

Supporting Information

Stabilization of M^{IV} (M = Ti, Zr, Hf, Ce, and Th) Using a Selenium Bis(Phenolate) Ligand

Andrew C. Behrle,¹ Jessica R. Levin,² Jee Eon Kim,² Jonathan M. Drewett,¹ Charles L. Barnes,¹
Eric J. Schelter,² and Justin R. Walensky^{1*}

¹ Department of Chemistry, University of Missouri-Columbia, 601 S. College Avenue,
Columbia, MO 65211-7600, USA

² P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of
Pennsylvania, Philadelphia, Pennsylvania 19104, USA

Table of Contents

| | |
|---|----|
| Synthesis of Na ₂ ^{Ar} OSeO..... | S2 |
| Synthesis of {Ce[^{Ar} OSeO] ₂ } ₂ {Na(THF) ₃ }..... | S2 |
| Figure S1. Cyclic voltammogram of Ti(^{Ar} OSeO) ₂ , 2..... | S3 |
| Figure S2. Linear plot of scan rate vs. peak currents for Ti(^{Ar} OSeO) ₂ , 2..... | S3 |
| Figure S3. Cyclic voltammogram of Th[^{Ar} OSeO] ₂ (THF) ₂ , 5..... | S4 |
| Figure S4. Cyclic voltammogram of Ce(^{Ar} OSeO) ₂ (THF) ₂ , 6..... | S4 |
| Figure S5. Cyclic voltammogram of [Ce(^{Ar} OSeO) ₂][Na(THF) ₃]..... | S5 |
| Figure S6. ¹ H NMR spectrum of Hf[^{Ar} OSeO] ₂ (THF)..... | S6 |
| Table S1. Electrochemical Data for 6..... | S7 |
| Table S2. Electrochemical data for [Ce(^{Ar} OSeO) ₂][Na(THF) ₃]..... | S8 |

Na₂^{Ar}OSeO. A 20 mL scintillation vial was charged with H₂^{Ar}OSeO, **1** (800 mg, 1.63 mmol) and THF (8 mL) was added. Then, NaN(SiMe₃)₂ (659 mg, 3.59 mmol) was added at room temperature and the reaction mixture was stirred for 4 h and filtered over a Celite pipette. The solution was concentrated, layered with hexanes and placed in a -23 °C freezer overnight to yield a white solid (828 mg, 95%). An NMR sample was taken in C₆D₆ and quenched with D₂O to ensure **1** was fully deprotonated.

{Ce[^{Ar}OSeO]₂}{Na(THF)₃}. A 20 mL scintillation vial was charged with Na₂^{Ar}OSeO, (200 mg, 0.375 mmol) and THF (6 mL) was added. A second 20 mL scintillation vial was charged with Ce(OTf)₃ (100 mg, 0.170 mmol) and THF (6 mL) was added. Both vials were placed in a -23 °C freezer for 10 minutes and the Na₂^{Ar}OSeO solution was added to Ce(OTf)₃. The reaction was allowed to stir for 15 h to yield a pale red colored solution. The reaction was filtered over a Celite pipette, concentrated, and layered with hexanes to yield a white precipitate (147 mg, 64%).
¹H NMR (C₆D₆, 25°C): δ 8.63 (s, 4H, ArH), 5.34 (s, 36H, ^tBuH), 4.86 (s, 4H, ArH), 2.72 (THF), 1.13 (s, 36H, ^tBuH), 1.00 (THF).

