Supporting Information for:

# Multi-electron C-O Bond Activation Mediated by A Family of Reduced Uranium Complexes

*John J. Kiernicki,[1] Brian S. Newell,[2] Ellen M. Matson,[1] Nickolas H. Anderson,[1] Phillip E. Fanwick,[1] Matthew P. Shores,[2] Suzanne C. Bart[1]**

[1] H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47906

[2] Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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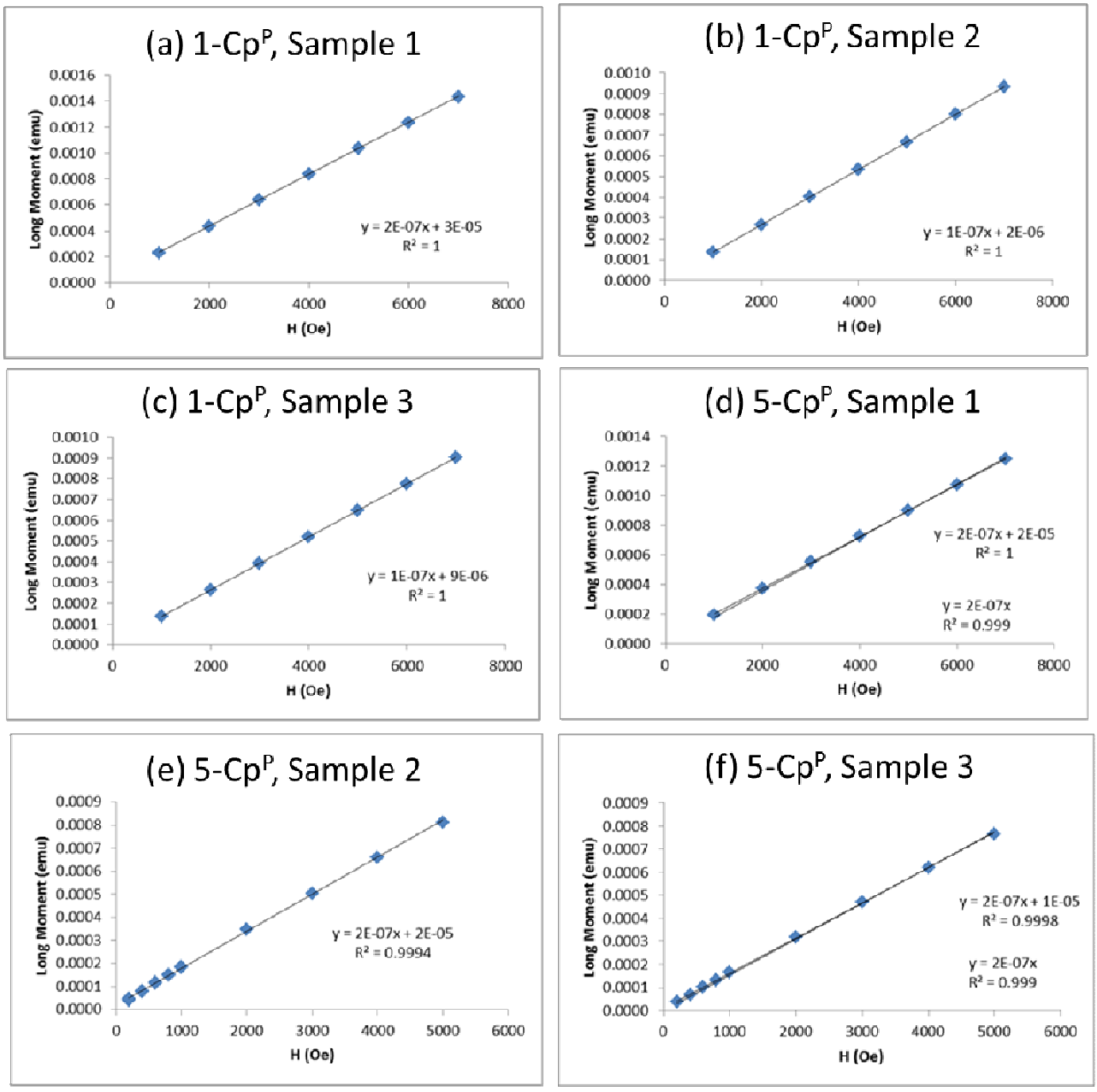


Figure S1. Tests for ferromagnetic impurities carried out at 100 K on independently synthesized samples of **1-Cp$^P$** (a-c) and **5-Cp$^P$** (d-f). Note: in (d) and (f) the second linear fit equation (without y-axis intercept) was forced to zero.

