

Supporting Information for:

**Isolation of a Uranium(III) Benzophenone Ketyl Radical that Displays
Redox-Active Ligand Behaviour**

*Ellen M. Matson, John J. Kiernicki, Nickolas H. Anderson, Phillip E. Fanwick, Suzanne C. Bart**

H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907

Table of Contents:

Experimental Details.....	2-4
Figure S1: ¹ H NMR spectrum of 2	5
Figure S2: Infrared spectrum of 2	5
Figure S3: Infrared spectrum of 2 with benzophenone overlay.....	6
Figure S4: ¹ H NMR spectrum from reaction of 2 with TEMPO.....	6
Figure S5: IR spectrum from reaction of 2 with TEMPO with benzophenone overlay.....	7
Figure S6: ¹ H NMR spectrum from reaction of 2 with N ₃ Mes.....	7
Figure S7: IR spectrum from reaction of 2 with N ₃ Mes.....	8
Crystallographic Experimental Information	9-10
References	11

General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a coldwell 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.¹ Benzene-*d*₆ was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze-pump-thaw cycles. Benzophenone (recrystallized from anhydrous diethyl ether) and (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (used as received) were purchased from Sigma Aldrich. Tp*₂UI² (**1-I**), Tp*₂U(bipy)³ (**1-bipy**), KC₈⁴, and 2,4,6-trimethylphenylazide (N₃Mes)⁵ were prepared according to literature procedures. Elemental analyses were performed by Complete Analysis Laboratories, Inc. in Parsippany, NJ.

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 299.992 MHz. All chemical shifts were 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 using an acquisition time of 0.5, 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. Infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrum RX I spectrometer on KBr salt plates. Samples were prepared by allowing the desired solution mixture to evaporate on

the salt plate. Electronic absorption measurements were recorded at 294 K in THF in sealed 1 cm quartz cuvettes with a Jasco V-670 spectrophotometer.

Single crystals 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 ($\lambda = 1.54184 \text{ \AA}$). Preliminary examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP⁶. The structures were solved using the structure solution program PATTY in DIRDIFF99.⁷ Refinement was performed on a LINUX PC using SHELX-97.⁶ The data were collected at a temperature of 150(1) K.

Preparation of Tp*₂U(OC•Ph₂) (2). A 20 mL scintillation vial was charged with Tp*₂UI (0.100 g, 0.104 mmol), an equivalent of benzophenone (0.019 g, 0.103 mmol), and approximately 10 mL of THF. While stirring, two equivalents of KC₈ (0.028 g, 0.206 mmol) were added, resulting in a slight color change to light purple. After 2 h volatiles were removed *in vacuo*. The product was extracted into 20 mL of pentane, and the slurry was filtered over Celite to remove by-products. The product was isolated by drying of the resulting purple solution and recrystallization from concentrated pentane, yielding a purple powder (0.082 g, 0.081 mmol, 75%). X-ray quality crystals of **2** were grown overnight from a concentrated pentane-toluene solution (20:1) at -35 °C. Due to the instability of complex **2**, elemental analysis was not obtained. ¹H NMR (C₆D₆, 25 °C): $\delta = -227.59$ (39, 2H, *p*-CH), -178.86 (30, 4H, *o*-CH), -50.58 (233, 6H, Tp*-CH₃), -3.74

(205, 6H, Tp*-CH₃), -3.33 (334, 6H, Tp*-CH₃), -1.90 (143, 6H, Tp*-CH₃), 1.31 (32, 2H, Tp*-CH), 1.34 (62, 2H, Tp*-CH), 3.36 (7, 6H, Tp*-CH₃), 4.16, (160, 2H, Tp*-CH), 18.63 (176, 6H, Tp*-CH₃), 22.05 (184, 2H, B-H), 93.86 (18, 4H, *m*-CH). IR: 2523, 2558 cm⁻¹ (B-H). UV-Vis (THF, 23 °C, 3.0 x 10⁻⁴ M): 556 nm (ε = 860 M⁻¹ cm⁻¹).

Alternative Synthesis of 2. A 20 mL scintillation vial was charged with Tp*₂U(2,2'-bipy) (0.100 g, 0.101 mmol) and approximately 3 mL of THF. Addition of benzophenone (0.018 g, 0.098 mmol) resulted in an immediate color change to purple. After removing solvents under reduced pressure, the purple product was extracted with pentane and dried to yield an inseparable mixture of Tp*₂U(OC•Ph₂) and 2,2'-bipyridine as confirmed by ¹H NMR spectroscopy.

