis. The reactions in eq 2.2 appear to be the first examples of insertion of CO$_2$ and COS into Bi–C bonds.

\[ \text{ECO (1 atm)} \quad \text{MeCN} \]

![Equation 2.2](image)

To examine the generality of the insertion reactivity in eq 2.2, analogous CO$_2$ reactions were examined with BiPh$_3$ and [Ar′Bi(C$_6$H$_2$′Bu$_2$-3,5-OH-4)][BPh$_4$], a molecule that is closely related to 1 in composition and structure, but contains a conventional aryl monoanionic ligand instead of an oxyaryl dianionic ligand. Complex [1-H][BPh$_4$] has the same atom connectivity as 1 except that the oxo ligand is protonated and the bond distances are normal for the (C$_6$H$_2$′Bu$_2$-3,5-OH-4)$^{1-}$ aryl ring, rather than quinoidal (see Figure 2.3). Neither BiPh$_3$ nor [1-H][BPh$_4$] react with CO$_2$ under the conditions of eq 2.2.

![Figure 2.1](image)

**Figure 2.1.** ORTEP$^9$ representation of Ar′Bi[O$_2$C(C$_6$H$_2$′Bu$_2$-3-5-O-4)-κ$^2$O,O′], 2, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure 2.2. ORTEP representation of $\text{Ar}^\prime\text{Bi}[\text{OSC(C}_6\text{H}_3\text{Bu}_2\text{-3-5-O-4)}\text{-}^{\kappa^2}\text{O,S}]$, \(3\), from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

![ORTEP representation of Ar\textsuperscript{\prime}Bi[OSC(C\textsubscript{6}H\textsubscript{3}Bu\textsubscript{2}-3-5-O-4)-\kappa^2O,S], 3, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

Figure 2.3. Bond distances in the oxyaryl, oxyarylcarboxy, and oxyarylthiocarboxy dianionic ligands of compounds 1, 2, and 3 and the normal bond lengths of the closely related monoanionic aryl ligand in [1-H][BPh\textsubscript{4}].

![Bond distances in the oxyaryl, oxyarylcarboxy, and oxyarylthiocarboxy dianionic ligands of compounds 1, 2, and 3 and the normal bond lengths of the closely related monoanionic aryl ligand in [1-H][BPh\textsubscript{4}].](image)

Structural Analysis of the Oxyarylcarboxy and Oxyarylthiocarboxy Complexes. X-ray crystallography revealed that 2 and 3 have structures similar to that of 1. As seen in Figures 2.1 and 2.2, complexes 2 and 3 each have their two polydentate ligands oriented at right angles. This provides a large amount of space around the metal as is typical for bismuth.\textsuperscript{1-8,10-13} Complex 1
also has its two ligand planes at 90°, but the orientation differs from that in 2 and 3. If the Ar′ ligand is in the yz plane in all three compounds, the dianionic ligands of 2 and 3 are in the xy plane, whereas the dianionic ligand in 1 is in the xz plane. The difference occurs presumably to minimize steric interactions between the oxyaryl ring and Ar′ since the oxyaryl ring is closer to bismuth in 1. In 2, the 178.5(2)° Bi1−C13−C14 angle leads to a 92.4(1)° angle between the Ar′ aryl ring and the aryl ring in the dianionic ligand. The analogous angles in 1 are 176.3(2)° and 96.1(1)°. These angles differ in 3, which has a 167.9(2)° Bi1−C13−C14 angle and a 95.71(6)° angle between the C6 rings of the two ligands.

The Ar′−Bi moieties of 2 and 3 are conventional like those in 1 and its precursor, Ar′BiCl₂,[1] Table 2.1. However, the dianionic ligands in 2 and 3 have unusual delocalized bonding as in 1 and in contrast to [1-H][BPh₄], as shown in Figure 2.3. For example, the 1.278(2) Å C(17)−O(3) and 1.258(2) Å C(17)−O(2) C−O(oxyaryl) bond distances of 2 and 3, respectively, are intermediate between single and double bonds (phenol C−O 1.364 Å, quinone C=O 1.220(2) Å[14]) like the 1.265(4) Å analogue in 1. The 1.435(4) and 1.407(3) Å C(13)−C(14) distances connecting the aryl ring to the CO₂ and COS carbon atoms in 2 and 3, respectively, are also both intermediate between single and double bonds. Since the C(15)−C(16) and C(18)−C(19) distances in 2 and 3 are the shortest in the aryl ring like the analogues in 1, both 2 and 3 have bond distance patterns consistent with quinoidal character. Hence, the structural parameters of the dianionic ligand in 1 are maintained after insertion of CO₂ and COS.
Table 2.1. Comparison of Bi–C and Bi–N distances involving the Ar′ ancillary ligand.

<table>
<thead>
<tr>
<th></th>
<th>Bi–C(Ar′) (Å)</th>
<th>Bi–N(Ar′) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.208(3)</td>
<td>2.517(3), 2.568(3)</td>
</tr>
<tr>
<td>2</td>
<td>2.215(3)</td>
<td>2.542(3), 2.549(3)</td>
</tr>
<tr>
<td>3</td>
<td>2.211(2)</td>
<td>2.544(2), 2.619(2)</td>
</tr>
<tr>
<td>[1-H][BPh₄]</td>
<td>2.202(3)</td>
<td>2.512(2), 2.547(2)</td>
</tr>
<tr>
<td>Ar′BiCl₂</td>
<td>2.224(4)¹⁵</td>
<td>2.571, 2.561</td>
</tr>
<tr>
<td>BiPh₃</td>
<td>2.268(8)¹⁵</td>
<td></td>
</tr>
</tbody>
</table>

Complexes 2 and 3 are diamagnetic like 1. However the characteristic splitting of the Ar′ protons in the ¹H NMR spectrum of 1, caused by the asymmetric geometry of the twisted pincer arms, was not observed: only a single set of resonance was observed for the Ar′ protons in each case. A resonance for the inserted carboxy carbon atom of 2 was located at 175.8 ppm in the ¹³C NMR spectrum of a ¹³C enriched version of 2. IR spectroscopy of 2 shows absorptions at 1545 and 1322 cm⁻¹ that fall in the range characteristic of asymmetric and symmetric stretching vibrations for carboxylate ligands.¹⁶,¹⁷ These absorptions shift to 1523 and 1305 cm⁻¹ (Hooke’s law calculation: 1512 and 1293 cm⁻¹) in the ¹³C enriched analogue. The IR spectrum of 3 contains absorptions at 1735 and 1597 cm⁻¹, attributable to C–O stretching vibrations that are similar to the 1710–1718 and 1559 cm⁻¹ absorptions of free carbonyl sulfide.¹⁸ An IR absorption at 1019 cm⁻¹ in 3 is in the 934–1043 cm⁻¹ C–S stretching region found in other metal-bound thiocarboxylate ligands.¹⁹–²¹

Protonation of 2 to Form a Carboxyphenol Complex. The structural uniqueness of the dianionic oxyaryl ligand of 1 was originally defined in part by examining its protonated analogue, [Ar′Bi(C₆H₄₂Bu₂-3,5-OH-4)][BPh₄], [1-H][BPh₄], which has normal bond distances in the aryl ring.⁸ A similar comparison was sought for 2. Addition of [Et₃NH][BPh₄] to 2 yielded a white solid in >85% yield identified as {Ar′Bi[O₂C(C₆H₄₂Bu₂-3-5-OH-4)-κ²O,O′]}[BPh₄], [2-
by elemental, spectroscopic, and crystallographic analysis, eq 2.3. The $^1$H NMR spectrum of [2-H][BPh$_4$] showed resonances typical for Ar$'$ and (BPh$_4$)$^{1-}$, as well as a resonance at 6.13 ppm that is consistent with an OH proton. A broad absorption at 3414 cm$^{-1}$ consistent with an OH group was observed by IR spectroscopy. X-ray crystallography confirmed the atomic connectivity in [2-H][BPh$_4$], but the low quality of the crystal did not allow detailed discussion of metrical parameters. However, an unrelated reaction involving 2 and [NO][BF$_4$] led to isolation of the analogous (BF$_4$)$^{1-}$ salt, namely {Ar$'$Bi[O$_2$C(C$_6$H$_5$Bu$_2$-3-5-OH-4)-$\kappa^2$O,O']}[$\text{BF}_4$], [2-H][BF$_4$], Figure 2.4, which did provide satisfactory data and thus allow for structural analysis.
Figure 2.4. ORTEP representation of \{Ar'Bi[O_2C(C_6H_2'Bu_2-3-5-OH-4)-\kappa^2O,O']}[BF_4], [2-H][BF_4], with thermal ellipsoids drawn at the 50\% probability level. Hydrogen atoms are omitted for clarity.

The now protonated monoanionic ligand in [2-H][BF_4], Figure 2.5, has typical aromatic carbon-carbon bond lengths like those found in [1-H][BPh_4] and distinct from the distances in 2. The C–O bond in [2-H][BF_4] at 1.374(10) Å is much longer than the 1.265(4) Å in 2 and is typical for carbon-oxygen single bonds in phenols.\textsuperscript{14} The Bi–O bonds in [2-H][BF_4] at 2.336(5) Å are slightly longer than to the analogous bonds in 2 at 2.276(2) and 2.278(2) Å and are within the range of ordinary bismuth carboxylates.\textsuperscript{23-28}
Figure 2.5. Bond distances in the oxyaryl and oxyarylcarboxy dianionic ligands of compounds 1 and 2 compared to the normal bond lengths of the closely related monoanionic carboxylate ligand in [2-H][BF₄].

**Density Functional Theory Analysis of the Oxyarylcarboxy and Oxyarylthiocarboxy Dianionic Ligands.** Density functional theory calculations on 2, [1-H][BPh₄], and [2-H]⁺ reveal structural minima that agree very well with the crystallographic data. In the case of 3, however, the converged calculated structure did not show the upward bend seen in Figure 2.2. This structural variation may be due to crystal packing. In both 2 and 3, the new dianionic ligands were found to have delocalized bonding with quinoidal character that was not present in the protonated version of 2, namely, [2-H]⁺. An analogous difference was observed in the calculations on 1 and [1-H][BPh₄].

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35
Figure 2.6. From left to right, HOMO of compounds 1, 2 and 3. All orbitals are drawn with a contour value of 0.05.

The highest occupied molecular orbitals (HOMOs) of 2 and 3 are compared with that of 1 in Figure 2.6. All three HOMOs are similar in the oxy parts of the ligands shown at the top of the figure. The HOMOs of 2 and 3 differ from 1 in the bottom part of the figure. In both 2 and 3, the HOMO has considerable C=C character between the ipso carbon and the carboxyl or thiocarboxyl carbon. This extends the quinoidal character of the ligands as seen in Scheme 2.2.

\[
\text{Ar}^{+}\text{Bi} \quad \text{O} \quad \text{O} \quad \text{=} \quad \text{O} \\
\text{Bu}^{+} \quad \text{Bu}^{+} \\
2
\]

\[
\text{Ar}^{+}\text{Bi} \quad \text{O} \quad \text{S} \quad \text{=} \quad \text{O} \\
\text{Bu}^{+} \quad \text{Bu}^{+} \\
3
\]

\[
\text{Ar}^{+} = 2,6-(\text{Me}_{2}\text{NCH}_{2})_{2}\text{C}_{6}\text{H}_{3}
\]

Scheme 2.2. Quinoidal Resonance Structures of the Dianionic Ligands of Compounds 2 and 3, Respectively, Showing Double Bond Character

This multiple bonding with the ipso carbon is not found in the HOMO of 1 nor in any other orbitals of 1: there is only a small interaction between the ipso carbon and bismuth. Hence
there is a higher negative charge on the ipso carbon in 1 that correlates with its reactivity with CO$_2$ and COS.

Natural population analyses (NPA) on 2 and 3 were compared with that of 1 and indicate that insertion of CO$_2$ and COS does not significantly affect the electron density on the formally dianionic ligands. In 1, the oxyaryl ligand has an NPA value of 0.7 electrons, and the analogous numbers for 2 and 3 are 1.0 and 0.8 electrons, respectively. NPA calculations on the ipso carbon of the dianionic ligand showed 4.515 electrons on C13 of 1 compared to 4.224 and 4.183 electrons for C14 of the oxyarylcarboxy and oxyaryltiocarboxy dianionic ligands of 2 and 3, respectively. The higher electron density on C13 in 1 is spread out to the carboxyl and thiocarboxyl groups in 2 and 3 so that C14 in those compounds has lower electron density. The electron density on C13 in 1 is also higher than the 4.435 and 4.347 values on the analogous carbons in the protonated conventional aryl complex, [1-H][BPh$_4$], and BiPh$_3$, respectively. This difference can be used to rationalize the CO$_2$ and COS insertion reactivity observed for 1 and not for [1-H][BPh$_4$] and BiPh$_3$.

Reactions of 1 with Silyl Halides and Pseudohalides. Complex 1 reacts with 1 equiv of trimethylsilyl chloride to form Ar′BiCl(C$_6$H$_2$Bu$_2$-3,5-OSiMe$_3$-4), 4, in over 85% yield as shown in eq 2.4. Ph$_3$SiCl reacts similarly to form Ar′BiCl(C$_6$H$_2$Bu$_2$-3,5-OSiPh$_3$-4), 5, in over 65% yield.

These reactions constitute formal addition of R$_3$SiCl over five bonds. NMR spectroscopy and
elemental analytical data are consistent with the compounds as formulated, but crystallographic confirmation of these compounds has been elusive.

In order to further explore the nature of these silylated products and in an attempt to derivatize 4 to crystallographically characterize an example of a Ar′Bi(monoanion)(C₆H₂Bu₂-3,5-OsiR₃-4) complex, 4 was treated with 1 equiv of AgOTf (OTf = CF₃SO₃⁻). A precipitate consistent with AgCl formed, and the desired triflate derivative was isolated, eq 2.5.

\[
\begin{align*}
\text{4} & \quad + \quad \text{AgOTf} \\
\rightarrow & \\
\text{6} & \quad \begin{bmatrix} \text{OTf} \end{bmatrix}
\end{align*}
\]

(2.5)

Although the chloride in 4 was replaced by the triflate, X-ray crystallography showed that the complex crystallized as an outer sphere triflate complex, i.e. [Ar′Bi(C₆H₂Bu₂-3,5-OsiMe₃-4)][CF₃SO₃], 6, Figure 2.7. The ¹H NMR spectrum of compound 4 shows a single broad peak for the NMe₂ protons of Ar′, while compound 6 has two singlets similar to that seen for 1. This difference may arise because the triflate ligand in 6 is outer sphere, while 4 may have the chloride ligand coordinated to the metal center.
Figure 2.7. ORTEP representation of [Ar′Bi(C₆H₂Bu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Structural evidence for the Ar′Bi(X)(C₆H₂Bu₂-3,5-OSiR₃-4) products in eq 2.4 in which X was coordinated to bismuth was obtainable by examining the reaction of 1 with the trimethylsilyl pseudohalide, Me₃SiCN. The reaction of 1 with Me₃SiCN in one case formed single crystals of the 1,5-addition product, namely, Ar′Bi(CN)(C₆H₂Bu₂-3,5-OSiMe₃-4), 7, that could be characterized by X-ray crystallography, Figure 2.8. Although 7 provided a desired structural
example, it was not the main product of the Me₃SiCN reaction. The predominant and most commonly obtained product of the reaction was the dicyanide complex, Ar′Bi(CN)₂, 8, eq 2.6. Single crystals of 8 were analyzed by X-ray crystallography, but a structure solution was not obtainable, possibly because of disorder.

\[
\text{1} \quad \xrightarrow{\text{Me₃SiCN}} \quad \text{7} \quad \text{+} \quad \text{8}
\]  

(2.6)

The formation of Ar′BiX₂ products from R₃SiX reactions with 1 as observed for 7 and 8 in eq 2.6 appears to be general. With Me₃SiN₃, NMR evidence for the initial 1,5-addition product, Ar′Bi(N₃)(C₆H₄′Bu₂-3,5-OSiMe₃-4) is observed, but the main product is Ar′Bi(N₃)₂, 9. In contrast to 8, this complex can be crystallographically characterized as shown in Figure 2.9.
Ar′BiX₂ products are also obtainable from R₃SiX reactions with 1 when X = Cl. When 1 is reacted with an excess of Me₃SiCl, the known dichloride, Ar′BiCl₂,¹ is formed quantitatively along with the silyl ether Me₃SiOC₆H₃ᵗBu₂-2,6,²⁰ which was identified by ¹H NMR spectroscopy and GC–MS, Scheme 2.3. This reaction can also be done stepwise: addition of Me₃SiCl to the initial reaction product, 4, also generates Ar′BiCl₂ and Me₃SiOC₆H₃ᵗBu₂-2,6. The isolation of this silyl ether indicates that the [(C₆H₂ᵗBu₂-3,5-OSiMe₃)⁻]⁻ unit in 4 has added hydrogen. When the reaction of 1 with excess Me₃SiCl was performed in CD₃CN, ²H NMR spectroscopy and GC–MS indicated that the ether product contained deuterium on the carbon atom previously attached to bismuth, i.e., Me₃SiOC₆H₂ᵗBu₂-2,6-D-4. Hence, solvent can be the source of hydrogen or deuterium.
Scheme 2.3. Direct synthesis of Ar′BiCl₂ and Me₃SiOC₆H₃′Bu₂-2,6 by 1 and excess Me₃SiCl and step-wise synthesis through compound 4.

To aid in NMR analysis of the complicated mixtures of Ar′Bi(X)(C₆H₂′Bu₂-3,5-OSiMe₃-4) and Ar′BiX₂ formed from reactions of Me₃SiX with 1, Ar′Bi(N₃)₂ and Ar′Bi(CN)₂ were independently synthesized by treatment of the previously reported bis(aryloxide) Ar′Bi(OC₆H₃Me₂-2,6)₂ with excess Me₃SiX reagent (X = N₃ and CN), eq 2.7. The byproduct from these reactions is the expected silyl ether, Me₃SiOC₆H₃Me₂-2,6, as confirmed by ¹H NMR spectroscopy and GC−MS.

Structural Analysis of 6, 7, and 9. Selected structural data for compounds 6, 7, and 9 are compared with those for 1, 2, 3, and [1-H][BPh₄], in Tables 2.4 and 2.5. The Bi−C(Ar′) and Bi−N(Ar′) distances of 6 and 9 are conventional and similar to the bond lengths in 1-3 and [1-
Compound 7 has a 0.04 Å longer Bi–C(Ar') distance of 2.255(2) Å along with significant relative asymmetry and lengthening in the Bi–N bonds of the nitrogen donating arms at 2.677(2) and 3.039(2) Å. The 3.039(2) Å bond length is still within the sum of the van der Waals radii of 3.9 Å. This asymmetry is not observed in solution since there is a single resonance for the NMe$_2$ protons in the $^1$H NMR spectrum.

Compounds 6 and 7 exhibit right angles between the planes of the two aromatic ligands as found in 1, 2, and [1-H][BPh$_4$], but not for 3. The C1–Bi1–C13 angles for 6 and 7 are 93.14(7)$^\circ$ and 96.74(7)$^\circ$, respectively. The 2.242(2) Å Bi–C(siloxyphenyl) distance in four coordinate 6 is similar to the 2.221(3) Å Bi–C(hydroxyphenyl) distance in [1-H][BPh$_4$] which also has an outer sphere anion. The 2.255(2) Å Bi–C($C_6H_2^tBu_2-3,5-OSiMe_3$) distance in 7 is also in this range. However, the 2.396(2) Å Bi–C(CN) distance in 7 is much larger than all the other Bi–C distances in these complexes. No other Bi–C(CN) complexes were found in the Cambridge Structural Database for comparison, but comparison of the only crystallographically characterized antimony cyanide, Me$_2$Sb(CN), and a typical Sb–C(aryl) bond does not show an analogous lengthening of the Sb–C(CN) (2.230(9) Å) bond distance relative to the typical Sb–C(aryl) (2.143(6) to 2.152(10) Å) bond in SbPh$_3$.

The 2.454(2) Å Bi–N(azide) distance in 9 is in the broad range of 2.32(2) to 2.487(2) Å analogs in [Bi(N$_3$)$_6$][PPh$_4$]$_3$, that contains only terminal azide ligands. The azide ligands in 9 are both linear with N–N–N angles of 178.5(2) and 179.1(2)$^\circ$ and attach to bismuth with Bi–N–N angles of 117.9(2)$^\circ$ and 117.8(2)$^\circ$. The analogous angles in [Bi(N$_3$)$_6$][PPh$_4$]$_3$ are 114.7(2)$^\circ$ to 122.9$^\circ$.

Regeneration of the Dianionic Oxyaryl Ligand from Ar'BiCl($C_6H_2^tBu_2-3,5-OSiMe_3$-4), 4. The reaction of 4 with 1 equiv of KOC$_6$H$_3^tBu_2-2,6$ does not lead to a simple substitution of
chloride in a reaction analogous to that observed with AgOTf in eq 2.5. Instead, the aryloxide reaction regenerates the dianionic oxyaryl ligand, \((C_6H_2'Bu_2-3,5-O-4)^{2-}\), and compound 1 with formation of the silyl ether \(Me_3SiOC_6H_2'Bu_2-2,6\) and KCl, eq 2.8.

\[
\text{OA}_\text{Ar} = OC_6H_2'Bu_2-2,6
\]

The reaction pathway initially considered for eq 2.8 was a radical process involving an \(Ar'Bi[OC_6H_2'Bu_2-2,6](C_6H_2'tBu_2-3,5-O'SiMe_3-4)\) intermediate that would undergo Bi−O homolysis as proposed for the synthesis of 1.\(^8\) This possibility was tested with the analogous reaction of 4 with a para-methyl substituted aryloxide, \(KOC_6H_2'Bu_2-2,6-Me-4\). With the para position substituted, this phenolate cannot form the aryl radical necessary in the radical pathway.\(^8\) However, the reaction of 4 with \(KOC_6H_2'Bu_2-2,6-Me-4\) also immediately gives the characteristic color change to dark red for the formation of 1. Complex 1 is indeed formed in this reaction and the byproduct silyl ether was identified as \((2,6-di-tert-butyl-4-methylphenoxy)trimethylsilane\)\(^{35}\) by \(^1\)H NMR spectroscopy and GC–MS. It is therefore more likely that the reaction of 4 with a phenolate follows a less complex mechanism, Scheme 2.4, in which the nucleophilic phenolate abstracts the \(Me_3Si\) group with concomitant KCl formation. This mechanism is consistent with the experimental observations.
Scheme 2.4. Possible Mechanism for Me₃Si Abstraction and the Reformation of 1 from 4 and KOC₆H₅Bu₂-2,6-Me-4

Interestingly, the addition of KOC₆H₅Bu₂-2,6 to the chloride complex, 4, leads to regeneration of 1 in a cyclic process, Scheme 2.5, that involves the net conversion of KOC₆H₅Bu₂-2,6 and Me₃SiCl to Me₃SiOC₆H₅Bu₂-2,6 and KCl. Although this particular transformation is not difficult to effect by other means, the reactions in Scheme 2.5 show that bismuth and the oxyaryl dianionic ligand can participate in cyclic reaction chemistry.

Scheme 2.5. Cyclic Synthesis of the Silyl Ether (2,6-Di-tert-butylphenyl)(trimethylsilyl)ether

Reaction of 1 with Iodine. The reaction of 1 with I₂ in THF affords Ar’BiI₂,¹ analogous to the Ar’BiX₂ species formed in eq 2.6 and Scheme 2.3, but the coproduct is 3,3’,5,5’-tetra-tert-butyl-4,4’-diphenoquinone,¹³,¹⁴ Scheme 2.6. The diphenoquinone identified by ¹H and ¹³C NMR spectroscopy and by GC–MS, is a common byproduct in bismuth aryloxide chemistry and has
been isolated from reactions of BiCl₃ and 3 equiv of LiOC₆H₅Bu₂-2,6 by Hanna and co-workers in a process thought to involve Bi−O bond homolysis. The reaction formally involves the two electron oxidation of the oxyaryl dianionic ligand by iodine as shown by the half reactions, but the mechanism of the transformation is unknown.

![Scheme 2.6](image)

\[
(C₆H₂'Bu₂-3,5-O-4)^{2-} \rightarrow \frac{1}{2} \text{diphenoquinone} + 2 \text{e}^- \\
I₂ + 2 \text{e}^- \rightarrow 2 \text{I}^-
\]

**Scheme 2.6.** Reaction of 1 with I₂ to Form the Coupled Product 3,3',5,5'-Tetra-tert-butyl-4,4'-diphenoquinone

**DISCUSSION**

Although CO₂ insertion into metal–carbon bonds is a characteristic organometallic reaction for most metals, it is not as common with main group metals. The reactions of CO₂ and COS with the oxylaryl complex Ar'Bi(C₆H₂'Bu₂-3,5-O-4), 1, appear to be the first examples of insertion of these substrates into Bi–C bonds. No other examples were found in literature searches. The fact that CO₂ does not react with BiPh₃ or with the aryl monoanion complex [Ar'Bi(C₆H₂'Bu₂-3,5-OH-4)][BPh₄], that is closely related to 1, indicates that this reactivity arises from the special electronic nature of the dianionic oxyaryl ligand.

The enhanced reactivity of the oxyaryl ligand in 1 can be rationalized with the resonance structures in Scheme 2.7. Resonance form D matches that expected in conventional Bi–C(aryl).
complexes that do not insert CO$_2$. However, quinoidal resonance structure E has enhanced negative charge at the para-carbon position that could lead to the observed reactivity with CO$_2$ and COS. Since the bond distances in 1 are in between those expected for D and E, structure E can be a significant contributor to reactivity. The higher charge at this para-carbon is not significantly stabilized by bismuth, as shown by the DFT calculations, Figure 2.6, and hence this carbon is more reactive than those in typical organobismuth complexes. Since the oxyaryl dianionic ligand is known only in 1, comparisons of its reactivity attached to other metals cannot be made.

Scheme 2.7. Two Resonance Structures for the Oxyaryl Dianionic Ligand of Compound 1.

Insertion of CO$_2$ and COS into the Bi–C bond of 1 generates two new dianionic ligands, [O$_2$C(C$_6$H$_2$Bu$_2$-3,5-O-4)-κ$^2$O,O]$_2^-$ and [OSC(C$_6$H$_2$Bu$_2$-3,5-O-4)-κ$^2$O,S]$_2^-$, both of which also show delocalized bonding as in the [C$_6$H$_2$Bu$_2$-3,5-O-4]$_2^{2-}$ dianion in 1. In the quinoidal resonance forms of these dianionic ligands, the −2 charge localized on the para-carbon in 1 (Structure E above) can be spread over three additional atoms as shown in Scheme 2.8.
**Scheme 2.8.** Possible Resonance Structures of the Oxyarylcarboxy Dianionic Ligand of Compound 2.

The reactivity of 1 with R₃SiCl, eq 2.4, can be rationalized by resonance structure D in Scheme 2.7. The anionic phenolate oxygen in that resonance form could be sufficiently nucleophilic to react with a trimethylsilyl group to form a strong Si–O bond. This would create a transient cationic species, [Ar‘Bi(C₆H₄’Bu₂-3,5-OSiR₃-4)]⁺, with an outer sphere X⁻ counteranion that could subsequently coordinate to bismuth to make 4 or 5. The synthesis of the outer sphere triflate salt, [Ar‘Bi(C₆H₄’Bu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6, shows that such cations can exist with the appropriate counteranion. These reactions are analogous to the protonation of 2 to make {Ar‘Bi[O₂C(C₆H₄’Bu₂-3-5-OH-4)O-κ²O,O’]}[BPh₄], [2-H][BPh₄], eq 2.4. The net result of nucleophilic attack on Me₃SiX reagents followed by capture of X⁻ by bismuth is formal addition of Si–X over five bonds.

The reaction of excess R₃SiX with 1 to produce Ar‘BiX₂, e.g., eq 2.6, and the stepwise reaction of Ar‘BiCl(C₆H₄’Bu₂-3,5-OSiMe₃-4), 4, with Me₃SiCl to make Ar‘BiCl₂, Scheme 2.3, are consistent with the stability of Ar‘BiX₂ complexes as end products. Ar‘BiX₂ complexes are commonly observed in reactions involving the [Ar‘Bi]²⁺ moiety.²,¹¹-¹³ The formation of the silyl ether product of this reaction, R₃SiOC₆H₅’Bu₂-2,6, is consistent with the hydrogen abstraction
chemistry frequently found in bismuth reactions. In CD$_3$CN, the hydrogen (deuterium) was found to originate from solvent.

Attempts to obtain structural data on the bismuth complexes in this study reveal some unexpected irregularities in the ability to obtain single crystals suitable for crystallography. For example, although Ar′BiCl$_2$, and Ar′Bi(OAr)$_2$ (OAr = [OC$_6$H$_3$Me$_2$-2,6]$^1^-$, [OC$_6$H$_3$Pr$_2$-2,6]$^1^-$, [OC$_6$H$_2$Bu$_2$-2,6-Me-4]$^1^-$)$^8$ readily crystallize, the X = Cl version of the Ar′Bi(X)(C$_6$H$_2$Bu$_2$-3,5-OSiR$_3$-4) series did not. Instead, the X = CN derivative gave good single crystals of this structural type even though it is difficult to isolate this compound compared to the main product of the reaction, Ar′Bi(CN)$_2$. The latter dicyanide did not give good crystal data in contrast to Ar′BiCl$_2$ and Ar′Bi(N$_3$)$_2$, which did give solvable data. Although complexes 1 and 2 both crystallize to provide good data, their protonated analogues [1-H][BPh$_4$] and [2-H][BPh$_4$], respectively, differed. Only for [1-H][BPh$_4$] was crystallographically acceptable data obtained. No patterns emerge from these data, but they do suggest that slight modification of components in [Ar′Bi]$^{2+}$ complexes may lead to crystallographically definable derivatives of new compounds.

CONCLUSION

The quinoidal character of the unusual oxyaryl dianionic ligand, (C$_6$H$_2$Bu$_2$-3,5-O-4)$^{2-}$, in the Bi$^{3+}$ complex Ar′Bi(C$_6$H$_2$Bu$_2$-3,5-O-4), 1, has led to the first insertion reactions of CO$_2$ and COS into Bi–C bonds. These reactions generate new dianionic ligands with quinoidal character, [O$_2$C(C$_6$H$_2$Bu$_2$-3-5-O-4)-κ$^2$O,O']$^{2-}$ and [OSC(C$_6$H$_2$Bu$_2$-3-5-O-4)-κ$^2$O,S]$^{2-}$ in 2 and 3, respectively. Reactions of 1 with silyl halides and pseudohalides Me$_3$SiX (X = Cl, CN, N$_3$) lead to formal addition of Si–X across five bonds to form Ar′Bi(X)(C$_6$H$_2$Bu$_2$-3,5-OSiR$_3$-4) complexes. These react with additional Me$_3$SiX to generate Ar′BiX$_2$ complexes and (2,6-di-tert-
butylphenyl)(trimethylsilyl) ether. Addition of KOC₆H₃Bu₂-2,6 to Ar′Bi(Cl)(C₆H₂Bu₂-3,5-OSiMe₂-4) regenerates I in a cyclic process that converts KOC₆H₃Bu₂-2,6 and Me₃SiCl to Me₃SiOC₆H₃Bu₂-2,6 and KCl using the bismuth complex in a cyclic fashion to facilitate the transformation.

**EXPERIMENTAL DETAILS**

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. ¹H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (¹³C NMR spectra on the 500 MHz spectrometer operating at 125 MHz, ¹⁹F NMR spectra on the DR400 spectrometer operating at 375 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. GC–MS spectra were collected on a ThermoTrace MS and GC–MS instrument. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. IR samples were prepared as KBr pellets on a Varian 1000 FTIR system. KOC₆H₃Bu₂-2,6 and KOC₆H₂Bu₂-2,6-Me-4 were synthesized via an adaptation of a literature procedure by treatment of the parent phenol with 1 equiv of KN(SiMe₃)₂ in toluene, followed by filtration of the resulting white solid, and washing with hexane. ¹¹² [Et₃NH][BPh₄] was synthesized by treatment of [Et₃NH][Cl] with NaBPh₄ in water, followed by filtration and drying under a high vacuum (10⁻⁵ Torr) for 48 h. ¹³CO₂ (99.98%), ¹³CO₂ (99%), and COS (96+ %) were purchased from Airgas, Cambridge Isotope Laboratories,
and Matheson, respectively. Phenol reagents were sublimed prior to use. Me$_3$SiN$_3$ and Me$_3$SiCN (Sigma-Aldrich) were distilled under argon before use. Me$_3$SiCl (Alfa Aesar, 98+%) and Ph$_3$SiCl (Sigma-Aldrich, 97%) were received packed under argon and used without further purification. Ar$'Bi$(OC$_6$H$_3$Me$_2$-2,6)$_2$ was prepared according to the literature.$^8$

**Ar$'Bi$(C$_6$H$_2$'Bu$_2$-3,5-O-4), 1.** This procedure is an improved route to 1 compared to that in the literature.$^8$ A white opaque suspension of KOC$_6$H$_3'Bu$_2$-2,6 (1.16 g, 4.74 mmol) in THF (15 mL) was slowly added by pipet into a stirred solution of Ar$'BiCl$_2 (1.00 g, 2.31 mmol) in THF (70 mL). The cloudy white mixture turned yellow, then orange, and finally a dark red color after mixing. After 4 h of stirring, the reaction solution was centrifuged and filtered to remove insoluble material. Addition of hexane (350 mL) to the stirred filtrate generated an orange insoluble material that was filtered, washed with additional hexane, and dried under a vacuum. This crude product was dissolved in THF and allowed to precipitate with the addition of hexane. This reduced the amount of HOC$_6$H$_3'Bu$_2$-2,6 byproduct and caused the color to become bright orange. This process was repeated 3 times to give analytically pure bright orange 1 (850 mg, 61%).

