ORGANOMETALLICS

Radical Reductive Elimination from Tetrabenzyluranium Mediated by an Iminoquinone Ligand

Ellen M. Matson,[†] Sebastian M. Franke,[‡] Nickolas H. Anderson,[†] Timothy D. Cook,[†] Phillip E. Fanwick,[†] and Suzanne C. Bart^{*,†}

[†]H. C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States [‡]Department of Chemistry and Pharmacy, Inorganic Chemistry, Friedrich Alexander University, Egerlandstraße 1, 91058 Erlangen, Germany

Supporting Information

ABSTRACT: Reductive elimination from U(CH₂Ph)₄ (**1-Ph**) mediated by 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]quinone (^{dipp}iq) was observed, resulting in the formation of (^{dipp}ap)₂U(CH₂Ph)₂(THF)₂ (**2**) (^{dipp}ap = 4,6di-*tert*-butyl-2-[(2,6-diisopropylphenyl)amido]phenolate) and bibenzyl. The crossover experiment with U(CD₂C₆D₅)₄ showed formation of bibenzyl-d₇, indicating that reductive elimination occurs in a stepwise fashion via benzyl radical extrusion, presumably through an iminosemiquinone tris-(benzyl) intermediate, (^{dipp}isq)U(CH₂Ph)₃. Synthesis of this intermediate was attempted by addition of the iminoquinone



ligand to $UI_3(THF)_4$ to form (^{dipp}isq) UI_3 (3), followed by alkylation with 3 equiv of benzylpotassium. However, this only resulted in the isolation of **2**. Reduction of **3** with KC₈ afforded the amidophenolate diiodide species (^{dipp}ap) $UI_2(THF)_2$ (4), maintaining the tetravalent oxidation state of the uranium and reducing the ligand. Attempts at the formation of **2** via addition of 2 equiv of benzylpotassium to **4** resulted in decomposition. The uranium mono(alkyl) (^{dipp}ap) $UI(CH_2Ph)(THF)_2$ (5) was observed upon addition of 1 equiv of benzylpotassium to **4**. All products have been characterized by ¹H NMR and electronic absorption spectroscopy. X-ray crystallography was employed to ascertain ligand reduction in **2**, **3**, and **5**.

INTRODUCTION

Reductive elimination is a key step in carbon–element bond formation and has been demonstrated to proceed by both radical (one-electron)^{1–3} and concerted (two-electron)⁴ pathways. High-valent transition-metal centers are favored for reductive elimination, as the two-electron-reduced products are often stable.⁵ In the case of uranium, Seyam and co-workers noted that C–C reductive elimination occurs from the fleeting uranium(VI) species UO₂Ph₂, forming biphenyl and unstable uranium(IV) oxide products.⁶ However, this is not a general reaction. In the case of UO₂R₂ (R = *i*Pr, *n*Bu, *t*Bu), β -hydride elimination and U–C homolytic cleavage pathways are operative.

More recently, reductive elimination has been demonstrated for tetravalent uranium compounds in the presence of additional substrates or oxidants, which avoids formation of an unstable divalent uranium product. For instance, Evans has demonstrated that $[Cp_2UH_2]_2$ is an effective multielectron reductant for PhSSPh and PhN=NPh (Scheme 1), generating $Cp_2U(SPh)_2$ and $Cp_2U(NPh)_2$, respectively, as well as for cyclooctatetraene to form $[Cp^*(COT)U]_2(\mu$ -COT).⁷ In all cases, formation of the product proceeds via the reductive elimination of dihydrogen from $[Cp_2UH_2]_2$. Similar reactivity has been noted in the case of the tuck-in, tuck-over compound $Cp^*U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2UCp_2^*$, which behaves Scheme 1. Reductive Elimination by Uranium Complexes

H-H Reductive Elimination H = H and H = HH = H

as a masked form of $[Cp_2^*U]$, generating the same products in the presence of the aforementioned reagents following C–H reductive elimination to restore the traditional η^5 -Cp^{*} coordination.⁸

Received: December 17, 2013 Published: April 7, 2014 Traditional two-electron reductive elimination reactions are rare for uranium, due to the tendency of this metal to undergo radical processes. However, redox-active ligands can control one-electron transfers, facilitating multielectron processes. These ligands have been widely used on uranium, including examples by Kiplinger and co-workers⁹ and our laboratory,¹⁰ which have demonstrated the use of α -diimine ligands in the synthesis of uranium(III) and -(IV) compounds. Schiff base ligands can be used to store electrons from uranium in a C–C bond, as shown by Mazzanti and co-workers.¹¹ Andersen and co-workers^{12,13} and our recent work¹⁴ have demonstrated that radical bipyridine ligands coordinated to low-valent uranium centers facilitate two-electron chemistry to generate U–N and U–O multiple bonds.

We recently reported that concerted C-C reductive elimination from $U(CH_2C_6H_5)_4$ (1-Ph) in the presence of $^{Mes}DAB^{Me}$ ($^{Mes}DAB^{Me}$ = ArN=C(Me)C(Me)=NAr, Ar =2,4,6-trimethylphenyl (Mes)) generates 1 equiv of bibenzyl and forms (MesDABMe)U(CH2Ph)2, which has a ligand that has been reduced by two electrons.¹⁵ Rather than a typical reductive elimination, where electrons reside on the metal center, in this case the electrons are stored in the ligand, preventing the formation of unstable divalent and zerovalent products. On the basis of this interesting result, reductive elimination of $U(CH_2C_6H_5)_4$ with the related iminoquinone ligand, 4,6-di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]quinone (dippiq), was explored to determine if analogous chemistry occurs and, if so, by what mechanism. Herein, we present the results of this study, along with additional experiments aimed at supporting mechanistic intermediates in the reductive elimination reaction.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert-atmosphere drybox under an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two -35 °C freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.¹⁶ Benzene- d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN, and Complete Analysis Laboratories, Inc., in Parsippany, NJ. 4,6-Di-*tert*-butyl-2-[(2,6-diisopropylphenyl)imino]-quinone (^{dipp}iq),¹⁷ UI₃(THF)₄,^{18,19} U(CH₂Ph)₄,¹⁵ KC₈,²⁰ and KCH₂Ph²¹ were synthesized following literature procedures.