Preparation of Tp*₂UNMes (3-UNMes) A 20 mL scintillation vial was charged with Tp*₂U(OC•Ph₂) (**2**) (0.050 g, 0.043 mmol) and dissolved in 2 mL of tetrahydrofuran. While stirring, 2,4,6-trimethylphenylazide (0.007 g, 0.043 mmol) was added via microsyringe and stirred for 30 min resulting in an immediate color change from purple to pink concomitant with N₂(g) evolution. An aliquot was removed for analysis. Volatiles were removed *in vacuo* from the remaining solution and the resulting solid was washed with *n*-pentane to afford dark pink powder (0.037 g, 0.033 mmol, 77%) identified as pure Tp*₂UNMes (**3-UNMes**) by comparison of the ¹H NMR spectrum to literature values.⁸

Preparation of Tp*₂UO (3-UO) A 20 mL scintillation vial was charged with Tp*₂U(OC•Ph₂) (**2**) (0.050 g, 0.043 mmol) and dissolved in 2 mL of tetrahydrofuran. While stirring, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (0.007 g, 0.045 mmol) was added as a solid resulting in an immediate color change to pink. An aliquot was removed for analysis after 5 min. Volatiles were removed from the remaining solution *in vacuo* to

afford pink powder (0.031g, 0.031 mmol, 72%) identified as pure $\text{Tp}^*\text{}_2\text{UO}$ (**3-UO**) by comparison of the ^1H NMR spectrum to literature values.⁹