$^1$H NMR (500 MHz, acetonitrile-$d_3$): $\delta$ 7.51 [m, 5H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$ and C$_6$H$_2$'Bu$_2$O], 3.88 [d, $^2J_{HH} = 14.7$ Hz, 2H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 2.67 [s, 6H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 2.26 [s, 6H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 1.24 [s, 18H, C$_6$H$_2$'Bu$_2$O]. $^{13}$C NMR (125 MHz, acetonitrile-$d_3$): $\delta$ 182.7 [i-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 174.5 [i-C$_6$H$_2$'Bu$_2$O], 159.0 and 139.6 [C$_6$H$_2$'Bu$_2$O], 149.7 [o-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 134.5, 129.0, and 127.7 [m- and p-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$ and C$_6$H$_2$'Bu$_2$O], 67.2 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 46.5 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 46.4 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 34.9 [$q$-C$_6$H$_2$(CMe$_3$)$_2$O], 29.1 [C$_6$H$_2$(CMe$_3$)$_2$O]. IR: 3045w, 2991w, 2943m, 2894m, 2840w, 2797w, 1554s, 1477s, 1432s, 1374m, 1354m, 1333m, 1300w, 1254m, 1202w, 1173w, 1127w, 1091s, 1034w, 1005m, 885w, 840s, 803w, 775w, 709w, 530w, 444m
cm\(^{-1}\). Anal. Calcd for C\(_{26}\)H\(_{39}\)N\(_2\)O\(_2\)Bi: C, 51.64; H, 6.51; N, 4.63. Found: C, 52.07; H, 6.99; N, 4.35.

\textbf{Ar'Bi[O\(_2\)C(C\(_6\)H\(_2\)Bu\(_2\)-3-5-O-4)-\kappa^2\text{O},\text{O'}]}, \textbf{2}. A 100 mL sealable side arm Schlenk flask was charged with bright orange 1 (130 mg, 0.22 mmol). Addition of acetonitrile (10 mL) formed a red solution. The flask was placed on a high vacuum line, degassed, and charged with 1 atm of carbon dioxide. After stirring at room temperature for 1 h, a yellow precipitate formed. The flask was degassed with three freeze–pump–thaw cycles and transferred to an argon-filled glovebox. The reaction mixture was concentrated under a vacuum, and the solids were collected via centrifugation, washed with hexane, and dried under a vacuum giving 2 as a yellow powder (102 mg, 73%). X-ray quality crystals were grown from a saturated acetonitrile solution at \(-30^\circ\text{C}\). \(^1\text{H}\) NMR (500 MHz, acetonitrile-\(d_3\)): \(\delta\) 7.70 [d, \(^2\text{J}_{HH} = 6.99\) Hz, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.64 [s, 2H, O\(_2\)C(C\(_6\)H\(_2\)Bu\(_2\)O)], 7.52 [t, 1H, \(^3\text{J}_{HH} = 14.8\) Hz, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 4.29 [s, 4H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 2.68 [s, 12H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 1.36 [s, 18H, O\(_2\)C(C\(_6\)H\(_2\)Bu\(_2\)O)]. \(^{13}\text{C}\) NMR (125 MHz, acetonitrile-\(d_3\)): \(\delta\) 130.6, 129.1, 127.8, and, 126.2 [m- and p- (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\) and O\(_2\)C(C\(_6\)H\(_2\)Bu\(_2\)O)], 68.7 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 46.3 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 35.6 [q-O\(_2\)C(C\(_6\)H\(_2\)(CMe\(_3\))\(_2\)O)], 30.7 [O\(_2\)C(C\(_6\)H\(_2\)(CMe\(_3\))\(_2\)O)]. IR: 3631w, 2951s, 2794w, 1665w, 1591s, 1546m, 1468s, 1424s, 1322s, 1010m, 841s, 694m cm\(^{-1}\). Anal. Calcd for C\(_{27}\)H\(_{39}\)N\(_2\)O\(_3\)Bi: C, 50.00; H, 6.06; N, 4.32. Found: C, 49.70; H, 5.93; N, 4.23. UV–Vis (MeCN): \(\lambda_{\text{max}}\) (nm), \(\varepsilon\) (M\(^{-1}\) cm\(^{-1}\)) 357, 15600; 249, 18600.

\textbf{Ar'Bi[O\(_2\)\(^{13}\text{C}\)(C\(_6\)H\(_2\)Bu\(_2\)-3-5-O-4)-\kappa^2\text{O},\text{O'})], \(\textbf{2-}^{13}\text{C}\).} The \(^{13}\text{C}\) analogue of 2 was prepared analogously from \(^{13}\text{CO}_2\) (90 mg, 73%). \(^{13}\text{C}\) NMR (125 MHz, acetonitrile-\(d_3\)): \(\delta\) 175.8 [O\(_2\)\(^{13}\text{C}\)(C\(_6\)H\(_2\)Bu\(_2\)O)] 130.6, 129.1, 127.8, and, 126.2 [m- and p-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\) and O\(_2\)C(C\(_6\)H\(_2\)Bu\(_2\)O)], 68.7 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 46.3 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 35.6 [q-
O₂C(C₆H₂(CMe₃)₂O), 30.7 [O₂C(C₆H₂(CMe₃)₂O)]. IR: 3631w, 2951s, 2794w, 1665w, 1591s, 1523m (calcd 1512), 1468s, 1424s, 1305s (calcd 1293), 1010m, 841s, 694m cm⁻¹.

Ar′Bi[OSC(C₆H₂Bu₂-3-5-O-4)-κ²O,S], 3. A 100 mL sealable side arm Schlenk flask was charged with bright orange 1 (150 mg, 0.25 mmol). Addition of acetonitrile (15 mL) formed a red solution. The flask was placed on a high vacuum line, degassed, and charged with 1 atm of carbonyl sulfide (COS) gas. After stirring at room temperature for 1 h, an orange precipitate formed. The flask was degassed with three freeze–pump–thaw cycles and moved into a nitrogen-filled glovebox. The solids were collected via centrifugation, washed with hexane, and dried under a vacuum giving 3 as an orange powder (108 mg, 65%). X-ray quality crystals were grown from a saturated acetonitrile solution at −30 °C. ¹H NMR (500 MHz, acetonitrile-d₃): δ 7.70 [d, 2J_HH = 7.34 Hz, 2H, (Me₂NCH₂)₂C₆H₃], 7.54 [t, 3J_HH = 14.8 Hz, 1H, (Me₂NCH₂)₂C₆H₃], 7.48 [s, 2H, OSC(C₆H₂Bu₂O)], 4.29 [s, 4H, (Me₂NCCH₂)₂C₆H₃], 2.67 [br s, 12H, (Me₂NCH₂)₂C₆H₃], 1.28 [s, 18H, OSC(C₆H₂Bu₂O)]. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 130.8, 129.6, 127.4, and 126.3 [m- and p-(Me₂NCH₂)₂C₆H₃ and OSC(C₆H₂Bu₂O)], 69.8 [(Me₂NCH₂)₂C₆H₃], 48.0 [br s, (Me₂NCH₂)₂C₆H₃], 36.5 [q-OSC(C₆H₂(CMe₃)₂O)], 30.3 [OSC(C₆H₂(CMe₃)₂O)]. IR: 2957s, 2816s, 2780s, 1735s, 1597m, 1448s, 1362m, 1296w, 1227s, 1185s, 1097s, 1019s, 843s, 792m, 758s, 713w, 618w cm⁻¹. Anal. Calcd for C₂₇H₃₉BiN₂O₂·CH₃CN: C, 49.34; H, 6.00; N, 5.96. Found: C, 49.30; H, 5.89; N, 5.47. UV–Vis (MeCN): λₘₐₓ (nm), ε (M⁻¹ cm⁻¹) 396, 38300; 270, 14400.

{Ar′Bi[O₂C(C₆H₂Bu₂-3-5-OH-4)-κ²O,O′][BPh₄], [2-H][BPh₄]}. A colorless solution of [Et₃NH][BPh₄] (130 mg, 0.31 mmol) in THF (12 mL) was slowly added to a stirred yellow suspension of 2 (190 mg, 0.29 mmol) in THF (5 mL). The reaction mixture quickly became a very pale yellow solution. After stirring at room temperature for 1 h, the solvent was removed
under a vacuum yielding a fluffy off-white powder. The crude product was further purified by recrystallization in acetonitrile at −30 °C yielding white needle-shaped crystals of \( [2\text{-H}][\text{BPh}_4] \) (254 mg, 88%). \(^1\)H NMR (500 MHz, acetonitrile-\(d_3\)): \( \delta \) 7.88 [d, \(^2\)J\text{HH} = 7.50 Hz, 2H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.78 [s, 2H, O\(_2\)C(C\(_6\)H\(_2\)\(^3\)Bu\(_2\)OH)], 7.65 [t, \(^3\)J\text{HH} = 15.0 Hz, 1H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 7.29 [m, 8H, m-\text{BPh}_4], 7.01 [m, 8H, o-\text{BPh}_4], 6.84 [m, 4H, p-\text{BPh}_4], 6.13 [s, 1H, O\(_2\)C(C\(_6\)H\(_2\)\(^3\)Bu\(_2\)OH)], 4.46 [s, 4H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 2.76 [s, 12H, (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 1.39 [s, 18H, O\(_2\)C(C\(_6\)H\(_2\)\(^3\)Bu\(_2\)OH)]. \(^{13}\)C NMR (125 MHz, acetonitrile-\(d_3\)): \( \delta \) 163.8 [\text{BPh}_4], 155.4 [O\(_2\)C(C\(_6\)H\(_2\)\(^3\)Bu\(_2\)OH)], 137.7 [BPh\(_4\)], 131.9, 129.5, 128.4, and 126.6 [m- and p- (Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\) and O\(_2\)C(C\(_6\)H\(_2\)\(^3\)Bu\(_2\)OH)], 122.8 [BPh\(_4\)], 69.1 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 47.1 [(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)], 35.2 [\text{q-O}_2\text{C(C}_6\text{H}_2(\text{CMe}_3)_2\text{OH})], 30.2 [O\(_2\)C(C\(_6\)H\(_2\)(CMe\(_3\))_2\text{OH})]. IR: 3620s, 3414br, 3057s, 2958s, 2872s, 2798m, 1948w, 1887w, 1817w, 1598s, 1562s, 1476s, 1388s, 1239s, 1117s, 1004s, 889m, 836s, 733s, 707s, 612s cm\(^{-1}\). Anal. Calcd for C\(_{50}\)H\(_{58}\)BN\(_2\)O\(_3\)Bi: C, 62.90; H, 6.12; N, 2.93. Found: C, 63.19; H, 5.99; N, 2.91.

\( \{\text{Ar'}\text{Bi}[\text{O}_2\text{C}(\text{C}_6\text{H}_2\text{Bu}_2\text{-3-5-OH-4})\text{-}\kappa^2\text{O, O'}]\}[\text{BF}_4] \), [2-H][BF\(_4\)]. A silylated scintillation vial was charged with an orange acetonitrile (10 mL) solution of 2 (75 mg, 0.12 mmol). Using a plastic spatula, cold [NO][BF\(_4\)] (14 mg, 0.12 mmol) was added as a solid to the stirred reaction mixture inducing rapid color changes to lime green, yellow, and finally dark red. The reaction mixture was allowed to stir for 5 min and then placed in a freezer at −30 °C over night. Multiple products were observed by \(^1\)H NMR and \(^{19}\)F NMR of the crude reaction mixture. Colorless X-ray quality crystals of [2-H][BF\(_4\)] were grown by THF evaporation at room temperature.

\( \text{Ar'Bi(Cl)}(\text{C}_6\text{H}_2\text{Bu}_2\text{-3,5-OSiMe}_3\text{-4}), \) 4. A scintillation vial was charged with bright orange 1 (100 mg, 0.17 mmol). Addition of THF (10 mL) formed a dark red solution. When a colorless solution of Me\(_3\)SiCl (22 μL, 0.17 mmol) in THF (10 mL) was added to the reaction
vessel, the mixture instantly turned clear and colorless. After 3 h, the mixture was an off-white suspension and was stored overnight at −30 °C to precipitate further product. The supernatant was decanted, and the white solids were washed with cold THF and collected by centrifugation. The white powder was dried under a vacuum to yield analytically pure 4 (101 mg, 86%). $^1$H NMR (500 MHz, acetonitrile-$d_3$): $\delta$ 8.02 [s, 2H, C$_6$H$_2$Bu$_2$OSiMe$_3$], 7.59 [s, 3H, m- and p- (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 4.13 [d, $^3$J$_{HH}$ = 14.8 Hz, 2H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 3.72 [d, $^3$J$_{HH}$ = 14.8 Hz, 2H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 2.52 [br s, 12H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 1.28 [s, 18H, C$_6$H$_2$Bu$_2$OSiMe$_3$], 0.32 [s, 9H, C$_6$H$_2$Bu$_2$OSiMe$_3$]. $^{13}$C NMR (125 MHz, acetonitrile-$d_3$): $\delta$ 188.4 [i-$^4$Me$_2$NCH$_2$C$_6$H$_3$], 255.4 [i-C$_6$H$_2$Bu$_2$OSiMe$_3$], 154.0 and 143.9 [C$_6$H$_2$Bu$_2$OSiMe$_3$], 150.6 [o-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 136.4 [C$_6$H$_2$Bu$_2$OSiMe$_3$], 129.3 [p-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 127.8 [m-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 67.8 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 47.0 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 35.3 [q-C$_6$H$_2$(CMe$_3$)$_2$OSiMe$_3$], 30.8 [C$_6$H$_2$(CMe$_3$)$_2$OSiMe$_3$], 2.53 [C$_6$H$_2$Bu$_2$OSiMe$_3$]. IR: 3037w, 2956m, 2903m, 2869m, 2835w, 2793w, 2711w, 1579w, 1551w, 1469m, 1451m, 1417m, 1392m, 1361m, 1256m, 1231m, 1202m, 1176w, 1150w, 1131m, 1070w, 1034w, 1003m, 910m, 843s, 770m, 710w, 676w, 637w, 562w, 528w, 481w, 451w, 412w cm$^{-1}$. Anal. Calcd for C$_{29}$H$_{48}$BiClN$_2$OSi: C, 48.83; H, 6.80; N, 3.93. Found: C, 48.93; H, 6.77; N, 3.84.

$^{1}$BiCl(BiCl$_2$(C$_6$H$_2$Bu$_2$)$_2$)$_{-3,5}$-OSiPh$_3$-4), 5. A scintillation vial was charged with bright orange 1 (100 mg, 0.17 mmol). Addition of THF (10 mL) formed a dark red solution. Addition of Ph$_3$SiCl (49 mg, 0.17 mmol) in THF (12 mL) caused no immediate change in appearance. After stirring overnight, the reaction mixture became a yellow suspension. The solids were collected by centrifugation and washed three times with THF to afford 5 as a white solid (99 mg, 67%). $^1$H NMR (500 MHz, acetonitrile-$d_3$): $\delta$ 7.85 [s, 2H, C$_6$H$_2$Bu$_2$OSiPh$_3$], 7.61 [s, 3H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 7.53 [t, $^3$J$_{HH}$ = 8.03 Hz, 6H, o-C$_6$H$_2$Bu$_2$OSiPh$_3$], 7.45 [m, 3H, p-
C₆H₄Bu₂OSiPh₃, 7.33 [t, JHH = 15.3 Hz, 6H, m-C₆H₄Bu₂OSiPh₃], 4.14 [d, JHH = 15.0 Hz, 2H, (Me₂NCH₂)₂C₆H₃], 3.82 [d, JHH = 15.0 Hz, 2H, (Me₂NCH₂)₂C₆H₃], 2.60 [br s, 12H, (Me₂NCH₂)₂C₆H₃], 0.91 [s, 18H, C₆H₄Bu₂OSiPh₃]. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 187.3 [i-(Me₂NCH₂)₂C₆H₃], 176.5 [i-C₆H₄Bu₂OSiPh₃], 154.7 and 145.8 [C₆H₄Bu₂OSiPh₃], 151.7 [o-(Me₂NCH₂)₂C₆H₃], 137.9 [C₆H₄Bu₂OSiPh₃], 137.4 [o-C₆H₄Bu₂OSiPh₃], 135.4 [C₆H₄Bu₂OSiPh₃], 131.5 [m-C₆H₄Bu₂OSiPh₃], 131.0 [p-C₆H₄Bu₂OSiPh₃], 129.4 [p-(Me₂NCH₂)₂C₆H₃], 129.1 [m-(Me₂NCH₂)₂C₆H₃] 69.0 [(Me₂NCH₂)₂C₆H₃], 48.4 [(Me₂NCH₂)₂C₆H₃], 37.2 [q-C₆H₂(CMe₃)₂OSiPh₃], 32.8 [C₆H₂(CMe₃)₂OSiPh₃]. IR: 2955m, 2866m, 1589w, 1468m, 1415s, 1223s, 1114s, 1002m, 907m, 842s, 774m, 742m, 701s, 573w, 510s, 453w cm⁻¹. Anal. Calcd for C₄₄H₅₄BiClN₂O₃Si: C, 58.76; H, 6.05; N, 3.11. Found: C, 57.65; H, 6.41; N, 3.11.

[Ar'Bi(C₆H₄Bu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6. A stirred white mixture of 4 (81 mg, 0.11 mmol) in THF (8 mL) rapidly turned clear and colorless upon the addition of AgOTf (31 mg, 0.12 mmol) in THF (3 mL). Subsequently, slow formation of a white precipitate occurred. After stirring overnight, the reaction mixture was centrifuged to remove off-white insoluble material consistent with silver chloride. The solvent was removed from the colorless supernatant under a vacuum to give 6 as a white powder (84 mg, 89%). X-ray quality crystals were grown from a saturated acetonitrile solution at −30 °C. ¹H NMR (500 MHz, acetonitrile-d₃): δ 7.91 [s, 2H, C₆H₂Bu₂OSiMe₃], 7.64 [s, 3H, (Me₂NCH₂)₂C₆H₃], 4.06 [d, JHH = 15.0 Hz, 2H, (Me₂NCH₂)₂C₆H₃], 3.77 [d, JHH = 15.0 Hz, 2H, (Me₂NCH₂)₂C₆H₃], 2.75 [s, 6H, (Me₂NCH₂)₂C₆H₃], 2.25 [s, 6H, (Me₂NCH₂)₂C₆H₃], 1.29 [s, 18H, C₆H₂Bu₂OSiMe₃], 0.33 [s, 9H, C₆H₂Bu₂OSiMe₃]. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 186.5 [i-(Me₂NCH₂)₂C₆H₃], 174.2 [i-C₆H₂Bu₂OSiMe₃], 155.8 [C₆H₂Bu₂OSiMe₃], 151.7 [o-(Me₂NCH₂)₂C₆H₃], 145.5
\[ \text{[C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 137.3 \quad \text{[C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 131.1 \quad \text{[(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 129.5 \]

\[ \text{[(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 68.7 \quad \text{[(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 48.3 \quad \text{[(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 36.6 \quad [q-\text{C}_6\text{H}_2(\text{CMe}_3)_2\text{OSiMe}_3], \quad 32.0 \quad [\text{C}_6\text{H}_2(\text{CMe}_3)_2\text{OSiMe}_3], \quad 3.6 \quad [\text{C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3]. \]

\(^1\text{F NMR (375 MHz, acetonitrile-}\text{d}_3\): \( \delta \quad -79.36 \quad \text{[s, 3F, C}_6\text{OSiMe}_3], \quad 128.19 \quad \text{[s, 12H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 3.85 \quad \text{[br s, 2H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 3.35 \quad \text{[br s, 2H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 2.19 \quad \text{[s, 12H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 1.31 \quad \text{[s, 18H, C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 0.36 \quad \text{[s, 9H, C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3]. \]

\(^1\text{H NMR (500 MHz, acetonitrile-}\text{d}_3\): \( \delta \quad 8.01 \quad \text{[s, 2H, C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 7.38 \quad \text{[s, 3H, m- and p- (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 3.85 \quad \text{[br s, 2H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 3.35 \quad \text{[br s, 2H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 2.19 \quad \text{[s, 12H, (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 1.31 \quad \text{[s, 18H, C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 0.36 \quad \text{[s, 9H, C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3]. \]

\(^1\text{H NMR (125 MHz, acetonitrile-}\text{d}_3\): \( \delta \quad 174.1 \quad \text{[}^1\text{C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 165.9 \quad \text{[CN], 152.6 and 142.7 [C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 150.0 \quad \text{[}^6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 136.4 \quad \text{[}^6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 128.51 \quad \text{[p- (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 128.19 \quad \text{[m- (Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 67.0 \quad \text{[(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 44.1 \quad [(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \quad 35.1 \quad \text{[}^6\text{C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 30.8 \quad \text{[}^6\text{C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3], \quad 2.70 \quad \text{[C}_6\text{H}_2^6\text{Bu}_2\text{OSiMe}_3]. \]

**Reaction of 1 with Excess Me3SiCl.** Me3SiCl (32 μL, 0.25 mmol) was added by microsyringe to a stirred dark red solution of 1 (50 mg, 0.08 mmol) in THF (5 mL). The reaction
mixture immediately became colorless and was stirred for 12 h. After solvent removal, the resulting white solid (52 mg) was stirred in hexane (5 mL) for 30 min, and the insoluble material was collected by centrifugation to yield an off white solid (20 mg) that was determined to be the known dichloride Ar′BiCl₂ by ¹H and ¹³C NMR spectroscopy. Solvent was removed from the mother liquor under reduced pressure affording a white solid determined to be (Me₃SiOC₆H₃Bu₂-2,6)²⁹ (7 mg) by ¹H NMR spectroscopy and GC–MS.

**Reaction of 4 with KOC₆H₃Bu₂-2,6.** A cloudy white mixture of 4 (90 mg, 0.13 mmol) in THF (8 mL) immediately turned dark red upon the addition of KOC₆H₂Bu₂-2,6 (32 mg, 0.13 mmol). After stirring overnight, the solvent was removed under reduced pressure, and the crude orange solid was stirred in hexane (8 mL) for 2 h. The mixture was centrifuged to recover orange solids (75 mg) that were identified as 1 by ¹H NMR spectroscopy. Hexane was removed from the supernatant under a vacuum to yield an off-white solid that was identified by ¹H NMR spectroscopy and GC–MS as (2,6-di-tert-butylphenoxy)trimethylsilane²⁹ (35 mg, 97%).

**Reaction of 4 with KOC₆H₃Bu₂-2,6-Me-4.** A cloudy white mixture of 4 (60 mg, 0.08 mmol) in THF (8 mL) immediately turned dark red upon the addition of KOC₆H₂Bu₂-2,6-Me-4 (22 mg, 0.08 mmol) in THF (3 mL). After stirring for 3 h, the solvent was removed under reduced pressure, and the crude orange solid was stirred in hexane (10 mL) for 15 min. The mixture was then centrifuged to recover orange solids (35 mg) that were identified as 1 by ¹H NMR spectroscopy. The hexane was removed from the supernatant under a vacuum to yield a white solid that was identified by ¹H NMR and GC–MS as (2,6-di-tert-butyl-4-methylphenoxy)trimethylsilane³⁵ (22 mg, 94%).

**Ar′Bi(CN)₂, 8.** Neat Me₃SiCN (24 μL, 0.19 mmol) was added via microsyringe to a stirred yellow solution of Ar′Bi(OC₆H₃Me₂-2,6)₂ (50 mg, 0.08 mmol) in THF (5 mL). The
yellow color faded, and a white precipitate began to form over 5 min. Stirring was continued for 1 h, and hexane (5 mL) was added. The mixture was filtered, and the filtrate was washed with a 1:1 THF/hexane (5 mL) mixture and dried under reduced pressure to afford 8 as a white solid (29 mg, 82%). Single crystals were grown from a concentrated MeCN solution stored at −30 °C overnight. 

\[ ^1H\text{ NMR at 298 K (500 MHz, acetonitrile-\textit{d}_3): } \delta 7.60 \text{ [d, } ^2J_{HH} = 7.5 \text{ Hz, 2H, } m-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 7.49 \text{ [t, } ^3J_{HH} = 7.5 \text{ Hz, 1H, } p-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 4.41 \text{ [br s, 2H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 4.04 \text{ [br s, 2H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 2.81 \text{ [br s, 6H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]. \]

\[ ^13C\text{ NMR (125 MHz, acetonitrile-\textit{d}_3): } \delta 152.1 \text{ [o-} (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 129.7 \text{ [p-} (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 128.7 \text{ [m-} (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 67.6 \text{ [(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 45.5 \text{ [br s, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 41.4 \text{ [br s, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]. \]

IR: 3046w, 2988w, 2967w, 2871m, 2834m, 2802m, 2782w, 2133m, 1579w, 1474m, 1454m, 1401w, 1359w, 1275w, 1253m, 1230w, 1212w, 1174w, 1147w, 1098w, 1036m, 1010s, 970w, 894w, 842s, 794m, 765m, 708w, 526w, 467w, 437w cm\(^{-1}\). Anal. Calcd for C\(_{14}\)H\(_{19}\)BiN\(_4\): C, 37.17; H, 4.24; N, 12.38. Found: C, 37.28; H, 4.08; N, 12.22.

The mother liquors isolated from the syntheses of Ar′Bi(CN)\(_2\), 8, and Ar′Bi(N\(_3\))\(_2\), 9, via this Ar′Bi(OC\(_6\)H\(_3\)Me\(_2\)-2,6\(_2\)-based route were dried to yield off white solids identified as (2,6-dimethylphenoxy)trimethylsilane.\(^{30}\)

**Ar′Bi(N\(_3\))\(_2\), 9, from 1.** Neat Me\(_3\)SiN\(_3\) (28 μL, 0.21 mmol) was added via microsyringe to a stirred dark red soluteion of 1 (55 mg, 0.09 mmol) in THF (5 mL). The red color faded, and a white precipitate began to form over 5 min. Stirring was continued for 1 h, and hexane (5 mL) was added. The solids were collected by filtration, washed with a 1:1 THF/hexane mixture (5 mL), and dried under reduced pressure to afford 9 as a white solid (40 mg, 96%). 

\[ ^1H\text{ NMR (500 MHz, acetonitrile-\textit{d}_3): } \delta 7.79 \text{ [d, } ^2J_{HH} = 7.5 \text{ Hz, 2H, } m-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 7.60 \text{ [t, } ^3J_{HH} = 7.5 \text{ Hz, 1H, } p-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 4.41 \text{ [br s, 2H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 4.04 \text{ [br s, 2H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3], \]

\[ 2.81 \text{ [br s, 6H, } (\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]. \]
$^1$H, $p$-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 4.31 [s, 4H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 2.82 [s, 12H, (Me$_2$NCH$_2$)$_2$C$_6$H$_3$]. $^{13}$C NMR (125 MHz, acetonitrile-$d_3$): $\delta$ 151.9 [o-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 129.5 [$p$-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 128.4 [m-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$], 67.8 [(Me$_2$NCH)$_2$C$_6$H$_3$], 45.5 [(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]. IR: 3046w, 2998w, 2965w, 2889w, 2864w, 2786w, 2033vs, 2012vs, 1578w, 1453m, 1423m, 1401w, 1352w, 1312m, 1263m, 1227w, 1211w, 1172w, 1158w, 1088w, 1029m, 999m, 986m, 955w, 911w, 841s, 782m, 708w, 638w, 613w, 480w, 454m cm$^{-1}$. Anal. Calcd for C$_{12}$H$_{19}$BiN$_8$: C, 29.75; H, 3.96; N, 23.14. Found: C, 30.14; H, 3.97; N, 23.08.

Ar′Bi(N$_3$)$_2$, 9, from Ar′Bi(OC$_6$H$_3$Me$_2$-2,6)$_2$. Me$_3$SiN$_3$ (28 μL, 0.21 mmol) was added by microsyringe to a stirred yellow solution of Ar′Bi(OC$_6$H$_3$Me$_2$-2,6)$_2$ (55 mg, 0.09 mmol) in THF (5 mL). The yellow color faded and a white precipitate formed over 3 min. Stirring was continued for 1 h and hexane (5 mL) was added. The solid was collected via centrifugation and dried under a vacuum to afford 9 as a white solid (40 mg, 96%) identified by $^1$H and $^{13}$C NMR spectroscopy. (2,6-Dimethylphenoxy)trimethylsilane$^{30}$ was isolated and identified as described above in the synthesis of 8.

Reaction of 1 with Iodine. Addition of a THF (2 mL) solution of iodine (31 mg, 0.12 mmol) to a stirred dark red solution of 1 (74 mg, 0.12 mmol) in THF (8 mL) caused the reaction mixture immediately to become pale yellow in color. Stirring was continued for 1 h, the mixture was filtered, and the solvent was removed from the filtrate. The resulting yellow solid was stirred in hexane (5 mL) for 1 h to extract the organic byproduct. The yellow insoluble material was separated by centrifugation (62 mg) and determined by X-ray crystallography to be Ar′BiI$_2$.$^{1}$ The hexane solution was evaporated under reduced pressure to yield a yellow solid (22 mg) identified by $^1$H and $^{13}$C NMR spectroscopy and GC−MS as the coupled product (3,3′,5,5′-tetra-tert-butyl-4,4′-diphenoquinone).$^{43,44}$
**X-ray Crystallographic Data.** Crystallographic information for complexes 2, 3, [2-H][BF₄], 6, 7, and 9 is summarized in Table 2.2 and 2.3. Selected bond distances are in Tables 2.4 – 2.5.

Table 2.2. X-ray data collection parameters for Ar′Bi[O₂C(C₆H₄′Bu₂-3-5-O-4)-κ²O,O'], 2, Ar′Bi[OSC(C₆H₄′Bu₂-3-5-O-4)-κ²O,S], 3, and {Ar′Bi[O₂C(C₆H₄′Bu₂-3-5-OH-4)-κ²O,O']}[BF₄], [2-H][BF₄].

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Table 2.3. X-ray data collection parameters for [Ar'Bi(C₆H₄Bu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6, Ar'Bi(CN)(C₆H₄Bu₂-3,5-OSiMe₃-4), 7, and Ar'Bi(N₃)₂, 9.

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<td>C₃₀H₄₈BiN₃Os</td>
<td>C₁₂H₁₀₉BiN₈•CH₃CN</td>
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<tr>
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<td>93(2)</td>
<td>88(2)</td>
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<tr>
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<td>8.2299(5)</td>
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<tr>
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<td>c (Å)</td>
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Table 2.4. Selected Bond lengths (Å) and angles (°) for compounds Ar′Bi(C₆H₂tBu₂-3,5-O-4), 1, Ar′Bi[O₂C(C₆H₂tBu₂-3-5-O-4)-κ²O₂O′], 2, Ar′Bi[OSC(C₆H₂tBu₂-3-5-O-4)-κ²O₂S], 3, [Ar′Bi(C₆H₂tBu₂-3,5-OH-4)][BPh₄], [1-H][BPh₄].

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<th>1</th>
<th>2</th>
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<td>Bi–C(Ar′)</td>
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<td>2.215(3)</td>
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<td>2.544(2),</td>
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<td>2.619(2)</td>
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<td>92.9(2)</td>
<td>98.8(2)</td>
<td>93.34(9)</td>
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Table 2.5. Selected Bond lengths (Å) and angles (°) for compounds {Ar′Bi[O₂C(C₆H₂tBu₂-3-5-OH-4)-κ²O₂O′]}[BF₄], 2-H][BF₄], [Ar′Bi(C₆H₂tBu₂-3,5-OSiMe₃-4)][CF₃SO₃], 6, Ar′Bi(CN)(C₆H₂tBu₂-3,5-OSiMe₃-4), 7, and Ar′Bi(N₃)₂, 9.

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<tr>
<th></th>
<th>2-H][BF₄]</th>
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<td>2.561(2)</td>
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<td>89.2(2)</td>
<td>93.14(7)</td>
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REFERENCES

(1) Soran, A. P.; Silvestru, C.; Breunig, H. J.; Balázs, G.; Green, J. C. Organometallics 2007, 26, 1196.
(22) Colorless crystals were isolated from the reaction of compound 2 and [NO][BF4] in acetonitrile. See chapter 4 for relevant NO chemistry.
(34) Villinger, A.; Schulz, A. Angew. Chem., Int. Ed. 2010, 49, 8017.
Chapter 3

Bismuth-Based Cyclic Synthesis of 3,5-Di-tert-butyl-4-hydroxybenzoic Acid
via the Oxyarylcarboxy Dianion, (O_{2}CC_{6}H_{2}'Bu_{2}O)^{2-}

INTRODUCTION

As described in Chapter 2, synthetic studies of bismuth aryloxide chemistry have led to a series of new dianionic ligands, specifically the oxyaryl (C_{6}H_{2}'Bu_{2}-3,5-O-4)^{2-}, oxyarylcarboxy [O_{2}C(C_{6}H_{2}'Bu_{2}-3,5-O-4)]^{2-}, and oxyarylthiocarboxy [OS(C_{6}H_{2}'Bu_{2}-3,5-O-4)]^{2-} dianions that contain both an oxo group and aryl, carboxy or thiocarboxy components.\(^{1,2}\) As shown in Scheme 3.1, these dianionic ligands are accessible by the reaction of the NCN phenyl pincer complex of bismuth dichloride, Ar′BiCl_{2} \([\text{Ar′} = 2,6-(\text{Me}_{2}NCH}_{2})_{2}C_{6}H_{3}]\), with potassium 2,6-di-tert-butylphenolate, KOAr.\(^{1,2}\) Precedent for the bismuth-based C–H bond activation in the first reaction in Scheme 3.1, which provides the synthetic access to these dianionic ligands, can be found in the use of bismuth in catalytic oxidation and ammonoxidation of propene to form acrolein and acrylonitrile in the SOHIO process.\(^{3-6}\) In those catalytic processes, bismuth is thought to perform the hydrogen abstraction necessary for the propene activation.\(^{3}\) The mild CO_{2} activation in the second reaction in Scheme 3.1 was the first observation of CO_{2} insertion into a bismuth carbon bond.\(^{2}\)

\(^{†}\) Portions of this chapter have been published: Kindra, D. R.; Evans, W. J. Dalton Transactions 2014, 43, 3052.
Scheme 3.1. Synthesis of complexes containing oxyaryl (1), oxyarylcarboxy (2), and oxyarylthiocarboxy (3) dianions.

