Multi-electron Reduction Facilitated by A Trianionic Pyridine(diimine) Ligand

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Experimental

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 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. Benzene-d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze-pump-thaw cycles. Elemental analysis was performed by Midwest Microlab, LLC, in Indianapolis. Azobenzene was purchased from Sigma Aldrich and used as received. $Cp^*_2UI(THF)$,[i] potassium graphite,[ii] and $^{Mes}PDI^{Me}$[iii] were prepared according to 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 $SiMe_4$ using ^1H (residual) chemical shifts of the solvent as a secondary standard. 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. The spectra for paramagnetic molecules were obtained using an acquisition time of 0.5 s; thus, the peak widths reported have errors of ±2 Hz. Electronic absorption spectroscopic measurements were recorded at 294 K in pentane in sealed 1 cm quartz cuvettes with a Jasco V-670 spectrophotometer.

Synthesis of Cp*U(PDI)(THF) (1). A 20 mL scintillation vial was charged with $Cp^*_2UI(THF)$ (0.100 g, 0.141 mmol), $^{Mes}PDI^{Me}$ (0.056 g, 0.141 mmol) and toluene. This was stirred for one hour, after which time 2 equivalents of KC_8 (0.038 g, 0.282 mmol) was added. After 3 hours of stirring, the solution was filtered over Celite to remove KCp*, KI, and graphite (C_8). The volatiles were removed *in vacuo*, yielding a brown solid. The resulting solid was stirred in pentane for 30 minutes. This solution was again filtered over Celite to remove unidentified side products. The solvent was removed under vacuum to afford **1** as a brown solid (0.072 g, 0.085 mmol, 60%). X-ray-quality single crystals were obtained by recrystallization from diethyl ether at -35° C. Analysis for $C_{41}H_{54}N_3OU$: calcd: C, 58.41; H, 6.46; N, 4.98; found: C, 58.51; H, 6.35; N, 4.96. ^1H NMR (C_6D_6, 25 °C): δ = -33.9 (48, 2H, THF-CH_2), -32.9 (48, 2H, THF-CH_2), -14.9 (48, 2H, THF-CH_2), -14.7 (48, 2H, THF-CH_2), -8.1 (22, 1H), -5.2 (18, 1H), -2.4 (5, 15H, Cp*-CH_3), 1.9 (4, 3H), 2.5 (4, 3H), 7.5 (7, 1H), 7.9 (7, 1H), 8.0 (7, 1H), 8.9 (16, 3H), 10.1 (7, 1H), 11.6 (14, 3H), 13.4 (10, 3H), 14.9 (10, 3H), 23.1 (12, 3H), 24.5 (38, 1H), 27.7 (14, 3H). μ_{eff} = 2.3 μ_B.

Synthesis of Cp*U(=NPh)$_2$(PDI) (2). A 20 mL scintillation vial was charged with 0.102 g (0.121 mmol) of Cp*U(^{Mes}PDI^{Me})(THF) (**1**) and 10 mL of toluene. While stirring, 0.022 g (0.121 mmol) of azobenzene was added. After stirring for 30 min, volatiles were removed *in vacuo*. The resulting solid was recrystallized by placing a pentane suspension (10 mL) in the freezer overnight to afford a dark brown solid (0.066 g, 0.069 mmol, 58%) assigned as Cp*U(PDI)(NPh)$_2$. Single, X-ray quality crystals were grown in a concentrated toluene/THF/pentane (10:2:1) solution at -35 ºC. Elemental analysis of $C_{49}H_{56}N_5U$: Calculated, C, 61.79; H, 5.92; N, 7.35. Found, C, 61.76; H, 5.89; N, 7.32. ^1H NMR (C_6D_6, 25 ºC) δ -10.85 (61, 12H, Ar- CH_3), -5.37 (44, 2H), -3.74 (19, 15H, Cp*-CH_3), 8.41 (10, 10H), 11.03 (17, 4H), 22.09 (14, 1H), 22.97 (90, 6H), 29.28 (7, 6H).