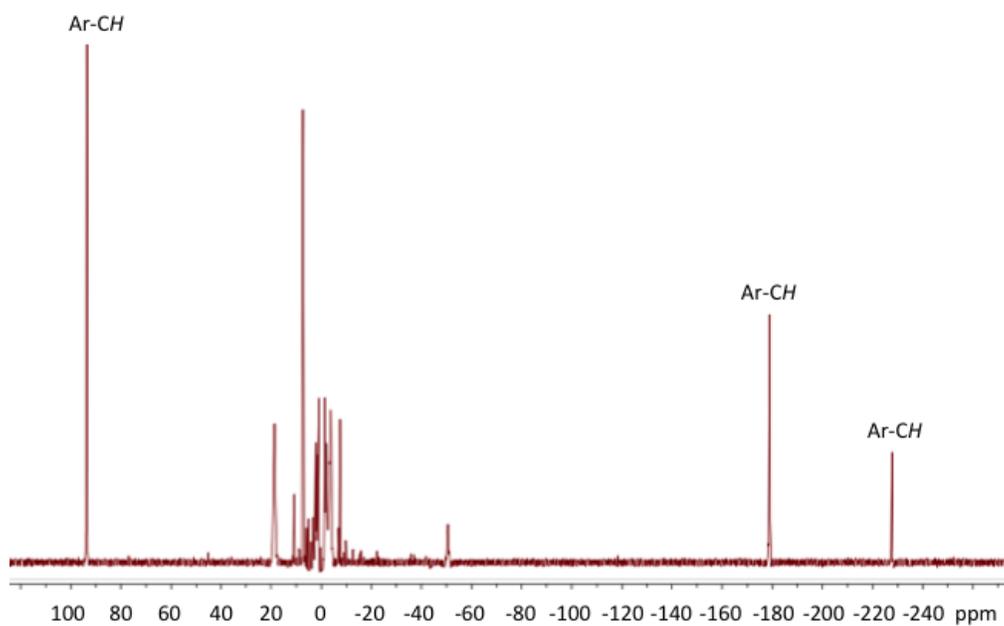


Figure S1: ^1H NMR (C_6D_6 , 23 °C) spectrum of **2**

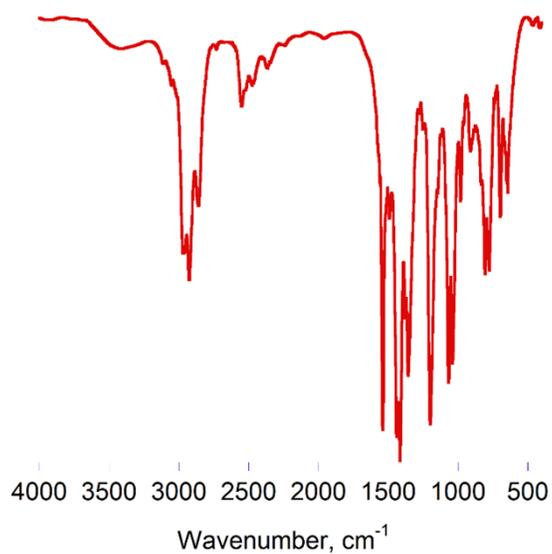


Figure S2: Infrared spectrum of **2**

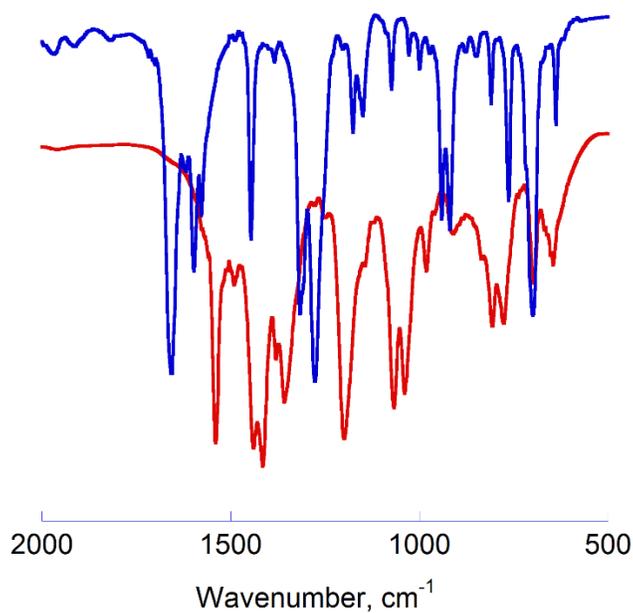


Figure S3: Infrared spectrum of **2** (red) with benzophenone (blue) overlay illustrating consumption of C=O stretch (1657 cm^{-1})

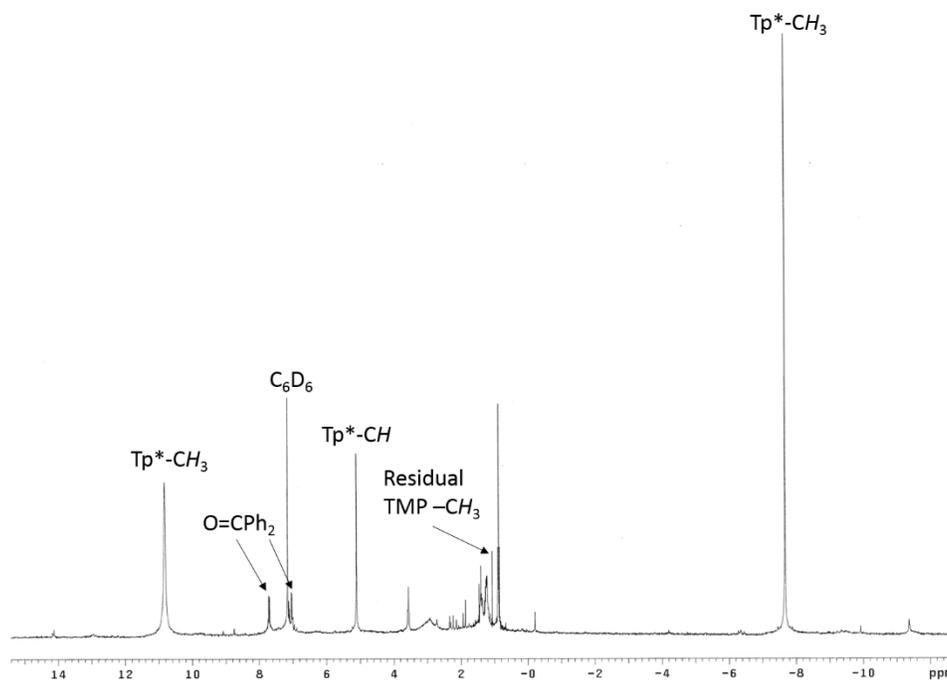


Figure S4: Crude ^1H NMR (C_6D_6 , $23\text{ }^\circ\text{C}$) spectrum from reaction of **2** with TEMPO resulting in the formation of **3-UO**

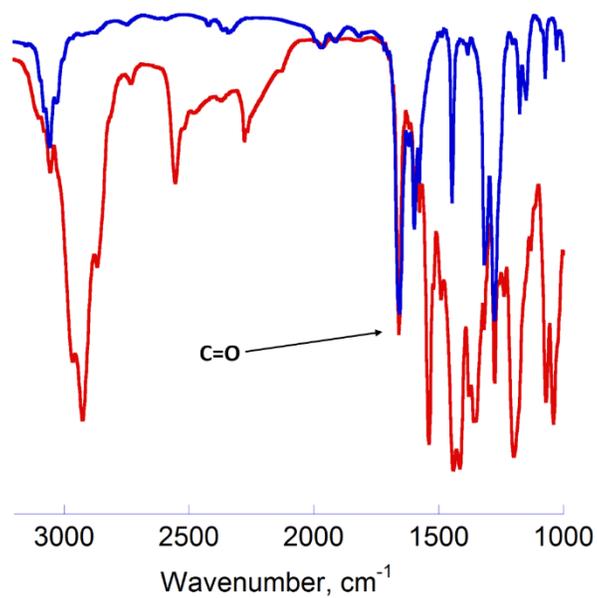


Figure S5: Infrared spectrum of crude mixture from reaction of **2** with TEMPO (red) resulting in formation of **3-UO**. Spectrum of benzophenone (blue) is overlaid to illustrate emergence of C=O stretch.