Exploration of the utility of these reactions and the new dianionic ligands in synthesis has revealed that this C–H and CO$_2$ activation chemistry can be used in a synthetic cycle to make 3,5-di-tert-butyl-4-hydroxybenzoic acid. This carboxylic acid is used in biomedical applications as a precursor to antiviral compounds$^7$ and to cyclooxygenase inhibitors.$^8$ Although it is not an expensive chemical, the published syntheses, which are largely in the patent literature,$^9$$^{12}$ typically functionalize the parent phenol with carbon dioxide by heating (80–210 °C) under high pressure (5–15 atm) with exposure to strong base.$^{11,12}$

The process described below demonstrates that bismuth, a metal rarely used in catalysis or CO$_2$ activation, can effect this synthesis in a cyclic manner at ambient temperatures under an atmosphere of carbon dioxide. Also reported in this chapter is the facile decarboxylation reaction of the oxyarylcarboxy intermediate in the cycle, Ar′Bi[O$_2$C(C$_6$H$_3$′Bu$_2$-3-5-O-4)-κ$^2$O,O′],
to show the reversible nature of this bismuth-centered CO₂ chemistry and the use of the oxyarylcarboxy dianion complex to make a silyl ether silyl ester in one step.

RESULTS

The first two reactions in Scheme 3.1 provide the oxyarylcarboxy dianion complex, Ar′Bi[O₂C(C₆H₄Bu₂-3-5-O-4)-κ²O₂O'], 2, which contains the conjugate base of the target compound, 3,5-di-tert-butyl-4-hydroxybenzoic acid, 10.¹³⁻¹⁵ Double protonation of 2 can be effected by [Et₃NH][Cl] in a reaction that reforms Ar′BiCl₂, the starting material in Scheme 3.1. As shown in Scheme 3.2, this sequence constitutes a cyclic process for the formation of 10 in which the (Ar′Bi)²⁺ unit is used catalytically. The net reaction is given in eq 3.1.

\[
2 \text{ KOAr} + \text{ CO}_2 + 2[\text{Et}_3\text{NH}][\text{Cl}] \rightarrow 10 + 2 \text{ KCl} + 2 \text{ Et}_3\text{N} + \text{ HOAr} \quad (3.1)
\]

The isolated yields of the individual reactions starting with the formation of 1 are (a) 61%, (b) 73% and (c) 88%, which combine for an overall yield of 39% for 10 with respect to bismuth. If the carboxylic acid is synthesized in a stepwise manner, but without isolating the intermediates, a final overall yield of 73% for 10 with respect to bismuth can be achieved. Ar′BiCl₂ is recovered in comparable yield. The identity and purity of 10 was demonstrated by GC-MS and ^1^H and ^1^3C NMR spectroscopy.¹⁵
Scheme 3.2. Reaction cycle for (a) C–H bond activation, (b) CO$_2$ insertion, and (c) protonation to make 3,5-di-tert-butyl-4-hydroxybenzoic acid using Ar′BiCl$_2$ catalytically.

Since the reagents, [Et$_3$NH][Cl] and KOAr, react to form 2,6-di-tert-butylphenol and KCl, and since [Et$_3$NH][Cl] protonates 1 to form [Ar′Bi(C$_6$H$_5$)$_2$′Bu$_2$-3,5-OH-4)][Cl], which does not insert CO$_2$, the sequence in Scheme 3.2 must be done in a cyclic stepwise manner rather than as a continuous catalytic process. In addition, there is spectroscopic evidence (Figure 3.1) that the first equivalent of [Et$_3$NH][Cl] reacts with 2 to form an intermediate such as Ar′Bi(Cl)[O$_2$C(C$_6$H$_5$)$_2$′Bu$_2$-3-5-OH-4)] that is susceptible to deprotonation by KOAr to regenerate 2. Unfortunately this compound always formed as a mixture with Ar′BiCl$_2$ and could not be isolated. The cyclic nature of the reaction facilitates the isolation of the product, since it is the only hexane soluble compound in the final reaction, (c).
Figure 3.1. $^1$H NMR spectrum of compound 2 and 1 equiv of [Et$_3$NH][Cl] in acetonitrile-$d_3$ showing evidence for the proposed intermediate Ar$'$Bi(Cl)[O$_2$C(C$_6$H$_5$Bu$_2$-3-5-OH-4)].

The use of [Et$_3$NH][BPh$_4$], instead of [Et$_3$NH][Cl], as a proton source was initially explored since the intermediate tetraphenylborate salt \{Ar$'$Bi[O$_2$C(C$_6$H$_5$Bu$_2$-3-5-OH-4)-$\kappa^2$O,O']$\}$[BPh$_4$], \textbf{[2-H][BPh$_4$]}, has already been described in Chapter 2. This ultimately proved unsuccessful, but led to an unexpected result. Colorless crystals with a different morphology than that observed for \textbf{[2-H][BPh$_4$]} were recovered from a concentrated acetonitrile solution of \textbf{[2-H][BPh$_4$]} stored at $-30$ °C for several days. These crystals were identified as the ligand redistribution product Ar$'$Bi[O$_2$C(C$_6$H$_5$Bu$_2$-3-5-OH-4)]$_2$, \textbf{11}, Figure 3.2, in which the Ar$'$Bi$^{2+}$ moiety is bound to two [O$_2$C(C$_6$H$_5$Bu$_2$-3-5-OH-4)]$^{1-}$ carboxylate ligands. The crystal structure contains two unique molecules in the unit cell that differ in the carboxylate coordination. One molecule contains one carboxylate ligand $\kappa^1$ bound to Bi and the other bound $\kappa^2$ as observed in
compound 2, [2-H][BPh₄], and [2-H][BF₄]. The other molecule contains two κ¹ bound carboxylate ligands. No evidence for the other expected ligand redistribution product, [Ar’Bi][BPh₄]₂, was observed and 11 was only observed to form under these conditions from {Ar’Bi[O₂C(C₆H₂Bu₂-3-5-OH-4)-κ²O,O’]}[BPh₄] or the (BF₄)⁻ analog, {Ar’Bi[O₂C(C₆H₂Bu₂-3-5-OH-4)-κ²O,O’]}[BF₄].

![ORTEP representation of both linkage isomers of Ar’Bi[O₂C(C₆H₂Bu₂-3-5-OH-4)]₂, 11, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

**Figure 3.2.** ORTEP¹⁶ representation of both linkage isomers of Ar’Bi[O₂C(C₆H₂Bu₂-3-5-OH-4)]₂, 11, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
All of the carboxylate ligands in 11 are monoanionic as confirmed by examination of the X-ray data. The C–O bond lengths range from 1.374(3) to 1.388(3) Å, which is consistent with C–O single bonds in phenols and are much longer than the intermediate distances of the dianionic oxyarylcarboxy ligand in compound 2. Similarly, the ring carbon-carbon bond distances in 11 do not show the short-long pattern seen in 1 and 2.

The bismuth–oxygen bonds of the κ1 ligands (two for Bi2 and one for Bi1) have similar bond distances at 2.352(2) Å (Bi1–O4), 2.341(2) Å (Bi2–O10), and 2.384(2) Å (Bi2–O7). The single κ2 bound ligand on Bi1 has bond distances of 2.650(2) and 2.450(2) Å. The asymmetry and length of the Bi–O[κ2-O2C(C6H5′Bu2-3-5-OH-4)] connection is different from the shorter, 2.336(5) Å, and symmetric Bi–O[κ2-O2C(C6H5′Bu2-3-5-OH-4)] attachment in {Ar′Bi(O2C(C6H5′Bu2-3-5-OH-4)-κ2O,O′)}[BF4], [2-H][BF4]. The remaining three Bi···O distances, 3.013 Å (Bi1–O5), 2.997 Å (Bi2–O11), and 3.452 Å (Bi2–O8), are each within the sum of the van der Waals radii of 3.8 Å.

An alternative route to 10 has been explored using potassium iodide to cleave the oxyarylcarboxy dianion, eq 3.2. This generates the dipotassium salt of 10, namely dipotassium 3,5-di-tert-butyl-4-oxidobenzoate, K2-10, and the NCN pincer diiodide, Ar′BiI2. Protonation of the dipotassium salt, K2-10, with two equiv of [Et3NH]Cl formed 10 in 70% overall yield. However, conversion of the NCN pincer diiodide, Ar′BiI2, back to the oxyarylcarboxy complex, 2, was surprisingly more difficult than that of the dichloride. The reaction of Ar′BiI2 and KOMe
analogous to the 4 h synthesis of 1\textsuperscript{1,2} from Ar'BiCl\textsubscript{2}, reaches completion only after 18 h. Hence, this KI route is not preferable to Scheme 3.2.

The oxyaryl complex 1 was reported to react with one and two equiv of R\textsubscript{3}SiX reagents (R = Me, Ph; X = CN, N\textsubscript{3}, Cl) to produce, in step-wise fashion, Ar'Bi(X)(C\textsubscript{6}H\textsubscript{4}Bu\textsubscript{2}-3,5-OSiR\textsubscript{3}-4) and Ar'BiX\textsubscript{2}, respectively.\textsuperscript{2} The analogous reaction of 1 equiv of trimethylsilyl chloride with the oxyarylcarboxy complex 2 did not produce an analogous isolable Ar'Bi(Cl)(O\textsubscript{2}CC\textsubscript{6}H\textsubscript{4}Bu\textsubscript{2}-3,5-OSiMe\textsubscript{3}-4) product. However, reaction of 2 with an excess of Me\textsubscript{3}SiCl produced Ar'BiCl\textsubscript{2} and the trimethylsilyl ether of the trimethylsilyl ester of 3,5-di-\textit{tert}-butyl-4-hydroxybenzoic acid, i.e., trimethylsilyl 3,5-di-\textit{tert}-butyl-4-(trimethylsilyloxy)benzoate, 12, eq 3.3. Compound 12 was characterized by NMR and IR spectroscopy and mass spectrometry in agreement with its formulation in eq 3.3.

\begin{equation}
\text{2} + 2 \text{Me}_3\text{SiCl} \rightarrow \text{(THF)} \rightarrow \begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array} + \begin{array}{c}
\text{'Bu}_3\text{Si} \\
\text{O}
\end{array}
\end{equation}

The oxyaryl dianion complex 1 was previously reported to react with one equiv of I\textsubscript{2}, to yield the known bismuth diiodide, Ar'BiI\textsubscript{2},\textsuperscript{18} and the product of coupling the aryl groups, (3,3',5,5'-tetra-\textit{tert}-butyl-4,4'-diphenoquinone), eq 3.4.\textsuperscript{19,20}

\begin{equation}
\text{1} \rightarrow \text{I}_2 \rightarrow \begin{array}{c}
\text{I} \\
\text{I}
\end{array} + \begin{array}{c}
\text{'Bu}_3\text{Si} \\
\text{O}
\end{array}
\end{equation}
An analogous reaction was performed with compound 2 to further explore the chemistry of the new oxyarylcarboxy dianionic ligand. Unexpectedly, this reaction quickly yielded the same products observed in eq 3.4, namely Ar′BiI₂ and the coupled aryl product, eq 3.5. These products required the oxyarylcarboxy ligand to undergo decarboxylation. To test this, the reaction was performed with the $^{13}$C labeled analog, 2-$^{13}$C, in a sealed J. Young NMR tube. Free $^{13}$CO₂ was observed by $^{13}$C NMR spectroscopy, confirming the rapid decarboxylation of the dianionic ligand in eq 3.5.

CONCLUSION

In conclusion, the C–H bond activation accessible from the bismuth NCN pincer complex, Ar′BiCl₂, can be combined with CO₂ activation and subsequent protonation to provide a cyclic route to 3,5-di-tert-butyl-4-hydroxybenzoic acid. The bismuth-based cycle requires only ambient temperature and 1 atm of CO₂ rather than a heated reaction under CO₂ pressure as previously reported and demonstrates the viability of using bismuth in CO₂ based processes. The oxyarylcarboxy dianion that is central to this cycle can be converted in one step to a silyl ether silyl ester derivative of 3,5-di-tert-butyl-4-hydroxybenzoic acid and it is easily decarboxylated with I₂.
EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. 1H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (13C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared neat on KBr salt plates on a Varian 1000 FT-IR system. GC-MS spectra were collected on a ThermoTrace MS and GC-MS instrument. High-resolution mass spectra (HRMS) were obtained from the UC Irvine Mass Spectrometry Facility. Potassium 2,6-di-tert-butylphenolate was synthesized via an adaptation of a literature procedure by treatment of the parent phenol with one equiv of KN(SiMe3)2 in toluene, followed by filtration of the resulting white solid, and washing with hexane.21 CO2 (99.98%) and 13CO2 (99%) were purchased from Airgas and Cambridge Isotope Laboratories, respectively. Phenol reagents were sublimed prior to use. [Et3NH][Cl] (≥ 99%) was purchased from Sigma-Aldrich. Ar′Bi(C6H2′Bu2-3,5-O-4), Ar′Bi[O2C(C6H2′Bu2-3-5-O-4)-κ2O,O΄], {Ar′Bi[O2C(C6H2′Bu2-3-5-OH-4)-κ2O,O΄]}[BPh4], and {Ar′Bi[O2C(C6H2′Bu2-3-5-OH-4)-κ2O,O΄]}[BF4] were prepared according to the literature.2

3,5-Di-tert-butyl-4-hydroxybenzoic Acid, 10. [Et3NH][Cl] (23 mg, 0.17 mmol) was added as a solid to a stirred yellow suspension of 2 (50 mg, 0.08 mmol) in THF (8 mL). After stirring for 30 min, the reaction mixture became clear and colorless. After stirring overnight, the solvent was removed under vacuum to yield an off-white solid which was stirred in hexane (10
mL) for 1 h. The insoluble material was collected by centrifugation and identified as Ar′BiCl₂ by ¹H and ¹³C NMR.¹⁸ Solvent was removed to yield the hexane soluble carboxylic acid, 10 (17 mg, 88%), identified by ¹H and ¹³C NMR spectroscopy and GC-MS.¹⁵

**Dipotassium 3,5-di-tert-butyl-4-oxidobenzoate, K₂-10.** Solid KI (77 mg, 0.46 mmol) was added to a stirring yellow mixture of 2 (100 mg, 0.15 mmol) in THF (10 mL). After stirring overnight, the solvent was removed by vacuum and the yellow solids washed with hexane (10 mL). The yellow solids were extracted with minimum THF and these extractions dried under vacuum to give K₂-10 as an off-white solid (35 mg, 70%). ¹H NMR (500 MHz, acetonitrile-d₃): δ 7.76 [s, 2H, KOC₆H₂tBu₂CO₂K], 1.38 [s, 18H, KOC₆H₂tBu₂CO₂K]. K₂-10 was protonated with 2 equiv of [Et₃NH][Cl] to yield 10, identified by GC-MS and ¹H NMR spectroscopy,¹⁵ and KCl.

**Trimethylsilyl 3,5-di-tert-butyl-4-((trimethylsilyl)oxy)benzoate, 12.** To a stirred yellow mixture of 2 (97 mg, 0.15 mmol) in THF (10 mL) was added excess Me₃SiCl (0.1 mL, 0.8 mmol) inducing a rapid fading of color, with the reaction mixture becoming clear and colorless after 20 min. After stirring overnight, the solvent was removed by vacuum and the white solids were stirred in hexane (10 mL). White insoluble material was collected and identified as Ar′BiCl₂ by NMR spectroscopy.¹⁸ Hexane was removed under vacuum to yield 12 as a white solid (43 mg, 73%). ¹H NMR (500 MHz, benzene-d₆): δ 8.42 [s, 2H, Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 1.30 [s, 18H, Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 0.37 [s, 9H, Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 0.30 [s, 9H, Me₃SiOC₆H₂tBu₂CO₂SiMe₃]. ¹³C NMR (125 MHz, benzene-d₆): δ 167.6 [Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 158.3 [Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 141.7 [Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 124.5 [Me₃SiOC₆H₂tBu₂CO₂SiMe₃], 35.7 [Me₃SiOC₆H₂(CMe₃)₂CO₂SiMe₃], 31.6 [Me₃SiOC₆H₂(CMe₃)₂CO₂SiMe₃], 4.1
[Me₃SiOC₆H₄Bu₂CO₂SiMe₃], 0.3 [Me₃SiOC₆H₄Bu₂CO₂SiMe₃]. IR: 3036w, 2958m, 1692s, 1601w, 1418m, 1364w, 1310s, 1250s, 1151m, 1124m, 906s, 851s, 780m, 639w cm⁻¹. HRMS (Cl+) m/z cald for C₄₁H₃₈O₃Si₂ (M+H)⁺ 395.2438, found 395.2439.

**Reaction of 2 with Iodine.** In an argon-filled glovebox, a brown THF (3 mL) solution of I₂ (33 mg, 0.13 mmol) was added to a stirred yellow mixture of 2 (85 mg, 0.13 mmol) in THF (8 mL). The reaction mixture quickly turned clear and red/brown. After stirring for 4 h, the solvent was removed under vacuum. The resulting yellow solids were extracted with hexane (10 mL) leaving off-white insoluble material identified by ¹H and ¹³C NMR spectroscopy as Ar′BiI₂. The red hexane extract was dried to yield red solids identified by ¹H and ¹³C NMR spectroscopy and GC-MS as the coupled product (3,3′,5,5′-tetra-tert-butyl-4,4′-diphenoquinone).⁰¹⁸

**Ar′Bi[O₂C(C₆H₄Bu₂-3-5-OH-4)]₂, 11, from [2-H][BPh₄].** A concentrated acetonitrile solution of [2-H][BPh₄] was allowed to stand at −30 °C for several days. X-ray quality crystals of different morphology than that observed for crystals of [2-H][BPh₄] grown under the same conditions were recovered and identified as 11. **Ar′Bi[O₂C(C₆H₄Bu₂-3-5-OH-4)]₂, 11, from [2-H][BF₄].** A concentrated acetonitrile solution of [2-H][BF₄] was allowed to stand at −30 °C for several days. Compound 11 was identified by X-ray crystallography.

**X-ray Crystallographic Data.** Crystallographic information for complexe 11 is summarized in Table 3.1. Selected bond distances are in Table 3.2.
### Table 3.1. X-ray data collection parameters for 11.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(C_{42}H_{61}BiN_{6}O_{6})<em>a / (C</em>{42}H_{61}BiN_{6}O_{6})<em>b * 3(CH</em>{3}CN)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1920.97</td>
</tr>
<tr>
<td>T(K)</td>
<td>88(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>24.4396(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>24.2866(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15.5450(6)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
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</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
</tr>
<tr>
<td>Volume Å³</td>
<td>8982.7(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calcd} (Mg/m³)</td>
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</tr>
<tr>
<td>μ (mm⁻¹)</td>
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</tr>
<tr>
<td>R1 [I &gt; 2.0σ(I)]</td>
<td>0.0262</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.0582</td>
</tr>
</tbody>
</table>

### Table 3.2. Selected bond lengths (Å) and angles (°) for compound Ar′Bi(O₂C(C₆H₄Bu₂-3-5-OH-4))₂, 11, compared to known compounds 2 and [2-H][BF₄].

<table>
<thead>
<tr>
<th>Bond Lengths/Angles</th>
<th>11</th>
<th>2</th>
<th>[2-H][BF₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi–C(Ar′)</td>
<td>2.208(3); 2.194(3)</td>
<td>2.215(3)</td>
<td>2.197(7)</td>
</tr>
<tr>
<td>Bi–N(Ar′)</td>
<td>2.582(2), 2.597(2); 2.577(2), 2.501(2)</td>
<td>2.542(3), 2.549(3)</td>
<td>2.513(6), 2.542(6)</td>
</tr>
<tr>
<td>Ar′–Bi–O(κ¹-O₂C(C₆H₄Bu₂-3-5-OH-4))</td>
<td>87.95(8), 86.91(9)</td>
<td>92.9(2)</td>
<td>89.2(2)</td>
</tr>
<tr>
<td>O–Bi–O</td>
<td>152.37(7); 166.71(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES

(15) Spectral Database for Organic Compounds (SDBS); 1H and 13C NMR; SDBS No.: 15294; RN 1421-49-4; http://sdb.siodb.aist.go.jp/sdb/sdb-bin/cre_index.cgi (accessed September 11, 2013).
Chapter 4

Nitric Oxide Insertion Reactivity with the Bismuth–Carbon Bond:
Formation of the Oximate Anion, \([\text{ON}=(\text{C}_6\text{H}_2\text{'Bu}_2\text{O})]^\text{1−}\), from the Oxyaryl Dianion, \((\text{C}_6\text{H}_2\text{'Bu}_2\text{O})^\text{2−}\)

INTRODUCTION†

Nitric oxide, NO, is a simple heterodiatomic molecule that is critical in many areas of science and technology.\(^1\text{−}^4\) It is a significant component in the atmospheric chemistry of smog,\(^5\) the industrial chemistry of nitric acid and its derivatives,\(^6\) and the biological chemistry of physiological processes related to nerve impulse, blood pressure, and immune systems.\(^7,8\) The radical nature of NO allows both oxidation to \((\text{NO})^\text{1+}\) and reduction to \((\text{NO})^\text{1−}\) to occur, whereas in biological systems, a protonated form designated HNO is accessible.\(^9\) Recently, the first example of an \((\text{NO})^\text{2−}\) complex was identified.\(^10\)

Due to this extensive chemistry, the reactivity of NO has been thoroughly examined with most of the elements in the periodic table.\(^1\text{1−}^3\text{3}\) An exception is with bismuth, a metal that historically has been understudied.\(^1\text{4}\) I now report bismuth NO chemistry and specifically, the NO reactivity of the previously reported \(\text{Ar''Bi(C}_6\text{H}_2\text{'Bu}_2\text{-3,5-O-4)}\), \(\text{I}\), \([\text{Ar''} = 2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\), a \(\text{Bi}^{3+}\) complex of the unusual oxyaryl dianion, \((\text{C}_6\text{H}_2\text{'Bu}_2\text{O})^\text{2−}\) described in Chapter 2.\(^1\text{5}\) The reactivity of NO was of interest to probe the chemistry of the Bi–C bond of this dianionic ligand that is generated by C–H bond activation and rearrangement from the reaction of \(\text{KOC}_6\text{H}_3\text{'Bu}_2\text{-2,6}\) with the NCN pincer stabilized bismuth dichloride, \(\text{Ar''BiCl}_2\), Scheme 4.1.\(^1\text{5}\)

† Portions of this chapter have been published: Kindra, D. R.; Casely, I. J.; Ziller, J. W.; Evans, W. J. *Chemistry A European Journal* DOI: 10.1002/chem.201404910
Complex 1 reacts with NO in contrast to BiPh₃ which, when exposed to 1 atm of NO gas for 24 h, shows no reaction.

![Scheme 4.1](image)

**Scheme 4.1.** Synthesis of Ar′Bi(C₆H₂′Bu₂-3,5-O-4), 1, and the reaction between 1 and CO₂.¹⁵,¹⁶

To fully identify the reaction products of this direct reaction of NO gas with the oxyaryl bismuth–carbon linkage in 1, independent syntheses were carried out with the NO delivery reagent Ph₃CSNO and with the previously reported bismuth complex of the oxyarylcarboxy dianion, [O₂C(C₆H₂′Bu₂-3-5-O-4)]²⁻, 2, formed from 1 and CO₂ (Scheme 4.1).¹⁶ This has led to the first examples of NO insertion into a bismuth–carbon bond, unusual NO insertion chemistry, and structural data on the quinoidal oximate ligand, [ON=(C₆H₂′Bu₂O)]¹⁻.¹⁷

**RESULTS AND DISCUSSION**

A red acetonitrile solution of the oxyaryl complex, Ar′Bi(C₆H₂′Bu₂-3,5-O-4), 1,¹⁵ reacted with NO at 1 atm, eq 4.1, to form a dark green solution that contains multiple products identified by ¹H NMR spectroscopy. Reactions conducted at low temperature (−35 °C) and with stoichiometric amounts of NO gas also gave complicated product mixtures. However, from the
room temperature reaction, yellow crystals of \([\text{Ar'}\text{Bi(ONC}_6\text{H}_2\text{-3,5-}^t\text{Bu}_2\text{-4-O})]_2(\mu\text{-O}),\ 13\), were obtained at \(-30\ °\ C\) from the crude acetonitrile reaction mixture, Figure 4.1. Subsequently, yellow crystals of \(\text{Ar'}\text{Bi(ONC}_6\text{H}_2\text{-3,5-}^t\text{Bu}_2\text{-4-O})_2,\ 14\), were obtained at room temperature from the same mother liquor, Figure 4.2. The structures of these products were defined by X-ray crystallography.

Figure 4.1. ORTEP\(^{18}\) representation of \([\text{Ar'}\text{Bi(ONC}_6\text{H}_2\text{-3,5-}^t\text{Bu}_2\text{-4-O})]_2(\mu\text{-O}),\ 13\), from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The two bismuth centers are bound by a bridging oxygen (O1).
Figure 4.2. ORTEP representation of Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)₂, 14, with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The reaction involves a relatively rare example of insertion into an M–X bond by NO gas. Although NO is highly reactive, it typically reacts either as a) an oxidant to form complexes of (NO)⁻; b) as a reductant to form complexes of (NO)¹⁺; or c) as an oxide delivery agent. Migratory insertion of bound (NO)⁻ ligands and insertion of (NO)¹⁺ by reaction with [NO][X] reagents, such as [NO][BF₄], are far more common than insertion reactions with nitric oxide gas.

In equation 4.1, the formal insertion of NO into the Bi–C bond of the (C₆H₂₄₄₃₅₆-O-4)²⁻ dianion generates the oximate ligand, [ON=(C₆H₂₄₄₃₅₆O)]⁻, which is present in both 13 and 14. The sodium salt of this oximate has been described as an intermediate formed in solution in reactions of NO with phenolates, but to my knowledge, it has not been previously isolated. Compound 13 contains two [Ar′Bi(oximate)]¹⁺ moieties linked by a bridging oxide, whereas 14 contains two oximate units bound to a single [Ar′Bi]²⁺ moiety. Because the N–O bond order in the oximate is one, the oxyaryl dianion is formally oxidized and the NO reduced in the reaction. Conversion of the oxyaryl dianion in 1 to the oximate monoanion creates a charge imbalance at
the Bi$^{3+}$ center allowing coordination of the oxide ligand in 13. The origin of the oxide is unknown, but it could arise from another equivalent of NO acting as an oxygen-delivery agent. The presence of the two oxyaryl-dianion-derived oximate ligands in 14 indicates that ligand redistribution is occurring under the reaction conditions.

Because 13 and 14 were formed as a mixture shown in eq 4.1, efforts were made to synthesize them in pure form from other precursors. The oxyarylcarboxy complex, Ar$^+$Bi[O$_2$C(C$_6$H$_2$Bu$_2$-3-5-O-4)-κ$^2$O,O'], 2, formed from 1 and CO$_2$, had previously been shown to undergo facile decarboxylation under mild conditions in a reaction with I$_2$ and therefore had the potential to act as a surrogate for 1. Accordingly, its reactivity with NO was examined. Compound 2 reacts with NO at atmospheric pressure to form an emerald green solution similar to that of the reaction mixture shown in eq 4.1. Yellow crystals identified as 13 by X-ray crystallography were isolated in >90% yield, eq 4.2, and allowed this oximate complex to be spectroscopically characterized in pure form (see below).

![Diagram](image)

When the reaction was performed in deuterated solvents in a sealed J. Young NMR tube, free carbon dioxide could be observed in the $^{13}$C NMR spectrum, confirming decarboxylation of the [O$_2$C(C$_6$H$_2$Bu$_2$-3-5-O-4)]$^{2-}$ ligand in 2 as part of the reaction process.
The isolation of pure 13 allowed the development of a route to isolate 14. Reaction of 13 with two equivalents of either [Et₃NH][Cl] or Me₃SiCl forms primarily one equivalent of Ar'BiCl₂ and one equivalent of 14, as was identified by NMR spectroscopy and X-ray crystallography, eq 4.3.

Again, ligand redistribution is apparently involved. Although a mixture was formed, as shown in eq 4.3, separation is now possible, because Ar'BiCl₂ is much less soluble in THF, and this allows 14 to be isolated in 45% yield with respect to bismuth. It is fortunate that the kinetics of these reactions allow the isolation of 14, because it also reacts with both [Et₃NH][Cl] and Me₃SiCl to make Ar'BiCl₂.

An additional by-product isolated from eq 4.2 was a small amount of the polymeric carbonate species [Ar'Bi(μ-κ¹:κ²-CO₃)]ₙ, as was identified by X-ray crystallography.²⁷ Formation of the carbonate as a minor product is reasonable, because free CO₂ is observed in the reaction vessel, and oxide formation was observed in the NO reaction, eq 4.1. Resonances consistent with small amounts of (Me₃Si)₂O²⁸ and the silylated oximate, Me₃SiON=(C₆H₄′Bu₂O), were observed by ¹H NMR and GC-MS techniques when 13 was reacted with Me₃SiCl.

Another approach to avoid the complicated mixture of products from the NO reaction in eq 4.1, was to examine reactions with the alternative NO source, Ph₃CSNO.²⁹ This reagent
reacted with 1 to form another fully characterized complex of the oximate ligand, the bright orange (Ph₃CS)(Ar′)Bi(ONC₆H₂-3,5-tBu₂-4-O), 15, eq 4.4. This complex can be obtained cleanly in >90% yield and was crystallographically identified, Figure 4.3. In this case, the “[Ar′Bi(ONC₆H₂tBu₂O)]¹⁺” unit was trapped by a (Ph₃CS)⁻ ligand before ligand redistribution or coordination to oxide occurred, as was found in eq 4.1. This demonstrates the value of the Ph₃CSNO reagent as a substitute for NO.
Figure 4.3. ORTEP representation of \((\text{Ph}_3\text{CS})(\text{Ar}')\text{Bi}(\text{ONC}_6\text{H}_2-3,5-\text{Bu}_2-4-\text{O})\), 15, from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The structures of 13–15 contain \([\text{Ar}'\text{Bi}]^{2+}\) moieties with conventional Bi–C(Ar’) bond lengths ranging from 2.184(3) to 2.235(4) Å.\(^{16}\) The 2.493(3) to 2.576(3) Å Bi–N bond lengths of the pincer arms in 14 and 15 are also typical for \([\text{Ar}'\text{Bi}]^{2+}\) compounds.\(^{16,27,30}\) However, in 13, there is asymmetry in its Bi–N bonds, in which one arm of each pincer ligand has typical bond lengths (2.629(4) and 2.636(4) Å), whereas the other is much longer (2.845(4) and 2.910(4) Å). The latter long bond lengths are still within the sum of the van der Waals radii of 3.9 Å, but
suggest less interaction as is sometimes observed with Ar'Bi$^{2+}$ complexes.$^{16,31}$ This is part of the flexible nature of the Ar' ligand.

The first structural data on the [ON=(C$_6$H$_2$Bu$_2$O)]$^{1-}$ oximate ligand, obtained in complexes 13–15, revealed metrical parameters that are consistent with the quiniodal structures drawn in eq 4.1–4.4. These are shown in Figure 4.4 in comparison with the dianionic ligands in 1 and 2. Two values are shown for each distance in 13 and 14, because they have two oximate ligands per molecule. Two of the C–C bonds in each of the [ON=(C$_6$H$_2$Bu$_2$O)]$^{1-}$ ligands in 13–15 are in the 1.347 to 1.358 Å range of a double bond and the C–O bond lengths, 1.232 to 1.239 Å, are also in the double-bond range.$^{32}$ In contrast, structures of the dianionic ligands in 1 and 2 are more delocalized.
Figure 4.4. Bond distances in the oximate ligands of compounds 13, 14, and 15 compared to the dianionic oxyaryl and oxyarylcarboxy ligands in 1 and 2, respectively. Compounds containing two oximate ligands (13 and 14) list both distances for each bond.

The analogous C–C distances in 1 and 2 are longer, 1.372(3) to 1.384(3) Å, as are the C–O bond lengths, 1.265(4) to 1.278(2) Å. The 1.315(4) to 1.336(4) Å C–N bonds in 13–15 are slightly longer than those typically found in organic oximes, R₂C=NOH (1.281 Å), and the 1.317(4) to 1.349(3) Å N–O bonds of the inserted (NO)⁻ moiety are in the single-bond range.