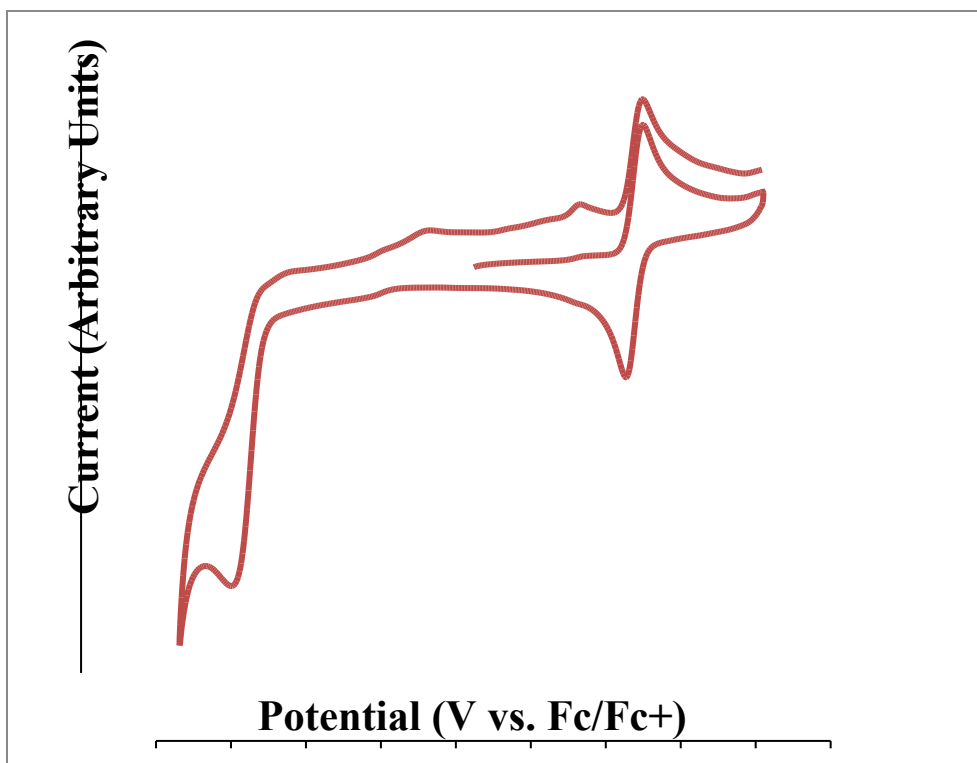


Figure S1. Cyclic voltammogram of $\text{Ti}(\text{ArOSeO})_2$, **2**, showing full scan with ligand-based oxidation at 0.99 V vs. Fc/Fc^+ .

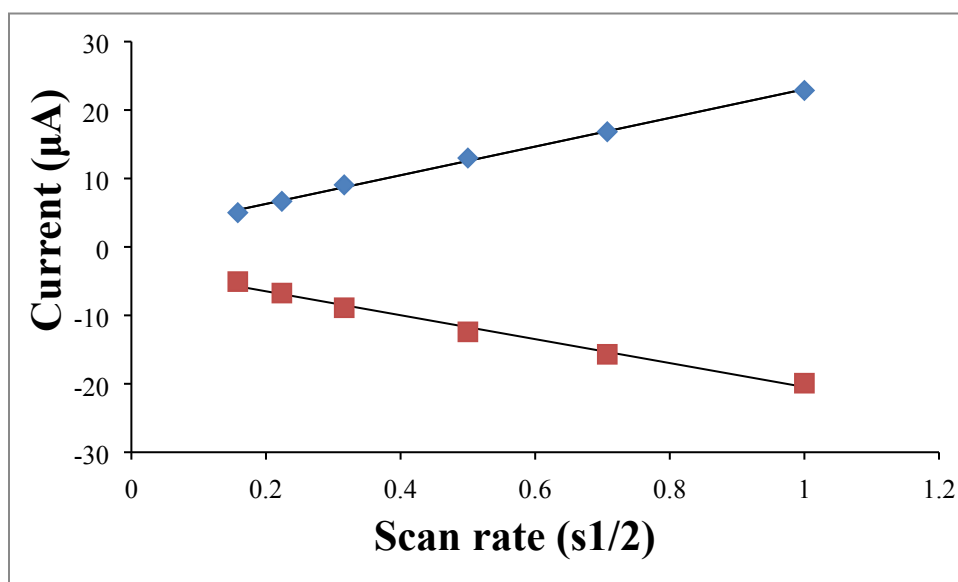


Figure S2. Linear plot of scan rate vs. peak currents for $\text{Ti}(\text{ArOSeO})_2$.