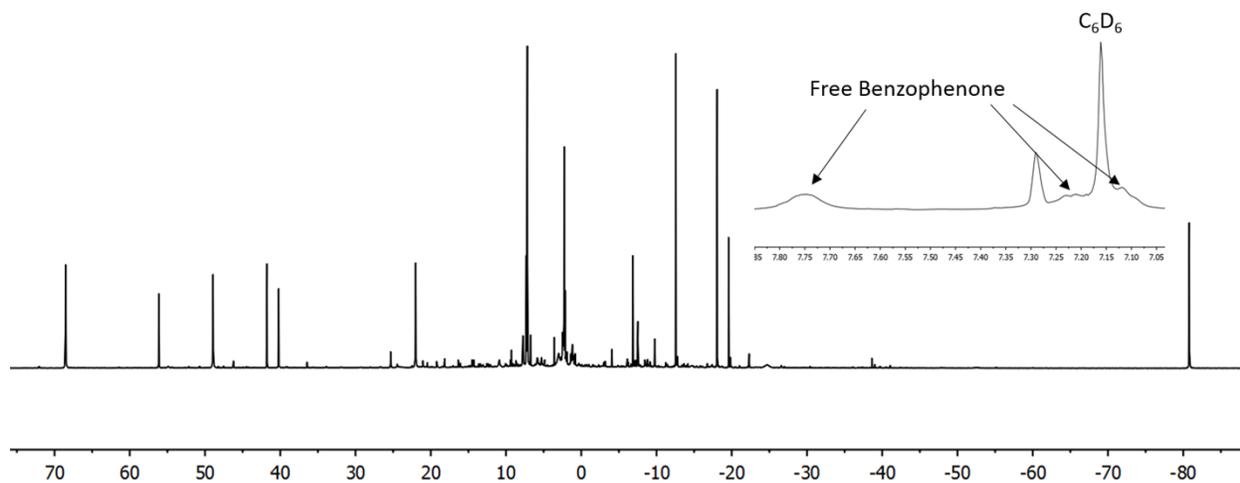


Figure S6: Crude ^1H NMR (C_6D_6 , 23 °C) spectrum of from reaction of **2** with 2,4,6-trimethylphenylazide resulting in the formation of **3-UNMes**. Inset displays formation of free benzophenone.

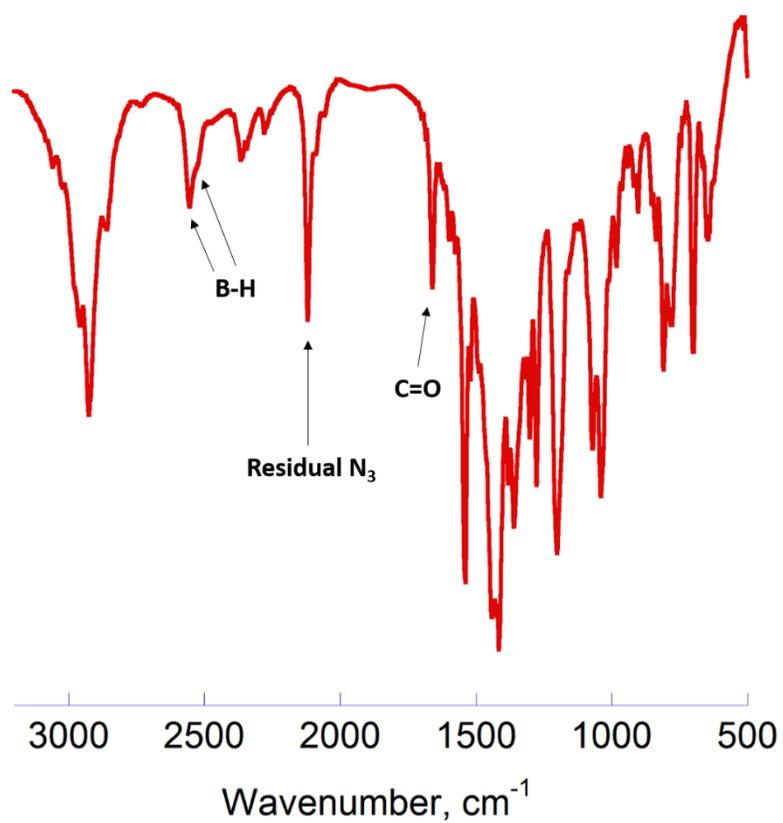


Figure S7: Infrared spectrum of crude mixture from reaction of **2** with 2,4,6-trimethylphenylazide resulting in formation of **3-UNMes**. Free benzophenone is indicated by

C=O.