Although the structural parameters are consistent in 13–15 and the Bi–C(Ar') distances of each are conventional, the Bi–O(oximate) bonds vary significantly in the three complexes as do the Bi–O–N angles: 2.277(3) Å [108.6(2)°] and 2.284(3) Å [103.1(2)°] for 13, 2.295(2) Å [105.6(2)°] and 2.364(2) Å [99.8(2)°] for 14, and 2.455(2) Å [95.8(2)°] for 15. More acute Bi–
O–N angles were found with the longer distances in 14 and 15. In comparison to these Bi–O lengths, the 2.053(3) and 2.090(3) Å Bi–O(oxide) distances in 13 are much shorter. The pairs of Bi–O(oximate) distances in 14 and the two Bi–O(oxide) distances in 13 show a surprising disparity within the pair considering they are from chemically equivalent bonds. In comparison, the Ar′Bi(OC₆H₃R₂-2,6)₂ series have Bi–O bonds that fall in a more narrow range: 2.2972(17) and 2.3068(17) Å for R = Me, 2.2969(16) and 2.3000(16) Å for R = iPr, and 2.350(3) and 2.321(3) Å for Ar′Bi(OC₆H₂Bu₂-2,6-Me-4). The larger Bi–O distance in 15 may arise due to the large size of the (Ph₃CS)⁻ ligand. However, [Ar′Bi(μ-κ¹:κ²-CO₃)]₄²⁻ also has long Bi–O bonds of 2.402(7), 2.411(8), and 2.412(7) Å. Overall, these structures demonstrate the flexibility of the (Ar′Bi)²⁺ unit to stabilize a diverse set of aryloxide-derived ligands with both localized and delocalized structures and variable Bi–O bond distances.

¹H NMR spectroscopy on the pure oximate products showed a 1:1 ratio of [ON=(C₆H₂Bu₂O)]⁻ to Ar′ resonances for 13 that is qualitatively similar to the spectrum of 14, which has a 2:1 ratio of resonances. The ¹H NMR spectrum of 15 differs in that the resonances of the methylene protons of the Ar′ ligand are split as is found for 1,¹⁶ as well as some other Ar′Bi²⁺ compounds in the literature.¹⁵,¹⁶,³³ Compounds 2, 13, and 14 did not show this splitting of the Ar′ ligand resonances, even though the solid-state structure of 13 showed two different types of Bi–N distances.

The UV-vis spectrum of 13 showed a solvent dependence, Figure 4.5, not found for 1, 2, 14, and 15. In THF and MeCN, complex 13 is green due to an absorption at λ = 639 nm (ε = 2900 M⁻¹cm⁻¹) in THF and 634 nm (ε = 1600 M⁻¹cm⁻¹) in MeCN, in addition to the maxima at approximately 375 nm (ε = 80000 M⁻¹cm⁻¹). The second absorption is not observed when 13 is dissolved in toluene, diethyl ether, or dichloromethane and 13 is yellow. In contrast, the yellow
orange complexes, 1, 2, 14, and 15, each show only single maxima at $\lambda = 467$ nm (6900 m$^{-1}$cm$^{-1}$), 379 nm (61700 M$^{-1}$cm$^{-1}$), 397 nm (37400 M$^{-1}$cm$^{-1}$), and 357 nm (15700 M$^{-1}$cm$^{-1}$), respectively. The large molar absorptivity values are consistent with p–p* transitions.34

![Graph showing UV-vis absorption spectra](image)

Figure 4.5. UV-vis of compound 13 in THF (black), DCM (red), Et$_2$O (green), MeCN (blue) and toluene (orange). In only THF and MeCN is the second absorption at ca. 600 nm present.

CONCLUSION

The reaction of NO with the oxyaryl dianion complex, Ar'Bi(C$_6$H$_2$'Bu$_2$-3,5-O-4), 1, has provided the first example of NO insertion into a Bi–C bond. This has led to the first fully characterized examples of the oximate ligand, [ON=(C$_6$H$_2$'Bu$_2$O)]$^{1-}$ in three different molecules, namely, [Ar'Bi(ONC$_6$H$_2$-3,5-'Bu$_2$-4-O)]$_2$(μ-O), 13, Ar'Bi(ONC$_6$H$_2$-3,5-'Bu$_2$-4-O)$_2$, 14, and
(Ph₃CS)(Ar′)Bi(ONC₆H₂-3,5-′Bu₂-4-O), 15. Although the C–C and C–O distances in these quinoidal oximates are similar, their Bi–O distances show surprising variation. The utility of carboxyaryloxy Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-O-4)-κ²O,O′] and Ph₃CSNO as synthetic substitutes for 1 and NO, respectively, was also demonstrated.

**EXPERIMENTAL DETAILS**

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water by using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze/pump/thaw cycles, and vacuum transferred before use. ¹H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (¹³C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FTIR system. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer and proved to be problematic with the oximate complexes compared to other Ar′Bi complexes. Incomplete combustion was often observed and multiple samples had to be analyzed. Nitric oxide (NO) gas was purchased from Aldrich (98.5%) and was passed through two U-shaped glass columns connected in series and cooled to −78 °C before use. [Et₃NH][Cl] (≥99%, Sigma–Aldrich) was used as purchased. Ph₃CSNO,²⁹ Ar′Bi(C₆H₂′Bu₂-3,5-O-4), 1,¹⁶ and Ar′Bi[O₂C(C₆H₂′Bu₂-3-5-O-4)-κ²O,O′], 2,¹⁶ were prepared according to the literature.
**Reaction of Ar′Bi(C₆H₂/₅Bu₂-3,5-O-4) with NO.** A 100 mL Schlenk flask fitted with a high-vacuum Teflon stopcock was charged with a red solution of 1 (100 mg, 0.17 mmol) in acetonitrile (10 mL). The flask was placed on a high-vacuum line, degassed, and charged with 1 atm of NO. After stirring at RT for 1 h, a dark green mixture was formed. The flask was degassed with three freeze/pump/thaw cycles and transferred to an argon-filled glovebox. Yellow crystals of [Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)]₂(μ-O), 13, suitable for X-ray diffraction analysis were isolated from a concentrated acetonitrile solution at −30 °C. Subsequently, yellow crystals of Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)₂, 14, suitable for X-ray diffraction analysis were isolated from a concentrated acetonitrile solution in an NMR tube that was left at RT for two days.

**Synthesis of [Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)]₂(μ-O), 13.** A Schlenk flask (100 mL) fitted with a high-vacuum Teflon stopcock was charged with a yellow suspension of 2 (100 mg, 0.15 mmol) in THF (12 mL). The flask was placed on a high-vacuum line, degassed, and charged with 1 atm of NO. After stirring at RT for 1 h, a dark red solution formed. The reaction mixture was stirred overnight and then degassed. Upon degassing a rapid color change to emerald green was effected. The flask was transferred to an argon filled glovebox and the solvent was removed under reduced pressure to give 13 as a green solid (90 mg, 91%). ¹H NMR (500 MHz, acetonitrile-d₃): δ 7.69 [d, 4H, m-(Me₂NCH₂)₂C₆H₃], 7.55 [t, 2H, p-(Me₂NCH₂)₂C₆H₃], 7.36 [s, 2H, ON=(C₆H₂/Bu₂O)], 7.20 [s, 2H, ON=(C₆H₂/Bu₂O)], 4.20 [s, 8H, (Me₂NCH₂)₂C₆H₃], 2.57 [s, 24H, (Me₂NCH₂)₂C₆H₃], 1.29 [s, 18H, ON=(C₆H₂/Bu₂O)], 1.20 ppm [s, 18H, ON=(C₆H₂/Bu₂O)]. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 187.9, 156.0, 134.1, 130.8, 129.2, 116.6 [(Me₂NCH₂)₂C₆H₃ and ON=(C₆H₂/Bu₂O)], 68.7 [(Me₂NCH₂)₂C₆H₃], 46.2 [br s, (Me₂NCH₂)₂C₆H₃], 36.2 [q-ON=(C₆H₂(CMe₃)₂O)], 35.8 [q-ON=(C₆H₂(CMe₃)₂O)], 30.1 ppm.
[ON=(C₆H₂(CMe₃)₂O)]. IR: 2954 s, 2924 s, 2858 s, 1604 m, 1453 s, 1357 s, 1296 s, 1247 s, 1103 m, 1060 m, 1016 s, 927 s, 883 w, 840 m cm⁻¹. Anal. Calcd for C₅₂H₇₈Bi₂N₆O₅: C, 48.60; H, 6.12; N, 6.54; found: C, 47.11; H, 6.02; N, 6.35. Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated acetonitrile solution at −30 °C.

**Synthesis of Ar′Bi(ONC₆H₂-3,5-Bu₂-4-O)₂, 14, from 13 and [Et₃NH][Cl].** Solid [Et₃NH][Cl] (27 mg, 0.19 mmol) was added to a stirred emerald green solution of 13 (120 mg, 0.10 mmol) in THF (10 mL). After stirring overnight, the reaction mixture was a dark yellow solution. The solvent was removed under vacuum leaving off-white solids that were stirred in a THF/hexane (2:3) solution. White solids were separated from the yellow supernatant by centrifugation and dried. The insoluble white solids were identified as the known Ar′BiCl₂ by ¹H NMR spectroscopy.³⁰ The soluble fraction upon drying gave an orange tacky solid, which was washed with hexane to give 14 as an orange solid (77 mg, 45% yield with respect to bismuth).

¹H NMR (500 MHz, acetonitrile-d₃): δ 7.79 [d, 2H, m-(Me₂NCH₂)₂C₆H₃], 7.58 [t, 1H, p-(Me₂NCH₂)₂C₆H₃], 7.42 [s, 2H, ON=(C₆H₂(Bu₂O))], 7.11 [s, 2H, ON=(C₆H₂(Bu₂O))], 4.29 [s, 4H, (Me₂NCH₂)₂C₆H₃], 2.65 [s, 12 H, (Me₂NCH₂)₂C₆H₃], 1.28 [s, 18H, ON=(C₆H₂(Bu₂O))], 1.22 ppm [s, 18H, ON=(C₆H₂(Bu₂O))].¹³C NMR (125 MHz, acetonitrile-d₃): δ 187.9, 138.9, 132.9, 130.4, 129.2, 117.0, and 112.5 [(Me₂NCH₂)₂C₆H₃ and ON=(C₆H₂(Bu₂O))), 68.9 [(Me₂NCH₂)₂C₆H₃, 47.0 [br s, (Me₂NCH₂)₂C₆H₃], 36.1 [q-ON=(C₆H₂(CMe₃)₂O)], 35.6 [q-ON=(C₆H₂(CMe₃)₂O)], 29.8 ppm [ON=(C₆H₂(CMe₃)₂O)]. IR: 2957s, 2918m, 2867m, 1608s, 1455s, 1388w, 1356s, 1299s, 1248s, 1091m, 1055s, 1014s, 924s, 883m, 840m, 746w, 709m cm⁻¹. Anal. Calcd for C₄₀H₉₉BiN₄O₄: C, 55.29; H, 6.84; N, 6.45; found: C, 55.65; H, 7.13; N, 6.44. Crystals of 3 suitable for X-ray crystallography analysis were grown from a concentrated acetonitrile solution at RT.
Synthesis of Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)₂, 14, from 13 and Me₃SiCl. Neat Me₃SiCl (25 μL, 0.20 mmol) was added by microsyringe to a stirred emerald green solution of 13 (120 mg, 0.10 mmol) in THF (12 mL), which gave a rapid color change to yellow. After stirring overnight, the yellow reaction mixture was dried under reduced pressure, and the crude product was stirred in hexane (10 mL) for 1 h. Separation by centrifugation gave off-white insoluble material, which was identified as Ar′BiCl₂ by NMR spectroscopy. The hexane-soluble yellow solids were identified as 14 by X-ray crystallography and NMR spectroscopy.

Synthesis of (Ph₃CS)(Ar′)Bi(ONC₆H₂-3,5-tBu₂-4-O), 15. A green solution of Ph₃CSNO (50 mg, 0.17 mmol) in THF (6 mL) was added to a stirred dark red solution of 1 (100 mg, 0.17 mmol) in THF (4 mL). The solution turned light orange after 1 h. After stirring overnight, solvent was removed under vacuum to give a red sticky solid. This crude product was washed with hexane to give 15 as a bright orange powder (140 mg, 93 %). ¹H NMR (500 MHz, benzene-d₆): δ 7.82 [d, 6H, m-(C₆H₅)₃CS], 7.72 [s, 1H, ON=(C₆H₂tBu₂O)], 7.66 [s, 1H, ON=(C₆H₂tBu₂O)], 7.28 [d, 2H, m-(Me₂NCH₂)₂C₆H₃], 7.14 [m, 6H, o-(C₆H₅)₃CS], 7.02 [t, 3H, p-(C₆H₅)₃CS], 6.96 [t, 1H, p-(Me₂NCH₂)₂C₆H₃] 3.85 [d, 2H, (Me₂NC₂H₃)], 3.78 [d, 2H, (Me₂NC₂H₃)], 2.13 [br s, 12H, (Me₂NCH₂)₂C₆H₃], 1.62 [s, 9H, ON=(C₆H₂tBu₂O)], 1.43 [s, 9H, ON=(C₆H₂tBu₂O)]. ¹³C NMR (125 MHz, benzene-d₆): δ 205.5, 187.1, 155.9, 152.7, 147.8, 134.3, 131.5, 130.3, 129.1, and 115.7 [(Me₂NCH₂)₂C₆H₃ and ON=(C₆H₂tBu₂O)] 144.9 [(C₆H₅)₃CS], 126.6 [(C₆H₅)₃CS], 69.0 [(Me₂NCH₂)₂C₆H₃], 46.2 [br s, (Me₂NCH₂)₂C₆H₃], 36.0 [q-ON=(C₆H₂(CMe₂)₂O)], 35.6 [q-ON=(C₆H₂(CMe₂)₂O)], 30.3 [ON=(C₆H₂(CMe₂)₂O)]. IR: 2954m, 2864m, 1588s, 1485s, 1447s, 1356s, 1293s, 1245s, 1116s, 1074m, 1017m, 940s, 885w, 841m, 745m, 703s cm⁻¹. The sample for elemental analysis was recrystallized from THF as a THF solvate: Anal. Calcd for C₄₅H₅₄BiN₃O₂S•C₄H₈O: C, 59.93; H, 6.36; N, 4.28; found: C,
60.78; H, 6.08; N, 3.56. Crystals suitable for X-ray crystallography were grown from a saturated acetonitrile solution at RT.

**Synthesis of \((\text{Ph}_3\text{CS})(\text{Ar'})\text{Bi(ONC}_6\text{H}_2\text{-3,5-tBu}_2\text{-4-O})\), 15 from 2.** A green solution of \(\text{Ph}_3\text{CSNO}\) (26 mg, 0.085 mmol) in THF (2 mL) was added to a stirred yellow suspension of 2 (55 mg, 0.085 mmol) in THF (8 mL). After stirring overnight, the red reaction mixture was dried under reduced pressure to give a red sticky solid. After washing with hexane, the bright orange powder (70 mg, 90%) was identified as 15 by NMR spectroscopy.

**X-ray Crystallographic Data.** Crystallographic information for complexes 13, 14, and 15 is summarized in Table 4.1.

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<td>(c) (Å)</td>
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<td>(β) (deg)</td>
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Table 4.2. Selected bond lengths (Å) and angles (°) for compounds Ar′Bi(C₆H₄tBu₂-3,5-O-4), 1, [Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)]₂(µ-O), 13, Ar′Bi(ONC₆H₂-3,5-tBu₂-4-O)₂, 14, and (Ph₃CS)(Ar′)Bi(ONC₆H₂-3,5-tBu₂-4-O), 15.

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<td>Bi–C(Ar′)</td>
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Table 4.3. Selected bond lengths (Å) and angles (°) for compounds (Ph₃CS)(Ar′)Bi(ONC₆H₂-3,5-tBu₂-4-O), 15.

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<td>Bi–S</td>
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<tr>
<td>Bi–S–C(Ph₃C)</td>
<td>107.06(10)</td>
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</table>
REFERENCES

(14) Reactions of $N_2O_3$ with organometallic main-group complexes including BiPh$_3$ have been described, but no bismuth products were reported: L. G. Makarova, K. A. Nesmeyanov, *Zh. Obshch. Khim.* 1939, 9, 771.
INTRODUCTION

Tripodal ligands with appended functionality that can act as H-bond donors and acceptors, Scheme 5.1, have been used to successfully investigate small molecule binding to transition metals in a controlled coordination environment. The ligands shown have a tris(2-aminoethyl)amine (tren) backbone accompanied with substituents to control the secondary coordination sphere, or binding pocket, around the axial position of the metal center. These tren-based ligands have proven capable of isolating and characterizing highly reactive transition metal species via intramolecular hydrogen-bonding between the axial ligand and the specifically tuned substituents of the tren ancillary ligand. For example, the ligand tris[(N′-tert-butylureaylato)-N-ethyl]aminato ([H₃buea]³⁻), Scheme 5.1a, with hydrogen bonding donor groups, has allowed the isolation and spectroscopic and structural characterization of the only example of a non-heme iron(III) complex with a terminal oxo ligand derived directly from dioxygen. More recently, the ligand N,N′,N″-[2,2′,2′′-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) ([MST]³⁻), Scheme 5.1b, which has three hydrogen bonding acceptor groups, was used to isolate a Mn³⁺-(μ-OH)–Ca²⁺ species capable of oxygen reduction. Although this approach has been used extensively with transition metals, less attention has been devoted to main group metals.

In efforts to learn more about the chemistry of bismuth oxygen bonds and to provide a platform to make Bi(O) and Bi(OH₂) moieties, the chemistry of bismuth with the tripodal ligand H-bond donor and H-bond acceptor ligands, [H₃buea]³⁻ and [MST]³⁻, has been investigated.
Reactions with the tridentate nitrogen ligand, N,N'((methylazanediyl)bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) ([TSB]$^{2-}$), Scheme 5.1c, which has one less nitrogen bonding arm than [MST]$^{3-}$, were also studied.

Since bismuth is one of the least studied metals in the periodic table, there are a few examples of bismuth in polydentate ligand environments of this type, much less with appended H-donor and acceptor functionality. There are only two reported examples of bismuth tren coordination complexes, N(CH$_2$CH$_2$NMe)$_3$Bi and N(CH$_2$CH$_2$NSiMe$_3$)$_3$Bi, and only the latter has been characterized by X-ray crystallography.

![Scheme 5.1](image)

**Scheme 5.1.** a) tris[(N'-tert-butylureaylato)-N-ethyl]aminato metal complex with hydrogen bond donor groups, M(H$_3$buea) b) N,N',N''-[2,2',2''-nitritrotres(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) metal complex with hydrogen bond accepting groups, M(MST) and c) N,N'((methylazanediyl)bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) with hydrogen bond accepting groups, M(TST).$^{2,3}$

**RESULTS AND DISCUSSION**

Following the reaction protocols useful in transition metal chemistry, Bi(OAc)$_3$ was reacted with H$_3$[buea]$^{3-}$. Although resonances consistent with a new product were observed by NMR spectroscopy, no isolable products were obtained. The chemistry of [MST]$^{3-}$ was next surveyed and in this case a characterizable product, Bi[MST], was obtainable. The synthesis of Bi[MST] was first accomplished by treatment of a dimethylacetamide (DMA) solution of N,N,N''-[2,2',2''-nitritrotres(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) with 3
equiv of NaH followed by the addition of Bi(OAc)$_3$, in accordance with previous literature methods for the synthesis of [MST]$^{3-}$ transition metal complexes.$^2$ However, difficulty in separating the poorly soluble Bi[MST] product from the NaOAc byproduct and the low yield (as assessed by NMR) encouraged the development of an alternative synthetic method. A yellow THF solution of Bi[N(SiMe$_3$)$_2$]$_3^5$ reacts rapidly with H$_3$[MST] to form Bi[MST], 16, as a white solid in $>90\%$ yield, eq 5.1. The analytically pure product was characterized by NMR and IR spectroscopy and X-ray crystallography to confirm the structure shown in Figure 5.1.

![ORTEP representation of Bi[MST], 16, drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.](image)

**Figure 5.1.** ORTEP$^6$ representation of Bi[MST], 16, drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.
The X-ray crystal structure determination revealed that Bi[MST] is an “empty cavity” complex with no ligands coordinated to bismuth on the axial position. This is rare in the chemistry of the [H₃buea]³⁻ and [MST]³⁻ ligands: only one example of an empty cavity has been crystallographically identified, [CoMST]⁻¹. On the other hand, bismuth frequently forms complexes with empty coordination positions.

The bismuth metal center lies out of the plane formed by the three anionic nitrogen atoms (N2, N3, N4) by 0.756 Å, as is evident from the three acute 70.02 to 70.66° N1–Bi–N_anionic angles. In comparison, in the neutral empty-pocket [CoMST]⁻¹, the metal is out of plane by only 0.206 Å with N1–Co–N_anionic bond angles between 83.79 and 84.33°. The bond lengths between bismuth and the three anionic nitrogen donor atoms in 16 fall in the narrow range 2.241(2) and 2.264(2) Å. The 2.438(2) Å Bi–N1 bond length with the neutral axial nitrogen is longer, as expected. These bond distances are comparable to those in [CoMST]⁻ analog (Co–N_anionic: 1.957(1) to 1.973(1) Å; Co–N1 bond: 2.114(1) Å) when the larger size of bismuth, 1.48 Å versus 1.26 Å for cobalt, is taken into account.

The coordination environment of bismuth in 16 is different from that reported for the only other crystallographically characterized bismuth tren compound, namely N(CH₂CH₂NSiMe₃)₃Bi. The latter complex has Bi–N_anionic bonds that are 0.1 Å shorter than observed in 16 and a significantly longer Bi–N bond to the neutral nitrogen, 3.021(4) Å. It is best described as a three-coordinate trigonal pyramid with a weak secondary interaction to the neutral nitrogen in one axial position and the other axial position unligated.

The electrochemical properties of 16 were explored using cyclic voltammetry (CV), Figure 5.2. No oxidative features were found but an irreversible reduction wave was observable at large negative potentials, −1.8 V vs ferrocene/ferrocenium. In an attempt to determine if these
features were metal or ligand based, cyclic voltammetry was performed on the analogous trivalent aluminum [MST]$^{3-}$ complex, Figure 5.2B. Since the CV of Al[MST] yielded no discernible features between 0.7 V and −2.2 V, the reduction features seen for 16 suggest the presence of a reduced bismuth species. Attempts to generate such a species chemically with KC$_8$ and cobaltocene were unsuccessful, however.

![Voltammogram](image)

**Figure 5.2.** (A) Voltammogram of Bi[MST], 16 (B) voltammogram of Al[MST] control. All CV performed in DMSO vs ferrocene/ferrocenium with 0.1 M of [Bu$_4$N][PF$_6$].

The low solubility of 16 in all solvents, even at elevated temperatures, complicated these studies. Reactions with strong oxidizing agents, e.g. pyridine-N-oxide, iodosylbenzene, ceric ammonium nitrate, and O$_2$, also failed to show formation of new products.
In an effort to find a more reactive ligand platform to pursue Bi(O) and Bi(OH$_2$) chemistry, the less sterically demanding ligand N,N'-(methylazanediyl)bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide), [TSB]$^{2-}$, was explored. Unlike the tetradentate [MST]$^{3-}$, [TSB]$^{2-}$ has only two chelating sulfonamide arms with the third arm being replaced by a methyl group bound to the apical nitrogen. This allows for significantly less steric congestion about the bismuth metal center while still providing a hydrogen bond accepting secondary coordination sphere.

The treatment of a THF solution of H$_2$[TSB] with two equiv of NaH, followed by addition of Bi(AcO)$_3$ yielded a complex reaction mixture containing multiple products as observed by $^1$H NMR spectroscopy. Recrystallization by hexane diffusion into a concentrated THF solution yielded colorless crystals that were identified by X-ray crystallography as the polymetallic cluster Bi$_5$Na$_2$O$_5$[TSB]$_5$, 17, Figure 5.3.
Figure 5.3. ORTEP representation of Bi₅Na₂O₅[TSB]₅, 17, drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. The coordination environment for Bi2, Bi3, Bi4, and Bi5 are shown.

Unfortunately, the quality of the data does not allow for specific discussion of the metrical parameters of compound 17. However, the connectivity of the polymetallic cluster is confirmed. The polymetallic cluster is approximately 1.2 x 1.8 nanometers in size. The five bismuth metal centers are in four unique coordination environments as shown in Figure 5.3. Bi2 and Bi5 are bound to a N-(2-((2-aminoethyl)(methyl)amino)ethyl)-4-methylbenzenesulfonamide ligand derived by cleavage of one of the two sulfonamide ligands from [TSB]²⁻. Each metal is also bound to two bridging oxide ligands. Bi4 is also coordinated to two oxide ligands but it is also bound by a [TSB]²⁻ ligand that contains all of its original sulfonamide groups. Bi3 is
likewise bound to a fully intact [TSB]$^{2-}$, but it is bound by a bridging oxide to a Na$_2$[TSB] moiety.

The coordination environment of Bi1, Figure 5.4, is different than that of Bi2-Bi5 in 17. Bi1 is bound to no [TSB]$^{2-}$ ligands and its primary coordination environment includes only bridging oxides that connect to all the other bismuth and sodium metals. The origin of the bridging oxide ligands is unclear.

![Coordination environment for Bi1 in compound 17 and surrounding bismuth and sodium metal centers.](image)

**Figure 5.4.** Coordination environment for Bi1 in compound 17 and surrounding bismuth and sodium metal centers.

**CONCLUSION**

The isolation of Bi[MST] indicates that bismuth can form coordination complexes with tripodal ligands with attached hydrogen bonding functionality. In the case of Bi[MST], the tendency of bismuth to have an open coordination site apparently overcomes the potential of the H-acceptor arms to stabilize a small ligand binding in the axial site. Efforts to fill the binding site with O$^{2-}$ and H$_2$O ligands were unsuccessful. Removal of one of the three arms of the [MST]$^{3-}$ ligands, leads to more diverse bonding opportunities as evidenced by the isolation of the complicated Bi$_5$Na$_2$O$_5$[TSB]$_5$ cluster.
EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use.

$^1$H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers ($^{13}$C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FT-IR system. $\text{H}_3[\text{MST}],^2 \text{H}_2[\text{TST}],^9$ and $\text{Bi}[\text{N(SiMe}_3)_2]_3$ were prepared as described in literature.

$\text{Bi}[\text{MST}], 16.$ N,N,N'-((2,2',2''-nitritolris(ethane-2,1-diyl))tris(2,4,6-trimethylbenzenesulfonylamine), $\text{H}_3[\text{MST}], (282$ mg, 0.407 mmol) in THF (10 mL) was added to a stirred yellow solution of $\text{Bi}[\text{N(SiMe}_3)_2]_3$ (287 mg, 0.416 mmol) in THF (5 mL). After 2 h at room temperature the reaction mixture became an opaque white suspension. The mixture was filtered and the recovered solids were washed once with THF and twice with Et$_2$O. The solids were collected and dried under vacuum to give 16 as a fluffy white solid (339 mg, 93%). X-ray quality crystals were grown from diffusion of Et$_2$O into a saturated DMA solution at room temperature. $^1$H NMR (500 MHz, DMSO-$_d_6$): $\delta$ 6.98 (s, 6H, Ar-H), 3.69 (t, 6H, CH$_2$), 3.44 (t, 6H, CH$_2$), 2.57 (s, 18H, $o$-CH$_3$), 2.26 (s, 9H, $p$-CH$_3$). $^{13}$C NMR (125 MHz, DMSO-$_d_6$): $\delta$ 139.9 ($p$-CH$_3$ArCH), 138.1 ($o$-CH$_3$ArCH), 131.3 (ArCH), 130.8 (SO$_2$ArCH), 60.0 (br, CH$_2$), 42.5 (CH$_2$), 23.2 ($o$-CH$_3$), 20.35 ($p$-CH$_3$). IR: 3421w, 2974m, 2920m, 2863m, 1604m, 1564m, 1454m, 1404m, 1291s, 1146s, 1125s, 1053s, 958s, 927s, 816s, 663s, 603s, 580m, 540s, 586m cm$^{-1}$. 

108
**Bi$_5$Na$_2$O$_5$[TSB]$_5$, 17.** Sodium hydride (10 mg, 0.40 mmol) was added as a solid to a stirred solution of N,N'((methylazanediyl)bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide), H$_2$[TSB], (80 mg, 0.19 mmol) in THF (10 mL). After 2 h, Bi(OAc)$_3$ (73 mg, 0.19 mmol) was added to the reaction mixture causing it to quickly turn clear and pale yellow. After stirring overnight, off-white insolubles were removed by centrifugation and the yellow supernatant was dried under reduced pressure to yield an off white solid (93 mg). X-ray quality crystals identified as 17 were grown by hexane diffusion into a concentrated THF solution.

**Table 5.1. X-ray data collection parameters for Bi[MST], 16, and Bi$_5$Na$_2$O$_5$[TST]$_4$, 17.**

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<td>empirical formula</td>
<td>C$<em>{33}$H$</em>{45}$BiN$_4$O$_6$S$_3$ • 2(C$_4$H$_9$NO)</td>
<td>C$<em>{81}$H$</em>{111}$Bi$<em>5$N$</em>{15}$Na$<em>2$O$</em>{21}$S$_8$ • 5(C$_4$H$_8$O)</td>
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$^a$ Definitions: R1 = Σ||F$_o$| |F$_c$| / Σ|F$_o$|, wR2 = [Σ[w(F$_o^2$ - F$_c^2$)$^2$] / Σ[w(F$_o^2$)$^2$]]$^{1/2}$
REFERENCES

Chapter 6

Facile Transfer of the Dianionic Oxyarylcarboxy Ligand, \([\text{O}_2\text{C(C}_6\text{H}_2\text{tBu}_2\text{-3,5-O-4})]^2-\), from Bismuth to Uranium: Isolation and Characterization of \((\text{C}_5\text{Me}_3)_2\text{U(Cl)[O}_2\text{C(C}_6\text{H}_2\text{tBu}_2\text{-3-5-OH-4}]}\)

INTRODUCTION

The unique dianionic ligands \((\text{C}_6\text{H}_2\text{tBu}_2\text{-3,5-O-4})^2-\), \([\text{O}_2\text{C(C}_6\text{H}_2\text{tBu}_2\text{-3,5-O-4})]^2-\), and \([\text{OSC(C}_6\text{H}_2\text{tBu}_2\text{-3,5-O-4})]^2-\), supported by the Ar′Bi\(^{2+}\) system, have proven to be excellent for expanding organometallic bismuth chemistry.\(^1\)–\(^5\) As described in Chapters 2 – 4, the dianionic ligands are capable of undergoing oxidation to form a variety of monoanionic derivatives: \([\text{O}_2\text{C(C}_6\text{H}_2\text{tBu}_2\text{-3-5-OH-4})]^1-\) by protonation, \((\text{C}_6\text{H}_2\text{tBu}_2\text{-3,5-OSiMe}_3\text{-4})^1-\) by silylation, and \([\text{ON=(C}_6\text{H}_2\text{tBu}_2\text{O})]^1-\) through oxidation by NO. However, given the already reduced nature of the dianionic ligands, further reduction has not been observed chemically or by electrochemical studies. This, combined with the fact that bismuth(III) is typically unreactive towards oxidizing and reducing agents,\(^6\) gives limited options for further small molecule activation.

Transferring the dianionic ligands to metals that offer greater reactivity could lead to unique chemistry. Transferring these oxygen bound ligands from bismuth is viable given the periodic trend of bond strength decreasing down a period. Bismuth, like most heavy metals, forms weak bonds.\(^7\) This is especially true in the case of bismuth–oxygen bonds.\(^6\)–\(^8\)

As described in Chapters 3 and 4, research with the Ar′Bi\(^{2+}\) [Ar′ = 2,6-(Me\(_2\)NCH\(_2\))\(_2\)C\(_6\)H\(_3\)] system revealed examples of facile ligand redistribution with the oxygen bound ligands \([\text{O}_2\text{C(C}_6\text{H}_2\text{tBu}_2\text{-3-5-OH-4})]^1-\) and \([\text{ON=(C}_6\text{H}_2\text{tBu}_2\text{O})]^1-\) to form the bis(ligand) compounds Ar′Bi[O\(_2\)C(C\(_6\)H\(_2\)tBu\(_2\)-3,5-OH-4)]\(_2\) and Ar′Bi(ONC\(_6\)H\(_2\)-3,5-tBu\(_2\)-4-O)\(_2\), respectively, from mono(ligand) precursors, Scheme 6.1.\(^1\)–\(^2\) In both cases, ligand redistribution occurs at ambient
temperature. In the case of \( \text{Ar}'\text{Bi}(\text{ONC}_6\text{H}_2-3,5-'\text{Bu}_2-4-\text{O})_2 \), redistribution can be induced with mild reagents such as \([\text{Et}_3\text{NH}]\text{[Cl]}\) and \(\text{Me}_3\text{SiCl}\).\(^2\) Although uncontrolled ligand redistribution can be a synthetic challenge, these results are encouraging in regards to controlled ligand transfer of the unique dianionic ligands, \((\text{C}_6\text{H}_2't\text{Bu}_2-3,5-'\text{O}_2-4)_{2}^-\) and \([\text{O}_2\text{C}(\text{C}_6\text{H}_2't\text{Bu}_2-3,5-'\text{O}_2-4)]_{2}^-\), to other metals. The favorable formation of \(\text{Ar}'\text{BiX}_2\) (\(X = \text{Cl}, \text{Br}, \text{or I}\))\(^3\) along with formation of stronger metal oxygen bonds could provide enough driving force for reactions to occur spontaneously at room temperature.