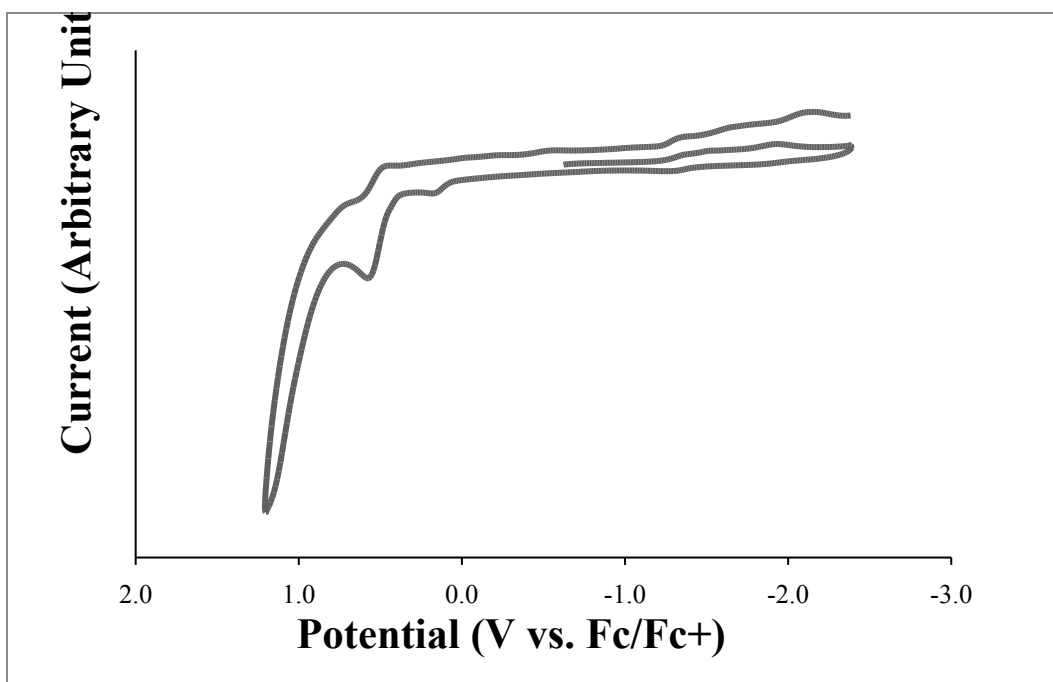


Figure S3. Cyclic voltammogram of $\text{Th}[\text{ArOSeO}]_2(\text{THF})_2$, **5**, showing full scan with ligand-based oxidations at 0.568 V and 0.178 V vs. Fc/Fc^+ .

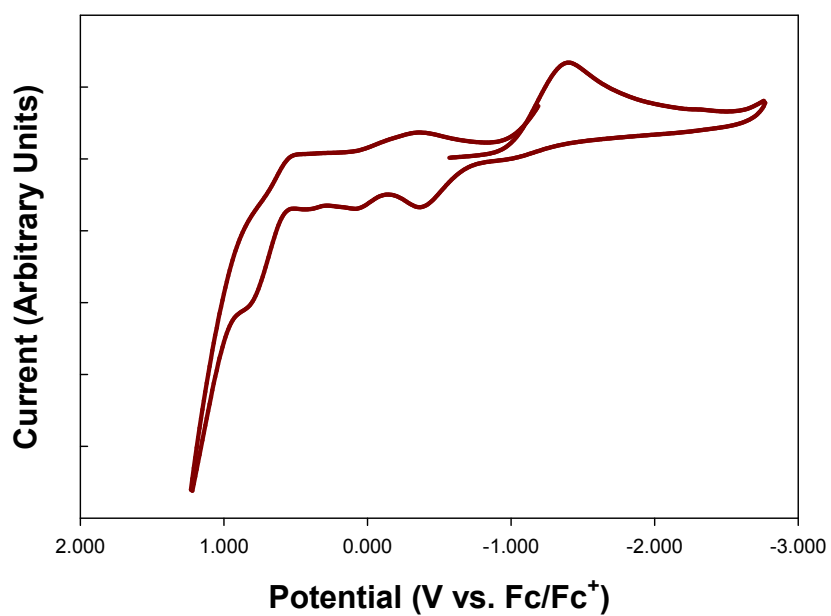


Figure S4. Cyclic voltammogram of $\text{Ce}(\text{ArOSeO})_2(\text{THF})_2$, **6**, showing full scan.

