Supporting Information for:

Utility of a Redox-Active Pyridine(diimine) Chelate in Facilitating Two Electron Oxidative Addition Chemistry at Uranium

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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 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.[1] Benzene-d6 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 Complete Analysis Laboratories, Inc., Parsippany, NJ. $Cp^PU(^{Mes}PDI^{Me})$ (**1**),[2] $Cp^PUI_2(^{Mes}PDI^{Me})$ (**2-I$_2$**),[2] NaTePh·1/2THF,[3] and iodosylbenzene dichloride[4] were prepared according to literature procedures. Thiophenol, benzeneselenol, diphenyldisulphide, diphenyldiselenide, diphenylditelluride, and phenylselenyl chloride were purchased from Sigma Aldrich and used as received. KSPh and KSePh were prepared by deprotonation of the corresponding thiol or selenol with potassium hydride at -78 °C in THF.

^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. 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.

Single crystals of **2-Cl$_2$** and **4-SePh** suitable for X-Ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Nonius KappaCCD image plate diffractometer equipped with a graphite crystal, incident beam monochromator. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å). Single crystals of **3** and **4-SPh** suitable 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 Kα radiation (λ = 1.54184 Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.[6] The structures were solved using the structure solution program PATTY in DIRDIFF99. Refinement was performed on a LINUX PC using SHELX-97.[10] The data were collected at a temperature of 150(1) K.

Synthesis of Cp^{P}UI$_2$(^{Mes}PDI^{Me}) (2-I$_2$) from Cp^{P}U(^{Mes}PDI^{Me}) (1). A 20 mL scintillation vial was charged with Cp^{P}U(^{Mes}PDI^{Me}) (**1**) (0.022 g, 0.027 mmol) in 2 mL of toluene and frozen in the coldwell. Upon thawing, I$_2$ (0.5 M in THF; 0.053 mL, 0.027 mmol) was added via microsyringe resulting in a slight colour change. Upon reaching RT, volatiles were removed *in vacuo*. Inspection of the crude mixture by ^{1}H NMR spectroscopy revealed formation (compared to literature)[2] of Cp^{P}UI$_2$(^{Mes}PDI^{Me}) (**2-I$_2$**) in quantitative fashion.

Synthesis of $Cp^PUCl_2(^{Mes}PDI^{Me})$ (2-Cl_2). A 20 mL scintillation vial was charged with 0.100 g (0.122 mmol) of $Cp^PU(^{Mes}PDI^{Me})$ (**1**) and 5 mL toluene and frozen in the coldwell. Upon thawing, 0.034 g (0.124 mmol) of iodosylbenzene dichloride was added and stirred for 15 minutes. Volatiles were removed, and the resulting mixture was recrystallized by slow evaporation of a concentrated diethyl ether solution at -35 °C, affording brown solid (0.057 g, 0.064 mmol, 52%) assigned as $Cp^PUCl_2(^{Mes}PDI^{Me})$ (**2-Cl_2**). Single, X-ray quality crystals were obtained by slow evaporation of a dilute diethyl ether solution at -35 °C. Elemental analysis of $C_{41}H_{46}N_3Cl_2U$: Calculated, C, 55.35; H, 5.21; N, 4.72. Found, C, 55.28; H, 5.06; N, 4.54. ^1H NMR (C_6D_6, 25 °C) δ = -46.67 (62, 1H, *p*-pyr-C*H*), -4.75 (8, 6H, Cp^P-$(CH_3)_2$), -2.84 (36, 12H, Ar-*o*-CH_3), -0.04 (26, 4H, Ar-*m*-C*H*), 2.04 (22, 2H, Cp^P-C*H*), 5.42 (129, 2H, Cp^P-C*H*), 6.34 (t, *J* = *6*, 1H, Cp^P-*p*-Ph-C*H*), 6.53 (t, *J* = *6*, 2H, Cp^P-*m*-Ph-C*H*), 6.79 (d, *J* = *6*, 2H, Cp^P-*o*-Ph-C*H*), 11.05 (9, 2H, *m*-pyr-C*H*), 14.55 (28, 6H, Ar-*p*-CH_3), 80.20 (490, 6H, N=CCH_3).

Synthesis of $Cp^PU(SePh)(Cl)(^{Mes}PDI^{Me})$ (3). A 20 mL scintillation vial was charged with 0.200 g (0.244 mmol) of $Cp^PU(^{Mes}PDI^{Me})$ (**1**) and 5 mL toluene and stirred. Phenylselenyl chloride (0.047 g, 0.245 mmol) was added and stirred for 5 min, followed by removal of volatiles *in vacuo*. The resulting solid was recrystallized from a saturated toluene solution layered with pentane, yielding brown solid (0.091 g, 0.090 mmol, 37%) assigned as $Cp^PU(SePh)Cl(^{Mes}PDI^{Me})$ (**3**). The mother liquor was further concentrated yielding an additional 0.037 g of **3** (52%). Single, X-ray quality crystals were obtained by layering an acetone solution of **3** with *n*-hexane at -35 °C. Elemental analysis of $C_{47}H_{51}N_3SeClU$: Calculated, C, 55.87; H, 5.09; N, 4.16. Found, C, 55.74; H, 5.21; N, 4.08. ^1H NMR (C_6D_6, 25 °C) δ = -77.54 (557, 1H, *p*-pyr-C*H*), -45.13 (127, 2H, Ar-C*H*), -

5.82 (110, 6H, -CH_3), -3.53 (33, 6H, -CH_3), -1.36 (82, 2H, Ar-C*H*), 0.79 (196, 6H, -CH_3), 3.32 (248, 2H, Ar-C*H*), 4.55 (1875, 1H, Cp^P-*p*-Ph-C*H*), 4.93 (32, 2H, Ph-C*H*), 5.62 (217, 2H, Ar-C*H*), 5.89 (28, 1H, Se-*p*-Ph-C*H*), 6.00 (28, 2H, Ph-C*H*), 7.85 (149, 2H, Ar-C*H*), 8.69 (58, 6H, -CH_3), 13.59 (82, 2H, Ar-*m*-C*H*), 15.88 (71, 2H, Ar-*m*-C*H*), 45.12 (439, 6H, N=CCH_3).