![Scheme 6.1](image)

**Scheme 6.1.** Previously observed ligand redistribution of oxygen bound ligands with the trivalent \(\text{Ar}'\text{Bi}^{2+}\) system.\(^1,2\)

In order to explore facile ligand transfer reactivity, \(\text{Ar}'\text{Bi}[\text{O}_2\text{C}(\text{C}_6\text{H}_2't\text{Bu}_2-3-5-'\text{O}-4)-\kappa^2\text{O},\text{O}']\), \(2\), was reacted with oxophilic metals containing halide ligands. It was anticipated that a metal capable of forming strong metal–oxygen bonds could exchange two metal halide bonds for the metal oxygen bonds of the dianionic ligand with formation of \(\text{Ar}'\text{Bi}(\text{halide})_2\). This chapter
describes an initial study of ligand transfer between compound \textbf{2} and oxophilic metal compounds and the characterization of the ligand transfer products.

**RESULTS**

The complexes of \textit{f}-element metals offered an ideal opportunity to pursue the ligand transfer of the dianionic ligand \([\text{O}_2\text{C}(\text{C}_6\text{H}_2\text{Bu}_2-3,5-\text{O}-4)]^{2-}\) given that the lanthanides and actinides make strong bonds to oxygen\textsuperscript{18-21} and form a wide range of carboxylates. A yellow THF suspension of \textbf{2} was reacted with the dark blue \text{SmI}_2(\text{THF})_2 to form a grey reaction mixture. \text{Ar}^{\prime}\text{BiI}_2 was extracted with THF and identified by NMR spectroscopy.\textsuperscript{10} The remaining black solids were poorly soluble in all solvents, possibly due to an oligomeric structure consisting of samarium and the \([\text{O}_2\text{C}(\text{C}_6\text{H}_2\text{Bu}_2-3,5-\text{O}-4)]^{2-}\) ligand.

\[ \text{2} + \text{SmI}_2(\text{THF})_2 \xrightarrow{\text{THF}} \left[ \text{SmO}_2\text{C} \right]^{\prime\prime} \text{Bu} \text{Bu} \text{Bu} \text{Bu} \text{Bu} + \text{Ar}^{\prime}\text{BiI}_2 \quad (6.1) \]

\textsuperscript{1}H NMR spectroscopy identified a new species and no resonances for the starting materials were observed. To further confirm ligand incorporation the analogous reaction with the carbon-\textsuperscript{13} enriched \textbf{2-\textsuperscript{13}C} was performed. \textsuperscript{13}C NMR spectroscopy of the black solids gave a resonance consistent with the presence of a ligand like \([\text{O}_2\text{C}(\text{C}_6\text{H}_2\text{Bu}_2-3,5-\text{O}-4)]^{2-}\) at 176.9 ppm. This is similar to the resonance observed for \textbf{2-\textsuperscript{13}C} at 175.8 ppm.\textsuperscript{3} IR spectroscopy of the black solids revealed resonances consistent with C–O asymmetric and symmetric stretches at
1534 and 1388 cm$^{-1}$, respectively,$^{23,24}$ that shift to 1505 and 1374 cm$^{-1}$ (Hooke’s law: 1500 and 1357 cm$^{-1}$) in the $^{13}$C enriched product. This suggests that there is a carboxylate ligand derived from 2 within the poorly soluble black oligomer, but further structural details could not be determined.

To avoid the potentially oligomeric product from the reaction in eq 6.1, the reaction of 2 with (C$_5$H$_5$)$_2$TiCl$_2$ was explored. Like the f-element metals, early transition metals are very oxophilic and should form M–O bonds stronger than the weak bismuth–oxygen bond. With the ancillary (C$_5$H$_5$)$_1$ ligands on the metal center, it was less likely that an insoluble oligomeric product could form. A yellow suspension of 2 in THF was reacted with a red solution of (C$_5$H$_5$)$_2$TiCl$_2$ in THF to quickly form an opaque red mixture. As in the previous reaction with SmI$_2$(THF)$_2$, the bismuth halogen complex, Ar′BiCl$_2$, was separated by centrifugation and identified in the product mixture by NMR spectroscopy, eq 6.2.$^{10}$ No starting materials were observable by NMR spectroscopy. Unfortunately, definitive spectroscopic evidence of ligand incorporation was not observable and X-ray quality crystals could not be grown from the product mixture.

A THF solution of (C$_5$Me$_5$)$_2$UCl$_2$$^{25}$ was reacted with compound 2 to form a red solution. After extracting the reaction mixture with hexane, 1 equiv (by mass balance) of Ar′BiCl$_2$ was identified by NMR spectroscopy and a new, hexane soluble, product was observed with 1:1 ratio
of \textsuperscript{t}Bu to (C\textsubscript{5}Me\textsubscript{5}) resonances. IR spectroscopy showed absorptions consistent with C–O stretches and \textsuperscript{13}C NMR spectroscopy identified a CO\textsubscript{2} moiety at 180.7 ppm.\textsuperscript{3} X-ray crystallography of multiple crystal crops revealed the structure of the monochloride complex, (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}U[O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}tBu\textsubscript{2}-3-5-OH-4)], \textbf{18}, Figure 6.1, eq 6.3. Evidently, the dianionic ligand [O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}tBu\textsubscript{2}-3,5-O-4)]\textsuperscript{2–} of the starting material was protonated to form the monoanionic carboxylate [O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}tBu\textsubscript{2}-3-5-OH-4)]\textsuperscript{1–}. It is possible that the crystals of \textbf{18} that were isolated are only a minor product of the reaction since there is no expected O–H stretch in the IR spectrum of bulk samples of \textbf{18}. An OH stretch is clearly observable in the protonated analog of \textbf{2}, \{Ar′Bi[O\textsubscript{2}C(C\textsubscript{6}H\textsubscript{2}tBu\textsubscript{2}-3-5-OH-4)-κ\textsuperscript{2}O,O′][BPh\textsubscript{4}]}[2-H][BPh\textsubscript{4}].\textsuperscript{3} However, if \textbf{18} is a minor product and there are multiple products from the reaction in eq 6.3, only one product is observable by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy.
Figure 6.1. ORTEP\textsuperscript{26} representation of (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}U(Cl)[O\textsubscript{2}C(\text{C\textsubscript{6}H\textsubscript{4}Bu\textsubscript{2}-3-5-OH-4})], 18, with thermal ellipsoids drawn at the 50\% probability level. Hydrogen atoms are omitted for clarity.

The structure of 18 has metrical parameters similar to those of other U\textsuperscript{4+} metallocenes. The U–Cl bond distance in compound 18 is 2.614(1) Å, similar to the starting material (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}UCl\textsubscript{2} at 2.583 Å.\textsuperscript{27} The U–Cp(centroid) distances of 2.444 and 2.455 Å are also typical for uranium metallocenes. The methyl displacements out the plane of the cyclopentadienyl ligands are 0.117 and 0.126 Å, an unexceptional value for uranium complexes.\textsuperscript{28} The Cp(centroid)–U–Cp(centroid) angle is 138.3° while the Cl–U–C(21) angle is 108.92(5)°.

Finally, the uranium–oxygen bonds are symmetric at 2.400(2) and 2.401(2) Å. With the larger size of uranium taken in account (covalent radii for U is 1.96 Å vs 1.48 Å for bismuth\textsuperscript{29}) these bonds are significantly shorter than for those seen in 2 (2.276(2) and 2.278(2) Å) and [2-H][BPh\textsubscript{4}] (2.336(5) Å).

Compound 18 has a carbon–oxygen bond length of 1.377(3) Å, typical for phenol carbon–oxygen single bonds,\textsuperscript{30} and ring carbon–carbon bonds are between 1.390(3) – 1.416(3)
Å. These parameters are consistent with a monoanionic carboxylate ligand and not the dianionic oxyarylcarboxylate ligand in the starting material,\(^3\) which has significant shortening of the carbon–oxygen bond (1.265(4) Å) and short-long pattern of carbon–carbon ring bonds between 1.372(4) – 1.465(4) Å.\(^3\) Compound 18 is therefore a tetravalent uranium species bound to four monoanionic ligands and not a pentavalent compound bound to three monoanions and one dianion.

To help confirm this formulation of compound 18, the room temperature magnetic moment was taken by the Evans’ method\(^31\) in benzene-\(d_6\). The experimentally determined magnetic moment of 18 was found to be 2.90 \(\mu_B\). This is not very close to the theoretical \(\mu_J\) approximation, \(\mu_J = g[J(J + 1)]^{1/2}\), of 3.58 \(\mu_B\) for the proposed \(5f^2\) U\(^{4+}\) ion. However, the experimentally observed values for room temperature magnetic moments of uranium compounds typically deviate significantly from this approximation (see Chapter 7).\(^32\) The 2.90 \(\mu_B\) value for compound 18 is within the 2.50 – 3.08 \(\mu_B\) range found for U(IV) compounds.\(^32\)

**DISCUSSION**

The reactions of compound 2 with SmI\(_2\)(THF)\(_2\) produced an insoluble black material spectroscopically characterized to contain a CO\(_2\) moiety of the type found in the \([O_2C(C_6H_2'Bu_2-3,5-O-4)]^{2-}\) dianionic ligand or in the \([O_2C(C_6H_2'Bu_2-3,5-OH-4))]\(^{1-}\) monoanion. However, further structural characterization was not possible given the product’s low solubility. It is likely that if a “Sm[O\(_2\)C(C\(_6\)H\(_2\)B\(_u_2\)-3,5-O-4)]” complex was made the small bite-angle \(\kappa^2\)-oxyarylcarboxylate ligand would not provide satisfactory steric shielding of the Sm\(^{2+}\) metal center. This could result in intermolecular bridging and an oligomeric structure. Further, redox active
divalent samarium, a common one electron reductant,\textsuperscript{33,34} could be the source of unwanted side reactions.

In an effort to remedy this problem compounds with sterically shielding ancillary ligands were explored. The Ti\textsuperscript{4+} complex, \((\text{C}_5\text{H}_5)_2\text{TiCl}_2\), did accomplish ligand transfer, but like in the reaction with SmI\textsubscript{2}, did not produce an isolable product. Only in the reaction with \((\text{C}_5\text{Me}_5)_2\text{UCl}_2\) was a product able to be isolated and characterized.

Though formal ligand transfer was accomplished in the reaction of compound 2 with \((\text{C}_5\text{Me}_5)_2\text{UCl}_2\), the structurally characterized product contains the protonated form of the oxyarylcarboxy dianionic ligand, i.e. the monoanionic carboxylate, \([\text{O}_2\text{C}(\text{C}_6\text{H}_2\text{tBu}_2\text{-}3\text{-}5\text{-OH}-4)]\textsuperscript{-}\). The source of this proton is unknown. The most acidic protons present in the reaction mixture are the benzyl protons of the Ar‘ ligand, which can be deprotonated with a strong base.\textsuperscript{35} However, the high yield (>90%) of Ar‘BiCl\textsubscript{2} makes it less likely that this is the source of the protons.

It is possible that the structurally characterized product, 18, is only a minor product of the reaction in eq 6.2. NMR spectroscopy and mass balance conclusively identified 1 equiv of Ar‘BiCl\textsubscript{2}, making it impossible for 1 equiv of 18 to also be formed (Cl balance). Further, IR spectroscopy revealed no O–H stretch consistent with the carboxylic ligand seen in the bismuth analog, \([\text{Ar‘Bi(O}_2\text{C}(\text{C}_6\text{H}_2\text{tBu}_2\text{-}3\text{-}5\text{-OH}-4))][\text{BPh}_4]\).\textsuperscript{3} Since IR stretches of OH groups are typically intense and broad, an absorption would be expected if 18 were the main product.

It is unknown if protonation of the dianionic ligand occurs before transfer to the uranium metal center or after. Uranium is significantly more electropositive (1.38 vs 2.02 for bismuth\textsuperscript{36}) which could increase the electron density delocalized across the oxyarylcarboxy ligand making it more reactive. However, the only evidence of ligand transfer with this system to date is with
monoanionic ligands. Hence, that initial protonation of the oxyarylcarboxy ligand may be necessary before transfer to uranium.

The experimentally observed magnetic moment for compound 18, 2.90 \( \mu_B \), is reasonable for tetravalent uranium complexes and only 0.11 \( \mu_B \) from the median value of all U\(^{4+} \) compounds (Chapter 7).\(^{32} \) In contrast pentavalent uranium complexes typically have magnetic moments of 1.64 to 2.38 \( \mu_B \).\(^{32} \) Further, uranium complexes with non-innocent redox active ligands often times give unusual magnetic moments (cf. \((C_5Me_4H)_3UNO,^{37} (C_5Me_5)_2U(2,2'-bpy)(R),^{38} \) and others; see Appendix B and Chapter 7) that deviate significantly from the average. The normal room temperature moment for 2 therefore helps support the formulation of the \([O_2C(C_6H_2^tBu_2-3-5-OH-4)]^{1-}\) monoanionic carboxylate ligand.

CONCLUSION

In conclusion the bismuth complex of the oxyarylcarboxy dianionic ligand, \([O_2C(C_6H_2^tBu_2-3,5-O-4)]^{2-}\) shows reactivity with oxophilic transition and f-element metal halides and the expected byproduct of ligand transfer Ar\(^t\)BiX\(_2\) is observed. Crystallographic evidence of ligand transfer was accomplished with \((C_5Me_5)_2UCl_2\) which yielded the tetravalent uranium carboxylate complex \((C_5Me_5)_2U(Cl)[O_2C(C_6H_2^tBu_2-3-5-OH-4)], 18.\)

EXPERIMENTAL

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried
over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. \textsuperscript{1}H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (\textsuperscript{13}C NMR spectra on the 500 MHz spectrometer operating at 125 MHz, \textsuperscript{19}F NMR spectra on the DR400 spectrometer operating at 375 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. IR samples were prepared as KBr pellets on a Varian 1000 FTIR system. Ar′Bi\textsubscript{O\textsubscript{2}}\textsubscript{2}C\textsubscript{6}H\textsubscript{2}Bu\textsubscript{2}-3-5-O-4)-κ\textsuperscript{2}O,O′]\textsuperscript{3}, Ar′Bi[O\textsubscript{2}\textsuperscript{13}C(C\textsubscript{6}H\textsubscript{2}Bu\textsubscript{2}-3-5-O-4)-κ\textsuperscript{2}O,O′]\textsuperscript{3}, (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}UCl\textsubscript{2}\textsuperscript{25} and SmI\textsubscript{2}(THF)\textsubscript{2}\textsuperscript{39} have been prepared according to literature.

**Reaction of 2 and SmI\textsubscript{2}(THF)\textsubscript{2}**. A THF (10 mL) solution of SmI\textsubscript{2}(THF)\textsubscript{2} (63 mg, 0.120 mmol) was added to a stirred orange suspension of 2 (75 mg, 0.120 mmol) in THF (5 mL) and allowed to stir overnight. The opaque yellow reaction mixture was separated by centrifugation to give black insoluble material and yellow supernatant. After removal of solvent under reduced pressure, the THF soluble product was identified as Ar′BiI\textsubscript{2} by NMR spectroscopy\textsuperscript{10} \textsuperscript{1}H NMR (500 MHz, benzene-\textsubscript{d}\textsubscript{6}): \(\delta\) 4.32 [s, 1H], 2.75 [s, 3H]. IR: 3634\textsuperscript{m}, 2957\textsuperscript{s}, 1598\textsuperscript{m}, 1534\textsuperscript{s}, 1485\textsuperscript{w}, 1388\textsuperscript{w}, 1326\textsuperscript{m}, 1240\textsuperscript{m}, 1160\textsuperscript{w}, 1117\textsuperscript{w}, 1026\textsuperscript{w}, 889\textsuperscript{w}, 793\textsuperscript{w} \textsuperscript{cm}^{-1}.

**Reaction of 2-\textsuperscript{13}C and SmI\textsubscript{2}(THF)\textsubscript{2}**. The 2-\textsuperscript{13}C reaction was performed analogously to the reaction with 2, but in a sealed J-Young NMR tube. \textsuperscript{13}C NMR (125 MHz, acetonitrile-\textsubscript{d}\textsubscript{3}): \(\delta\) 176.9 (\textsuperscript{13}CO\textsubscript{2}). IR: 3634\textsuperscript{m}, 2957\textsuperscript{s}, 1598\textsuperscript{m}, 1505\textsuperscript{s} (calcd 1500), 1485\textsuperscript{w}, 1374\textsuperscript{s} (calcd 1357), 1326\textsuperscript{m}, 1240\textsuperscript{m}, 1160\textsuperscript{w}, 1117\textsuperscript{w}, 1026\textsuperscript{w}, 889\textsuperscript{w}, 793\textsuperscript{w} \textsuperscript{cm}^{-1}.

**Reaction of 2 and (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}TiCl\textsubscript{2}**. A THF (10 mL) solution of (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}TiCl\textsubscript{2} (19 mg, 0.08 mmol) in THF (10 mL) was added to a stirred orange suspension of 2 (50 mg, 0.08 mmol) in THF (5 mL) and allowed to stir over night. The dark red reaction mixture was separated by
centrifugation to give an off-white insoluble identified by NMR spectroscopy as Ar′BiCl₂ in CD₃CN.¹⁰

(C₅Me₅)₂U(Cl)[O₂C(C₆H₂'Bu₂-3-5-OH-4)], 18. A THF (10 mL) solution of (C₅Me₅)₂UCl₂ (100 mg, 0.17 mmol) was added to a stirred orange suspension of 2 (110 mg, 0.17 mmol) in THF (5 mL) and allowed to stir overnight. After stirring overnight the solvent was removed under reduced pressure to give dark red solids. The crude product were stirred in hexane and then separated by centrifugation to give off-white insoluble material and red supernatant. The off-white solids were identified as Ar′BiCl₂ by NMR spectroscopy.¹⁰ Removal of hexane gave 18 as a red solid (88 mg, 64%). X-ray quality crystals were grown from a concentrated hexane solution at −30 °C. ¹H NMR (500 MHz, benzene-d₆): δ 8.07 [s, 30H, (C₅Me₅)], 1.32 [s, 2H, O₂C(C₆H₂'Bu₂O)], −1.81 [s, 18H, O₂C(C₆H₂'Bu₂O)]. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 148.3 [O₂C(C₆H₂'Bu₂O)], 134.3[O₂C(C₆H₂'Bu₂O)], 124.8[(C₅Me₅)], 29.9 [q-O₂C(C₆H₂(CMe₃)₂O)], 27.6 [(C₅Me₅)], −30.6 [O₂C(C₆H₂(CMe₃)₂O)]. IR: 3616m, 2956s, 2907s, 1595m, 1486m, 1453m, 1399s, 1351m, 1241m, 1159w, 1023w, 841w, 790m, 708m cm⁻¹. Magnetic moment (Evans method, benzene-d₆): 2.90 µB.

(C₅Me₅)₂U(Cl)[O₂¹³C(C₆H₂'Bu₂-3-5-OH-4)], 18.¹³C. The ¹³C analogue of 18 was prepared analogously from 2-¹³C in a sealed J-Young NMR Tube. ¹³C NMR (125 MHz, acetonitrile-d₃): δ 180.7 [O₂C(C₆H₂'Bu₂O)], 148.3 [O₂C(C₆H₂'Bu₂O)], 134.3[O₂C(C₆H₂'Bu₂O)], 124.8[(C₅Me₅)], 29.9 [q-O₂C(C₆H₂(CMe₃)₂O)], 27.6 [(C₅Me₅)], −30.6 [O₂C(C₆H₂(CMe₃)₂O)].

**X-ray Crystallographic Data.** Crystallographic information for 18 is summarized in Table 6.1. Selected bond distances are in Table 6.2.
Table 6.1. X-ray data collection parameters for \((\text{C}_5\text{Me}_5)_2\text{U}([\text{O}_2\text{C}([\text{C}_6\text{H}_5\text{Bu}_2-3-5-\text{OH}-4])]\), 18.

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</tr>
<tr>
<td>(b) ((\text{Å}))</td>
<td>13.4864(7)</td>
</tr>
<tr>
<td>(c) ((\text{Å}))</td>
<td>17.0256(9)</td>
</tr>
<tr>
<td>(\alpha) (deg)</td>
<td>81.3685(6)</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>77.3187(5)</td>
</tr>
<tr>
<td>(\gamma) (deg)</td>
<td>77.5097(6)</td>
</tr>
<tr>
<td>Volume (\text{Å}^3)</td>
<td>2015.48(18)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) ((\text{Mg/m}^3))</td>
<td>1.449</td>
</tr>
<tr>
<td>(\mu) ((\text{mm}^{-1}))</td>
<td>4.127</td>
</tr>
<tr>
<td>(R1^\text{a}) [(I &gt; 2.0\sigma(I))]</td>
<td>0.0218</td>
</tr>
<tr>
<td>(\text{wR}2^\text{a}) (all data)</td>
<td>0.0575</td>
</tr>
</tbody>
</table>

Table 6.2. Selected bond lengths (Å) and angles (°) for compound \((\text{C}_5\text{Me}_5)_2\text{U}([\text{O}_2\text{C}([\text{C}_6\text{H}_5\text{Bu}_2-3-5-\text{OH}-4])]\), 18, compared to 2 and [2-H][BF_4].

<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>1</th>
<th>[2-H][BF_4]</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp(cent)})–(\text{U}–\text{Cp(cent)})</td>
<td>138.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{O}–\text{M}–\text{O})</td>
<td>57.61(8)</td>
<td>56.01(18)</td>
<td>54.51(6)</td>
</tr>
<tr>
<td>((\text{O}_2\text{C})–(\text{C}_6\text{H}_5\text{Bu}_2\text{O}))</td>
<td>1.435(4)</td>
<td>1.468(10)</td>
<td>1.476(3)</td>
</tr>
<tr>
<td>(\text{M}–\text{O})</td>
<td>2.276(2), 2.278(2)</td>
<td>2.336(5), 2.336(5)</td>
<td>2.400(2), 2.401(2)</td>
</tr>
</tbody>
</table>
REFERENCES

(22) See introduction for more details on bismuth-aryl bonds and relevant literature.
Chapter 7

Magnetic Susceptibility of Uranium Complexes

INTRODUCTION†

It has been pointed out repeatedly in the literature\textsuperscript{1-10} that evaluating the magnetic susceptibility of uranium complexes is not as straightforward as it is for transition metal and lanthanide complexes. For any metal complex, the magnetic moment arises from the sum of the contributions of the ground state and the low-lying thermally accessible excited states as well as any temperature-independent magnetism in the system. For most 4f\textsuperscript{n} lanthanides, the ground state is defined by a \( ^{2S+1}L_J \) Russell–Saunders term because spin–orbit coupling is large and ligand field splitting is small due to the limited radial extension of the 4f orbitals. Room temperature magnetic moments can be approximated for most of the lanthanides by \( \mu_J = g[J(J + 1)]^{1/2} \) and correlated with oxidation state.\textsuperscript{11-15} This approximation does not apply to Sm\textsuperscript{3+} and Eu\textsuperscript{3+} because they have low-lying excited states, but the range of their experimental values is well defined.\textsuperscript{11-15} The situation is more complicated for d\textsuperscript{n} transition metals where the ligand field effects are strong and can diminish the contribution of the orbital angular momentum to the magnetic moment (orbital quenching). However, an operational solution exists for transition metal complexes: a spin-only approximation, \( \mu_S = 2[S(S + 1)]^{1/2} \), can be used as a starting point and then modified for orbital contributions depending on the d\textsuperscript{n} configuration and symmetry.\textsuperscript{11-14}

The actinides are intermediate between lanthanides and transition metals in the sense that the greater radial extension of the 5f orbitals means that ligand field effects cannot be ignored,

\[ \text{Portions of this chapter have been published: Kindra, D. R.; Evans, W. J. Chem. Rev. 2014, 114, 8865.} \]
yet spin-orbit coupling is large.\textsuperscript{1-3,5-10,12} In a case where two effects can be comparable, finding a simple model is usually more difficult. Neither the spin-only $\mu_S$ approximation used for transition metals nor the total angular momentum $\mu_J$ approximation used for the lanthanides is adequate for uranium, although $\mu_J$ is often used as an inexact starting point. A detailed theoretical analysis on actinide magnetism has recently been published that defines these issues more formally.\textsuperscript{3}

A further complication for uranium is that the $\mu_J$ values of 3.62 and 3.58 $\mu_B$ often used to approximate magnetism for $\text{U}^{3+}$ and $\text{U}^{4+}$, respectively, are similar enough to be within the experimental error of typical measurements. It is therefore difficult to differentiate $\text{U}^{3+}$ and $\text{U}^{4+}$ from room-temperature magnetic moments.\textsuperscript{6-10} As a consequence, it is preferable to obtain variable-temperature data with a superconducting quantum interference device (SQUID) or vibrating sample magnetometer (VSM) since the magnetic moment of a $5f^2$ $\text{U}^{4+}$ ion typically approaches zero at low temperature due to a singlet ground state. This does not occur with half-integral $5f^3$ $\text{U}^{3+}$ and $5f^1$ $\text{U}^{5+}$. Unfortunately, although variable-temperature analysis is the state-of-the-art method to evaluate the magnetism of uranium complexes, such data are not always easily obtained by all research groups and even the shapes of variable-temperature plots are not always consistent for a given ion.\textsuperscript{16-24}

Despite these difficulties, many claims of oxidation state based on room-temperature magnetic moments are in the literature. These claims often cite other papers with similar magnetic moments to support the oxidation state assignment without mentioning the papers in which different magnetic moments were observed for that oxidation state.

No comprehensive collection of magnetic data on uranium complexes has ever been assembled to survey the actual range of data in the literature. It was of interest to determine if
there were any trends in the ranges of magnetic moments reported for uranium complexes and the frequency of typically observed values. Magnetic data on over 400 complexes of uranium in the common +3, +4, and +5 oxidation states were collected and a statistical analysis was made of the values versus the oxidation state assigned to each complex. This compilation allows magnetic data on new uranium complexes to be compared to the full range of data in the literature. This should aid in determining if new complexes exhibit typical or unusual magnetic properties.

RESULTS

Appendix B contains the room-temperature and low temperature magnetic moment of each monometallic uranium complex surveyed. Statistical analyses of the data on the monometallic complexes for each oxidation state at both room and low temperature are presented in Table 7.1. For each oxidation state, the following values are given: the average, the median, the standard deviation, $\sigma$, the upper and lower quartile, $q_u$ and $q_l$, respectively, and the number of measurements, n.

Table 7.1. Statistical analysis of all monometallic uranium complexes reported for room temperature and low temperature (1.8 – 5 K).

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Median</th>
<th>Std. Dev$^{25}$</th>
<th>$q_u^{26}$</th>
<th>$q_l^{26}$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Room Temp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$^{3+}$</td>
<td>3.13</td>
<td>3.14</td>
<td>0.44</td>
<td>2.90</td>
<td>3.49</td>
<td>103</td>
</tr>
<tr>
<td>U$^{4+}$</td>
<td>2.77</td>
<td>2.79</td>
<td>0.39</td>
<td>2.50</td>
<td>3.08</td>
<td>243</td>
</tr>
<tr>
<td>U$^{5+}$</td>
<td>2.07</td>
<td>2.04</td>
<td>0.51</td>
<td>1.64</td>
<td>2.38</td>
<td>95</td>
</tr>
<tr>
<td><strong>Low Temp</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$^{3+}$</td>
<td>1.84</td>
<td>1.81</td>
<td>0.46</td>
<td>1.57</td>
<td>2.11</td>
<td>33</td>
</tr>
<tr>
<td>U$^{4+}$</td>
<td>0.84</td>
<td>0.69</td>
<td>0.54</td>
<td>0.50</td>
<td>1.10</td>
<td>91</td>
</tr>
<tr>
<td>U$^{5+}$</td>
<td>1.18</td>
<td>1.13</td>
<td>0.25</td>
<td>1.00</td>
<td>1.40</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 7.1 presents a histogram of the room temperature magnetic moments for monometallic U$^{3+}$, U$^{4+}$, and U$^{5+}$ complexes to allow visualization of the range of data on complexes of the different uranium ions. Figure 7.2 presents histograms of the room temperature magnetic moments for each oxidation state individually. Figure 7.3 presents analogous histograms of the low temperature magnetic moments.

**Figure 7.1.** Histogram of the uranium magnetic moments for monometallic complexes of the three common oxidation states with U$^{3+}$, U$^{4+}$, and U$^{5+}$ in black, grey, and white, respectively. Histogram bin widths are 0.20 $\mu_B$. 
Figure 7.2. Room temperature magnetic moments of monometallic U$^{3+}$ (top, green), U$^{4+}$ (middle, orange), and U$^{5+}$ (bottom, blue) complexes in $\mu_B$. Histogram bin widths of 0.20, y-axis are not to scale.
Figure 7.3. Low temperature (1.8 – 5 K) magnetic moments ($\mu_B$) of monometallic U$^{3+}$ (top, green), U$^{4+}$ (middle, orange), and U$^{5+}$ (bottom, blue) complexes in $\mu_B$. Histogram bin widths of 0.20, y-axis are not to scale.
DISCUSSION

Appendix B shows that the range of room temperature magnetic moments for each of the common paramagnetic uranium ions is large and the overlap is extensive: reported data range from $1.75 - 3.8$, $1.36 - 3.79$, and $1.24 - 3.77 \, \mu_B$ for $\text{U}^{3+}$, $\text{U}^{4+}$, and $\text{U}^{5+}$, respectively. As a consequence, any room temperature magnetic moment between 1.75 and 3.77 $\mu_B$ could be claimed to be within the full range of $\text{U}^{3+}$, $\text{U}^{4+}$, or $\text{U}^{5+}$! However, the histograms show trends that follow the number of unpaired electrons: the moments for $\text{U}^{3+}$ tend to be higher than those of $\text{U}^{4+}$, which tend to be higher than those of $\text{U}^{5+}$ (Figures 7.2 and 7.3). The range of values between the upper and lower quartiles, i.e., the middle 50% of the values, shows ranges with less overlap: $2.90 - 3.49$, $2.50 - 3.08$, and $1.64 - 2.38 \, \mu_B$ for $\text{U}^{3+}$, $\text{U}^{4+}$, and $\text{U}^{5+}$, respectively. There is still significant overlap between $\text{U}^{3+}$ and $\text{U}^{4+}$ at this 50% population level, but there is no overlap with $\text{U}^{5+}$. This overlap reflects statements in earlier papers indicating that room temperature magnetic moments are inadequate for differentiating $\text{U}^{3+}$ and $\text{U}^{4+}$.\textsuperscript{6-10}

The ranges of the low temperature magnetic moments for $\text{U}^{3+}$, $\text{U}^{4+}$, and $\text{U}^{5+}$ also overlap: $1.00 - 3.1$, $0.0 - 3.2$, and $0.7 - 1.67 \, \mu_B$, respectively. These are more difficult to compare since the lowest temperature reported is not uniform from one complex to another. The ranges of low temperature magnetic moments for the middle 50% of each ion are more distinct: $1.57 - 2.11$, $0.50 - 1.10$, and $1.00 - 1.40 \, \mu_B$ for $\text{U}^{3+}$, $\text{U}^{4+}$, and $\text{U}^{5+}$, respectively. There is no overlap between the range for $\text{U}^{3+}$ and $\text{U}^{4+}$ and the overlap between $\text{U}^{4+}$ and $\text{U}^{5+}$ is minimal. Hence, low temperature data, when available, are the most valuable.

Moreover, as pointed out in numerous papers on variable temperature magnetic data, the shape of the curve in a magnetic moment or $\chi T$ versus temperature plot is often more
informative in differentiating oxidation states. The susceptibility of a $5f^2\, U^{4+}$ complex should drop drastically toward a diamagnetic ground state at some low temperature (typically around 50 K), whereas the susceptibility of the half integral spin systems, $5f^3\, U^{3+}$ and $5f^1\, U^{5+}$, should go to non-zero values at low temperature. Three representative variable temperature plots for complexes of $U^{3+}$, $U^{4+}$, and $U^{5+}$ are shown in Figure 7.4. The results of Meyer and co-workers on a series of related $(^{\alpha} ArO)$_3tacn complexes are used to illustrate the relative shape and slope of the curves found in typical variable temperature plots for the three uranium ions.
Figure 7.4. Examples of $\mu_B$ versus temperature plots for a series of related $^{\text{Ad}}\text{ArO}_3\text{tacn}$ complexes from Meyer and co-workers:$^6$ (A) $\text{U}^{3+}$ complexes [($^{\text{t-Bu}}\text{ArO}_3\text{tacn})\text{U}$], (1), [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}$], (1-Ad), and [($^{\text{t-Bu}}\text{ArO}_3\text{tacn})\text{U}(\text{NCCMe}_3$)], (4); (B) $\text{U}^{4+}$ complexes [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}(\text{N}_3$)], (U(IV)-N3), [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}(\text{Cl})$], (U(IV)-Cl), [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}(\text{Br})$], (U(IV)-Br), and [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}(\text{I})$], (U(IV)-I); (C) the $\text{U}^{5+}$ complex [($^{\text{Ad}}\text{ArO}_3\text{tacn})\text{U}(\text{NSi(CH}_3)_3$)]. Reprinted with permission from *Chemical Communications* 2006, 1353.
The data were examined further to see if other trends could be discerned. Comparison of the room temperature magnetic moments determined in the solid state (SQUID, VMS, Gouy balance) versus solution state (Evans method) revealed no significant difference for either the U$^{3+}$ or the U$^{4+}$ complexes. The medians of the two populations were within 0.1 $\mu_B$ of each other for each ion. For the U$^{5+}$ ion, however, a significant difference was present between the solid and solution state room temperature moments. The median solution state value was 1.75 $\mu_B$ vs. a solid state value of 2.18 $\mu_B$, a difference nearly four times that seen for the other ions. It is unclear what could cause this difference and it may be a statistical artifact from unusually large U$^{5+}$ values reported in some solid state measurements (cf. 3.10, 3.70, 3.77 $\mu_B$) and the small sample size (n = 13) for solution state U$^{5+}$ ion measurements. It should also be noted that in the rare instances in which both solid state and solution state room temperature magnetic moments are reported, across all oxidation states the magnetic moments from the two methods can deviate by as much as 0.7 $\mu_B$, although 0.1 – 0.3 $\mu_B$ differences are more typical.