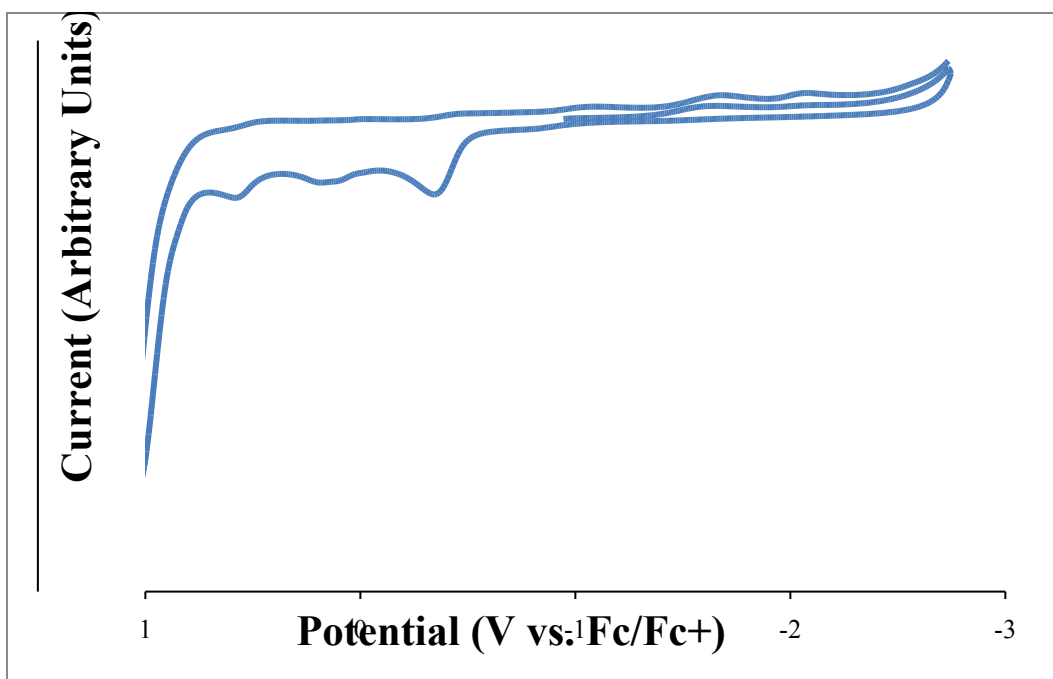


Figure S5. Cyclic voltammogram of $[\text{Ce}(\text{ArOSeO})_2][\text{Na}(\text{THF})_3]$ showing full scan with ligand-based oxidations at 0.58 V vs. Fc/Fc⁺.