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are reported relative to the peak for SiMe₄, using ¹H (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained by using an acquisition time of 0.5 s; thus, the peak widths reported have an error of ± 2 Hz. For paramagnetic molecules, the ¹H NMR data are reported with the chemical shift, followed by the peak width at half-height in hertz, the integration value, and (where possible) the peak assignment. Electronic absorption spectroscopic measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Jasco V-6700 spectrophotometer.

The cyclic voltammograms of the free ligands ^{dipp}iq and ^{Mes}DAB^{Me} were recorded in 0.2 M (n-Bu)₄NPF₆ solution (tetrahydrofuran, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy-carbon working electrode (diameter 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of analyte is always

1.0 mM. The ferrocenium/ferrocene couple was observed at 0.645 V (vs Ag/AgCl) under the noted experimental conditions.

Single crystals of $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (2), $(^{dipp}isq)-UI_3(THF)_2$ (3), and $(^{dipp}ap)U(I)(CH_2Ph)(THF)_2$ (5) for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high-intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with Cu K α radiation ($\lambda = 1.54184$ Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.²² The structures were solved using the structure solution program PATTY in DIRDIF99.²³ Refinement was performed on a LINUX PC using SHELX-97.²² The data were collected at a temperature of 150(1) K.

Preparation of $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (2). A 20 mL scintillation vial was charged with $U(CH_2Ph)_4$ (0.050 g, 0.083 mmol) and approximately 5 mL of THF. The brown-red solution was cooled to -35 °C. In a separate vial, 1 equiv of ^{dipp}iq (0.031 g, 0.082 mmol) was dissolved in approximately 2 mL of THF. The ligand was added to the uranium solution dropwise with vigorous stirring. No obvious color change observed. After 30 min of stirring, solvents were removed under reduced pressure. The product, 2, was extracted with ether and recrystallized at -35 °C (0.069 g, 0.073 mmol, 83%). ¹H NMR (C_6D_6 , 25 °C): δ -19.34 ($\omega_{0.5}$ = 967 Hz, 8H, THF), -12.89 ($\omega_{0.5}$ = 75 Hz, 9H, C(CH)_3), -10.08 ($\omega_{0.5}$ = 154 Hz, 12H, CH(CH₃)₂), -6.48 ($\omega_{0.5}$ = 261 Hz, 4H), -1.39 ($\omega_{0.5}$ = 44 Hz, 2H), 3.32 ($\omega_{0.5}$ = 165 Hz, 2H) 3.52 ($\omega_{0.5}$ = 27 Hz, 9H, C(CH)_3), 4.71 ($\omega_{0.5}$ = 42 Hz, 1H), 6.73 ($\omega_{0.5}$ = 23 Hz, 4H), 15.24 ($\omega_{0.5}$ = 475 Hz, 4H), 20.85 ($\omega_{0.5}$ = 140 Hz, 1H), 23.92 ($\omega_{0.5}$ = 783 Hz, 8H, THF).

Alternative Synthesis of 2. A 20 mL scintillation vial was charged with (dipp isq)UI₃(THF)₂ (0.100 g, 0.088 mmol) and approximately 4 mL of THF. The solution was cooled to -35 °C. Three equivalents of benzylpotassium (0.036 g, 0.274 mmol) was dissolved in 10 mL of THF and added dropwise to the uranium solution, resulting in an instantaneous color change from brown to red. After filtration over Celite to remove KI, THF was removed under reduced pressure. The product, 2, was recrystallized from a concentrated solution of ether and toluene (4/1) in high yields (0.074 g, 0.078 mmol, 89%). Crystals suitable for X-ray analysis were grown from a concentrated ether and toluene mixture (8/1). Anal. Calcd for C₃₄H₅₃N₁O₃I₂U: C, 61.07; H, 7.15; N, 1.48. Found: C, 60.91; H, 6.96; N, 1.37.

Preparation of (^{dipp}isq)UI₃(THF)₂ (3). A 20 mL scintillation vial was charged with UI₃(THF)₄ (0.100 g, 0.110 mmol) and approximately 10 mL of diethyl ether. To the blue-purple slurry was added 1 equiv of the brown-red solid ^{dipp}iq (0.042 g, 0.112 mmol) by difference, resulting in an instant color change to brown-yellow. After the mixture was stirred for 30 min, solvents were removed under reduced pressure, resulting in isolation of the product, 3, in quantitative yields. Anal. Calcd for C₃₄H₅₃NO₃I₃U: C, 37.61; H, 4.92; N, 1.29. Found: C, 37.26; H, 4.82; N, 1.24. ¹H NMR (C₆D₆, 25 °C): δ –26.92 ($ω_{0.5} = 129$ Hz, 1H), –17.50 ($ω_{0.5} = 103$ Hz, 9H, C(CH)₃), –9.37 ($ω_{0.5} = 17$ Hz, 2H, o-CH), –1.39 (47, 1H), 1.57 ($ω_{0.5} = 1266$ Hz, 12H, CH(CH)₂), –11.58 ($ω_{0.5} = 16$ Hz, 1H), 13.62 ($ω_{0.5} = 314$ Hz, 9H, C(CH)₃), 40.61 ($ω_{0.5} = 673$ Hz, 8H, THF), 43.80 ($ω_{0.5} = 90$ Hz, 2H), 45.62 ($ω_{0.5} = 1224$ Hz, 8H, THF).