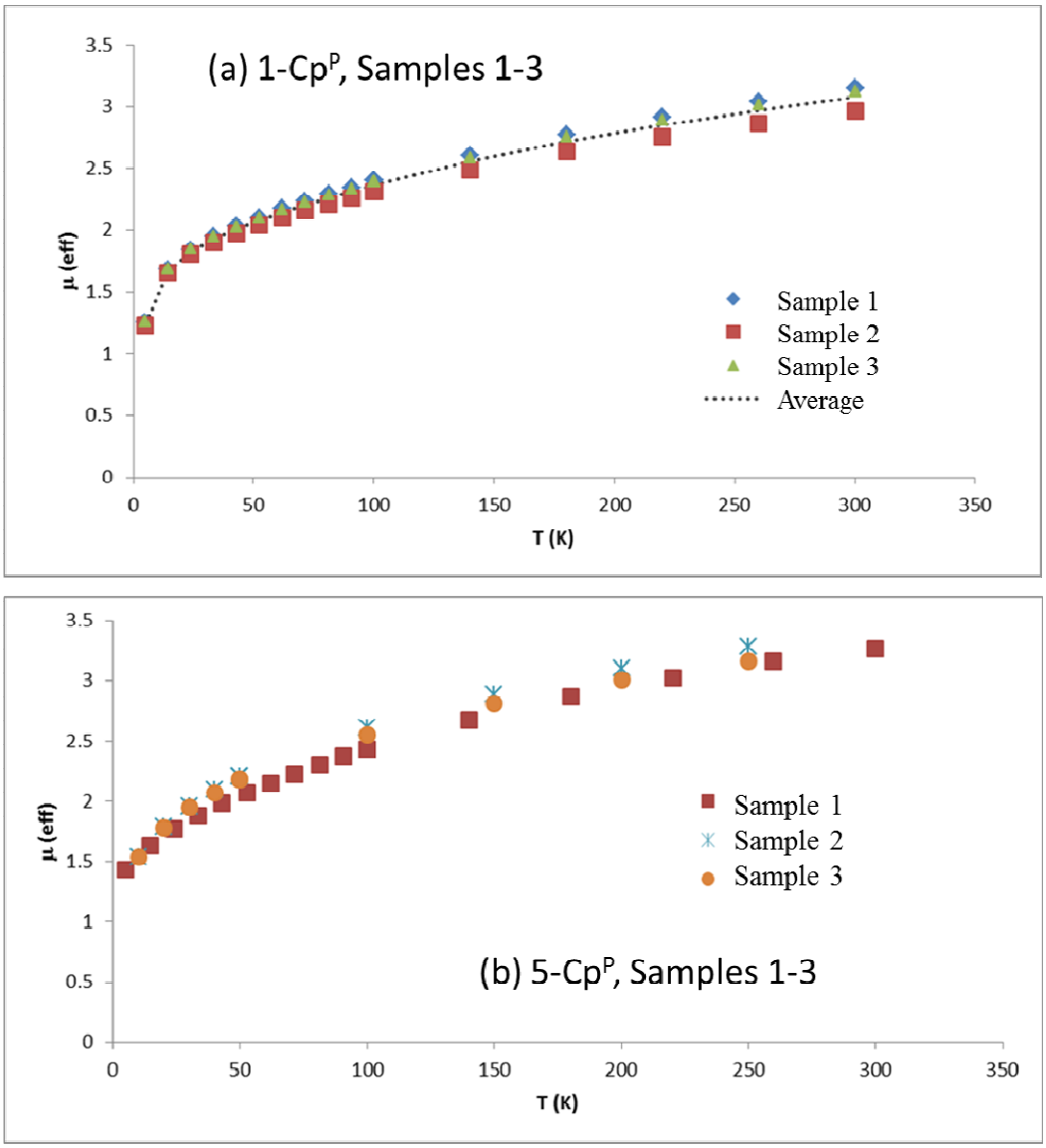


Figure S2. Sample-by-sample variability of effective magnetic moment (versus temperature) for **1-Cp$^P$** (a) and **5-Cp$^P$** (b). Susceptibility data were collected at 1000 Oe measuring field.