Synthesis of Cp^{P}U(EPh)$_2$(^{Mes}PDI^{Me}) (E = S, Se, Te) (4-EPh) from Cp^{P}U(^{Mes}PDI^{Me}) and PhEEPh. The following procedure is representative of all compounds of the type **4-EPh**. A 20 mL scintillation vial was charged with Cp^{P}U(^{Mes}PDI^{Me}) (**1**) (0.100 g, 0.122 mmol) in 5 mL of toluene and cooled to -35 °C. A separate vial containing diphenyldisulphide (0.027g, 0.124 mmol) in toluene (2 mL) was added dropwise to the first while stirring. Following stirring for 5 min, volatiles were removed in vacuo. The resulting solid was washed with pentane and dried, yielding brown powder (0.081 g, 0.078 mmol, 64%) assigned as Cp^{P}U(SPh)$_2$(^{Mes}PDI^{Me}) (**4-SPh**). Single, X-ray quality crystals were obtained from a saturated diethyl ether solution layered with pentane at -35 °C. Elemental analysis of $C_{53}H_{56}N_3S_2U$: Calculated, C, 61.37; H, 5.44; N, 4.05. Found, C, 61.27; H, 5.28; N, 3.96. ^{1}H NMR (C_6D_6, 25 ºC) δ = -83.83 (254, 1H, *p*-pyr-C*H*), -32.46 (66, 2H, *m*-pyr-C*H*), -3.87 (90, 2H, Cp^P-C*H*), -2.68 (4, 6H, -CH_3), 1.32 (23, 12H, Ar-*o*-CH_3), 2.10 (5, 4H, Ar-*m*-C*H*), 2.25 (d, *J* = *6*, 2H, Cp^P-*o*-Ph-C*H*), 3.28 (18, 6H, -CH_3), 5.00 (t, *J* = *6*, 2H, Ar-C*H*), 5.14 (t, *J* = *8*, 2H, S-*p*-Ph-C*H*), 5.26 (t, *J* = *6*, 1H, Cp^P-*p*-Ph-C*H*), 7.39 (d, *J* = *6*, 4H, S-*o*-Ph-C*H*), 10.62 (33, 4H, S-*m*-Ph-C*H*), 15.20 (8, 2H, Ar-C*H*), 44.56 (209, 6H, N=CCH_3). **4-SePh**: Brown powder (Yield = 96%). Single, X-ray quality crystals were obtained from a saturated THF solution layered with an equal volume of *n*-hexane. Elemental analysis of $C_{53}H_{56}N_3Se_2U$: Calculated, C, 56.29; H, 4.99;

N, 3.72. Found, C, 56.16; H, 4.89; N, 3.66. ^{1}H NMR (C_6D_6, 25 ºC) δ = -68.30 (3, 1H, *p*-pyr-C*H*), -15.59 (50, 2H, *m*-pyr-C*H*), -6.06 (91, 2H, Ar-C*H*), -2.92 (12, 6H, -C*H*$_3$), -2.36 (4, 6H, -C*H*$_3$), -1.95 (13, 12H, Ar-*o*-C*H*$_3$), 1.36 (4, 4H, Ar-*m*-C*H*), 2.12 (4, 1H, Cp^P-*p*-Ph-C*H*), 5.05 (t, *J = 6*, 2H, Ar-C*H*), 5.78 (t, *J = 6*, 2H, Ar-C*H*), 6.21 (d, *J = 6*, 2H, Ar-C*H*), 7.66 (13, 4H, Ar-C*H*), 10.63 (20, 4H, Ar-C*H*), 12.99 (7, 2H, Ar-C*H*), 29.28 (106, 6H, N=CC*H*$_3$). **4-TePh**: Brown Powder (Yield = 88%). Elemental analysis of $C_{53}H_{56}N_3Te_2U$: Calculated, C, 51.83; H, 4.60; N, 3.42. Found, C, 51.71; H, 4.71; N, 3.33. ^{1}H NMR (C_6D_6, 25 ºC) δ = -41.84 (45, 1H, *p*-pyr-C*H*), -8.90 (7, 6H, -C*H*$_3$), -8.68 (8, 12H, Ar-*o*-C*H*$_3$), -2.35 (3, 6H, -C*H*$_3$), -0.76 (4, 4H, Ar-*m*-C*H*), -0.22 (37, 2H, Ar-C*H*), 3.56 (19, 6H, N=CC*H*$_3$), 4.69 (30, 2H, Ar-C*H*), 7.03 (5, 2H, Ar-C*H*), 7.61 (t, *J = 8*, 2H, Ar-C*H*), 8.32 (t, *J = 8*, 1H, Cp^P-*p*-Ph-C*H*), 9.02 (t, *J = 8*, 2H, Ar-C*H*), 9.69 (t, *J = 6*, 4H, -Te-*m*-Ph-C*H*), 11.97 (d, *J = 8*, 2H, Cp^P-*o*-Ph-C*H*), 13.05 (d, *J = 6*, 4H, Te-*o*-Ph-C*H*).