Preparation of (^{dipp}ap)Ul₂(THF)₂ (4). A 20 mL scintillation vial was charged with (^{dipp}isq)Ul₃(THF)₂ (0.100 g, 0.088 mmol) and approximately 4 mL of THF. One equivalent of KC₈ (0.012 g, 0.088 mmol) was added by difference, resulting in a darkening of the solution. After it was stirred for 10 h, the solution was filtered over Celite to remove the byproducts KI and graphite. After solvents were removed under reduced pressure, the product, 4, was isolated as a dark brown powder (0.064 g, 0.063, 72%). Anal. Calcd for C₃₄H₅₃N₁O₃I₂U: C, 40.21; H, 5.26; N, 1.38. Found: C, 40.39; H, 5.24; N, 1.23. ¹H NMR (C₆D₆, 25 °C): δ –11.49 ($\omega_{0.5}$ = 1252 Hz, 4H, THF), -9.58 (d, ³J_{HH} = 6, 12H, CH(CH₃)₂), -8.43 ($\omega_{0.5}$ = 213 Hz, 4H, THF), -7.21 ($\omega_{0.5}$ = 494 Hz, 4H, THF), 1.55 ($\omega_{0.5}$ = 21 Hz, 9H, C(CH)₃), 3.27 ($\omega_{0.5}$ = 29 Hz, 1H, CH), 5.35 ($\omega_{0.5}$ = 8 Hz, 9H, C(CH)₃), 6.50 ($\omega_{0.5}$ =

Scheme 2. Synthetic Routes and Potential Intermediate for the Generation of Complex 2



395 Hz, 4H, THF), 7.14 ($\omega_{0.5}$ = 4 Hz, 2H), 14.30 ($\omega_{0.5}$ = 11 Hz, 2H, CH(CH₃)), 19.39 ($\omega_{0.5}$ = 47 Hz, 1H, CH). **Preparation of (^{dipp}ap)U(I)(CH₂Ph)(THF)₂ (5).** A 20 mL

scintillation vial was charged with (dippap)UI2(THF)2 (0.050 g, 0.053 mmol) and approximately 5 mL of THF and cooled to -35 °C. In a separate vial, 2 equiv of KCH₂Ph was dissolved in 3 mL of THF. The bright orange solution was added dropwise to the brown uranium solution with vigorous stirring, resulting in a color change to red. After 3 h at room temperature, the solution was filtered over Celite to remove KI. Volatiles were removed under reduced pressure. The product, 5, was recrystallized from a diethyl ether and pentane mixture (2/1) in good yield (0.030 g, 0.031 mmol, 59%). X-ray-quality crystals were grown from a toluene:pentane (1/3) solution at -35 °C. Analysis for C41H60NIO3U•1/2(C7H8): Calcd. C, 62.21; H, 7.60; N, 1.58. Found C, 61.97; H, 7.32; N, 1.55. ¹H NMR (C₆D₆, 25 °C): δ $-68.02 (\omega_{0.5} = 533 \text{ Hz}), -37.79 (\omega_{0.5} = 520 \text{ Hz}), -19.67 (\omega_{0.5} = 358$ Hz), -17.11 ($\omega_{0.5} = 333$ Hz), -14.06 ($\omega_{0.5} = 742$ Hz), -10.35 ($\omega_{0.5} =$ 535 Hz), -6.34 ($\omega_{0.5}$ = 505 Hz), -3.04 ($\omega_{0.5}$ = 457 Hz), 0.35 ($\omega_{0.5}$ = 105 Hz), 3.00 ($\omega_{0.5}$ = 157 Hz), 15.00 ($\omega_{0.5}$ = 93 Hz), 29.56 ($\omega_{0.5}$ = 395 Hz), 39.47 ($\omega_{0.5}$ = 450 Hz), 44.40 ($\omega_{0.5}$ = 407 Hz), 173.44 ($\omega_{0.5}$ = 585 Hz).

RESULTS AND DISCUSSION

Reductive elimination studies commenced with the addition of 1 equiv of ^{dipp}iq to 1-Ph, which resulted in no perceptible color change (Scheme 2). The reaction mixture was stirred for 15 min before volatiles were removed under reduced pressure. After workup, analysis of the crude product by ¹H NMR spectroscopy showed a sharp signal at 2.78 ppm, corresponding to the methylene protons of bibenzyl. Also in the spectrum were 12 paramagnetically broadened and shifted signals ranging from -19.34 to 23.92 ppm, consistent with a C_s-symmetric product. This would be expected for the formation of the desired amidophenolate uranium bis(benzyl) product (^{dipp}ap)- $U(CH_2Ph)_2(THF)_2$ (2; dippap = 4,6-di-tert-butyl-2-[(2,6diisopropylphenyl)amido]phenolate). Signals for the two tertbutyl groups and the methyl protons of the isopropyl groups are located at -12.89, 3.52, and -10.08 ppm, respectively. Additionally, two broad resonances integrating to 8H are located at -19.34 and 23.92 ppm, corresponding to the protons of two THF ligands. Four signals for the two chemically equivalent benzyl groups are also present.

To unambiguously determine the identity of 2, crystals suitable for X-ray diffraction were grown from a solution of diethyl ether and toluene (5/1) at -35 °C. Data collection at 150 K yielded unpublishable data, most likely on account of a phase transition at that temperature; thus, publishable data

were obtained at 200 K. Refinement of the data revealed the formation of $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (2), which features a six-coordinate uranium center in a distorted-octahedral geometry (Figure 1, Table 1). The U1–O1 distance of



Figure 1. Molecular structure of 2 shown with 30% probability ellipsoids. Hydrogen atoms and solvent molecules have been removed for clarity.