The compilation of data contained several series of closely related complexes that allowed the inspection of trends in magnetic moment based on ligand field strength. Variation in magnetic moments is sometimes explained by suggesting that stronger field ligands can quench orbital contributions to magnetism and this is used as evidence for 5f covalency. Ligand trends are discussed below as a function of metal oxidation state.

Data on four simple trivalent uranium halide salts, UX$_3$, are available. The 3.67, 3.7, 3.57, and 3.65 $\mu_B$ values for X = F, Cl, Br, and I, respectively, are all considerably higher than the average U$^{3+}$ value of 3.13 $\mu_B$ and they do not follow a periodic trend. The common trivalent uranium starting material U[N(SiMe$_3$)$_2$]$_3$ has three reported values: 2.51, 3.07, and
Comparing the median and most recent value for U[N(SiMe$_3$)$_2$]$_3$ with other simple trivalent homoleptic coordination compounds also fails to give a correlation of moment versus ligand field strength: U[N(SiMe$_3$)$_2$]$_3$ (3.07 µB), U[CH(SiMe$_3$)$_2$]$_3$ (3.0 µB), and U(OC$_6$H$_3$-Bu$'$-2,6)$_3$ (3.3 µB).\textsuperscript{41} Comparison of the magnetic moments of the trivalent cyclopentadienyl series (C$_5$Me$_5$)$_3$U (3.1 µB),\textsuperscript{42} (C$_5$H$_4$SiMe$_3$)$_3$U (3.28 µB),\textsuperscript{43} [C$_5$H$_3$(SiMe$_2$)$_2$]$_3$U (3.32 µB),\textsuperscript{44} and [C$_5$H$_3$(CMe$_2$)$_2$]$_3$U (3.37 µB)\textsuperscript{44} reveals there is not a large variation as a function of ligand. Likewise, the 2.6, 2.5, and 2.6 µB\textsuperscript{45} values for the U$^{3+}$ hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) complexes, Tp$_2$U(CH$_3$), Tp$_2$U(CH$_2$Ph), and Tp$_2$U(CH$_2$SiMe$_3$), are similar. In contrast, a significant variation in magnetic moments is found for the tacn series [(t$_5$Bu$_3$ArO)$_3$tacn]U (2.92 µB),\textsuperscript{6} [(t$_5$Ad$_3$ArO)$_3$tacn]U (2.83 µB),\textsuperscript{6} [(t$_5$Neop$_3$MeArO)$_3$tacn]U (2.49 µB),\textsuperscript{46} and [(t$_5$Dia$_3$ArO)$_3$tacn]U (3.04 µB)\textsuperscript{8} even though the differences in ligands are distant from the metal center.

A mixed picture of ligand effects is also found with U$^{4+}$ complexes. The salts, UF$_4$ and UCl$_4$, both have similar measured moments of 3.29 and 3.30 µB, respectively, which like the trivalent analogs are significantly higher than the U$^{4+}$ average (2.77 µB) and show no correlation with ligand field strength since they are equivalent.\textsuperscript{47} A series of U$^{4+}$ tacn halide complexes [(t$_5$Ad$_3$ArO)$_3$tacn]U(X)] (X = Cl, Br, and I) all have measured moments of approximately 2.9 µB,\textsuperscript{48} thereby showing no significant ligand effects. Tris(2-aminoethyl)amine (tren)-based tetravalent uranium complexes, [N(CH$_2$CH$_2$NR)$_3$]U(X), show inconsistency despite only slight modifications to the R groups of the tren ligands: R = SiMe$_2$Bu$_i$\textsuperscript{,49} X = Cl (3.19 µB), Br (3.14 µB), and I (3.08 µB); R = Si$i$Pr$_3$\textsuperscript{,50} X = F (2.4 µB), Cl (2.01 µB), and I (2.4 µB); R = SiMe$_3$,\textsuperscript{130,135} X = Cl (2.8 µB) and I (2.79 µB). On the other hand, the U[N(SiMe$_3$)$_2$]$_3$X complexes
with \( X = \text{Cl} \) (2.8 \( \mu_B \)), \( F \) (2.91 \( \mu_B \)), \( \text{BH}_4 \) (2.6 \( \mu_B \)), \( \text{Me} \) (2.7 \( \mu_B \)), \( H \) (2.6 \( \mu_B \)), \( \text{N(SiMe}_3)_2 \) (2.94 \( \mu_B \)) have more variation, but the values do not follow ligand field strength. However, several pairs of \( U^{4+} \) complexes do have lower magnetic moments for the member with the stronger ligand field: 3.32 and 3.11 \( \mu_B \) for \([\text{C}_5\text{H}_3(\text{CMe}_3)_2]_2\text{UCl}_2\) and \([\text{C}_5\text{H}_3(\text{CMe}_3)_2]_2\text{UF}_2\), 2.65 and 2.45 \( \mu_B \) for \((\text{C}_5\text{H}_5)_3\text{USH}\) and \((\text{C}_5\text{H}_5)_3\text{UOH}\), and 2.9 and 2.7 \( \mu_B \) for \( \text{Tp*UI}_2(\text{THF}) \) and \( \text{Tp*UI}_2(2,2'-\text{bpy}) \), respectively.

Unlike the simple trivalent and tetravalent uranium halides, which all have magnetic moments higher than the average for the oxidation state, the pentavalent halides, \( UX_5 \), have magnetic moments that bracket the 2.07 \( \mu_B \) average for \( U^{5+} \): 1.26 and 2.37 \( \mu_B \) for \( \text{UCl}_5 \) and \( \alpha-\text{UF}_5 \), respectively. Again, these compounds do not show a trend of lower moment with increased ligand field strength; the example higher in the spectrochemical series of ligand field strengths has the higher moment. The family of pentavalent complexes \([(\text{AdArO})_3\text{tacn})\text{U(NSiMe}_3)]\), \([(\text{tBuArO})_3\text{tacn})\text{U(NSiMe}_3)]\), \([(\text{DiaArO})_3\text{tacn})\text{U(NMes)}]\), \([(\text{AdArO})_3\text{tacn})\text{U(NMes)}]\), and \([(\text{tBuArO})_3\text{tacn})\text{U(NMes)}]\) has a wide range of room temperature magnetic moments of 2.0, 2.34, 2.55, 2.40, and 2.35 \( \mu_B \), respectively, and the values are not regular in terms of either the tacn ligand or the imido ligand. An extensive series of pentavalent uranium complexes of the formula \((\text{C}_5\text{Me}_5)_2\text{U(=N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)(X)\) where \( X = \text{OTf} \) (2.65 \( \mu_B \)), \( \text{SPh} \) (2.48 \( \mu_B \)), \( \text{OPh} \) (2.38 \( \mu_B \)), \( \text{NPh}_2 \) (2.27 \( \mu_B \)), \( \text{CCPh} \) (2.22 \( \mu_B \)), and \( \text{N=CPh}\_2 \) (2.03 \( \mu_B \)) shows magnetic moments that decrease with increasing ligand field strength. However, the halide series of the same parent compound, \((\text{C}_5\text{Me}_5)_2\text{U(=N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)(X)\) where \( X = \text{F} \) (2.22 \( \mu_B \)), \( \text{Cl} \) (2.42 \( \mu_B \)), \( \text{Br} \) (2.42 \( \mu_B \)), and \( I \) (2.34 \( \mu_B \)), does not show a periodic trend based on
ligand.\textsuperscript{60} Hence, currently there is no evidence of consistent correlation between ligand field strength and magnetic moment for any of the uranium oxidation states.

**CONCLUSION**

This study has examined the actual magnetic moment data in the literature to evaluate statements in the literature correlating magnetism with composition of uranium complexes. A survey of the magnetic moment data reported on over 500 uranium complexes shows that there is significant overlap between measured values of complexes of U\textsuperscript{3+}, U\textsuperscript{4+}, and U\textsuperscript{5+}. Since each ion has a large range of values and since there is so much overlap between the ranges, it is difficult to use room temperature values to assign oxidation states based on comparisons with other complexes. Since the overlap observed in the ranges of the low-temperature magnetic moments of U\textsuperscript{3+}, U\textsuperscript{4+}, and U\textsuperscript{5+} is smaller, low-temperature (1.8–5.0 K) values are more useful in assigning oxidation state. Ultimately, the shape of the $\mu$ versus $T$ curves and the tendency of $\mu$ to approach zero (U\textsuperscript{4+}) or not (U\textsuperscript{3+} and U\textsuperscript{5+}) are the most valuable magnetic indicators of oxidation state. These conclusions can now be made on the basis of all the magnetic data on uranium complexes currently in the literature. This survey also shows that there is no simple correlation of magnetic moment and ligand field strength. This compilation will also allow future data to be evaluated in terms of how typical a newly determined magnetic moment is for a given type of complex. If further correlations can be made, this compilation should provide the basis for discerning them as more data are collected.
REFERENCES

(25) Standard deviation was calculated by the following equation, where $x_i$, $\bar{x}$, and $n$ are the individual observations, the average, and population size, respectively. $\sigma = \sqrt{\Sigma [(x_i - \bar{x})^2 / (n - 1)]}$. 

138
(26) The upper quartile \((q_u)\) has the property that 75% of the observations fall short of \(q_u\) and 25% exceed it. The lower quartile \((q_l)\) has the analogous property in that 75% of the observations exceed \(q_l\) and 25% fall short.


(40) Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. Organometallics 1989, 8, 855.


Chapter 8

Samarium Metallocene Chemistry in Carbon Dioxide Activation and Reductive Carbon-Carbon Coupling

INTRODUCTION†

The chemistry of the lanthanides is unique compared to that of transition metals. In contrast to the more extensively studied transition metals, the f-element lanthanides are dominated by a single oxidation state, Ln(III),¹ are historically considered to participate in only ionic bonding,² and have similar reactivity in their trivalent states. It was this lack of redox chemistry and diverse reactivity that led to the lanthanides being long overlooked in organometallic chemistry.

These assumptions were first challenged in earnest with the study of samarium metallocene chemistry spearheaded by the Evans’ lab.³ Organosamarium chemistry using pentamethylcyclopentadienyl ligands, (C₅Me₅)¹⁻, ligands allowed for the isolation and study of novel divalent and trivalent samarium metallocenes, namely (C₅Me₅)₂Sm and (C₅Me₅)₃Sm,⁴,⁵ Scheme 8.1. Each of these samarium metallocenes led to a wealth of chemistry including but not limited to: small molecule activation,⁶⁻⁸ carbon-carbon bond formation,⁹,¹⁰ polymerization,⁸ nitrogen fixation¹¹ and the first examples of sterically induced reduction (SIR).¹²

Scheme 8.1. The trivalent and divalent organosamarium compounds \((C_5\text{Me}_5)_2\text{Sm}\) and \((C_5\text{Me}_5)_3\text{Sm}\).\(^4,5\)

With the success of the decamethylsamarocene system, this chemistry has been expanded to the rest of the lanthanides with successful examples of nitrogen fixation\(^13\) and the isolation and characterization of molecular divalent Ho, Er, Pr, Gd, Tb, and Lu complexes of the general formula \([Cp^\prime_3\text{Ln}][\text{K(cryptand)}]\) \((Cp^\prime = C_5\text{H}_4\text{SiMe}_3)\).\(^14,15\) These new isolable divalent species promise to further expand the reaction chemistry of the lanthanides. Despite the great potential of the new, more reducing, divalent lanthanides, their thermal instability and sterically burdened metal center must first be navigated.\(^14\) Study of the divalent samarium \((C_5\text{Me}_5)_2\text{Sm(THF)}_x\) is still a valuable system for organometallic reduction chemistry and small molecule activation.

Carbon dioxide is an attractive raw material for the synthesis of carbon-containing compounds due to its low cost and abundance.\(^16\) However, it has always been underutilized due to its unreactive nature (the strength of the C=O bonds make it a thermodynamically very stable molecule). In this context, the reduction of CO\(_2\) by highly reducing metals is an attractive process. Low-valent f-block elements have especially been of great interest in the last few years. Such f-element complexes have shown their ability to convert CO\(_2\) into various products, such as oxos, oxalates, and carbonates.\(^7,17-22\) CO\(_2\)-mediated isocyanate and carbamate formations have also been observed by multiple bond metathesis,\(^23\) as well as productive C–C bond formations by CO\(_2\) insertions in uranium complexes.\(^24,25\) The reactivity of f-block-element complexes with COS and CS\(_2\) has also been investigated experimentally.\(^7,25-29\)
The ability of samarium(II) to reduce carbon dioxide\textsuperscript{7} and, separately, to effect carbon-carbon coupling\textsuperscript{9,10} makes divalent samarium a potential candidate for coupling of CO\textsubscript{2} to form longer carbon chains. The coupling of CO\textsubscript{2} to form (O\textsubscript{2}CCO\textsubscript{2})\textsuperscript{2−} oxalate by (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm\textsuperscript{7} is an example of both these processes at once. Although further coupling with the samarium oxalate is unlikely, this reduction and coupling demonstrates the attractiveness of the system as a starting point for exploration of organometallic mediated CO\textsubscript{2} coupling. Such chemistry would have enormous environmental and industrial impacts on the global scale\textsuperscript{30} and is being actively pursued by a number of research groups\textsuperscript{31,32}.

Detailed theoretical studies have been undertaken by Professor Laurent Maron and Professor François Nief to give insight into the reaction mechanisms of samarium(II) metallocene complexes in carbon dioxide chemistry and carbon-carbon bond formation. In support of these theoretical studies, targeted experimental work was also performed at UCI to strengthen theoretical predictions with synthetic results. Reported in this chapter are the results of these studies along with the synthesis and characterization of a bimetallic samarium CO\textsubscript{2} insertion product and two bimetallic samarium complexes formed by reductive carbon-carbon bond formation of pyridine and 1-hexyne, respectively.

RESULTS AND DISCUSSION

\textbf{CO\textsubscript{2} Activation by [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm]\textsubscript{2}(\mu-O).} DFT calculations were performed by Professor Maron on the reaction of (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm(THF)\textsubscript{2} with carbon dioxide which was reported to form the oxalate, [(C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Sm]\textsubscript{2}(\mu-\kappa^2:\kappa^2\text{-O\textsubscript{2}CCO\textsubscript{2}}), by the Evans group in 1998, eq 8.1.\textsuperscript{7} As part of
the Maron theoretical study, it was predicted that \([((C_5Me_5)_2Sm)_2(\mu-O))_2\), [19] would react with carbon dioxide to form a \((\mu-\kappa_1:\kappa_2-\text{CO}_3)^{2-}\) carbonate complex, Scheme 8.2. The long known samarium oxide had been considered, like all the bridging lanthanide metallocene oxides, to be a synthetic dead end; but its reactivity with \(\text{CO}_2\) had never been formally explored.

\[\text{Scheme 8.2. Mechanistic proposals for the reduction of } \text{CO}_2 \text{ by low-valent Sm(II) complexes, as found in the literature.}\]

The theoretical prediction was explored by reacting a benzene solution of [19] with 1 atm of carbon dioxide. After exposing the reaction mixture to tetrahydrofuran the predicted
Samarium carbonate was isolated in 72% yield as a THF solvate: \([(C_5Me_5)_2Sm(THF)]_2(\mu-\kappa^1:\kappa^2-CO_3), \text{eq } 8.2.\]

\[
\text{19} \quad \begin{array}{c}
\text{Sm--O--Sm} \\
\text{1) benzene, CO}_2 \text{ (1 atm), 1 h} \\
\text{2) THF}
\end{array} \quad \text{20} \quad \text{(8.2)}
\]

Complex \textbf{20} was characterized by NMR and IR spectroscopy and elemental analysis and its molecular structure was established by X-ray crystallography, Figure 8.1. The IR spectrum contained absorptions at 1616, 1437, and 844 cm\(^{-1}\) consistent with bridging carbonates\(^{35,36}\). These absorptions shifted to 1563, 1402, and 818 cm\(^{-1}\) in the analogous compound \(20^{13}\text{C}\), in good agreement with predictions based on Hooke’s law calculations, 1579, 1405, and 824 cm\(^{-1}\), respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sm20_graph.png}
\caption{ORTEP\(^{37}\) representation of \([(C_5Me_5)_2Sm(THF)]_2(\mu-\kappa^1:\kappa^2-CO_3), \text{eq } 8.2.\), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.}
\end{figure}
A single \((\text{C}_5\text{Me}_5)^1\)^− \(^1\text{H}\) NMR resonance was observed for 20 in benzene-\(d_6\), despite the \(\kappa^1:\kappa^2\) asymmetric solid state crystal structure. Variable temperature NMR spectroscopy in toluene-\(d_8\) was unable to resolve separate resonances at temperatures as low as \(-75\ °\text{C}\), consistent with the \((\text{CO}_3)^2^-\) moiety being fluxional between the two metal centers in solution, a characteristic observed in other f-block bridging carbonates: \{[(^t\text{BuArO})_3\text{mes}]\text{U}]_2(\mu-\kappa^2:\kappa^2-\text{CO}_3),\}^{38} [\text{U}(\eta-\text{C}_8\text{H}_6\{\text{SiPr}_3-1,4\})_2(\eta-\text{C}_5\text{Me}_4\text{H})]_2(\mu-\eta^1:\eta^2-\text{CO}_3),^{39} \{\text{U}(\eta-\text{C}_8\text{H}_6\{\text{SiPr}_3-1,4\})_2(\eta-\text{C}_5\text{Me}_4\text{H})]_2(\mu-\eta^1:\eta^2-\text{CO}_3),^{39} \{[(\text{C}_4\text{H}_2\text{NMe})\text{CET}_2]_2[(\text{C}_4\text{H}_2\text{N})\text{CET}_2]\text{Sm}]_2(\mu-\kappa^2(\text{O},\text{O}'):\kappa^2(\text{O},\text{O}'')-\text{CO}_3).\}^{17} The \(^{13}\text{C}\) NMR carbonate resonance, observable only for 20-\(^{13}\text{C}\), was located at 205 ppm.

The crystal structure of 20, Figure 8.1, shows C–O bond distances in the \((\text{CO}_3)^2^-\) moiety of 1.279(4), 1.288(4), and 1.295(4) Å, suggesting a significant degree of delocalization within the dianion as the typical C–O and C=O bond lengths are 1.43 and 1.22 Å, respectively.\(^{40}\) An analogous compound, the Sm(III) porphyrinogen carbonate, \{[(\text{C}_4\text{H}_2\text{NMe})\text{CET}_2]_2[(\text{C}_4\text{H}_2\text{N})\text{CET}_2]\text{Sm}]_2(\mu-\kappa^2(\text{O},\text{O}'):\kappa^2(\text{O},\text{O}'')-\text{CO}_3),\} has similar C–O bond distances of 1.276(4) and 1.317(7) Å.\(^{17}\) The 2.211(2) Å Sm–O(\(\kappa^1\)-\text{CO}_3) bond distance in 20 is similar to the 2.1645(14) Å C–O(OPh) distance in \((\text{C}_5\text{Me}_5)\text{Sm(THF)(OPh)}).^{41}\) Additionally, the 2.392(2) and 2.398(2) Å Sm–O(\(\kappa^2\)-\text{CO}_3) distances are similar to the 2.388(3) and 2.409(3) Å Sm–O distances in \((\text{C}_5\text{Me}_5)\text{Sm(κ}^2-\text{O}_2\text{C}_5\text{Me}_5)\)\(^{42}\) and the 2.383(5) and 2.389(5) Å Sm–O distances in \{[(\text{C}_5\text{Me}_5)\text{Sm}]_2(\mu-\eta^2:\eta^2-\text{O}_2\text{CCO}_2).\}^7\)

The Sm–C(\(\text{C}_5\text{Me}_5\)) average distance in 20 is 2.760(3) Å for the two \((\text{C}_5\text{Me}_5)^1\) rings bound to Sm1 and 2.721(3) Å for the rings bound to Sm2. The 0.039 Å difference is due to the larger steric crowding and higher coordination number of Sm1 from being bound \(\kappa^2\) to the \((\text{CO}_3)^2^-\) moiety while Sm2 is bound \(\kappa^1\). These values are typical for trivalent samarium(III) \((\text{C}_5\text{Me}_5)^1\) complexes.\(^{43}\) The methyl groups are displaced away from the metal center 0.142 to
0.157 Å out of the plane of the cyclopentadienyl rings, a metric for the degree of steric crowding around f-element metalloccenes. These values indicate no unusual steric crowding.

Although DFT analysis ultimately found that the carbonate forming reaction pathway, Scheme 8.2, was unfavorable compared to the pathway that produced the oxalate, the analysis did correctly predict that \( [(C_5Me_5)_2Sm](\mu-O), \) 19, was reactive with CO\(_2\). This was unexpected since it originally was thought that oxides of this type were synthetic dead ends. Compound 19 and all the bridging lanthanide metalloccene oxides should now be re-considered as synthons. Compound 20 can be easily synthesized analytically pure in good yield (72%) and therefore it too is attractive for future reactivity studies.

**Ligand Influence on the Redox Chemistry of Organosamarium Complexes.** It has long been reported that the metal-ligand bonding of lanthanide complexes is mostly ionic. However, there is irrefutable evidence that the ligand environment does affect the reactivity and reducing power of divalent samarium. This is best exemplified by the chemistry of SmI\(_2\) which has greatly enhanced reducing power in the presence of the strongly donating hexamethylphosphoramide (HMPA) ligand. Despite this well known example, surprisingly little is known about ligand effects on the reducing power and reactivity of samarium(II) metalloccenes.

Previous experimental work by the Nief group explored the reaction of thulium(II) metalloccenes with pyridine. Their research found that only the complex with the more donating cyclopentadienyl ligands led to isolation of a reductively coupled pyridine complex, namely \([\text{Cp}^{\text{III}}_2\text{Tm}]_2[\mu-(\text{NC}_5\text{H}_5-\text{C}_5\text{H}_5\text{N})] \) (\(\text{Cp}^{\text{III}} = 1,2,4-(t\text{Bu})_3\text{C}_5\text{H}_2\)), eq 8.3. This complex is
presumably formed through electron transfer to pyridine followed by dimerization of the intermediate radical. However, an isolable product from the reaction of a thulium metallocene with a sterically equivalent but less donating ligand, i.e., $2,5^\prime$-Bu$_2$-3,4-Me$_2$C$_4$P (Dtp), could not be found and further studies to explore this ligand effect were required.$^{51}$

Using two ligands, Scheme 8.3, that are sterically similar while having different degrees of electron donation, the same model reaction with pyridine was explored with divalent samarium. In conjunction with this experimental work, DFT mechanistic analysis was performed by the Nief and Maron groups to explore the effects that different ligand environments have on this redox chemistry.

**Scheme 8.3.** The two cyclopentadienyl ligands used in this experiment. The (C$_4$Me$_4$P)$^{1-}$ ligand is significantly less donating while being sterically similar to (C$_5$Me$_5$)$^{1-}$.

With small modifications to the ligand environment, (C$_5$Me$_5$)$^{1-}$ vs (C$_4$Me$_4$P)$^{1-}$, the reactivity of the samarium(II) species was drastically altered in a model reaction with pyridine, Scheme 8.4, similar to that originally observed for thulium.$^{51}$

[Diagram of reaction scheme]
Scheme 8.4. Reaction of (C₄Me₄P)₂Sm and (C₅Me₅)₂Sm(THF)₂ with pyridine illustrating the significant effect small changes to the ligand environment can have on divalent samarium chemistry.⁵²

The reaction between (C₅Me₅)₂Sm(THF)₂ and excess pyridine in diethyl ether yielded a samarium(III) bimetallic species bridged by coupled pyridines, [(C₅Me₅)₂Sm(C₅H₅N)]₂(μ-C₁₀H₈N₂), 21. Complex 21 was characterized by ¹H and ¹³C NMR and IR spectroscopy. Elemental analysis was consistent with a composition of 21 with one neutral pyridine ligand removed. The molecular structure of 21 was confirmed by X-ray crystallography, Figure 8.2.

Figure 8.2. ORTEP representation of [(C₅Me₅)₂Sm(C₅H₅N)]₂(μ-C₁₀H₈N₂), 21, drawn at 50% probability level. Hydrogen atoms and co-crystallized solvent molecules omitted for clarity.

(C₅Me₅)₂Sm(THF)₂ performs a one electron reduction of pyridine and concomitant carbon–carbon bond formation to produce complex 21, analogous to that observed in the reaction between Cp”Tm and pyridine.⁵¹ This contrasts with the reaction of (C₄Me₄P)₂Sm and pyridine,
studied by Professor Nief’s research group, which simply yields the bis(pyridine) adduct with no redox activity observed. This model reaction illustrates the significant effect of ligand environment on samarium(II) redox chemistry.

The solid-state structure of 21 is symmetrical around the center of the C28–C28’ bond, thus imposing an anti conformation of the 4,4’-dihydrobis(4,4’-pyridine)-1,1’-diyl bridging ligand. The same conformation was also found in [TmI₂(C₅H₅N)₄]₂[μ-(NC₅H₅–C₅H₅N)]⁵³ and in [Cp''₂Tm]₂[μ-(NC₅H₅–C₅H₅N)].⁵¹ The Sm–C(C₅Me₅) average distance is 2.751(2) Å, and the Cp(centroid)–Sm–Cp(centroid) angle is 136.1°. Both are typical for samarium(III) metallocenes.⁴³ The methyl displacements in the (C₅Me₅)¹⁻ rings are 0.174 - 0.177 Å, which are also typical values for samarium metallocenes.⁴⁴ The oxidation of the Sm(II) metal center of (C₅Me₅)₂Sm(THF)₂ to Sm(III) in compound 21 is reflected by the characteristic ¹³C NMR resonance of trivalent samarium⁵⁴ and by the Sm–N(pyridine) distance, which is shorter in 21 at 2.547(2) Å than in the divalent (C₄Me₄P)₂Sm(py)₂ at 2.644(4) and 2.688(4) Å.

The DFT studies performed by Maron on this model reaction determined a reaction pathway involving a single electron transfer as the key step in the overall dimerization mechanism. The results are in good agreement with the experimental data detailed above and allow for an important insight into the effects of ligand environment on lanthanide reactivity and the electronic structure of samarium(II) compounds bearing η⁵-cyclopentadienyl ligands.⁵²

Reductive Coupling of Alkynes with (C₅Me₅)₂Sm. The reaction of samarium metallocenes with terminal alkynes has been reportedⁱ⁰ to lead to dimerization and facile reductive coupling of the alkyne to form a bimetallic complex, eq 8.4. The importance of such
single electron transfer (SET) and coupling reactions by low valent lanthanide and actinide complexes has encouraged greater mechanistic and theoretical study of such reactions. A more detailed synthetic analysis of the reactivity of \( (C_5\text{Me}_5)_2\text{Sm} \) was conducted in conjunction with detailed theoretical analysis.

Addition of neat 1-hexyne to a dark green solution of \( (C_5\text{Me}_5)_2\text{Sm} \) immediately afforded observable bubbling and a dark red/brown color, consistent with analogous reactivity reported in literature.\(^{10}\) Red solids were isolated and \( 22 \) was identified as \([((C_5\text{Me}_5)_2\text{Sm})_2(\mu-\eta^2:\eta^2-\text{BuC}_4\text{Bu})\) based on spectroscopy, elemental analysis, and X-ray crystallography, Figure 8.3, eq 8.5.
Figure 8.3. ORTEP representation of [(C₅Me₅)₂Sm]₂(μ-η²:η²-BuC₄Bu), 22, drawn at 25% probability level. Hydrogen atoms are omitted for clarity.

Compound 22 was characterized by ¹H and ¹³C NMR and IR spectroscopy and elemental analysis. ¹H NMR spectroscopy showed five resonances consistent with the solid state structure of 22, Figure 8.3, in which all four (C₅Me₅)¹⁻ rings are equivalent and the C21 and C21' atoms have lost hydrogen upon coupling. However, conclusively confirming the loss of the C21 and C21’ protons by spectroscopic techniques was not possible, and had to be determined experimentally (vide infra). The ¹³C NMR spectrum showed typical resonances for the ring and methyl carbons of a bis(pentamethylcyclopentadienyl)samarium(III) species at 115.8 and 19.5 ppm, respectively. Resonances for the trienediyl carbons are shifted more downfield, 19.5 to 11.5 ppm, relative to the pentamethylcyclopentadienyl resonances.

The bond distances of C22–C21 and C21–C21’ are 1.311(3) and 1.327(5) Å, respectively. These are intermediate between alkyne (1.20 Å) and alkene (1.34 Å) bond lengths. This is consistent with a decrease in bond order between C22–C21 and the formation of a new double
bond between the two formally independent alkyne moieties. This is similar to the previously reported complex \([\text{(C}_5\text{Me}_5\text{)}_2\text{Sm}]_2(\mu-\eta^2:\eta^2-\text{PhCH}_2\text{CH}_2\text{C}=\text{C}=\text{CH}_2\text{CH}_2\text{Ph})\)\(^{10}\) which has bond lengths of 1.286(11) and 1.353(17) Å in an analogous structure. The C23–C22–C21 and C22–C21–C21′ angles of \(22\) are 127.7(2)° and 152.4(3)°, respectively, which are in between the 120° of carbon–carbon double bonds and the 180° of carbon–carbon triple bonds. The Sm–C(C\(_5\)Me\(_5\)) average distance is 2.728(3) Å with a methyl displacement of 0.165 – 0.167 Å, both of which are typical for samarium(III) complexes.\(^{43,44}\)

The samarium metal center in \(22\) has bond lengths to C22 and C21 of 2.459(2) and 2.701(2) Å, respectively, suggesting a much greater interaction between samarium and C22 than C21. This is also seen in the previously published examples of samarium metallocene trienediyl complexes with the samarium metal center being about 0.2 Å closer to one carbon than the other.\(^{10}\)

In order to probe the mechanism for the formation of \(22\), the reaction between \((\text{C}_5\text{Me}_5)\text{Sm}(\text{BPh}_4)\)\(^{56}\) and the potassium salt of 1-hexyne, \(\text{KC}≡\text{CC}_4\text{H}_9\), synthesized by deprotonation of the alpha carbon with potassium hydride, was performed, eq 8.6. Addition of off-white hex-1-yn-1-ylpotassium as a solid to a stirring solution of red \((\text{C}_5\text{Me}_5)\text{Sm}(\text{BPh}_4)\) yielded a white insoluble product consistent with KBPh\(_4\) and a tacky red solid. The product of eq

\[
\begin{align*}
2 \cdot \text{Sm(BPh}_4) & + 2 \cdot \text{K}≡\text{Bu} \xrightarrow{\text{benzene}} \text{22} \\
& -2 \cdot \text{KBPh}_4
\end{align*}
\]
8.6 was conclusively identified as 22 by NMR spectroscopy and X-ray crystallography. With the absence of the alpha-carbon proton in hex-1-yn-1-ylpotassium it is logical that formation of 22 must proceed through the loss of the alpha-carbon protons in eq 8.5.

The experimental work detailed above helped corroborate with the DFT mechanistic studies performed by the Maron group. This work has further explored the reductive carbon-carbon coupling of alkynes.

CONCLUSION

The synthetic work reported here has provided experimental data in support of DFT studies of low valent samarium reactivity. These studies are specifically relevant to the activation and coupling of carbon dioxide along with the effects of ligand environment on lanthanide reactivity, a still inadequately understood aspect of f-element chemistry, and the carbon-carbon bond formation via reductive coupling of pyridine and alkynes. These DFT studies prompted the experimental work which led to the isolation of three new samarium bimetallic complexes, namely [(C₅Me₅)₂Sm(THF)]₂(µ-κ¹:κ²-CO₃), 20, [(C₅Me₅)₂Sm(C₅H₅N)]₂(µ-C₁₀H₈N₂), 21, and [(C₅Me₅)₂Sm]₂(µ-η²:η²-BuC₄Bu), 22. Compound 20 is the first reported reaction of [(C₅Me₅)₂Sm]₂(µ-O) in the 27 years since its initial publication.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques, under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were
purchased from Cambridge Isotope Laboratories, dried over NaK alloy, degassed by three
freeze-pump-thaw cycles, and vacuum transferred before use. $^1$H NMR spectra were recorded
on Bruker DR400, GN500, or CRYO500 MHz spectrometers ($^{13}$C spectra on the CRYO500
spectrometer operating at 125 MHz) at 298 K unless otherwise stated, and referenced internally
to residual protio-solvent resonances. Elemental analyses were conducted on a Perkin-Elmer
2400 Series II CHNS elemental analyzer. Carbon dioxide (99.98%) was purchased from Airgas
and used without further purification. The potassium salt of 1-hexyne, hex-1-yn-1-ylpotassium,$^{10}$ (C$_5$Me$_5$)$_2$Sm(BPh$_4$),$^{56}$ (C$_5$Me$_5$)$_2$Sm(THF)$_2$,$^{57}$ (C$_5$Me$_5$)$_2$Sm,$^{4}$ and [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-O)$^{33}$ were synthesized according to literature. 1-hexyne and pyridine were dried over molecular
sieves and degassed by three freeze-pump-thaw cycles prior to use.