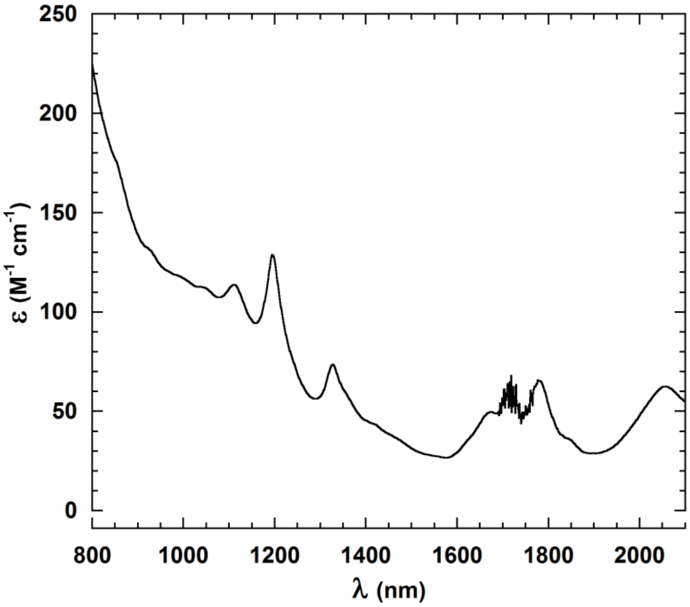

Figure S1. Near-infrared spectrum of **1** recorded in pentane at 294 K. Note: Sharp peaks at ~1680–1750 nm are solvent overtones.

Crystallography

Single crystals for X-ray diffraction were coated with polybutenes in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image-plate diffractometer. Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program *XPREP*.[iv] The structures were solved using the structure solution program *PATTY* in *DIRDIFF99*.[v] Refinement was performed on a LINUX PC using *SHELX-97*.[4] The data were collected at a temperature of 150(1) K.

Crystal Data for **1**: $C_{41}H_{54}N_3OU$, M = 842.928, triclinic, a = 11.08720(10), b = 17.1526(3), c = 20.6160(3) Å, α = 69.3710(8)°, β = 82.2600(8)°, δ = 89.3760(6)°, U = 3632.99(9) Å^3, T = 150(1) K, space group P-1 (no. 2), Z = 4, 72,464 reflections measured, 17,105 unique (R_{int} = 0.046) which were used in all calculations. The final R_1 = 0.0230 and w$R(F^2)$ = 0.0470 (all data).

Crystals Data for **2**: $C_{49}H_{56}N_5U{*}C_4H_8O,C_7H_8$, M = 1117.294, monoclinic, a = 18.6610(7), b =

22.0109(8), *c* = 26.2485(7) Å, β = 90.9021(18)°, *U* = 10780.1(6) $Å^3$, *T* = 150(1) K, space group *P 1 21/n 1(no. 14)*, *Z* = 8, 112,480 reflections measured, 19,423 unique (R_{int} = 0.072) which were used in all calculations. The final R_1 = 0.0590 and w$R(F^2)$ = 0.1830 (all data).

Sample ID: Compound **1**, Formula: $C_{41}H_{44}N_3OU$

DATA COLLECTION

A brown chunk of $C_{41}H_{44}N_3OU$ having approximate dimensions of 0.30 x 0.28 x 0.23 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Mo K_α radiation (λ = 0.71073 Å) on a Nonius KappaCCD equipped with a graphite crystal, incident beam monochromator.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 72464 reflections in the range 1 < q < 27°. The triclinic cell parameters and calculated volume are: a = 11.08720(10), b = 17.1526(3), c = 20.6160(3)Å, α = 69.3710(8), β =82.2600(8), δ = 89.3760(6)°, V = 3632.99(9)$Å^3$. For Z = 4 and F.W. = 842.94 the calculated density is 1.54 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[vi] was 0.46° indicating good crystal quality. The space group was determined by the program XPREP.[4] 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 2q of 55.7°.