2.147(2) Å²⁴⁻²⁶ and the U1–N2 distance of 2.328(3) Å^{27–30} are consistent with anionic bonds between uranium and the heteroatoms. Upon reductive elimination of bibenzyl, two-electron reduction of the iminoquinone ligand occurred, generating the dianionic amidophenolate resonance form (^{dipp}ap). Thus, the U–N and U–O bonds in **2** are similar to those reported for the uranium amidophenolate (^{dipp}ap)₂U-(THF)₂ (U–O = 2.163(3), 2.155(3); U–N = 2.304(3), 2.317(3) Å).³¹ Elongation of the N–C (1.420(5) Å) and O–C (1.369(4) Å) distances in comparison to the structural parameters of the oxidized free ligand (N–C = 1.287(2) Å, O–C = 1.221(6) Å)¹⁷ lends further support for ligand reduction, as do analogous bond distances to (^{dipp}ap)₂U-(THF)₂. The U–O(THF) distances of 2.510(3) and 2.470(2) Å are as expected for dative uranium–oxygen interactions.

The U–C distances for the methylene carbons of 2 (2.517(3) and 2.490(4) Å) are within the range of previously observed U(IV)–benzyl methylene carbon distances (2.456–2.538 Å).^{15,32–38} Interesting features of the uranium–benzyl

Table 1. Structura	al Parameters	(Bond	Distances	in Á	and
Angles in deg) fo	r Compounds	2 and	3		

distance or angle	2	3
U1-O1	2.147(2)	2.154(4)
U1-N2	2.328(3)	2.570(5)
O1-C11	1.369(4)	1.346(8)
N2-C12	1.401(5)	1.350(8)
C11-C12	1.420(5)	1.426(8)
U1-051	2.470(2)	2.499(4)
U1-O61	2.510(3)	2.484(4)
U1-C30	2.517(3)	
U1-C40	2.490(4)	
U1–I1		3.0140(4)
U1-I2		3.0126(4)
U1-I3		3.0136(5)
U1-C30-C31	105.3(3)	
U1-C40-C41	95.5(2)	
O(X)1 - U1 - O(X')1	162.85(9)	68.20(15)
	(X=5, X'=6)	(X = 2, X' = 3)

interactions are the U-C-C bond angles of 105.3(3) and 95.5(2)°, which are significantly smaller than those of η^{1} uranium benzyl complexes (116.6(10)-134.2(4)°),³⁹⁻⁴¹ indicating higher hapticity. To determine the hapticity of the benzyl groups, two parameters, Δ and Δ' , were calculated for each benzyl substituent in 2, according to literature procedures,⁴² where $\Delta = [MC_o - MCH_2] - [MC_{ipso} - MCH_2]$ and $\Delta' = [MC_o' - MCH_2] - [MC_{ipso} - MCH_2]$ (Table 2). In these calculations, MC_0 is the shorter metal-toortho carbon contact length, MC_o' is the longer metal-to-ortho contact length, MCH₂ is the metal-to-methylene carbon bond length, and MC_{ipso} is the metal-to-ipso carbon bond length. Although the Δ and Δ' values are within the appropriate range for η^4 -benzyl substituents,^{15,34,42} the U–C_o bond distances are extremely long, suggesting a lower hapticity. This argument is further supported by the U-C-C angles in 2, which are larger than those for the η^4 -benzyl groups reported for 1-Ph $(82.7(4) - 89.4(4)^{\circ}).^{15}$

In addition to structural parameters, electronic absorption spectroscopy was employed to provide insight into the oxidation state of the uranium center in **2**. A spectrum was collected from 280 to 2100 nm in THF at ambient temperature (Figure 2). Bands with low molar absorptivities were noted in the near-infrared region of the spectrum, as is commonly observed for uranium(IV) complexes.^{9,10,31,43,44} This spectrum is reminiscent of those of other tetravalent uranium complexes with redox-active ligands, such as $(dpp-BIAN)_2U(THF)$ (dpp-BIAN = 1,2-bis((2,6-diisopropylphenyl)imino)-



Figure 2. Electronic absorption spectroscopy of $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (2) (red), $(^{dipp}ap)UI_2(THF)_2$ (4) (blue), and $(^{dipp}ap)UI(CH_2Ph)(THF)_2$ (5) (green) in THF at ambient temperature. The inset shows the near-infrared region of the spectrum. Solvent overtones, ranging between 1600 and 1800 nm, have been removed for clarity.

acenaphthene))⁹ and $(^{\text{Mes}}\text{DAB}^{\text{Me}})_2\text{U}(\text{THF})$ and $\text{Cp}_2\text{U}-(^{\text{Mes}}\text{DAB}^{\text{Me}}).^{10}$ Thus, the electronic absorption spectroscopic data agree with the formulation of a tetravalent uranium center, as supported by crystallographic data. No significant features were observed in the visible region as would be expected for either the iminoquinone ligand or its one-electron-reduced iminosemiquinone [isq]⁻ counterpart, further supporting two-electron reduction of $^{\text{dipp}}$ iq to the amidophenolate [ap]²⁻ during formation of **2**.

To investigate the mechanism for reductive elimination from **1-Ph** to form bibenzyl, a crossover experiment was performed. To an equimolar ratio of $U(CH_2C_6H_5)_4$ and $U(CD_2C_6D_5)_4$ was added 2 equiv of ^{dipp}iq. Following workup, separation of the organometallic and organic products was achieved by filtration through a silica gel plug. Analysis of the organics by GC/MS showed bibenzyl, bibenzyl- d_{14} , and the radical crossover product bibenzyl- d_7 in a statistical mixture (25:25:50) (Figure S7, Supporting Information), supporting the notion that C–C reductive elimination occurs by a radical mechanism via U–C homolytic cleavage.

compd	$MC_i - MCH_2^a$	$MC_o - MCH_2^{b}$	$MC_{o'} - MCH_2^{c}$	Δ^d	Δ'^{e}	ref
(dmpe)U(CH ₂ Ph) ₃ CH ₃	0.22	0.55	0.91	0.33	0.69	34
$Cp*U(CH_2Ph)_3$	0.34	0.89	0.94	0.56	0.61	27
$U(CH_2Ph)_4 (1-Ph)^f$	0.24	0.71	0.83	0.47	0.59	15
$(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (2)	0.51	1.00	1.28	0.49	0.77	this work
	0.69	1.28	1.53	0.59	0.83	
$(^{dipp}ap)U(I)(CH_2Ph)(THF)_2$ (5)	0.62	1.08	1.49	0.46	0.87	this work