Crystallographic Details

Experimental: Compound 2

DATA COLLECTION

A violet needle of $C_{43}H_{54}B_2N_{12}OU$, $0.5(C_7H_7)$ having approximate dimensions of 0.20 x 0.10 x 0.04 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_α radiation ($\lambda = 1.54184\text{\AA}$) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 36165 reflections in the range $3 < \theta < 72^\circ$. The triclinic cell parameters and calculated volume are: $a = 11.0395(8)$, $b = 13.5231(9)$, $c = 17.6638(18)$ \AA , $\alpha = 72.590(5)$, $\beta = 86.210(5)$, $\gamma = 67.426(4)^\circ$, $V = 2319.9(3)$ \AA^3 . For $Z = 2$ and F.W. = 1060.21 the calculated density is 1.52 g/cm^3 . The refined mosaicity from DENZO/SCALEPACK¹⁰ was 1.68° indicating very poor crystal quality. The space group was determined by the program XPREP². There were no systematic absences; the space group was determined to be P-1(#2).

The data were collected at a temperature of 150(1) K. Data were collected to a maximum 2θ of 146.0° .

DATA REDUCTION

A total of 36165 reflections were collected, of which 7556 were unique. Frames were integrated with DENZO-SMN¹⁰.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 102.3 /mm for Cu K_α radiation. An empirical absorption correction using SCALEPACK¹⁰ was applied. Transmission coefficients ranged from 0.536 to 0.664. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 8.4% based

on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99⁷. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $1/[s^2(F_o^2) + (0.1558P)^2 + 2.2566P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".¹¹ 7556 reflections were used in the refinements. However, only the 7371 reflections with $F_o^2 > 2s(F_o^2)$ were used in calculating R1. The final cycle of refinement included 589 variable parameters and converged (largest parameter shift was < 0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \sum |F_o - F_c| / \sum F_o = 0.068$$

$$R2 = \text{SQRT} (\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2) = 0.179$$

The goodness-of-fit parameter was 1.09. The highest peak in the final difference Fourier had a height of $4.81 \text{ e}/\text{A}^3$. The minimum negative peak had a height of $-2.15 \text{ e}/\text{A}^3$.

Refinement was performed on a LINUX PC using SHELX-97⁶. Crystallographic drawings were done using programs ORTEP¹² and PLUTON¹³.

Alert level B: PLAT029_Alert_3_B

Response: Data completeness is indicated to be 95.9%. Symmetry was reexamined and determined to be correct for the crystal.

References

- (1) Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K. and Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
- (2) Sun, Y., McDonald, R., Takats, J., Day, V. W. and Eberspacher, T. A. *Inorg. Chem.* **1994**, *33*, 4433-4434.
- (3) Kraft, S. J., Fanwick, P. E. and Bart, S. C. *Inorg. Chem.* **2010**, *49*, 1103-1110.
- (4) Chakraborty, S.; Chattopadhyay, J.; Guo, W.; Billups, W. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 4486.
- (5) L. P. Spencer, R. Altwer, P. Wei, L. Gelmini, J. Gauld and D. W. Stephan, *Organometallics* **2003**, *22*, 3841–3854.
- (6) Sheldrick, G. M. *Acta. Cryst.* **2008**, *112*, A64.
- (7) Beurskens, P. T., Beurskens, G., de Gelder, R., Garcia-Granda, S., Gould, R. O. and Smits, J. M. M. DIRDIF2008 Program System, Crystallography Laboratory, University of Nijmegen: The Netherlands, 2008.
- (8) Matson, E. M.; Crestani, M. G.; Fanwick, P. E.; Bart, S. C. *Dalton Trans.* **2012**, *41*, 7952.
- (9) Kraft, S. J.; Walensky, J.; Fanwick, P. E.; Bart, S. C. *Inorg. Chem.* **2010**, *49*, 7620.
- (10) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
- (11) "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, (1992), Tables 4.2.6.8 and 6.1.1.4
- (12) C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976)
- (13) Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.