Synthesis of $Cp^PU(EPh)_2(^{Mes}PDI^{Me})$ (E = S, Se) (3-EPh) from $Cp^PUI_2(^{Mes}PDI^{Me})$ and KEPh. A 20 mL scintillation vial was charged with 0.280 g (0.261 mmol) of $Cp^PUI_2(^{Mes}PDI^{Me})$ (**2-I$_2$**) and 10 mL of THF. While stirring, 0.078 g (0.526 mmol) of KSPh was added. After stirring for 2 h, the brown-orange solution was filtered over Celite. Volatiles were removed *in vacuo* and the resulting solid was washed with pentane to afford brown solid (0.225 g, 0.217 mmol, 83%) identified as $Cp^PU(SPh)_2(^{Mes}PDI^{Me})$ (**4-SPh**). **4-SePh**: (Yield = 92%).

Synthesis of $Cp^PU(TePh)_2(^{Mes}PDI^{Me})$ (4-TePh) from $Cp^PUI_2(^{Mes}PDI^{Me})$ and NaTePh•1/2THF. A 20 mL scintillation vial was charged with 0.100 g (0.093 mmol) of $Cp^PUI_2(^{Mes}PDI^{Me})$ (**2-I$_2$**) and 10 mL of THF. While stirring, 0.050 g (0.190 mmol) of NaTePh•1/2THF was added. After stirring for 2 h, volatiles were removed. The residue was dissolved in toluene and filtered over Celite. Following the removal of volatiles, the crude product was recrystallized by layering a THF solution with an equal volume of *n*-pentane at -35 ºC affording brown solid (0.093 g, 0.078 mmol, 81%) identified as $Cp^PU(TePh)_2(^{Mes}PDI^{Me})$ (**4-TePh**).

Crossover Experiment of Oxidative Addition of PhEEPh to $Cp^PU(^{Mes}PDI^{Me})$. A 20 mL scintillation vial was charged with 0.050 g (0.061 mmol) of $Cp^PU(^{Mes}PDI^{Me})$ (**1**) dissolved in 4 mL of toluene and chilled to -35 °C. A seperate vial was charged with diphenyldisulphide (0.007 g, 0.032 mmol) and diphenyldiselenide (0.010 g, 0.032 mmol) in 2 mL of toluene and added to the vial containing $Cp^PU(^{Mes}PDI^{Me})$ (**1**). The reaction mixture was stirred 1 hr before volatiles were removed *in vacuo*. The crude reaction mixture was inspected via ^1H NMR spectroscopy revealing the presence of **4-SPh**, **4-SePh**, and a third product assigned as $Cp^PU(SPh)(SePh)(^{Mes}PDI^{Me})$ (**4-SPh/SePh**). **4-SPh/SePh**: ^1H NMR (C_6D_6, 25 ºC) δ = -74.99 (149, 1H, *p*-pyr-C*H*), -24.69 (47, 2H, *m*-pyr-C*H*), -2.43 (3, 6H, -CH_3), -1.87 (8, 2H, Ar-C*H*), -1.08 (14, 6H, -CH_3), 0.31 (15, 6H, -CH_3), 0.63 (20, 6H, -CH_3), 1.50 (8, 1H, Ar-C*H*), 1.66 (9, 2H, Ar-C*H*), 1.92 (8, 2H, Ar-C*H*), 2.17 (8, 1H, Ar-C*H*), 3.59 (d, *J* = *8*, 2H, X-*o*-Ph-C*H*), 5.57 (t, *J* = *8*, 2H, X-*m*-Ph-C*H*), 5.70 (t, *J* = *8*, 1H, X-*p*-Ph-C*H*), 6.92 (7, 2H, Ar-C*H*), 8.17 (d, *J* = *6*, 2H, Cp^P-*o*-Ph-C*H*), 9.27 (33, 2H, Ar-C*H*), 12.08 (26, 2H, Ar-C*H*), 14.29 (8, 2H, Ar-C*H*), 36.70 (136, 6H, N=CCH_3).

Crossover Control Experiments:

4-SPh + 4-SePh: A J-Young NMR tube was charged with 0.005 g each of $Cp^PU(SPh)_2(^{Mes}PDI^{Me})$ and $Cp^PU(SePh)_2(^{Mes}PDI^{Me})$ in 1 mL of C_6D_6. Inspection by ^1H NMR spectroscopy revealed no interconversion. The tube was subsequently heated at 75 °C overnight.

Inspection by ^{1}H NMR spectroscopy again revealed neither the presence of $Cp^{P}U(SPh)(SePh)(^{Mes}PDI^{Me})$ **4-SPh/SePh** nor significant product decomposition.

PhS-SPh + PhSe-SePh: A J-Young NMR tube was charged with 0.005 g each of diphenyldisulfide and diphenyldiselenide in 1 mL in C_6D_6 and vigorously shaken for 2 min. Inspection by ^{1}H NMR spectroscopy revealed only resonances for PhS-SPh and PhSe-SePh. Peaks attributable to PhS-SePh were not present.

Table S1. Experimental bond distances and angles of **2-Cl$_2$**, **3**, **4-SPh**, **4-SePh**.