Table 2. Hapticity Values for 2 and 5

^{*a*}Average metal to ipso carbon bond length minus metal to methylene carbon bond length. ^{*b*}Average metal to shorter ortho carbon bond length minus metal to methylene carbon bond length. ^{*c*}Average metal to longer ortho carbon bond length minus metal to methylene carbon length. d [MC_{ortho} – MCH₂] – [MC_{ipso} – MCH₂]. ^{*e*}[MC_{ortho'} – MCH₂] – [MC_{ipso} – MCH₂]. ^{*f*}Shortest contacts.

Radical reductive elimination to form **2** is in contrast to that noted in the formation of $({}^{\text{Mes}}\text{DAB}{}^{\text{Me}})U(\text{CH}_2\text{C}_6\text{H}_5)_2$ ¹⁵ which has been established to proceed through a concerted mechanism. We reasoned that initial coordination of the iminoquinone ligand to tetrabenzyluranium results in benzyl radical extrusion with concurrent ligand reduction to form the monoanionic iminosemiquinone intermediate $({}^{\text{dipP}}\text{isq})U(\text{CH}_2\text{Ph})_3$ (Scheme 2). This species could subsequently eject an additional benzyl radical to generate **2** and bibenzyl.

This hypothesis is supported by the cyclic voltammogram (CV) for ^{dipp}iq recorded in THF, which shows a reversible oneelectron reduction to form the stable monoanionic iminosemiquinone ligand (^{dipp}isq)⁻ at -0.664 V (vs Ag/AgCl) (Figure S1, Supporting Information) when sweeping between -1.5 and 1.6V.⁴⁵ In comparison, the CV for ^{Mes}DAB^{Me} shows a quasireversible one-electron reduction at -0.839 V, indicating that [^{Mes}DAB^{Me}]⁻ is not stable. With regard to the mechanism for reductive elimination from tetrabenzyluranium, observation of the radical pathway for ^{dipp}iq may be due to the lower reduction potential, which generates a stable monoanion that facilitates radical elimination. Because this reduction is irreversible for ^{Mes}DAB^{Me}, the two-electron concerted elimination is favored.

To determine the viability of (dippisq)U(CH2Ph)3 as an intermediate in the formation of 2, independent synthesis was attempted by salt metathesis of (^{dipp}isq)UI₃ with benzylpotassium. On the basis of the reduction potential of dippiq, we reasoned that addition of the iminoquinone ligand to $UI_3(THF)_4$ would generate (^{dipp}isq)UI₃. Exposure of a dark blue solution of $UI_3(THF)_4$ to 1 equiv of (^{dipp}iq) results in an instantaneous color change to yellow-brown. After workup, the product was isolated as a brown powder in quantitative yield. ¹H NMR analysis revealed 10 broad resonances ranging from -26.92 to 45.62 ppm, supporting the assignment of the product as the uranium iminosemiquinone species (dippisq)- $UI_3(THF)_2$ (3). Two resonances are visible at -17.50 and 13.62 ppm (9H each), corresponding to the two tert-butyl groups of the ligand. Additionally, a signal integrating to 12H corresponding to the symmetric isopropyl methyl substituents is located at 1.57 ppm. Two broad resonances at 40.61 and 45.62 ppm (8H each) correspond to two coordinated THF ligands.

Compound 3 was further characterized by X-ray crystallography of brown crystals grown from a concentrated THF solution layered with pentane at -35 °C. Refinement of the crystallographic data confirmed the assignment of the product as $(^{dipp}isq)UI_3(THF)_2$, which features a seven-coordinate uranium center in a distorted-capped-octahedral geometry (Figure 3, Table 1). The U–I distances of 3.0126(4), 3.0136(5), and 3.0140(4) Å are shorter than those reported for the starting material $UI_3(THF)_4$ (3.103(2), 3.119(2), and 3.167(2) Å),¹⁸ consistent with the decrease in ionic radius that accompanies oxidation from U(III) to U(IV). The U-I distances compare favorably with those reported for $UI_4(OEt_2)$ (2.964 Å),⁴⁶ $UI_4(dioxanes)_2$ (2.964 Å),⁴⁷ and $UI(O(2,6-di-tert-butyl)phenyl)_3$ (3.011 Å).⁴⁸ The U–O(THF) distances of 2.484(4) and 2.499(4) Å are similar to those of the starting material, which range from 2.48(1) to 2.56(2) Å.¹⁸ The short U1-O1 distance of 2.154(4) Å is consistent with an anionic interaction, as observed in the structural parameters of 2. An U1-N1 distance of 2.570(5) Å elongated from that of 2 is noted and is outside the range of uranium(IV) amide linkages (2.161–2.298 Å), suggesting a neutral U–N interaction.^{27–30,49} These parameters are also consistent with the uranium(IV)



Figure 3. Molecular structure of 3 shown with 30% probability ellipsoids. Hydrogen atoms and solvent molecules have been removed for clarity.

bis(iminosemiquinone), $[(^{R}isq)_2UCl]_2$ (R = tBu, dipp), which has short U–O distances (2.151(6), 2.150(6) Å) and longer U–N distances (2.568(7), 2.563(7) Å).³¹