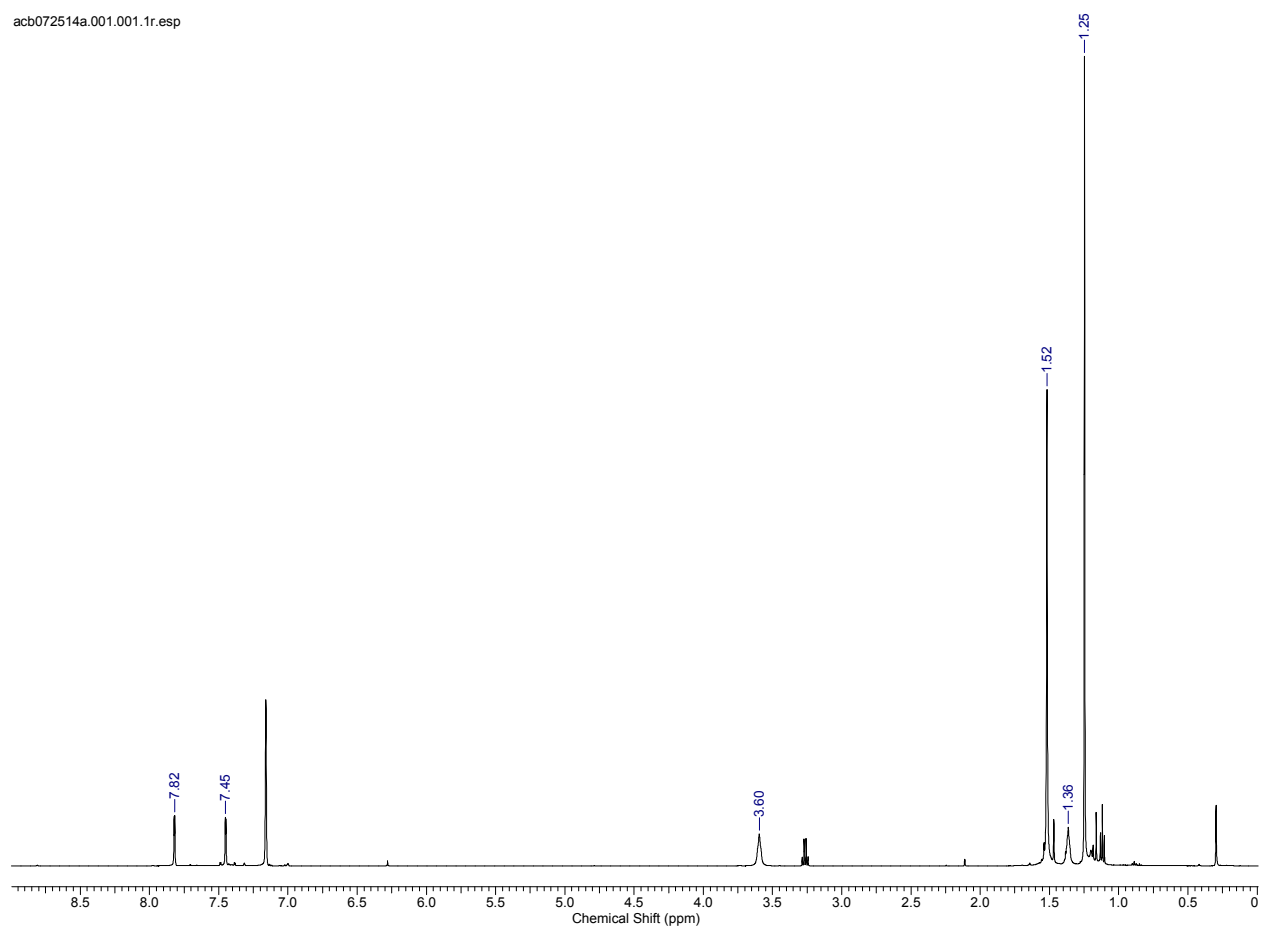


Figure S6. ¹H NMR spectrum of Hf[^{Ar}OSeO]₂(THF), **4** with product chemical resonances labelled.

Table S1. Electrochemical Data for **6**.

| Scan rate (mV/sec) | E_{pa} [V vs. Fc] | E_{pc} [V vs. Fc] | ΔE [V] | I_{pa}/I_{pc} |
|-----------------------|------------------------|------------------------|-------------------|-----------------|
| 1000 | -0.380 | -1.390 | 1.010 | 0.657 |
| 500 | -0.410 | -1.350 | 0.940 | 0.609 |
| 250 | -0.430 | -1.300 | 0.870 | 0.606 |
| 100 | -0.460 | -1.240 | 0.780 | 0.567 |
| 50 | -0.490 | -1.200 | 0.710 | 0.417 |

Table S2. Electrochemical data for $[\text{Ce}(\text{ArOSeO})_2][\text{Na}(\text{THF})_3]$.

| Scan rate (mV/sec) | E_{pa} [V vs. Fc] | E_{pc} [V vs. Fc] | ΔE [V] | I_{pc}/I_{pa} |
|-----------------------|------------------------|------------------------|-------------------|-----------------|
| 1000 | -0.305 | -0.515 | 0.210 | 2.81 |
| 500 | -0.325 | -0.495 | 0.170 | 2.62 |
| 250 | -0.345 | -0.485 | 0.140 | 2.84 |
| 100 | -0.355 | -0.485 | 0.130 | 3.02 |
| 50 | -0.375 | -0.485 | 0.110 | 3.30 |