[(C$_5$Me$_5$)$_2$Sm(THF)]$_2$(μ-$κ^1$:κ$^2$-CO$_3$), 20. In a 100 mL sidearm Schlenk flask attached to
a high vacuum line, a stirred yellow mixture of [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-O) (117 mg, 0.140 mmol) in
benzene (5 mL) was exposed to CO$_2$ at 1 atm for 1 h. The flask was evacuated to the vapor
pressure of the solvent and moved into an argon-filled glovebox. Orange-yellow solids were
isolated by centrifugation and washed once with benzene (5 mL). The solids were dissolved in
THF to form a golden yellow solution. Removal of THF under vacuum gave 20 as a yellow
solid (103 mg, 72%). The bulk product was further purified via extraction with 5 mL of hexane
and recrystallized at −35° C. $^1$H NMR (500 MHz, benzene-$d_6$): δ 1.58 (s, 60H, C$_5$Me$_5$). $^{13}$C
NMR (125 MHz, benzene-$d_6$): δ 117.5 (C$_5$Me$_5$), 18.4 (C$_5$Me$_5$). IR: 2965s, 2904s, 2857s,
2723w, 1616w, 1536w, 1437s, 1260w, 1084m, 1022m, 869m, 844m, 803w, 659w cm$^{-1}$. Anal.
Calcd for 2•THF, C$_{45}$H$_{68}$O$_4$Sm$_2$: C, 55.51; H, 7.04. Found: C, 55.49; H, 6.88.

[(C$_5$Me$_5$)$_2$Sm(THF)]$_2$(μ-$κ^1$:κ$^2$-$^{13}$CO$_3$), 20-$^{13}$C. The $^{13}$C analogue of 20 was prepared
analogously from $^{13}$CO$_2$. $^{13}$C NMR (125 MHz, benzene-$d_6$): δ 205.4 (CO$_3$), 117.2 (C$_5$Me$_5$), 18.3
(C₅Me₅). IR: 2966s, 2902s, 2722w, 1563w (calcd 1579), 1402s (calcd 1405), 1260w, 1084m, 1022m, 868m, 818m (calcd 824), 754w, 659w cm⁻¹.

\[ [(C₅Me₅)₂Sm(C₅H₅N)]_2(\mu-C₁₀H₈N₂), \textbf{21}. \] Pyridine (79 mg, 1.0 mmol) dissolved in diethyl ether (10 mL) was added to a stirred solution of (C₅Me₅)₂Sm(THF)₂ (225 mg, 0.400 mmol) in diethyl ether (5 mL). The dark purple solution quickly turned dark red upon addition. After 1 h, the solvent was removed under vacuum to yield \textbf{21} as a red powder (237 mg, 90%). The bulk product was further purified via recrystallization in THF at −35° C. Crystals suitable for X-ray diffraction were grown from a saturated THF solution or a saturated toluene/hexane solution at −35° C. \(^1\)H NMR (500 MHz, benzene-\(d_6\)): \(\delta\) 6.32 (s, 3H, py), 4.52 (s, 1H, py), 3.85 (s, 2H, py), 3.30 (s, 3H, py), 2.90 (s, 2H, py), 1.45 (s, 2H, py), 1.58 (s, 1H, py), 1.35 (s, 60H, C₅Me₅), 0.96 (s, 1H, py). \(^1^3\)C NMR (125 MHz, benzene-\(d_6\)): \(\delta\) 115.4 (C₅Me₅), 94.2 (py), 72.9 (py), 17.6 (C₅Me₅). IR: 3020w, 2964m, 2903s, 2856s, 2753w, 1633s, 1600s, 1561s, 1442s, 1379w, 1276s, 1209m, 1125w, 1009w, 968s, 728m, 706m, 625m, 579w cm⁻¹. Anal. Calcd for \textbf{21}–C₅H₅N, C₅₅H₇₅N₃Sm₂: C, 61.23; H, 7.01; N, 3.89. Found: C, 61.33; H, 7.38; N, 3.88.

\[ [(C₅Me₅)₂Sm]_2(\mu-\eta^2:\eta^2-BuC₄Bu), \textbf{22}, \textit{from (C₅Me₅)₂Sm}. \] In a glovebox, 1-hexyne (22 \(\mu\)L, 0.19 mmol) was added to a stirred dark green solution of (C₅Me₅)₂Sm (75 mg, 0.18 mmol) in toluene (6 mL). Within 3 min. the mixture was red-brown. After stirring for 25 min the solvent was removed under vacuum leaving a \textbf{22} as a red tacky solid (90 mg, 100%). Crystals suitable for X-ray diffraction were grown from a saturated toluene solution at −35° C. \(^1\)H NMR (500 MHz, benzene-\(d_6\)): \(\delta\) 1.52 (s, 60H, C₅Me₅), −1.20 (t, 6H, CH₃), −1.70 (br, 4H, CH₂), −2.20 (br, 4H, CH₂), −14.4 (br, 4H, CH₂). \(^1^3\)C NMR (125 MHz, benzene-\(d_6\)): \(\delta\) 115.8 (C₅Me₅), 20.5 (CH₃), 19.5 (C₅Me₅), 18.2 (CH₂), 18.0 (CH₂), 11.5 (CH₂). IR: 2958s, 2905s, 2858s, 2724w,
1491w, 1438m, 1378m, 1020w, 608w cm$^{-1}$. Anal. Calcd for C$_{52}$H$_{78}$Sm$_2$: C, 62.21; H, 7.83. Found: C, 62.15; H, 7.92.

$[(C_5Me_5)_2Sm](\mu-\eta^2:\eta^2$-BuC$_4$Bu), 22, from (C$_5$Me$_5)_2Sm(BPh$_4$). KCCBu (16 mg, 0.14 mmol), prepared from 1-hexyne and KH, was added as a solid to a stirred mixture of (C$_5$Me$_5)_2Sm(BPh$_4$) (100 mg, 0.135 mmol) in 10 mL of benzene. After stirring at ambient temperature overnight, white insoluble material consistent with KBPh$_4$ was removed by centrifugation. Removal of solvent from the red supernatant gave a tacky red solid that was dissolved in toluene and filtered to remove a small amount of red insoluble material. Solvent removal gave tacky red solids that analyzed as pure 22 by $^1$H NMR spectroscopy. Red crystals were obtained from a saturated toluene solution at $-35$ °C that were identified as 22.

**X-ray Crystallographic Data.** Crystallographic information for complexes 20, 21, and 22 is summarized in Table 8.1. Selected bond distances are in Table 8.2.
Table 8.1. X-ray data collection parameters for \[[(C_5\text{Me}_5)_2\text{Sm(THF)}_2]\] (μ-κ\(^1\):κ\(^2\)-CO\(_3\)), 20, \[[(C_5\text{Me}_5)_2\text{Sm(C}_5\text{H}_5\text{N})_2]\] (μ-C\(_{10}\text{H}_8\text{N}_2\)), 21, and \[[(C_5\text{Me}_5)_2\text{Sm}]_2(μ-η\(^2\):η\(^2\)-BuC\(_4\text{Bu}\)), 22.

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<th>20</th>
<th>21</th>
<th>22</th>
<th>(C(_5\text{Me}_5))(_2)Sm(^4)</th>
<th>19(^{33,44})</th>
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<td>C(<em>{52})H(</em>{78})Sm(_2)•2(C(_5\text{H}_8))</td>
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<td>198(2)</td>
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<td>Monoclinic</td>
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<td></td>
</tr>
<tr>
<td>space group</td>
<td>P(_1)</td>
<td>P2(_i)/c</td>
<td>C2/c</td>
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<td></td>
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<tr>
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<td>10.1899(6)</td>
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<td>b (Å)</td>
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<td>14.1166(9)</td>
<td>14.0443(5)</td>
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<td>c (Å)</td>
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<td>22.5205(14)</td>
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<td>3222.0(3)</td>
<td>5881.0(4)</td>
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<tr>
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Table 8.2. Selected bond lengths (Å) and angles (°) for compounds \[[(C_5\text{Me}_5)_2\text{Sm(THF)}_2]\] (μ-κ\(^1\):κ\(^2\)-CO\(_3\)), 20, \[[(C_5\text{Me}_5)_2\text{Sm(C}_5\text{H}_5\text{N})_2]\] (μ-C\(_{10}\text{H}_8\text{N}_2\)), 21, and \[[(C_5\text{Me}_5)_2\text{Sm}]_2(μ-η\(^2\):η\(^2\)-BuC\(_4\text{Bu}\)), 22 compared to known compounds \[(C_5\text{Me}_5)_2\text{Sm}\] and \[[(C_5\text{Me}_5)_2\text{Sm}]_2(μ-O)\], 19.

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<td>5.489(2)</td>
<td>4.189(1)</td>
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158
REFERENCES

Appendix A

Synthesis, Characterization, and Reduction Chemistry of Alkaline Earth Metallocenes

INTRODUCTION

This appendix describes the synthesis, characterization, and initial reduction chemistry of alkaline earth metallocenes. The previously reported series of lanthanide divalent complexes of the general formula \([(C_5H_4SiMe_3)_3Ln][K(chelate)]\) (Ln = all lanthanides but promethium; chelate = 18-crown-6 or 2.2.2.-cryptand),\(^1\)\(^\text{3}\) Scheme A.1, allowed for study of this rare oxidation state of the lanthanides. Synthesized by reduction of the parent trivalent, \((C_5H_4SiMe_3)_3Ln\), with \(KC_8\), the oxidation state of these synthetic divalent complexes was assigned based on X-ray crystallography, UV-vis, EPR spectroscopy (for Ln = Y, Gd, and Lu only), and DFT calculations.\(^1\)\(^\text{3}\)

\[
\text{M} = \text{Ln, U}
\]

Scheme A.1. Molecular formulas of lanthanum, uranium, and thorium divalent complexes previously reported in literature.

Many of the new \(\text{Ln}^{2+}\) ions, in addition to the newly reported uranium and thorium analogs, \([(C_5H_4SiMe_3)_3U][K(\text{crypt})]^4\) and \([(C_5H_3(SiMe_3)_2)_3\text{Th}][K(18-\text{crown-6})]^5\) Scheme A.1,
were once thought inaccessible given that their calculated reduction potentials (−2.7 to −3.9, vs NHE, for Lu, Y, Pr, Ho, Er, La, Ce, Tb, and Gd; −4.9 V for Th)\textsuperscript{6,7} where greater than that of the potassium (−2.9 vs NHE) reductant. However, DFT theoretical studies shows that the trigonal planar environment of the three \((\text{C}_5\text{H}_4\text{SiMe}_3)\)\textsuperscript{−} ligands leads to an empty \(d_z^2\) metal orbital that allows for reduction to the \(4f^n 5d^1\) Ln\textsuperscript{2+} electron configuration.\textsuperscript{1-3} This formulation is supported by the UV-vis, DFT and X-ray crystallography of the divalent compounds.\textsuperscript{1-3} It contrasts with the classic divalent ions (Eu, Yb, Sm, Tm, Dy, Nd) which are best described as \(4f^{n+1}\) systems.\textsuperscript{8,9}

As a means to probe this system further, the alkaline earth analogs were synthesized to provide closed shell divalent ions in the same \([(\text{C}_5\text{H}_4\text{SiMe}_3)_3]\)\textsuperscript{3−} trigonal planar environment, for comparison to the new Ln\textsuperscript{2+} ions. This could provide more stable compounds for study since the f element complexes have limited thermal instability.\textsuperscript{2} In addition, these alkaline earth complexes would have neither d nor f electrons and hence the spectroscopic data would arise solely from the ligands. These complexes would also be diamagnetic allowing for NMR analysis. Like the f-element lanthanides, the alkaline earth metals participate in primarily ionic bonding\textsuperscript{10,11} and should therefore be satisfactory surrogates. Using different metals (Ca, Sr, or Ba) and more sterically demanding cyclopentadienyl ligands allows for tuning reactivity and stability.\textsuperscript{12}

In the process of synthesizing these alkaline earth metallocenes, attempts at reducing the divalent alkaline earth metals to monovalent, M\textsuperscript{1+}, ions was undertaken. Previously reported examples of molecular monovalent alkaline earth compounds are extremely rare: an inverse sandwich calcium complex \([(\text{THF})_2\text{Ca}\{\mu-\text{C}_6\text{H}_3-1,3,5-\text{Ph}_3}\}\text{Ca}(\text{THF})_3]\),\textsuperscript{13} reported in 2009, and two Mg(I) dimeric complexes: \([\text{Mg(Priso)}]_2\) and \([\text{Mg(Nacnac)}]_2\),\textsuperscript{14} (Priso = (Ar)NC\[N(i\text{Pr})_2]\)N(Ar); Nacac = [(Ar)NC(Me)]\textsubscript{2}CH) reported in 2007, are the only examples
found in the literature. No examples of monovalent complexes for the heavier group 2 metals (Sr and Ba) have been reported.

RESULTS AND DISCUSSION

Synthesis of Alkaline Earth Metallocenes: Examples of alkaline earth metallocenes in the literature are not uncommon,\textsuperscript{15} and include the tri-substituted $[\text{C}_5\text{H}_2\text{(SiMe}_3\text{)}_3]_2\text{M}$ ($\text{M} = \text{Mg, Ca, Sr, Ba}$) metallocenes.\textsuperscript{16} Following this literature example, 2 equiv of $\text{K(C}_5\text{H}_4\text{SiMe}_3\text{)}$ were reacted with anhydrous $\text{BaI}_2$ and $\text{CaI}_2$ in THF to afford colorless THF soluble products in each case, eq A.1. Along with recovery of 1 equiv (by mass balance) of $\text{KI}$, $^1\text{H}$ NMR spectroscopy shows a single product consistent with $\text{(C}_5\text{H}_4\text{SiMe}_3\text{)}_2\text{M}$ in each case ($\text{M} = \text{Ba, 23-Ba; Ca, 23-Ca}$). Only one set of resonances for the $\text{SiMe}_3$ group and ring protons in 23 is observed, which indicates that the two cyclopentadienyl rings are equivalent on the NMR time scale. This is consistent with that reported for the analogous $[\text{C}_5\text{H}_2\text{(SiMe}_3\text{)}_3]_2\text{M}$ complexes.\textsuperscript{16}

\[
\text{MI}_2 + 2 \text{K(C}_5\text{H}_4\text{SiMe}_3\text{)} \rightarrow \text{(C}_5\text{H}_4\text{SiMe}_3\text{)}_2\text{M} - 2 \text{KI} \quad \text{(A.1)}
\]

$\text{M} = \text{Ba, 23-Ba; Ca, 23-Ca}$

Compounds 23-Ba and 23-Ca were each reacted with a THF solution of $\text{K(C}_5\text{H}_4\text{SiMe}_3\text{)}$ and 2.2.2.-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) to yield the alkaline earth complex $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{M}][\text{K(crypt)}]$ ($\text{M} = \text{Ba, 24-Ba; Ca, 24-Ca}$), eq A.2. NMR spectroscopy revealed a single product with 3:1 cyclopentadienyl to 2.2.2.-cryptand resonance and with only one set of resonance for the cyclopentadienyl ligands. This suggests that the $\text{M}^{2+}$ ions interact with the three anionic, $\text{(C}_5\text{H}_4\text{SiMe}_3\text{)}^{-}$, ligands equally on the NMR time scale. This is consistent with the structural characterization of the lanthanide analogs,
[(C₅H₄SiMe₃)₃Ln][K(crypt)], which shows uniform bonding parameters to all three ligands.¹⁻³ Unfortunately there is a significant difference in solubility between 24-Ba and 24-Ca and the lanthanide analogous, hindering growth of X-ray quality crystals in the alkaline earth compounds.

\[
(C₅H₄SiMe₃)₂M + K(C₅H₄SiMe₃) \xrightarrow{2.2.2\text{-cryptand}} [(C₅H₄SiMe₃)₃M][K(crypt)] \tag{A.2}
\]

\[23\]

\[M = \text{Ba, 24-Ba; Ca, 24-Ca}\]

Reduction Chemistry of Alkaline Earth Metallocenes: Theoretical studies of the heavier s-block metals have shown that barium has significant 5d character in its bonding interactions¹¹ and that a purely ionic description of its bonding is not sufficient.¹⁷ Given the theoretical and spectroscopic characterization that the Ln²⁺ ions are accessible because of an available dₓ² orbital in the \[(C₅H₄SiMe₃)_3\]³⁻ ligand system,² it was prudent to investigate the potential of effecting the same reduction towards the alkaline earth analogs, namely compound 24.

Off-white compound 24-Ba was dissolved in THF in the presence of 1.1 equiv of 2.2.2-cryptand and rapidly passed through a column of packed KC₈ producing a dark blue effluent. This dark blue product, 25-Ba, is thermally unstable and will decompose to a colorless solution, which is characterized by NMR spectroscopy and X-ray crystallography to contain \([K(crypt)][C₅H₄SiMe₃]\), over a few hours at room temperature. Even when stored at low temperature, −30 °C, 25-Ba decomposes overnight. No evidence of \((C₅H₄SiMe₃)₂Ba\) was observed.

Despite this instability, initial spectroscopic characterization has been possible. X-band EPR spectroscopy was taken on a 5:1 THF:Et₂O solution of freshly made dark blue 25-Ba which showed an isotropic signal, Figure A.1a, at room temperature and a rhombic line shape at 77 K,
Figure A.1b. The isotropic room temperature signal has a $g_{iso}$ value of 2.00 and a narrow line width, both consistent with an organic based radical.\textsuperscript{18} A metal based radical could possibly show hyperfine splitting due to the nuclear spin of Ba-135 and Ba-137 (3/2 +), though these isotopes only make up 17.8\% of barium’s total natural abundance.\textsuperscript{19} The only reported example of Ca$^{1+}$ ion has a room temperature EPR signal which does not show hyperfine splitting from the calcium (Ca-43, natural abundance 0.135\%, nuclear spin of 7/2−), and a $g_{iso}$ value of 2.0023.\textsuperscript{18}

\begin{figure}
\includegraphics[width=\textwidth]{epr_spectra.png}
\caption{X-band EPR spectra of a 5:1 THF:Et$_2$O solution of 25-Ba at a) 293 K and b) 77 K.}
\end{figure}

The UV-vis spectrum of 25-Ba, Figure A.2, shows a broad absorption centered at 903 nm with an approximate extinction coefficient of 25,000 M$^{-1}$ cm$^{-1}$. The half-life of 25-Ba, determined by following the disappearance of this intense absorption with UV-vis, shows the room temperature half-life to be approximately 12 min. This is considerably less stable than most of the Ln$^{2+}$ analogs, which have room temperature half-lives between 20 days and 2.3 h. Only the smallest lanthanide, lutetium, had a similar half-life of 19 min.\textsuperscript{2}
In efforts to improve the stability of compound 25 to allow further characterization, the calcium analog, 25-Ca, was synthesized under the same conditions. The 6-coordinate ionic radius of Ba\(^{2+}\), 149 pm, is significantly larger than the analogous 6-coordinate La\(^{3+}\) (117.2 pm) ionic radius, the largest of the lanthanides\(^{20}\). Ca\(^{2+}\) has a 6-coordinate ionic radius of 114 pm, within the range of the lanthanides, and it was hoped this would reflect a significant improvement in compound 25 stability. Unfortunately the stability was drastically decreased, with the dark blue of 25-Ca lasting only ca. 30 s, even when synthesized with pre-cooled reaction materials at −30 °C.

In the pursuit of more stable alkaline earth compounds, the more sterically demanding cyclopentadienyl ligand, \([C_5H_5(SiMe_3)_2]\)^{1−}, was used to form complexes analogous to 23-Ba and 24-Ba, namely \([C_5H_5(SiMe_3)_2]_2Ba\), 26, and \([{C_5H_5(SiMe_3)_2}]_3Ba][K(\text{crypt})]\), 27. Similarly, the 18-crown-6 analog of 24-Ba, \([(C_5H_5SiMe_3)_3Ba][K(18-C-6)]\), 28, was synthesized to see if the
potassium chelating agent would impact stability. In both cases, the reduction of 27 and 28 under the conditions described above resulted in products less stable relative to 25-Ba with total lifetimes of ca. 3 min and 1 min respectively. Additionally, compound 28 was unstable at room temperature.

Reactivity of Reduced Barium Complex 25-Ba: The thermal instability of 25-Ba prevented structural characterization, but it did not prevent its use in reactivity studies. The dark blue effluent produced by passing 24-Ba through a packed column of KC₈ was dripped directly into a stirred vial containing phenanthrene in THF, Scheme A.2. The dark blue reactant instantly turned dark green/yellow upon mixing with phenanthrene.
Scheme A.2. Schematic diagram of the KC₈ column used to produce 25-Ba (dark blue) and dripped directly onto a THF solution of phenanthrene, immediately producing the dark green/yellow product mixture.

The dark green/yellow reaction mixture is NMR silent with exception of peaks consistent with K(C₅H₄SiMe₃). EPR spectroscopy in 5:1 THF:Et₂O solution shows an isotropic signal with poorly resolved hyperfine splitting at room temperature, Figure A.3a, and no hyperfine structure at 77 K, Figure A.3b. It is likely that the room temperature hyperfine splitting is a result of proton coupling, not coupling to the Ba-135/Ba-137 nucleus.¹⁸
The dark green/yellow product of Scheme A.2 is much more stable than 25-Ba, but structural characterization has still been elusive. Reaction with other arene reagents is currently being investigated. The reaction of 25-Ba with toluene produces a green product with a total life time of <5 s. It is therefore prudent to first focus on larger, easier to reduce arenes such as anthracene, biphenyl, and naphthalene.

**CONCLUSIONS**

Although the synthetic studies outlined in this appendix have resulted in thermally unstable and highly reactive compounds that are difficult to crystallographically characterize, further work could produce results of high impact. Full characterization of [(C₅H₄SiMe₃)₃M][K(crypt)], 24, would be a valuable analog to the recently reported Ln²⁺ compounds of the same connectivity and geometry. Further, this alkaline earth compound would
be one of the few none f-element complexes featuring three cyclopentadienyl ligands.\textsuperscript{21} Reduction of 24 with KC\textsubscript{8} produces a species that is thermally unstable. The use of more sterically demanding cyclopentadienyl ligands, smaller metals, and different potassium chelating agents did not improve the stability of the reduced species. Reactivity is possible, however, and more stable products can be formed to help characterize the nature of these reduced species.

**EXPERIMENTAL DETAILS**

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water by using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze/pump/thaw cycles, and vacuum transferred before use. \textsuperscript{1}H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (\textsuperscript{13}C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FTIR system. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer. UV–vis spectra were collected in THF at 298 K using a Varian Cary 50 Scan UV–vis spectrophotometer. EPR spectra were collected using X-band frequency (9.3–9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge, and the magnetic field was calibrated with DPPH (g = 2.0036). Barium iodide (BaI\textsubscript{2}) and calcium iodide (CaI\textsubscript{2}) were purchased from Aldrich as anhydrous powders in sealed ampoules and used without further purification. 2.2.2.-cryptand (Aldrich) was dried overnight under high vacuum before use, 18-crown-6 (Aldrich) was
sublimed prior to use. $\text{K(C}_5\text{H}_4\text{SiMe}_3)_{22}$ and $\text{KC}_8^{23}$ was prepared by literature methods. $\text{K[C}_5\text{H}_3(\text{SiMe}_3)_2]$ was prepared from $\text{K(C}_5\text{H}_4\text{SiMe}_3)$ in an analogous procedure to the preparation of $\text{K(C}_5\text{H}_4\text{SiMe}_3)$ from $\text{K(C}_5\text{H}_5)$.\textsuperscript{22}

$\text{(C}_5\text{H}_4\text{SiMe}_3)_2\text{Ba, 23-Ba.}$ A THF (5 mL) solution of $\text{K(C}_5\text{H}_4\text{SiMe}_3)$ (180 mg, 1.0 mmol) was added to a stirred THF (10 mL) solution of $\text{BaI}_2$ (200 mg, 0.5 mmol). After stirring overnight the reaction mixture was white and opaque with insoluble material. After separation by centrifugation the light yellow supernatant was dried under reduced pressure to afford a tacky off-white solid. This sold was washed in hexane and dried further to give 23-Ba as an off-white powder (200 mg, 95%). $^1\text{H NMR (500 MHz, acetonitrile-}d_3): \delta 6.02 [s, 4\text{H, (C}_5\text{H}_4\text{SiMe}_3)], 5.94 [s, 4\text{H, (C}_5\text{H}_4\text{SiMe}_3)], 0.18 [s, 18\text{H, (C}_5\text{H}_4\text{SiMe}_3)].$ $^{13}\text{C NMR (125 MHz, acetonitrile-}d_3): \delta 117.4 [(C}_5\text{H}_4\text{SiMe}_3), 116.9 [(C}_5\text{H}_4\text{SiMe}_3), 112.8 [(C}_5\text{H}_4\text{SiMe}_3), 1.2 [(C}_5\text{H}_4\text{SiMe}_3)].$

$\text{(C}_5\text{H}_4\text{SiMe}_3)_2\text{Ca, 23-Ca.}$ Compound 23-Ca is synthesized analogously to 23-Ba by the reaction of $\text{CaI}_2$ (83 mg, 0.28 mmol) and $\text{K(C}_5\text{H}_4\text{SiMe}_3)$ (99 mg, 0.56 mmol). 23-Ca was isolated as an off-white powder (81 mg, 92%).

$[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{Ba][K(crypt)], 24-Ba.}$ A solution of 2.2.2.-crypt (130 mg, 0.35 mmol) and $\text{K(C}_5\text{H}_4\text{SiMe}_3)$ (61 mg, 0.35 mmol) in THF (5 mL) was added to a stirred solution of 23-Ba (140 mg, 0.35 mmol) in THF (5 mL). After stirring overnight, the reaction mixture was dried under reduced pressure and the tacky off-white solid washed with hexane and dried further to give 24-Ba as an off-white powder (162 mg, 84 %). $^1\text{H NMR (500 MHz, acetonitrile-}d_3): \delta 5.87 [s, 6\text{H, (C}_5\text{H}_4\text{SiMe}_3)], 5.75 [s, 6\text{H, (C}_5\text{H}_4\text{SiMe}_3)], 3.56 [m, 12\text{H, crypt}], 3.52 [m, 12\text{H, crypt}], 2.52 [m, 12\text{H, crypt}], 0.15 [s, 27\text{H, (C}_5\text{H}_4\text{SiMe}_3)].$
[(C₅H₄SiMe₃)₃Ca][K(crypt)], 24-Ca. Compound 24-Ca is synthesized analogously to 24-Ba by the reaction of 23-Ca (100 mg, 0.30 mmol), K(C₅H₄SiMe₃) (45 mg, 0.32 mmol), and 2.2.2.-crypt (96 mg, 0.32 mmol). 24-Ca was isolated as an off-white powder (210 mg, 76%).

Reduction of 24-Ba with KC₈, 25-Ba. A THF (5 mL) solution of 24-Ba (30 mg, 0.03 mmol) and 2.2.2.-crypt (13 mg, 0.030 mmol) was rapidly passed through a packed column of KC₈ to afford a dark blue solution. UV–vis (THF) λₘₐₓ, nm (ε, M⁻¹ cm⁻¹): 903 (25,000).

Reaction of 24-Ca with KC₈, 25-Ca. A THF (5 mL) solution of 24-Ca (100 mg, 0.10 mmol) and 2.2.2.-crypt (48 mg, 0.13 mmol) was rapidly passed through a packed column of KC₈ to afford a dark blue solution that rapidly (5 – 10 s) decomposed to a light yellow solution.

Synthesis of [C₅H₃(SiMe₃)₂]₂Ba, 26. Compound 26 was synthesized analogously to 23-Ba by reaction of BaI₂ (100 mg, 0.3 mmol) with K[C₅H₃(SiMe₃)₂] (130 mg, 0.51 mmol) in THF (10 mL). 26 was isolated as an off-white powder. ¹H NMR (500 MHz, acetonitrile-d₃): δ 6.19 [s, 2H, C₅H₃(SiMe₃)₂], 6.12 [s, 4H, C₅H₃(SiMe₃)₂], 0.15 [s, 36H, C₅H₃(SiMe₃)₂].

{[C₅H₃(SiMe₃)₂]₃Ba}[K(crypt)], 27. A THF (5 mL) solution of K[C₅H₃(SiMe₃)₂] (67 mg, 0.27 mmol) and 2.2.2.-crypt (100 mg, 0.3 mmol) was added to a stirred THF (5 mL) solution of 26. After stirring overnight the solvent was removed under reduced pressure and the tacky solid was washed with hexane and dried further to give 27 as an off-white powder (303 mg, 95%). ¹H NMR (500 MHz, acetonitrile-d₃): δ 6.15 [s, 3H, C₅H₃(SiMe₃)₂], 6.05 [s, 6H, C₅H₅(SiMe₃)₂], 3.56 [m, 12H, crypt], 3.51 [m, 12H, crypt], 2.52 [m, 12H, crypt], 0.11 [s, 54H, C₅H₃(SiMe₃)₂].

Reduction of 27 with KC₈. A THF (5 mL) solution of 5 (33 mg, 0.030 mmol) and 2.2.2.-crypt (12 mg, 0.030 mmol) was rapidly passed through a packed column of KC₈ to afford a dark blue solution that turned colorless after 2 – 3 min.
[(C₅H₄SiMe₃)₃Ba][K(18-C-6)], **28.** Compound **28** is synthesized analogously to **24-Ba** by the reaction of **24-Ba** (100 mg, 0.2 mmol), K(C₅H₄SiMe₃) (43 mg, 0.24 mmol), and 18-crown-6 (68 mg, 0.24 mmol) in THF (10 mL). **28** was isolated as an off-white powder that decomposed after 48 hours.

**Reduction of 28 with KC₈.** A THF (5 mL) solution of **28** (50 mg, 0.1 mmol) and 18-crown-6 (33 mg, 0.13 mmol) was rapidly passed through a packed column of KC₈ to afford a dark blue solution that turned colorless after 1 min.

**Reaction with Phenanthrene.** A THF (5 mL) solution of **24-Ba** (30 mg, 0.03 mmol) and 2.2.2.-crypt (13 mg, 0.030 mmol) was passed through a packed column of KC₈ to afford a dark blue solution, **25-Ba**. This dark blue effluent was passed directly onto a stirred THF (5 mL) solution of phenanthrene (8 mg, 0.04 mmol). The dark green/yellow reaction mixture was stirred for 35 min, layered with cold hexane (10 mL) and placed in a −30 °C freezer over night. Dark green solids were decanted and dried under reduced vacuum (20 mg).
REFERENCES

Appendix B

Room Temperature and Low Temperature Magnetic Data of
U$^{3+}$, U$^{4+}$, and U$^{5+}$ ions

This appendix presents a compilation of magnetic moment data on mono- and bi-metallic uranium complexes found in literature up to August 2014. The room-temperature magnetic moment of each monometallic uranium complex surveyed, Table B.1, as well as the moment measured at low temperature (1.8–5 K) when variable-temperature studies were performed, are reported below. Complexes are named as they are in the original literature, and data are grouped according to the oxidation state assigned by the authors. The formal oxidation state assignment by the original authors, which is usually based on other data including spectroscopic, crystallographic, and DFT studies, is maintained in this review. Data are listed in order of increasing room temperature magnetic moments for each oxidation state as low temperature data are not always available and the lowest temperatures examined are not always the same. Complexes described only on the basis of synthesis and elemental analysis are reported as well as complexes fully characterized by X-ray crystallography and other spectroscopic methods. Magnetic moments not directly given in the text of papers were determined from plots of $\chi T$ or $\mu$ versus temperature. Only monometallic complexes are included in this survey to avoid complications of metal–metal interactions in polymetallic species.

Table B.2 presents the room-temperature and low temperature (when available) magnetic moment for homovalent bimetallic complexes. Finally, a list of abbreviations for the compounds surveyed is given.
Table B.1. Room temperature (RT) and low temperature (LT) magnetic moments ($\mu_B$) of monometallic uranium complexes in various formal oxidation states, $U^{n+}$, and formal coordination numbers (CN) determined by various methods (E = Evans Method; F = Faraday Method; G = Gouy Balance; S = SQUID; V = VSM). Values determined from graphs of $\chi T$ or $\mu$ vs. temperature are denoted with a † superscript.