One-electron ligand reduction was also evident by comparison of the intraligand bond distances of **3**. The C–O bond distance of 1.346(8) Å has been elongated from that of the free ligand ^{dipp}iq (1.221(2) Å),¹⁷ indicating reduction of the C=O bond order from 2 to 1, as in complex **2**. The C–N bond distance of 1.350(8) Å in **3** is longer than that of the oxidized ligand (1.287(2) Å)¹⁷ and is within the range of distances of organometallic complexes with [isq]⁻ radical ligands, ranging from 1.33 to 1.36 Å.^{50,51} The ^{dipp}isq ligand in **3** shows structural parameters similar to those for the [isq]⁻ radical anion in (^{tBu}isq)₂MCl₂ (M = Zr, Hf) (1.33–1.36 Å) (Chart 1).⁵⁰ The C1–C2 bond length of 1.443(9) Å has been

Chart 1. Comparison of Bond Distances (Å) in 3 with Those of Iminosemiquinone Complexes (^{Bu}isq)₂MCl₂ (M = Zr, Hf)



shortened from that of dipp isq (1.519(2) Å), as expected. Structural similarities of the radical ligand in **3** and 4,6-di-*tert*-butyl-2-[(*tert*-butyl)imino]semiquinone (tBu isqH) are also noted.⁴⁵

The electronic absorption spectrum of 3, collected from 280 to 2100 nm in THF at ambient temperature, shows weak bands $(30-110 \text{ M}^{-1}\text{cm}^{-1})$ at low energy for f-f transitions of the f² U(IV) center (Figure S6, Supporting Information).^{31,43,44} At

higher energies, a broad feature at 763 nm ($\varepsilon = 627 \text{ M}^{-1} \text{ cm}^{-1}$) for the open-shell iminosemiquinone ligand dominates the spectrum. The transition falls within the range of bands observed in the electronic absorption spectra of organometallic complexes containing a [isq]⁻ ligand, including (^{tBu}isq)₂M(X)₂ (M = Ti, Zr, Hf; X = F, Cl, Br)^{50,51} and (^Risq)₂UCl₂ (R = tBu, Ad, dipp).⁴⁰

Support for the presence of the iminosemiquinone ligand $[^{dipp}isq]^{-}$ in 3 was obtained using variable-temperature SQUID magnetometry. For comparison, compound 2, which has a closed-shell amidophenolate ligand, $[^{dipp}ap]^{2-}$, was also measured (Figure 4). Typical magnetic moments for uranium-



Figure 4. Temperature-dependent SQUID magnetization data (1 T) for compounds **2** (red) and **3** (blue) plotted as magnetic moment (μ_{eff}) vs temperature (*T*). Data were corrected for diamagnetism, and reproducibility was checked on multiple independently synthesized samples.

(IV) species show a steady drop in μ_{eff} as the temperature is lowered, decreasing from ~3.0 (300 K) to ~0.5 μ_B (4 K), consistent with a poorly isolated singlet ground state arising from ligand field effects.^{43,44,52} Data obtained for compound **2** fit within this established range and show a magnetic moment of 2.39 μ_B at 300 K, which decreases to 0.63 μ_B at 4 K and to 0.47 μ_B at 2 K. Three independently synthesized solid samples of **3** were measured over the same range, and the collected data display a similar variable-temperature behavior. At 300 K, the magnetic moment is 3.23 μ_B ; however, at low temperature, a magnetization of 1.50 μ_B is measured. This high value at low temperature is typical for charge-separated uranium(IV) species with radical anionic ligands, including [((^{Ad}ArO)₃tacnU^{IV}(CO₂^{•-})], ⁵² [((^{tBu}ArO)₃tacn)-U^{IV}(OC•^{tBu}Ph₂)], ⁴³ and [((^{tBu}ArO)₃tacn)U^{IV}(η^2 -NNCPh₂)], ⁵³

Scheme 3. Formation and Reactivity of Complex 4

which have magnetic moments of 1.51 (5 K), 1.61 (4 K), and 1.75 $\mu_{\rm B}$ (4 K), respectively. Thus, the magnetic moment observed for 3 is due to the magnetic contribution from the $[^{\rm dipp}isq]^-$ radical ligand, supporting its formulation as a charge-separated uranium(IV) species with an iminosemiquinone ligand. Contributions from the trivalent uranium tris(iodide) resonance structure $(^{\rm dipp}iq)UI_3({\rm THF})_2$ cannot be eliminated on the basis of the data collected.

With the successful synthesis of **3**, alkylation to form $(^{dipp}isq)U(CH_2Ph)_3$ was attempted (Scheme 2). Three equivalents of benzyl potassium were added to a THF solution of **3**, resulting in an instantaneous color change to red with concurrent precipitation of KI. After workup, the isolated red solid was recrystallized from a concentrated diethyl ether solution. The ¹H NMR spectrum for this product was recognizable as that for $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$ (**2**), and analysis of the solution also showed $^{1}/_{2}$ equiv of bibenzyl. The unsuccessful attempt at isolation of $(^{dipp}isq)U(CH_2Ph)_3$ highlights the reactive nature of this compound and suggests the possible formation of this species during radical reductive elimination to produce **2**.

Since the formation of **2** is accompanied by the reduction of the iminosemiquinone ligand to the amidophenolate, the reduction chemistry of 3 was investigated further. Exposure of $(^{dipp}isq)UI_3(THF)_2$ to 1 equiv of KC₈ resulted in immediate darkening of the solution. After filtration and removal of solvents in vacuo, a brown-yellow solid was isolated (Scheme 3). Analysis by ¹H NMR spectroscopy showed 11 resonances broadened and shifted by the paramagnetic uranium center. Two large resonances integrating to 9H each are located at 1.55 and 5.35 ppm, corresponding to the tert-butyl groups of the ligand. A large doublet located at -9.58 ppm integrating to 12H is assigned to the methyl groups of the isopropyl groups on the aryl ring. Four broad singlets (-11.49, -8.43, -7.21,and 6.50 ppm), integrating to 4H each, indicate coordination of two THF molecules and support assignment of the product as $(^{dipp}ap)UI_2(THF)_2$ (4).