DATA REDUCTION

A total of 72464 reflections were collected, of which 17105 were unique. Frames were integrated with DENZO-SMN.[6]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 45.0 /mm for Mo K_α radiation. An empirical absorption correction using SCALEPACK[6] was applied. Transmission coefficients ranged from 0.123 to 0.363. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 4.6% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[5] 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 $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.0089P)^2+0.0000P]$ where $P=(Fo^2 +2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[vii] 17105 reflections were used in the refinements. However, only the 9941 reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 855 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S |Fo - Fc| / S Fo = 0.023$$

$$R2 = SQRT (S w (Fo^2 - Fc^2)^2 / S w (Fo^2)^2) = 0.043$$

The goodness-of-fit parameter was 1.03. The highest peak in the final difference Fourier had a height of 0.80 e/A^3. The minimum negative peak had a height of -0.74 e/A^3.

Refinement was performed on a LINUX PC using SHELX-97.[4] Crystallographic drawings were done using programs ORTEP,[viii] and PLUTON.[ix]

Sample ID: **2**, Formula: $C_{49}H_{56}N_5U,C_4H_8O,C_7H_8$

DATA COLLECTION

A green plate of $C_{49}H_{56}N_5U,C_4H_8O,C_7H_8$ having approximate dimensions of 0.20 x 0.15 x 0.10 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_α radiation (λ = 1.54184Å) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of112480 reflections in the range 2 < q < 70°. The monoclinic cell parameters and calculated volume are: a = 18.6610(7), b = 22.0109(8) c = 26.2485(7) Å, β = 90.9021(18)°, V = 10780.1(6)Å^3. For Z = 8 and F.W. = 1117.31 the calculated density is 1.38 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[6] was 0.60° indicating moderate crystal quality. The space group was determined by the program ABSEN.[x] From the systematic presences of:

h0l h+l=2n
0k0 k=2n

and from subsequent least-squares refinement, the space group was determined to be P 1 21/n 1(# 14).

The data were collected at a temperature of 150(1)K. Data were collected to a maximum 2q of 140.5°.

DATA REDUCTION

A total of 112480 reflections were collected, of which 19423 were unique. Frames were integrated with DENZO-SMN.[6]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 88.0 /mm for Cu K_α radiation. An empirical absorption correction using SCALEPACK[6] was applied. Transmission coefficients ranged from 0.298 to 0.415. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 7.2% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[5] 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 $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.1039P)^2+25.5086P]$ where $P=(Fo^2 +2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[7] 19423 reflections were used in the refinements. However, only the 16093 reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included1235 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\ |Fo - Fc|\ /\ S\ Fo = 0.059$$

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2\ /\ S\ w\ (Fo^2)^2\ ) = 0.173$$

The goodness-of-fit parameter was 1.06. The highest peak in the final difference Fourier had a height of 2.89 e/A^3. The minimum negative peak had a height of -1.95 e/A^3.

Refinement was performed on a LINUX PC using SHELX-97.[4] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

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[i] Mohammad, A.; Cladis, D. P.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. *Chem Commun.* **2012**, *48*, 1671-1673.

[ii] Chakraborty, S.; Chattopadhyay, J.; Guo, W.; Billups, W. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 4486-4488.

[iii] Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849-850.

[iv] Sheldrick, G. M. *Acta Cryst., Sect. A* **2008**, *A64*, 112-122.

[v] P. T. Beurskens, G. Beurskens, R. deGelderS. Garcia-Granda, R. O. Gould, and J. M. M. Smits, *The DIRDIF2008 Program System*. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands, **2008**.

[vi] Z. Otwinowski and W. Minor, *Methods Enzymol.*, **1997**, *276*, 307.

[vii] "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, **1992**, Tables 4.2.6.8 and 6.1.1.4

[viii] C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, **1976**.

[ix] A. L. Spek, *J. Appl. Cryst.*, **2003**, *36*, 7.

[x] P. C. McArdle, *J. Appl. Cryst.*, **1996**, *29*, 306.