Distance (Å) or Angle (°)	**2-Cl$_2$ (X1 = X2 = Cl)**	**3 (X1 = Se; X2 = Cl)**	**4-SPh (X1 = X2 = S)**	**4-SePh (X1 = X2 = Se)**
U-N1	2.497(4)	2.485(6)	2.526(5)	2.529(3)
U-N2	2.402(4)	2.367(7)	2.375(5)	2.356(3)
U-N3	2.440(4)	2.491(7)	2.480(5)	2.531(3)
N1-C2	1.320(6)	1.314(11)	1.301(9)	1.325(5)
C2-C3	1.447(7)	1.459(11)	1.460(10)	1.434(6)
C3-C4	1.396(7)	1.386(12)	1.370(10)	1.389(5)
C4-C5	1.380(7)	1.384(12)	1.379(11)	1.375(6)
C5-C6	1.379(7)	1.387(12)	1.363(11)	1.376(6)
C6-C7	1.391(7)	1.389(12)	1.409(10)	1.384(5)
N2-C3	1.378(6)	1.381(10)	1.377(9)	1.390(5)
N2-C7	1.383(6)	1.384(11)	1.378(9)	1.386(5)
C7-C8	1.438(7)	1.431(12)	1.448(10)	1.448(5)
N3-C8	1.324(6)	1.319(11)	1.322(8)	1.316(5)
U-Ct	2.510	2.509	2.520	2.542
U-X1	2.7382(12)	2.8729(11)	2.7440(16)	2.8694(4)
U-X2	2.6246(13)	2.621(2)	2.7404(16)	2.9032(5)
X1-U-X2	157.60(4)	160.43(6)	163.82(5)	166.564(16)
C27-X1-U	--	111.4(11)	113.8(2)	109.43(12)
C33-X2-U	--	--	112.5(2)	107.90(12)

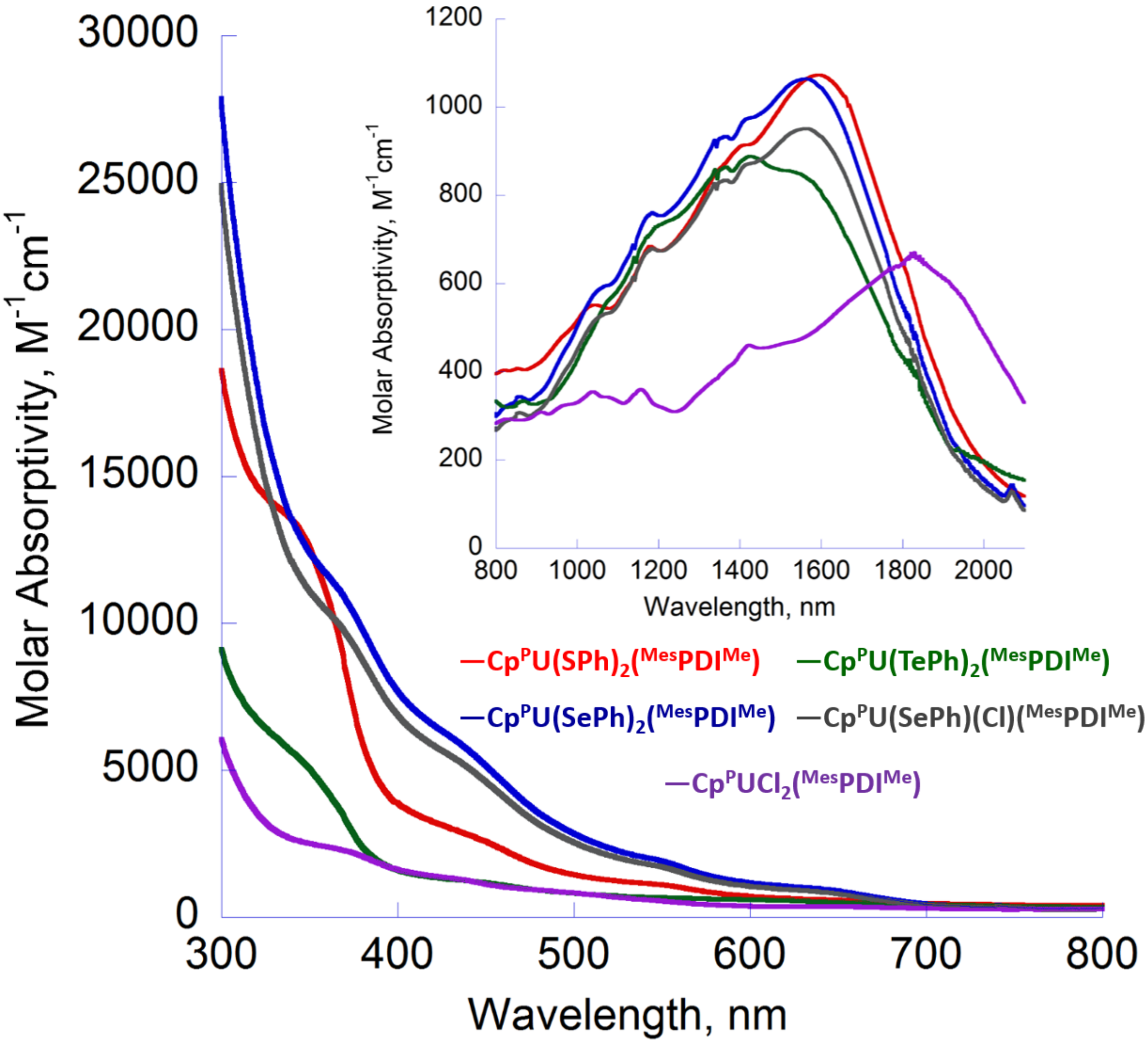

Figure S1. Electronic absorption spectra of **2-Cl$_2$** (purple), **3** (grey), **4-SPh** (red), **4-SePh** (blue), and **4-TePh** (green) recorded in tetrahydrofuran from 300-2100 nm at ambient temperature. Solvent overtones from 1670-1760 nm have been removed for clarity.