The ^{dipp}isq ligand in 3 serves as an electron sink during reduction to form (^{dipp}ap)UI₂(THF)₂, which maintains the thermodynamically preferred +4 oxidation state of the uranium. This is confirmed by the electronic absorption spectrum of 4, which shows loss of the absorbance for the iminosemiquinone ligand (763 nm), supporting ligand reduction to the amidophenolate form (Figure 2). Furthermore, weakly intense but sharp f–f transitions found in the near-IR region of the spectrum confirm the presence of a tetravalent uranium center^{43,44} and are similar to those previously observed for



Organometallics

the family of amidophenolate species $(^{R}ap)_{2}U(THF)_{2}$ (R = tBu, Ad, dipp).³¹

Interestingly, alkylation of 4 with 2 equiv of benzylpotassium did not result in the formation of **2** via salt metathesis as expected (Scheme 3). ¹H NMR spectroscopy revealed no resonances consistent for $(^{dipp}ap)U(CH_2Ph)_2(THF)_2$; instead, only a sharp signal for bibenzyl was noted. The observed decomposition supports that ligand-assisted extrusion of a benzyl radical is an essential mechanistic step in the formation of **2**. Treating **4** with 1 equiv of KCH₂Ph, however, affords the mono(benzyl) uranium(IV) product $(^{dipp}ap)U(CH_2Ph)-(THF)_2$ (**5**). This formulation is supported by the 19 broad resonances, ranging from -68.02 to 173.44 ppm, observed in the ¹H NMR spectrum due to asymmetry.

Structural details of **5** were elucidated by X-ray crystallography of crystals grown from a concentrated solution of pentane. Although only non-merohedral twinned crystals could be obtained, refinement of publishable quality structural data gave a pseudo-octahedral uranium compound, $(^{dipp}ap)UI-(CH_2Ph)(THF)_2$ (**5**) (Figure 5, Table 3). The U1–N120



Figure 5. Molecular structure of 5 shown with 30% probability ellipsoids. Hydrogen atoms and solvent molecules have been removed for clarity.

Table 3. Structural Parameters (Distances in Å and Angles in deg) for 5

U1-0110	2.121(8)	U1-0131	2.451(8)
U1-N120	2.299(9)	U1-O141	2.443(9)
O1-C111	1.383(11)	U1-C10	2.441(13)
N2-C112	1.404(12)	U1-I1	3.1045(10)
C111-C112	1.389(16)		
U1-C10-C11	99.0(7)	O131-U1-O141	162.5(2)

distance of 2.299(9) Å and the U1–O110 distance of 2.121(8) Å are similar to the corresponding distances of complex 2, supporting the notion that $[^{dipp}ap]^{2-}$ is maintained during the reaction. The U1–I1 distance of 3.1045(10) Å is similar to distances reported for 3. The U1–C10 distance of 2.441(13) Å and U1–C10–C11 bond angle of 99.0(7)° are similar to those reported for 2. While hapticity calculations are on par for η^4 coordination, the long calculated U–C_o distances (~4 Å) once again support a lower hapticity, indicating coordination of the benzyl substituent similar to that of 2. Although alkylation to generate 5 was successful, the inability to synthesize 2 via salt

metathesis of 4 highlights the importance of the reductive elimination reaction in generating uranium dialkyl complexes.

CONCLUSIONS

In summary, the iminoquinone ligand ^{dipp}iq effectively mediates carbon-carbon reductive elimination from tetrabenzyluranium to form 2. The accompanying redox chemistry does not occur at the uranium center but rather at the ligand, which is reduced to the amidophenolate dippap, stabilizing the low-valent products. In contrast to the α -diimine ligand ^{Mes}DAB^{Me}, ^{dipp}iq forces a radical reductive elimination pathway, as supported by a crossover experiment, likely due to the stability of the iminosemiquinone intermediate. Attempts to isolate the potential intermediate $(^{dipp}isq)U(CH_2C_6H_5)_3$ through alkylation of 3 led only to formation of 2 and bibenzyl. While the overall reductive elimination is a two-electron process, the iminoquinone ligand has a stable iminosemiquinone intermediate as observed in the cyclic voltammogram, facilitating two radical events to form 2. The studies presented here highlight the ability of the iminoquinone ligand to mediate carbon-carbon reductive elimination, support alkylation chemistry, and alter the mechanism for reductive elimination by tetrabenzyluranium on the basis of ligand redox potentials.

ASSOCIATED CONTENT

Supporting Information

Figures, text, and CIF files giving details of the syntheses and electrochemical, spectroscopic, and crystallographic data. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for S.C.B.: sbart@purdue.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Purdue University and the National Science Foundation (CHE-1149875). SCB is a Cottrell Scholar funded by the Research Corporation.

REFERENCES

(1) Gansaeuer, A.; Fleckhaus, A.; Lafont, M. A.; Okkel, A.; Kotsis, K.; Anoop, A.; Neese, F. J. Am. Chem. Soc. 2009, 131, 16989–16999.

(2) Tromp, M.; van Strijdonck, G. P. F.; van Berkel, S. S.; van den Hoogenband, A.; Feiters, M. C.; de Bruin, B.; Fiddy, S. G.; van der Eerden, A. M. J.; van Bokhoven, J. A.; van Leeuwen, P. W. N. M.; Koningsberger, D. C. Organometallics **2010**, *29*, 3085–3097.

(3) Hulley, E. B.; Wolczanski, P. T.; Lobkovsky, E. B. J. Am. Chem. Soc. 2011, 133, 18058–18061.

(4) Xu, H.; Bernskoetter, W. H. J. Am. Chem. Soc. 2011, 133, 14956–14959.

(5) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2005.

(6) Seyam, A. M. Inorg. Chim. Acta 1983, 77, L123-L125.

(7) Evans, W. J.; Miller, K. A.; Kozimor, S. A.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. Organometallics 2007, 26, 3568–3576.

(8) Evans, W. J.; Montalvo, E.; Kozimor, S. A.; Miller, K. A. J. Am. Chem. Soc. 2008, 130, 12258–12259.