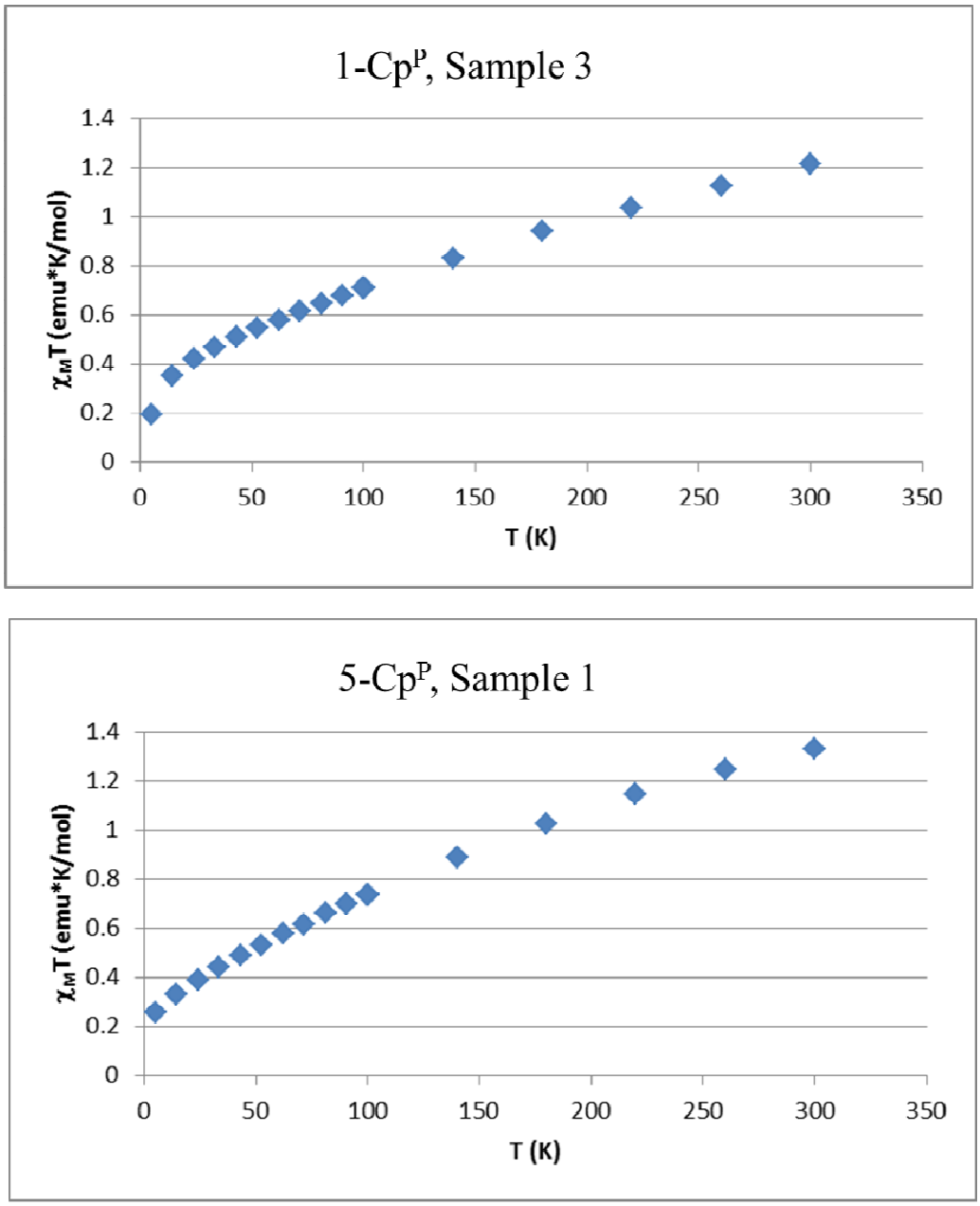





Figure S3. Variable temperature magnetic susceptibility data for **1-Cp$^P$** (top) and **5-Cp$^P$** (bottom) plotted in cgs units.