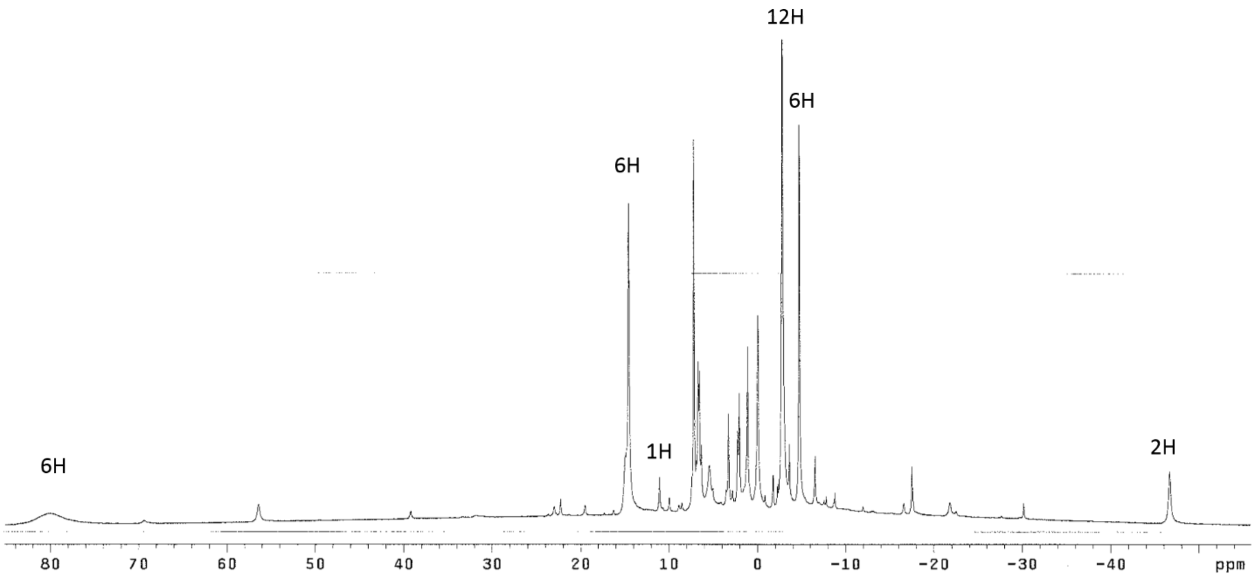

Figure S2. ^{1}H NMR spectrum of Cp^{P}UCl$_2$(^{Mes}PDI^{Me}) (**2**) (C_6D_6, 23 °C) with integration values shown.

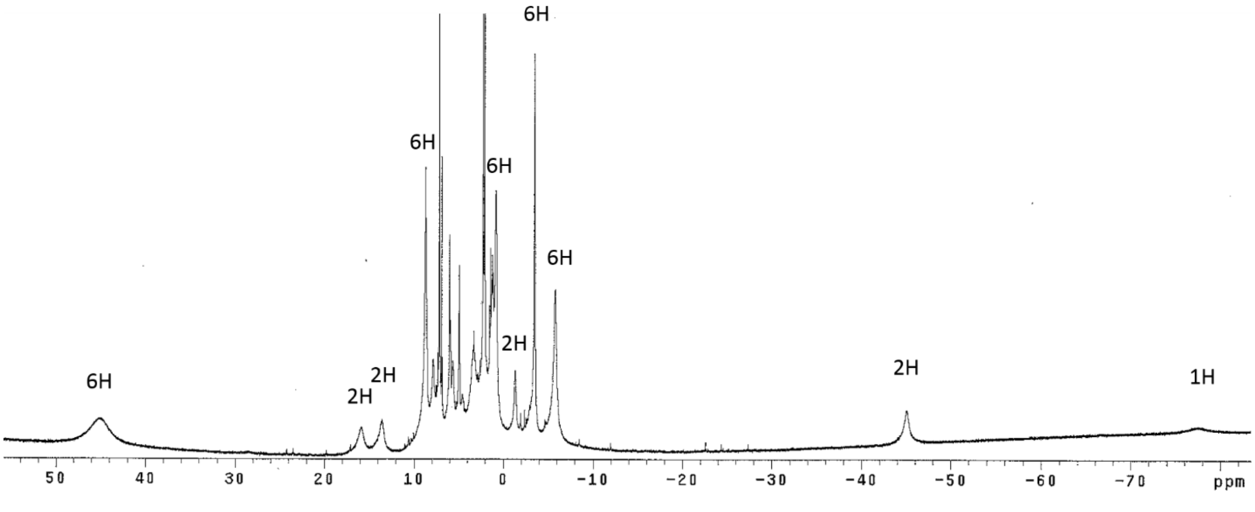

Figure S3. ^{1}H NMR spectrum of Cp^{P}U(SePh)(Cl)(^{Mes}PDI^{Me}) (**3**) (C_6D_6, 23 °C) with integration values shown.