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<th>LT $\mu$ (Temperature in K)</th>
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Rb₂UCl₃ +3 S 3.49 53
U(BH₄)₃(2,2,2-cryptand) +3 F 3.5 55
K₂UBr₅ +3 6 S 3.52 56
NH₄UCl₄·4H₂O +3 F 3.53 57
UO₂ +3 F 3.56 49
Cs₅LiUCl₆ +3 S 3.56 53
K₂UCl₅ +3 F 3.56 41
UBr₃ +3 9 V 3.57 58
RbUCl₄·3H₂O +3 F 3.57 59
[U(NN′₃)(CH₂PMe₃)] +3 5 E 3.60 20
U(L¹°mes)(CpMe₂) +3 6 E 3.61 37
U₁ +3 9 V 3.65 2.67 (5) 58
SrUCl₅ +3 6.5 15
UF₃ +3 9 G 3.67 60
UOBr +3 9 F 3.67 49
UCl₃ +3 9 V 3.70 58
KUCl₂·3H₂O +3 F 3.70 59
U(HCOO)₃ +3 9 G 3.70 61
U[UBr₃(C₂H₅PMe₃)₂] +3 5 S 3.7¹ 1.3¹ (2) 62
NH₄UCl₄·3H₂O +3 F 3.71 59
KUCl₂·4H₂O +3 F 3.72 57
Rb₂U₁ +3 6 S 3.73 53
RbUCl₄·4H₂O +3 F 3.74 57
K₂U₁ +3 6 S 3.75 53
K₂UCl₅ +3 F 3.77 52
[U(BIPM)₃(H)I]₂(THF) [solid state] +3 5 S 3.8¹ 3.1¹ (1.8) 63
(C₅Me₅)₂U(UNO) +4 10 S 1.36 0.33 (1.8) 64
UL·(1-phenylpiperazine) +4 V 1.76 65
CP₂U(µ⁶-DABMe₆) +4 8 S 1.79 0.40 (2) 66
(µ⁶-DABMe₆)₂U(THF) +4 5 S 1.91 0.68 (2) 66
Cp₃U(2,2′-bpy)(COHPh₂) +4 9 1.93 6
[Li(THF)]₂U[O(OrBu)₆] +4 6 S 1.98 0.20 (2) 67
(η²-Ph₂PNPr₃)UCl +4 7 E 1.99 68
[UCl(Tren)₂(TIPS)] +4 5 S 2.01 0.50 (1.8) 40
(η²-Ph₂PNPr₃)₂U +4 8 E 2.03 68
Cp₃U(2,2′-bpy)(COHPh) +4 9 2.04 6
U(SO₂)²⁺·2.2 DMF +4 G 2.04 69
Cp₃U(2,2′-bpy)(COH(furan)) +4 9 2.07 6
[U(Tren)₃](THF)₂[BPh₄] +4 6 E 2.10 70
[(η⁶-ArO)₂N]U(N₃) +4 7 S 2.14 0.34 (2) 71
[NN₃]UCCPh₂(Li•THF) +4 6 S 2.14 0.5¹ (2) 72
U₁(EtO)₂ +4 6 E 2.15 73
[U(BIPM)₃(CO)(CH₂CH₂H₂O-2)]⁻·2³⁻· N₂O₃·Cl₂(THF) +4 S 2.17 0.41 (1.8) 74
[(η⁶-Me₃ArO)₃mes]U[(15C₅)Na(THF)]·3-Na +4 6 S 2.19 0.71 (5) 2
[(CH₃)₂COT]₂U  +4  10  V  2.2  75

[{{(µ⁴-Me)ArO}₃mes}U][K], 2-K  +4  7  S  2.21  0.85 (5)  2

[{{(µ⁴-Me)ArO}₃mes}U][[(18C6)K(THF)], 3-K  +4  6  S  2.22  0.65 (5)  2

[U(BIPMP)₄(tacn)]₂(THF)₂  +4  7  S  2.22  0.75 (1.8)  76

[Ph₅BuP]₄[UCl₄]  +4  S  2.22  67

U(ClO₄)₂·2(1,4-di-methylpiperazine)·THF  +4  V  2.22  65

(C₃Me₅)₂UBr  +4  10  E  2.3  77

(C₃Me₅)₂UCl  +4  10  E  2.3  77

Cp²U(PD)(thf)  +4  7  E  2.3  78

[{{(µ⁴-Me)ArO}₃mes}U][Na], 2-Na  +4  7  S  2.32  0.64 (5)  2

UCI₂·3DPA  +4  G  2.32  79

[Ph₅BuP]₄[UBr₅]  +4  S  2.33  67

U(NCS)₂·(1,4-di-methylpiperazine)  +4  V  2.34  65

UCI₂·2.5DMA  +4  G  2.35  79

Dicyclobutonouranocene  +4  10  V  2.36  80

[(µ⁶-HArO)₃mes]U[(dibahb)]  +4  7  S  2.37  0.54 (5)  3

[Cp²Co]₂[U{OB(C₅F₅)₃}₂]₂(neacn)₂  +4  6  S  2.37  0.8¹ (2)  81

(C₃Me₅)₂U(acnac)  +4  6  S  2.39  0.47 (2)  82

(C₃Me₅)₂UF  +4  10  E  2.4  77

[U(Tren)⁺(PH)(K–2,2,2-cryptand)]  +4  5  S  2.4¹  0.8¹ (1.8)  83

[U(I)(Tren)⁺]  +4  5  S  2.4¹  0.6¹ (1.8)  84

[U(F)(Tren)⁺]  +4  5  S  2.4¹  0.5¹ (1.8)  84

[U(NH₃)(Tren)⁺]  +4  5  S  2.4¹  0.6¹ (1.8)  84

[C₃Me₅]₂[Co₃(tacn)₃]  +4  5  E  2.4  85

[U(C₅H₅NC(O)NC(O)UCl₄·0.5C₅H₄]  +4  10  V  2.4  86

[U(C₅H₅N(CH₂CH₂CH₂CH₂CH₃)]₂  +4  9  V  2.42  87

UCI₂·3MFA  +4  G  2.42  79

U(COT)₂  +4  10  V  2.43  88

U(N(CH₂CH₂CH₂CH₂CH₃)]₄  +4  4  V  2.44  89

[U(Tren)⁺(PH)][K(B15C₅)₂]  +4  5  S  2.45  1.04 (1.8)  83

Cp₃UOH  +4  10  G  2.45  0.56 (4.2)  90

[Li(THF)₂][U(N=C‘BuPh)]  +4  5  S  2.45  0.94 (4)  91

U(NCS)₂·(2,5-dimethylpiperazine)  +4  V  2.45  65

UCI₂·2.5DEA  +4  G  2.46  79

UCI₂·2.5McAl  +4  F  2.47  79

[U(I)(HC(SiMe₃)₂NAr⁺)](THF)  +4  5  E  2.48  93

UCI₂·2.5DMF  +4  G  2.48  79

Cp²U(2,2’-bpy)(COMe)₂  +4  9  2.49  6

[(µ⁶-HArO)₂tacn]U(OMe)  +4  7  S  2.5¹  1.3¹ (5)  94

[(µ⁴-ArO)₂tacn]U(OMe)  +4  7  S  2.5¹  1.1¹ (5)  94

[U(N(N₃)(NEt₁)]  +4  5  E  2.50  95

[(CH₃)₂COT]₂U  +4  10  S  2.5  75

UCI₂·2.5BuL  +4  F  2.52  92

[U(Cp²)(N(CH₂H₂py)]₂][BPh₄]  +4  9  S  2.53  0 (2)  5

[U(Cl)(C₂H₂N·2-NSiMe₃)]  +4  7  E  2.54  96
UC1•4BAN +4 +4 G 2.55 79
UC1Cl•5DMA +4 +4 G 2.56 79
\{[(CH2)2]•calix[4]tetrapyrrole\}•ULi(C2H5)2(THF)2 +4 9 G 2.58 50
[U(N(CH2CH3)2SiMe2)2(CH2CH2NSiMe2CHBPh2)]•(THF)] +4 6 E 2.59 97
(C8H12)2U +4 10 G 2.59 1.21 (5) 98
UC1•3MAA +4 +4 G 2.59 79
[U(N(SiMe2)2)2]•H +4 4 G 2.6 39
BH2UN(SiMe2)2] +4 3 E 2.6 99
[U(N3)(TrenTIPS)] +4 5 S 2.61 0.41 (1.8) 84
[U(TrenTIPS)2](PH3) +4 5 S 2.61 0.61 (1.8) 83
\{N[(CH3)3P]2C6H4\}•UCl +4 8 S 2.6 0.41 (1.8) 100
U(CH2C8H4) +4 4 G 2.60 101
Tp\•U(NPh) +4 7 G 2.6 102
[U(C(PPh3)2NMes)2] +4 6 E 2.61 103
[U(C(PPh2NSiMe2)2](Cl)(μ-Cl)2Li(thf)]2 +4 6 S 2.62 0.34 (1.8) 104
U(salen)Cl•bipy +4 8 S 2.62 105
(L8)U1 +4 5 E 2.63 105
\[U(BIPM)\]•UCl2 •(C(NCy)2)-C,N,N',N'''(Cl)(μ-Cl)2Li(THF)]2 +4 S 2.64 0.22 (1.8) 74
Cp2USH +4 10 G 2.65 0.52 (4.2) 90
[C8H12COT]2U +4 10 V 2.65 75
Bis(tetrahydrobenzo[8]annulene)uranium +4 10 V 2.65 106
UCp3(C8H4N2) +4 11 V 2.67 107
(η5-Pr3PNMes)UI +4 7 E 2.67 68
UC1•4VaL +4 G 2.67 92
U(O-2,6-Bu2C6H4)4 +4 4 G 2.68 108
U(N(CH2CH2CH2)2) +4 4 V 2.69 89
Na3UF7 +4 2.69 109
(C8Me2)2U•(-NC(CH3)(3-F-C8H4)2)2 +4 8 S 2.71 0.61 (2) 110
\{[N(SiMe2)2]•U(CH2Si)N(SiMe2)\} +4 4 E 2.7 39
MeU[N(SiMe2)2] +4 4 E 2.7 99
\{[(2HArO)2]tacn]U(η5-3-phen(Ind))] +4 8 S 2.7 1.2 (5) 24
\[^{18}BuNON\]U(η5-C5Me3)CH3 +4 7 E 2.7 111
[U(EtCH(Me)NDipp][Et(CH2)2Ndipp][N(SiMe2)2]2 +4 4 E 2.70 37
(dmpe)U(CH2C8H4)4 +4 6 G 2.70 101
Tpa•U(NMes) +4 7 G 2.7 102
Tpa•U(NAd) +4 7 G 2.7 102
U(OSiMe2)2•bipy +4 8 E 2.7 112
\{[(1DMF,DMF)ArO]3]tacn\}UCl +4 7 S 2.71 0.40 (2) 113
U(O)(CMes2)H4 +4 4 2.71 42
\{[(2HArO)2]tacn]U(dbahh)] +4 7 S 2.7 1.16 (5) 3
[U\{HC(SiMe2)2NaR]]•(THF)]2 +4 6 E 2.72 93
UCl•2DMBA +4 G 2.72 79
\[UL4\] L=OCMe2CH3[1-C(NCHCHN')Pr] +4 7 E 2.72 114
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<td>[U(C6H6N-2-NSiMe3)2]4</td>
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[U(Cl)[HC(SiMe₂NAr)₃]](THF) +4 5 E 2.88 93

UCI₄·BAM +4 G 2.88 79

UCI₄·4EA +4 G 2.88 79

[(t⁴ArO)₂tacn]U[CO₂] +4 7 S 2.89 1.51 (5) 122

[U{(NHCMe₂SiPr₂)NCH₂CH₂N(SiMe₂)₃}₂] +4 5 S 2.89 0.74 (1.8) 84

[(t⁴ArO)₂tacn]U(I) +4 7 S 2.9¹ 0.7¹ (5) 122

[(t⁴ArO)₂tacn]U(Br) +4 7 S 2.9¹ 0.7¹ (5) 122

[(t⁴ArO)₂tacn]U(Cl) +4 7 S 2.9¹ 0.7¹ (5) 122

[⁺⁻NON]U(C₂H₅₂) +4 5 E 2.90 111

[U{(CH₂CH₂NSiPr₂)₂(CH₂CH₂NSiPr₂)₂}C[HNMeCH₂]] +4 5 E 2.90 133

[Et₂N][U(NCS)₂(bipy)₂] +4 S 2.90 0.35 (2) 135

FU[N(SiMe₂)₂]₃ +4 4 2.91 42

U(U(N)₂Ar₃) +4 4 E 2.92 29

U(acac)₄ +4 8 S 2.92 136

[U(BIPM₃p)(Cl)(μ-Cl)₂(Li)(tmeda)(OCPH₂)] +4 7 E 2.93 76

[U(N(SiMe₂)₂)₂] +4 4 S 2.94 1.3¹ (2) 137

[U(N(SiMe₂H)₂)] +4 4 E 2.94 39

[Li(DME)₂][U(CH₂SiMe₂)]₃ +4 5 S 2.96 1.89 (2) 67

UCI₄·6AcA +4 G 2.96 79

Tp²U(η²-Se₂) +4 8 S 2.98 0.94 (4) 138

(NPN)₂U[η²-(N,N')=N-N=CPh₂] +4 7 E 2.99 139

[[(t⁴ArO)₂(PhCN)]tacn]U(enolate) +4 8 S 3.00 0.47 (3.5) 140

[U(BIPM₃pΣH)(Cl)₂(THF)] +4 7 S 3.0¹ 0.4¹ (1.8) 63

U(ClO₄)₂·(1,4-di-methylpiperazine) +4 V 3.0 65

U(TTA)₄ +4 8 S 3.01 136

[U(Tren₃TMS)[N(SiMe₂)₂]₂] +4 5 E 3.03 70

[U(NCy₂)[HC(SiMe₂NAr)₃](THF)] +4 5 E 3.04 93

UBr₄·(1,4-dimethylpiperazine) +4 V 3.05 65

[U(BIPM₃p)(μ-Cl)₂(Li)(tmeda)(OCPBu⁺)] +4 7 E 3.08 76

[U(NN₃)₂] +4 5 E 3.08 95

U(bac)₄ +4 8 S 3.08 136

UCI₄·4DPF +4 G 3.08 79

[⁺⁻NON]U(N(SiMe₂)₂) +4 4 E 3.09 141

[Li(THF)₂][U(CH₂Bu)₃] +4 5 S 3.09 2.36 (2) 67

Cp²UF₂ +4 8 S 3.11 42

UO₂ +4 8 S 3.11 136

Cp²UF₄(₃Mes)PDI₃Mes) +4 8 S 3.12 1.25 (5) 142

[⁺⁻NON]U(C₂Ph₂) +4 5 S 3.12 0.5¹ (2) 72

[U(N(SiMe₂)₂SiMe₂CH₂BBNH)₂] +4 4 E 3.12 143

UCI₄·4MF +4 G 3.13 144

[(t⁴ArO)₂tacn]U(Cl) +4 7 S 3.13 0.69 (2) 35

[U(BIPM₃p)(μ-Cl)₂(Li)(OE₂)(tmeda)] +4 7 S 3.13 0.66 (1.8) 76

UCI₄·4MF +4 G 3.13 79

[U(NN₃)₅Br] +4 5 E 3.14 95
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<td>[(⁻⁵⁺&lt;sup&gt;Me₃Si&lt;/sup&gt;ArO₂)tacn]U(O)</td>
<td>+5</td>
<td>7 S</td>
<td>1.98</td>
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<td>[UN(Tren&lt;sup&gt;2&lt;/sup&gt;PP)][Na(12C₄)₂]</td>
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<td>2.40</td>
<td>1.64 (5)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,6'-Pr₂-C₆H₃)(Cl)</td>
<td>+5</td>
<td>8 S</td>
<td>2.42</td>
<td>1.4² (2)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,6'-Pr₂-C₆H₃)(Br)</td>
<td>+5</td>
<td>8 S</td>
<td>2.42</td>
<td>1.4² (2)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,6'-Bu₂-C₆H₃)(F)</td>
<td>+5</td>
<td>8 S</td>
<td>2.46</td>
<td>1.0² (2)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,6'-Pr₂-C₆H₃)(SPh)</td>
<td>+5</td>
<td>8 S</td>
<td>2.48</td>
<td>1.1² (2)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,4,6'-Bu₁-C₆H₃)(Cl)</td>
<td>+5</td>
<td>8 S</td>
<td>2.51</td>
<td>1.0³ (2)</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,4,6'-Bu₁-C₆H₃)(I)</td>
<td>+5</td>
<td>8 S</td>
<td>2.53</td>
<td>1.0³ (2)</td>
</tr>
<tr>
<td>[(⁻⁴⁺ArO₂)tacn]U(NTMS)</td>
<td>+5</td>
<td>7 S</td>
<td>2.55</td>
<td>1.26 (5)</td>
</tr>
<tr>
<td>[UO₂Py₃]I·py</td>
<td>+5</td>
<td>E</td>
<td>2.6</td>
<td>172</td>
</tr>
<tr>
<td>(C₅Me₃)₂U(=N-2,6'-Pr₂-C₆H₃)(OTf)</td>
<td>+5</td>
<td>8 S</td>
<td>2.65</td>
<td>1.1¹ (2)</td>
</tr>
<tr>
<td>UCl₃(2-mcpyp)₂</td>
<td>+5</td>
<td>G</td>
<td>2.68</td>
<td>167</td>
</tr>
<tr>
<td>UCl₃(diphen)</td>
<td>+5</td>
<td>G</td>
<td>2.70</td>
<td>171</td>
</tr>
<tr>
<td>UCl₃(pyp)₂</td>
<td>+5</td>
<td>G</td>
<td>2.74</td>
<td>167</td>
</tr>
<tr>
<td>UCl₃(EBDPP)</td>
<td>+5</td>
<td>G</td>
<td>2.76</td>
<td>167</td>
</tr>
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</table>
\[ \text{UCl}_6(\text{dipy})\text{Cl} \quad +5 \quad \text{G} \quad 2.78 \quad 167 \]
\[ \text{UCl}_3\text{PhTeTePh} \quad +5 \quad \text{G} \quad 2.84 \quad 167 \]
\[ \text{UCl}_3(\text{oxineH})_4 \quad +5 \quad \text{G} \quad 2.84 \quad 167 \]
\[ \text{UCl}_3(\text{phen})_2 \quad +5 \quad \text{G} \quad 2.86 \quad 167 \]
\[ [\text{Li(THF)}][(\text{THF})(\text{Me}_{2}\text{Si})_2\text{NLiO}(\text{THF})]_2(\text{L})] \quad +5 \quad 7 \quad \text{S} \quad 2.86 \quad 0.88 (2) \quad 176 \]
\[ \text{UCl}_3\text{PhSeSePh} \quad +5 \quad \text{G} \quad 3.10 \quad 171 \]
\[ [\text{U}(\text{dbabhl})_2][\text{nBu}_2\text{N}] \quad +5 \quad 6 \quad \text{S} \quad 3.70 \quad 1.16 (5) \quad 177 \]
\[ \text{UCl}_3(\text{enbissal})_2 \quad +5 \quad \text{G} \quad 3.77 \quad 167 \]

\(^a\)Formal coordination number for inorganic salts given when available in the literature.\(^a\)

\(^b\)Magnetic measurement performed for this work.

**Table B.2.** Room temperature (RT) and low temperature (LT) magnetic moments (\(\mu_B\)) of bimetallic uranium complexes in various formal oxidation states, \(\text{U}^{\text{n+}}\), and formal coordination number (CN) determined by various methods (\(E = \text{Evans Method; F = Faraday Method; G = Gouy Balance; S = SQUID; V = VSM}\)). Values determined from graphs of \(\chi T\) or \(\mu\) vs. temperature are denoted with a † superscript. Values reported without specifying if per uranium metal or per formula unit are denoted with a § superscript.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxid. State</th>
<th>CN(^a)</th>
<th>Method</th>
<th>RT (\mu) ((\mu_B))</th>
<th>LT (\mu) ((\mu_B)) (Temperature in K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\mu\text{-toluene})\text{U}_2(\text{N}[\text{Bu}]\text{Ar})_4)</td>
<td>+3</td>
<td>5</td>
<td>S</td>
<td>1.5</td>
<td>0.25 (5)</td>
<td>43</td>
</tr>
<tr>
<td>((\text{NNI})_2\text{U}_2(\mu-\eta^5:\eta^5-C_6\text{H}_6))</td>
<td>+3</td>
<td>5</td>
<td>S</td>
<td>1.8</td>
<td>0.74 (5)</td>
<td>179</td>
</tr>
<tr>
<td>(<a href="">(\text{Me}_{2}\text{Si})_2\text{N}[\text{C}_6\text{Me}_3]\text{U}_2</a>)</td>
<td>+3</td>
<td>7</td>
<td>E</td>
<td>1.8</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>([\text{Li(THF)}]_2[\text{U}_2(\text{-CH}_2\text{-})<em>2\text{r-calix}[4]\text{tetrapyrrole}]</em>{\mu-I})</td>
<td>+3</td>
<td>8</td>
<td>S</td>
<td>1.99</td>
<td>0.55 (2)</td>
<td>181</td>
</tr>
<tr>
<td>([\text{C}_6\text{Me}_3\text{C}_6\text{H}_6]\text{U}_2](\mu-\eta^5:\eta^5-C_6\text{H}_6))</td>
<td>+3</td>
<td>9</td>
<td>E</td>
<td>2.1</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>([\text{[(DtbpoO)]_2U}_2(\mu-\eta^5:\eta^5-C_6\text{H}_6))</td>
<td>+3</td>
<td>5</td>
<td>E</td>
<td>2.7</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>([\text{[(SiMe}_3\text{)]_2}\text{U}_2(\eta^5-\eta^5-C_6\text{H}_6))</td>
<td>+3</td>
<td>5</td>
<td>E</td>
<td>2.7</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>([\text{[U(OSi(OBU)_2]_2(\mu-\eta^5:\eta^5-C_6\text{H}_6)]}_2)</td>
<td>+3</td>
<td>5</td>
<td>S</td>
<td>2.78</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>([\text{[U(NN))]_3}\mu^2-\eta^7-\eta^7-\eta^7\text{N_2}]</td>
<td>+3</td>
<td>5</td>
<td>E</td>
<td>3.22</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>([\text{[U[N(Me_5Si)]_2]_2(\mu-N(H)(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)]}_2)</td>
<td>+3</td>
<td>5</td>
<td>S</td>
<td>3.53</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>(\text{RbU}_2\text{Cl}_7)</td>
<td>+3</td>
<td>5</td>
<td>S</td>
<td>3.74</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>([\text{[U(BIPM)}^{\text{TMSS}}(\text{H})_2(\mu-\eta^5:\eta^5-C_6\text{H}_2\text{CH}_3)])</td>
<td>+3</td>
<td>7</td>
<td>S</td>
<td>3.50</td>
<td>2.17 (1.8)</td>
<td>63</td>
</tr>
<tr>
<td>([\text{[((\text{Ar})_2O)]_2}(\mu-\eta^5:\eta^5-C_6\text{H}_2\text{CH}_3)])</td>
<td>+4</td>
<td>8</td>
<td>S</td>
<td>1.65</td>
<td>0.26 (2)</td>
<td>(184)</td>
</tr>
<tr>
<td>(<a href="%5Cmu-%5Ctext%7BNPh%7D">\text{[(NNI)]}_2</a>_2)</td>
<td>+4</td>
<td>4</td>
<td>S</td>
<td>1.9</td>
<td>0.6 (5)</td>
<td>185</td>
</tr>
<tr>
<td>([\text{UF}_2(\text{H}_2\text{O})_2\text{O}_2\text{C}_6\text{H}_3]_2)</td>
<td>+4</td>
<td>S</td>
<td>2.04</td>
<td>0.2 (5)</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>([\text{[U(Tren)}^{\text{TMSS}}]_2(\mu-O)])</td>
<td>+4</td>
<td>5</td>
<td>E</td>
<td>2.09</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>([\text{[K(THF)]_2}][\text{K(THF)}_2]\text{U}_2(\text{CH}_2\text{C}_6\text{H}_3)]_2)</td>
<td>+4</td>
<td>6</td>
<td>S</td>
<td>2.11</td>
<td>0.34 (2)</td>
<td>67</td>
</tr>
<tr>
<td>([\text{K}_2(\text{U(OSi(OBu)_2)]_2}(\mu-\eta^5:\eta^5-C_6\text{H}_6)])</td>
<td>+4</td>
<td>6</td>
<td>S</td>
<td>2.23</td>
<td>0.4 (2)</td>
<td>183</td>
</tr>
<tr>
<td>([\text{DtbpoO}]_2\text{UOCOCO(ODtbpo)}_2)</td>
<td>+4</td>
<td>4</td>
<td>E</td>
<td>2.3</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>([\text{[((\text{Ar})_2O)]_2}(\mu-\eta^7:\eta^7-\text{Se}_4)])</td>
<td>+4</td>
<td>7</td>
<td>S</td>
<td>2.30</td>
<td>0.39 (2)</td>
<td>(184)</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{[HC(SiMe}_2\text{NAr}^\text{+})_2\text{]}\text{[U(Cl)(\text{\textmu-Cl})\text{U(THF)}_2]} & \quad +4 \quad 6 \quad \text{E} \quad 2.79^{\text{§}} \quad 93 \\
\text{[U(NEi)}_2\text{]} & \quad +4 \quad 4 \quad \text{S} \quad 2.81^{\text{§}} \quad 197 \\
\text{[[BIPM}^{\text{TMS}}\text{]}\text{[U(Cl)(\text{\textmu-Cl})_2\text{U(THF)}_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.1^{\text{§}} \quad 0.7^{\text{†}} (1.8) \quad 63 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.2^{\text{§}} \quad 0.4^{\text{†}} (2) \quad 198 \\
\text{[Na([Ne-Bu]}\text{Ar})_2]\text{[U[CH}_2\text{CH}_3\text{NSiMe}_2\text{]}\text{[CH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2]} & \quad +4 \quad 6 \quad \text{E} \quad 3.22^{\text{§}} \quad 199 \\
\text{[N(\text{\textmu-NSiMe}_2\text{]}\text{[\text{\textmu-Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.3^{\text{§}} \quad 0.4^{\text{†}} (2) \quad 198 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.4^{\text{§}} \quad 0.5^{\text{†}} (2) \quad 200 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.5^{\text{§}} \quad 0.5^{\text{†}} (2) \quad 200 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.4^{\text{§}} \quad 0.5^{\text{†}} (2) \quad 200 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.4^{\text{§}} \quad 0.5^{\text{†}} (2) \quad 200 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.3^{\text{§}} \quad 0.6^{\text{†}} (5) \quad 32 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.5^{\text{§}} \quad 0.7^{\text{†}} (2) \quad 198 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.6^{\text{§}} \quad 0.6^{\text{†}} (2) \quad 198 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.64^{\text{§}} \quad 0.93^{\text{§}} (5) \quad 32 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 6 \quad \text{S} \quad 3.74^{\text{§}} \quad 0.71^{\text{(2)}} \quad 9 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 8 \quad \text{S} \quad 3.75^{\text{§}} \quad 0.71^{\text{(2)}} \quad 9 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{E} \quad 3.82^{\text{§}} \quad 0.71^{\text{(2)}} \quad 63 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 3.8^{\text{§}} \quad 0.7^{\text{†}} (2) \quad 198 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 5 \quad \text{S} \quad 4.00^{\text{§}} \quad 0.69^{\text{(1.8)}} \quad 202 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 7 \quad \text{S} \quad 4.0^{\text{§}} \quad 1.1^{\text{†}} (2) \quad 198 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +4 \quad 5 \quad \text{G} \quad 5.17^{\text{§}} \quad 50 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 6 \quad \text{S} \quad 1.35 \quad 0.31^{\text{(2)}} \quad 183 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 7 \quad \text{S} \quad 1.53 \quad 0.31^{\text{(2)}} \quad 183 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 5 \quad \text{G} \quad 1.54 \quad 0.31^{\text{(2)}} \quad 156 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 10 \quad \text{S} \quad 2.08 \quad 0.31^{\text{(2)}} \quad 165 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 10 \quad \text{S} \quad 2.12 \quad 1.30^{(5)} \quad 165 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 6 \quad \text{S} \quad 2.13 \quad 0.97^{(2)} \quad 183 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 5 \quad \text{S} \quad 2.26 \quad 0.8^{(1.8)} \quad 40 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 6 \quad \text{S} \quad 2.40 \quad 0.59^{(1.8)} \quad 204 \\
\text{[Na([DAhO}_2\text{]}\text{[U(\text{\textmu-N})\text{U([Ne-Bu]}\text{Ar})_2]} & \quad +5 \quad 6 \quad \text{S} \quad 3.22^{\text{§}} \quad 0.88^{(1.8)} \quad 205 \\
\end{align*}
\]

\(^{a}\text{Formal coordination number for inorganic salts given when available in the literature.}\)
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>18C6</td>
<td>18-crown-6 ether</td>
</tr>
<tr>
<td>12C4</td>
<td>12-crown-4 ether</td>
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<tr>
<td>AA</td>
<td>acetamide</td>
</tr>
<tr>
<td>AAN</td>
<td>acetanilide</td>
</tr>
<tr>
<td>AcA</td>
<td>acrylamide</td>
</tr>
<tr>
<td>dippap</td>
<td>4,6-di-tert-butyl-2-[(2,6-diisopropylphenyl)-amido]phenolate</td>
</tr>
<tr>
<td>B15C5</td>
<td>benzo-15-crown-5 ether</td>
</tr>
<tr>
<td>bac</td>
<td>benzoyleacetonato</td>
</tr>
<tr>
<td>BAM</td>
<td>benzamide</td>
</tr>
<tr>
<td>BAN</td>
<td>benzanilide</td>
</tr>
<tr>
<td>BcMe</td>
<td>dihydrobis(methylimidazolyl)borate</td>
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<tr>
<td>BpMe</td>
<td>dihydrobis(methylpyrazolyl)borate</td>
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<td>bpy; bipy</td>
<td>2,2′-bipyridine</td>
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<td>BIPMDipp</td>
<td>C(PPh₂NDipp)₂; Dipp = C₆H₃-2,6-iPr₂</td>
</tr>
<tr>
<td>BIPMmes</td>
<td>C(PPh₂NMes)₂; Mes = C₆H₂-2,4,6-Me₃</td>
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<td>C(PPh₂NSiMe₃)₂</td>
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<td>BuL</td>
<td>γ-butyrolactam</td>
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<tr>
<td>CaL</td>
<td>ε-caprolactam</td>
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<tr>
<td>COT</td>
<td>C₈H₈</td>
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<tr>
<td>Cp</td>
<td>C₅H₅</td>
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<tr>
<td>Cp*</td>
<td>C₅Me₅</td>
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<tr>
<td>Cp′</td>
<td>C₅H₄SiMe₃</td>
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<tr>
<td>Cp&quot;</td>
<td>1,3-(Me₃Si)₂C₄H₃</td>
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<tr>
<td>Cp⁺⁺</td>
<td>1,3-(Me₃C)₂C₅H₃</td>
</tr>
<tr>
<td>CpP</td>
<td>1-(7,7-dimethylbenzyl)cyclopentadienide</td>
</tr>
<tr>
<td>cupf</td>
<td>cupferronato</td>
</tr>
<tr>
<td>MesDABMe</td>
<td>ArN=C(Me)C(Me)=NAr; Ar = 2,4,6-trimethylphenyl</td>
</tr>
<tr>
<td>dbm</td>
<td>dibenzoylethano</td>
</tr>
<tr>
<td>DEB</td>
<td>diethynylbenzene</td>
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<tr>
<td>DEA</td>
<td>N,N′-diethylacetamide</td>
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<tr>
<td>dipp</td>
<td>C₆H₃-2,6-iPr₂</td>
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<tr>
<td>DMA</td>
<td>N,N′-dimethylacetamide</td>
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<td>DMBA</td>
<td>N,N′-dimethylbenzamide</td>
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<tr>
<td>DMF</td>
<td>N,N′-dimethylformamide</td>
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<td>dmpe</td>
<td>1,2-bis(dimethylphosphino)ethane</td>
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<td>DPA</td>
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<tr>
<td>DPF</td>
<td>N,N′-diphenylformamide</td>
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<tr>
<td>dpp-BIAN</td>
<td>1,2-bis(2,6-diisopropylphenylimino)-acenaphthylene</td>
</tr>
<tr>
<td>EA</td>
<td>N-ethylacetamide</td>
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</tbody>
</table>
enbissal  ethylenebis(salicylaldimine)
gu      guanine
Hdbabh  2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene
IMC:    tetramethylimidazol-2-ylidene
isq     iminosemiquinone
MA      N-methylacetamide
MAA     N-methylacetanilide
MBuL    N-methyl-γ-butyrolactam
MCaL    N-methyl-ε-caprolactam
mcpy    2-mercaptopyrindine
MF      N-methylformamide
MFA     N-methylformanilide
′BuNON  [′BuNH(SiMe2)]2O
ODtbp   OC6H3-Bu′-2,6
ophen   o-phenanthroline
OTtbp   OC6H2-Bu′-2,4,6
Oxine   8-hydroxyquinoline
PDI     pyridine-(diimine)
\text{MesPDI}^\text{Me}  2,6-((\text{Mes})N=CMe)2-C5H3N; \text{Mes} = C6H2-2,4,6-Me3
Pipz    piperazine
Pn*     C_{14}H_{18}
Pz       pyrazolate
T       tropolono
terpy   2,2′:6′,2″-terpyridine
tfac    trifluoroacetylacetonato
tmma   N,N,N′,N′-tetramethylmalonamide
Tp*; TpMe2 hydrotris(3,5-dimethylpyrazolyl)borate)
tren    tris(2-aminoethyl)amine
TTA     thenoyltrifluoroacetonato
Val     δ-valerolactam
REFERENCES