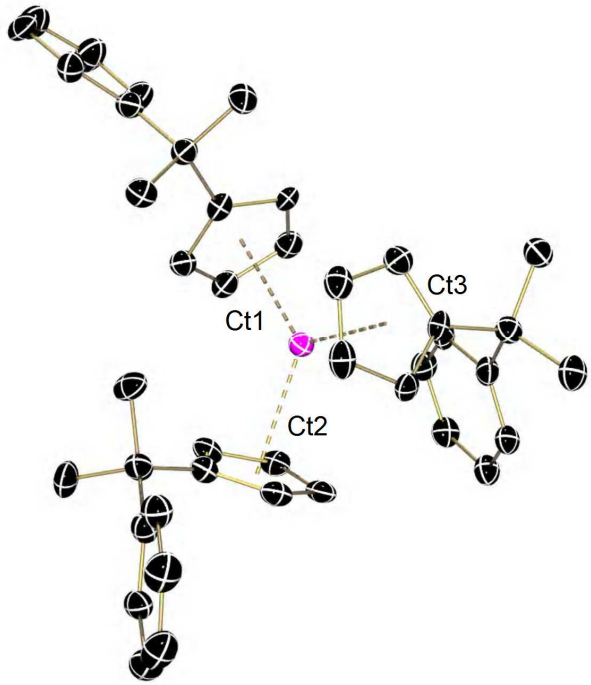


Figure S4 Molecular structure of $\mathbf{Cp^{P}_{3}U}$ shown with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances: U1-Ct1: 2.568; U1-Ct2: 2.528; U1-Ct3: 2.527 Å.

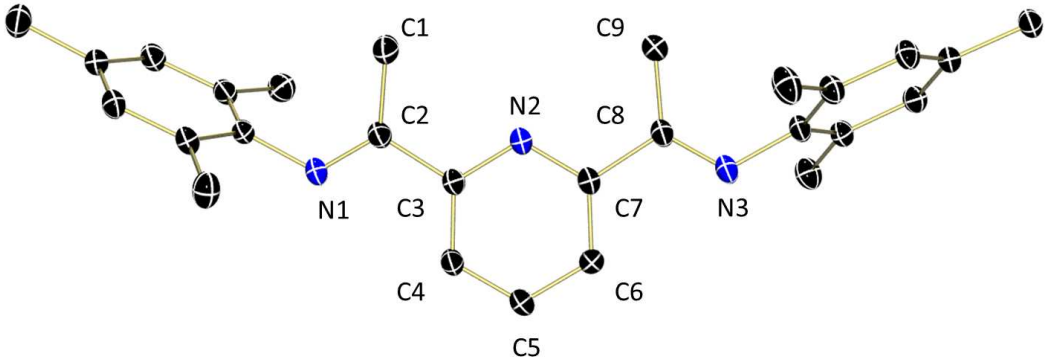


Figure S5 Molecular structure of $^{Mes}PDI^{Me}$ shown with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Single, X-ray quality crystals were obtained from a saturated n-pentane solution at -35 °C.