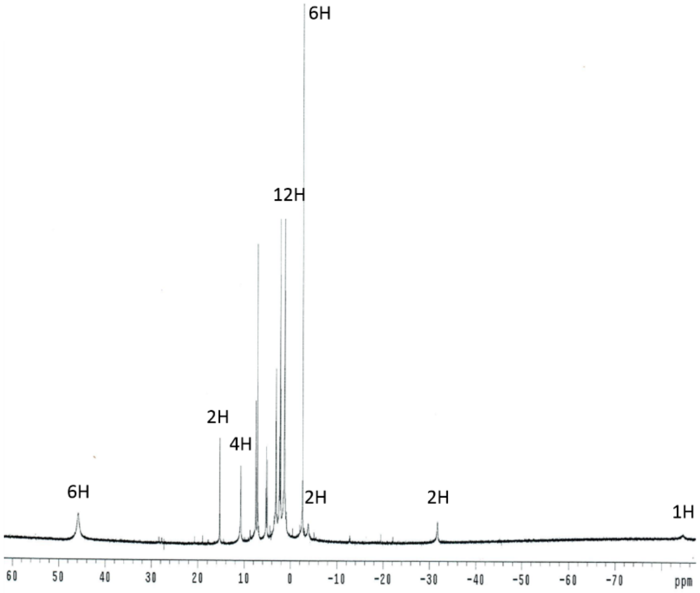

Figure S4. ^{1}H NMR spectrum of Cp^{P}U(SPh)$_2$(^{Mes}PDI^{Me}) (**4-SPh**) (C_6D_6, 23 °C) with integration values shown.

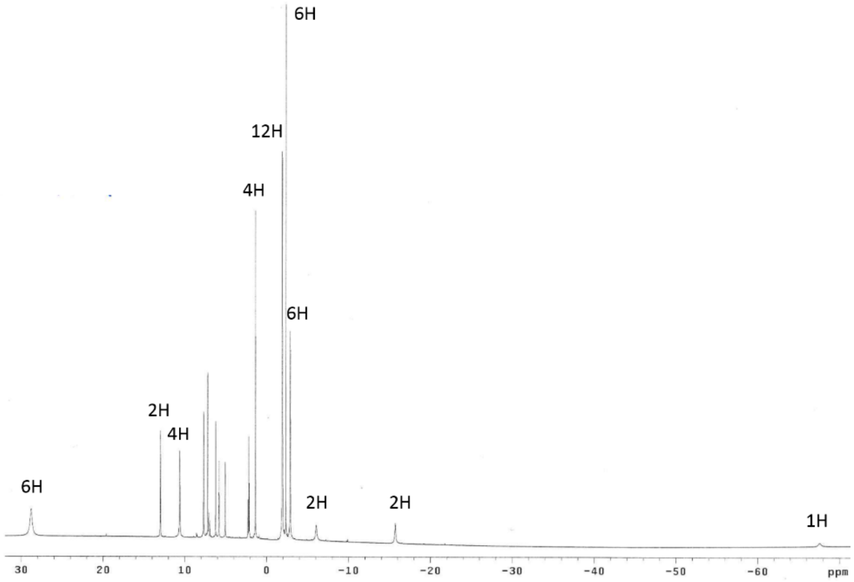

Figure S5. ^{1}H NMR spectrum of Cp^{P}U(SePh)$_2$(^{Mes}PDI^{Me}) (**4-SePh**) (C_6D_6, 23 °C) with integration values shown.

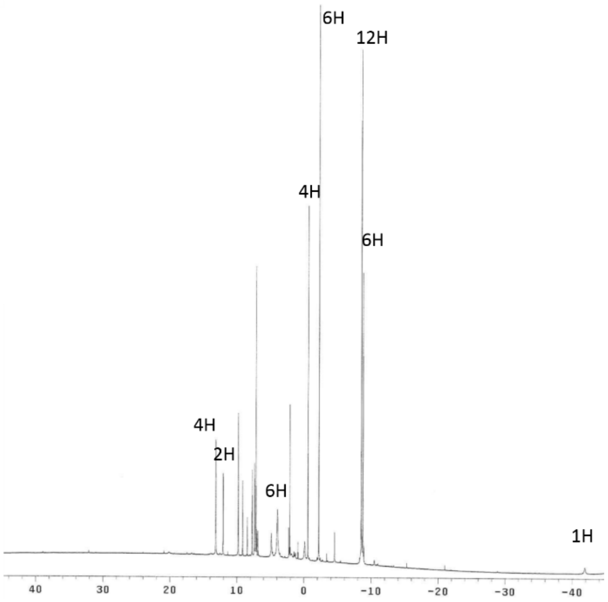

Figure S6. ^{1}H NMR spectrum of Cp^{P}U(TePh)$_2$(^{Mes}PDI^{Me}) (**4-TePh**) (C_6D_6, 23 °C) with integration values shown.