(9) Schelter, E. J.; Wu, R.; Scott, B. L.; Thompson, J. D.; Cantat, T.; John, K. D.; Batista, E. R.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2009**, *49*, 924–933. (10) Kraft, S. J.; Williams, U. J.; Daly, S. R.; J. Schelter, E.; Kozimor, S. A.; Boland, K. S.; Kikkawa, J. M.; Forrest, W. P.; Christensen, C. N.; Schwarz, D. E.; Fanwick, P. E.; Clark, D. L.; Conradson, S. D.; Bart, S. C. *Inorg. Chem.* **2011**, *50*, 9838–9848.

- (11) Camp, C.; Andrez, J.; Pécaut, J.; Mazzanti, M. Inorg. Chem. 2013, 52, 7078-7086.
- (12) Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251–4264.
- (13) Zi, G.; Blosch, L. L.; Jia, L.; Andersen, R. A. Organometallics 2005, 24, 4602-4612.
- (14) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. Inorg. Chem. 2010, 49, 1103–1110.
- (15) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. J. Am. Chem. Soc. 2012, 134, 6160-6168.
- (16) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518–1520.
- (17) Abakumov, G. A.; Cherkasov, V. K.; Piskunov, A. V.; Meshcheryakova, I. N.; Maleeva, A. V.; Poddel'skii, A. I.; Fukin, G. K. Dokl. Chem. **2009**, 427, 168–171.
- (18) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. Inorg. Chem. 1994, 33, 2248-2256.
- (19) Clark, D. L.; Sattelberger, A. P. Inorg. Synth. 1997, 31, 307-315. (20) Chakraborty, S.; Chattopadhyay, J.; Guo, W.; Billups, W. E.
- Angew. Chem., Int. Ed. 2007, 46, 4486–4488. (21) Lochmann, L.; Lim, D. J. Organomet. Chem. 1971, 28, 153–158.
- (22) Sheldrick, G. M. Acta Crystallogr. **2008**, A64, 112–122.
- (23) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda,
- S.; Gould, R. O.; Smits, J. M. M. DIRDIF2008 Program System;
- University of Nijmegen, Nijmegen, The Netherlands, 2008. (24) Edwards, P. G.; Andersen, R. A.; Zalkin, A. J. Am. Chem. Soc.
- **1981**, *103*, 7792–7794. (25) Hitchcock, P. B.; Lappert, M. F.; Singh, A.; Taylor, R. G.;
- Brown, D. J. Chem. Soc., Chem. Commun. 1983, 561–563.
- (26) Broderick, E. M.; Gutzwiller, N. P.; Diaconescu, P. L. Organometallics 2010, 29, 3242-3251.
- (27) Graves, C. R.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. Organometallics 2008, 27, 3335–3337.
- (28) Mansell, S. M.; Perandones, B. F.; Arnold, P. L. J. Organomet. Chem. 2010, 695, 2814-2821.
- (29) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. Nat. Chem. 2010, 2, 723–729.
- (30) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. Polyhedron 2006, 25, 484–492.
- (31) Matson, E. M.; Opperwall, S. R.; Fanwick, P. E.; Bart, S. C. Inorg. Chem. 2013, 52, 7295–7304.
- (32) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. J. Am. Chem. Soc. 2005, 127, 1338–1339.
- (33) Jantunen, K. C.; Burns, C. J.; Castro-Rodriguez, I.; Da Re, R. E.; Golden, J. T.; Morris, D. E.; Scott, B. L.; Taw, F. L.; Kiplinger, J. L. Organometallics **2004**, *23*, 4682–2692.
- (34) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. Organometallics 2002, 21, 5978–5982.
- (35) Jantunen, K. C.; Haftbaradaran, F.; Katz, M. J.; Batchelor, R. J.; Schatte, G.; Leznoff, D. B. *Dalton Trans.* **2005**, 3083–3091.
- (36) Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W. J. Am. Chem. Soc. 2009, 131, 15512–15521.
- (37) Duhovic, S.; Khan, S.; Diaconescu, P. L. Chem. Commun. 2010, 46, 3390–3392.
- (38) Hayes, C. E.; Leznoff, D. B. Organometallics 2010, 29, 767–774.
 (39) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. J. Am.
- Chem. Soc. 2011, 133, 4948-4954.
- (40) Kiplinger, J. L.; John, K. D.; Morris, D. E.; Scott, B. L.; Burns, C. J. Organometallics **2002**, *21*, 4306–4308.
- (41) Monreal, M. J.; Diaconescu, P. L. Organometallics 2008, 27, 1702–1706.
- (42) Edwards, P. G.; Andersen, R. A.; Zalkin, A. Organometallics 1984, 3, 293-298.
- (43) Lam, O. P.; Anthon, C.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. J. Am. Chem. Soc. **2008**, 130, 6567–6576.

- (44) Marks, T. J. Progress in Inoganic Chemistry; Wiley: New York, 1979; Vol. 25.
- (45) Carter, S. M.; Sia, A.; Shaw, M. J.; Heyduk, A. F. J. Am. Chem. Soc. 2008, 130, 5838–5839.
- (46) Carmichael, C. D.; Jones, N. A.; Arnold, P. L. *Inorg. Chem.* **2008**, 47, 8577–8579.
- (47) Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. Organometallics **2011**, 30, 2031–2038.
- (48) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D.; Smith, W. H. Inorg. Chem. **1994**, 33, 4245–4254.
- (49) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. J. Am. Chem. Soc. 2003, 125, 14264–14265.
- (50) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. Inorg. Chem. **2008**, 47, 10522–10532.
- (51) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. Inorg. Chem. 2005, 44, 5559–5561.
- (52) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757–1759.
- (53) Lam, O. P.; Feng, P. L.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. J. Am. Chem. Soc. **2008**, 130, 2806–2816.