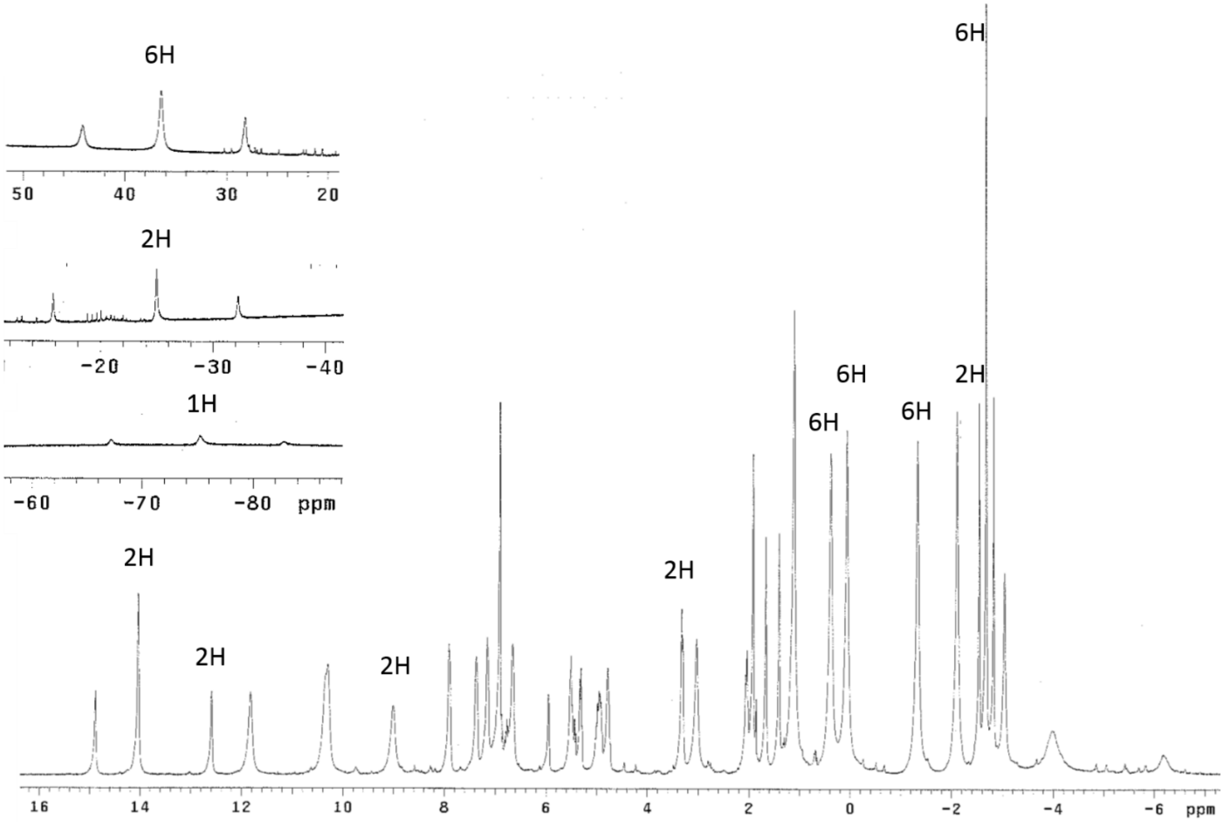

Figure S7. ^{1}H NMR spectrum of Cp^{P}U(SPh)(SePh)(^{Mes}PDI^{Me}) (**4-SPh/SePh**) obtained from crossover experiment. Upfield and downfield protons are inset to increase clarity (C$_6$D$_6$, 23 °C) with integration values shown.

Crystallographic Details

Experimental: 2-Cl_2

DATA COLLECTION

A brown plate of $C_{41}H_{46}Cl_2N_3U$, $C_4H_{10}O$ having approximate dimensions of 0.20 x 0.20 x 0.04 mm was mounted on a nylon loop 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 36296 reflections in the range 1 < θ < 28°. The monoclinic cell parameters and calculated volume are: a = 8.22010(10), b = 24.8482(5) c = 20.3997(5) Å, β = 92.7080(10)°, V = 4162.08(14) Å^3. For Z = 4 and F.W. = 963.90 the calculated density is 1.54 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[5] was 0.45° indicating good crystal quality. The space group was determined by the program XPREP.[6] From the systematic presences of:

h0l l=2n
0k0 k=2n

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

The data were collected at a temperature of 150(1) K. Data were collected to a maximum 2θ of 56.6°.

DATA REDUCTION

A total of 36296 reflections were collected, of which 10180 were unique. Frames were integrated with HKL3000.[5]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 40.7 /mm for Mo K_α radiation. An empirical absorption correction using SCALEPACK[5] was applied. Transmission coefficients ranged from 0.313 to 0.850. 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 Patterson heavy-atom method which revealed the position of the U atom. The remaining atoms were located in succeeding difference Fourier syntheses. All 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 $\Sigma w(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $w=1/[\sigma^2(Fo^2)+(0.0480P)^2]$ where $P=(Fo^2+2 Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[7] 10180 reflections were used in the refinements. However, only the 6451 reflections with $F_o^2>2\sigma(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 481 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.038$$

$$R2 = SQRT (\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2) = 0.083$$

The goodness-of-fit parameter was 0.96. The highest peak in the final difference Fourier had a height of 1.76 e/A^3. The minimum negative peak had a height of -1.59 e/A^3.

Refinement was performed on a LINUX PC using SHELX 2013.[6] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

Experimental: 3

DATA COLLECTION

An orange of $C_{47}H_{51}ClN_3SeU$, 0.5(C_3H_6O) having approximate dimensions of 0.05 x 0.05 x 0.03 mm was mounted on a nylon loop 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 of 42978 reflections in the range 2 < θ < 67°. The monoclinic cell parameters and calculated volume are: a = 42.342(2), b = 8.3362(4) c = 24.4297(12) Å, β = 101.179(4)°, V = 8459.5(7)Å^3. For Z = 8 and F.W. = 1039.43 the calculated density is 1.63 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[5] was 0.47° indicating good crystal quality. The space group was determined by the program XPREP.[6] From the systematic presences of:

hkl h+k=2n
h0l l=2n

and from subsequent least-squares refinement, the space group was determined to be C 1 2/c 1(#15).

The data were collected at a temperature of 150(1) K. Data were collected to a maximum 2θ of 135.8°.

DATA REDUCTION

A total of 42978 reflections were collected, of which 7389 were unique. Frames were integrated with HKL3000.[5]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 126.5 /mm for Cu K_α radiation. An empirical absorption correction using SCALEPACK[5] was applied. Transmission coefficients ranged from 0.378 to 0.684. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 6.4% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[10] 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 $\Sigma w(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as w=1/[σ. Scattering factors were taken from the "International Tables for Crystallography".[7] 7389 reflections were used in the refinements. However, only the 5742 reflections with $F_o^2>2\sigma(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 508 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.047$$

$$R2 = SQRT (\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2) = 0.094$$

The goodness-of-fit parameter was 1.06. The highest peak in the final difference Fourier had a height of 0.98 e/A^3. The minimum negative peak had a height of -1.38 e/A^3.

Refinement was performed on a LINUX PC using SHELX2013.[6] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

Experimental: 4-SPh

DATA COLLECTION

A red plate of $C_{53}H_{56}N_3S_2U$, $C_4H_{10}O$ having approximate dimensions of 0.20 x 0.16 x 0.05 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_α radiation (λ = 1.54184 Å) 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 51617 reflections in the range 3 < θ < 68°. The monoclinic cell parameters and calculated volume are: a = 11.8172(4), b = 19.4061(7) c = 24.4379(8) Å, β = 99.239(3)°, V = 5531.5(3)Å^3. For Z = 4 and F.W. = 1111.34 the calculated density is 1.33 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[5] was 0.74° indicating moderate crystal quality. The space group was determined by the program XPREP.[6] 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 2θ of 137.0°.

DATA REDUCTION

A total of 51617 reflections were collected, of which 9730 were unique. Frames were integrated with DENZO-SMN.[5]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 92.5/mm for Cu K_α radiation. An empirical absorption correction using SCALEPACK[5] was applied. Transmission coefficients ranged from 0.472 to 0.630. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 9.4% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[10] 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 $\Sigma w(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[\sigma^2(Fo^2)+(0.1458P)^2+5.7493P]$ where $P=(Fo^2 +2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[7] 9730 reflections were used in the refinements. However, only the 8699 reflections with $F_o^2>2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 588 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma\ |Fo - Fc|\ /\ \Sigma\ Fo = 0.065$$

$$R2 = SQRT\ (\ \Sigma\ w\ (\ Fo^2 - Fc^2\ )^2\ /\ \Sigma\ w\ (Fo^2)^2\ ) = 0.186$$

The goodness-of-fit parameter was 1.10. The highest peak in the final difference Fourier had a height of 4.14 e/A^3. The minimum negative peak had a height of -1.76 e/A^3. Residual electron density was adjusted using the SQUEEZE option in PLATON.[9]

Refinement was performed on a LINUX PC using SHELX-97.[6] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

Experimental: 4-SePh

DATA COLLECTION

An orange needle of $C_{53}H_{56}N_3Se_2U$, $2(C_4H_8O)$ having approximate dimensions of 0.50 x 0.31 x 0.17 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Mo K_α radiation (λ = 0.71073Å) 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 49413 reflections in the range $1 < \theta < 27°$. The monoclinic cell parameters and calculated volume are: a = 11.7186(2), b = 26.9121(4) c = 17.5708(3) Å, β = 100.6420(10)°, V = 5446.03(15)$Å^3$. For Z = 4 and F.W. = 1275.22 the calculated density is 1.56 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[5] was 0.73° indicating moderate crystal quality. The space group was determined by the program XPREP.[6] 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 2θ of 55.7°.

DATA REDUCTION

A total of 49413 reflections were collected, of which 12859 were unique. Frames were integrated with DENZO-SMN.[5]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 43.6/mm for Mo K_α radiation. An empirical absorption correction using SCALEPACK[5] was applied. Transmission coefficients ranged from 0.413 to 0.466. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 6.3% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[10] The remaining atoms were located in succeeding difference Fourier syntheses. All 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 $\Sigma w(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[\sigma^2(Fo^2)+(0.0265P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[7] 12859 reflections were used in the refinements. However, only the 8039 reflections with $F_o^2>2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 632 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma\ |Fo - Fc|\ /\ \Sigma\ Fo = 0.037$$

$$R2 = SQRT\ (\ \Sigma\ w\ (\ Fo^2 - Fc^2\ )^2\ /\ \Sigma\ w\ (Fo^2)^2\ ) = 0.064$$

The goodness-of-fit parameter was 0.92. The highest peak in the final difference Fourier had a height of 1.07 e/A^3. The minimum negative peak had a height of -1.16 e/A^3.

Refinement was performed on a LINUX PC using SHELX-97.[6] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

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(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, pp 1518.

(2) Kiernicki, J. J.; Newell, B. S.; Matson, E. M.; Anderson, N. H.; Fanwick, P. E.; Shores, M. P.; Bart, S. C. *Inorg. Chem.* **2014**, *53*, pp 3730-3741.

(3) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *Inorg. Chem.* **2009**, *48*, pp 2693–2700.

(4) Tao, J.; Tran, R.; Murphy, G. K. *J. Am. Chem. Soc.* **2013**, *135*, pp 16312-16315.

(5) Z. Otwinowski and W. Minor, Methods Enzymol., 276, 307 (1997).

(6) Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, pp 112.

(7) "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, (1992), Tables 4.2.6.8 and 6.1.1.4.

(8) C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).

(9) Spek, A. L. *J. Appl. Cryst* **2003**, *36*, pp 7.

(10) Beurskens, P. T.; Beurskens, G.; deGelder, R.; Garcia-Granda; Gould, R. O.; Smits, J. M. M. The DIRDIF2008 Program System. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands, (2008).