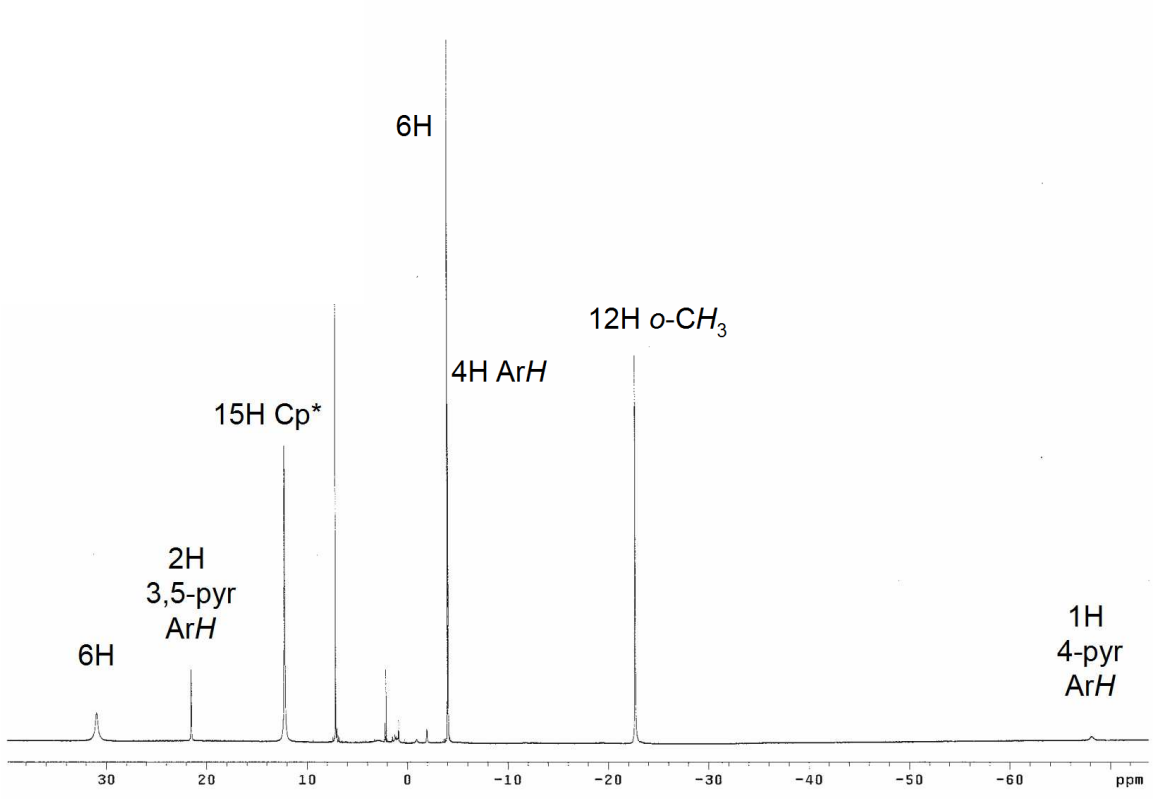


Figure S6 $^{1}$H NMR spectrum (23 °C) of Cp*UI$_2$($^{Mes}$PDI$^{Me}$) in $C_6D_6$

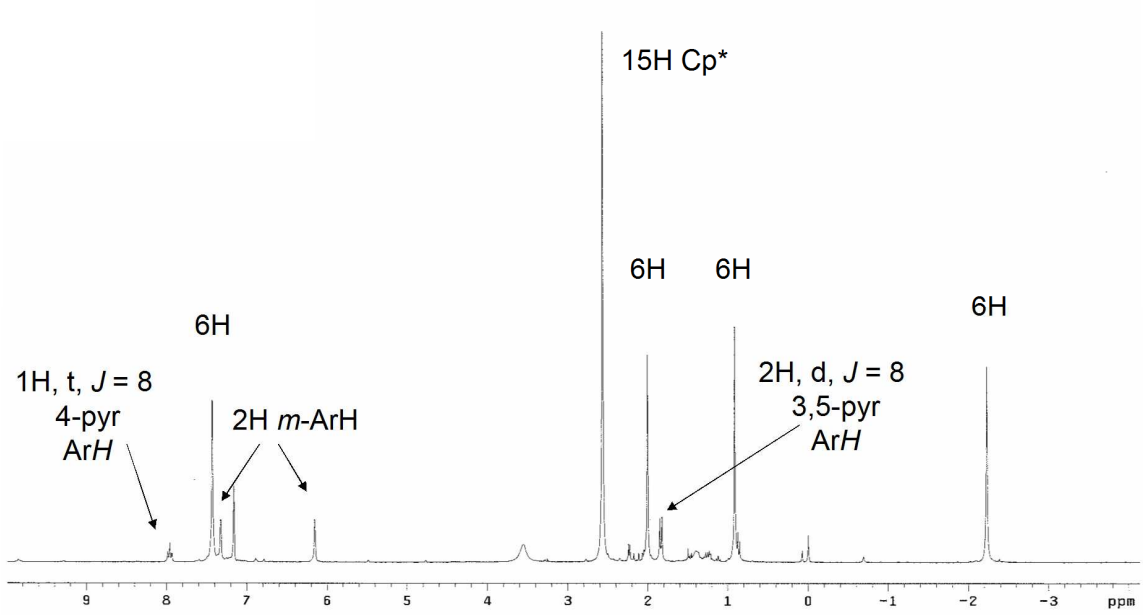


Figure S7 $^{1}$H NMR spectrum (23 °C) of Cp*UI($^{Mes}$PDI$^{Me}$) in $C_6D_6$

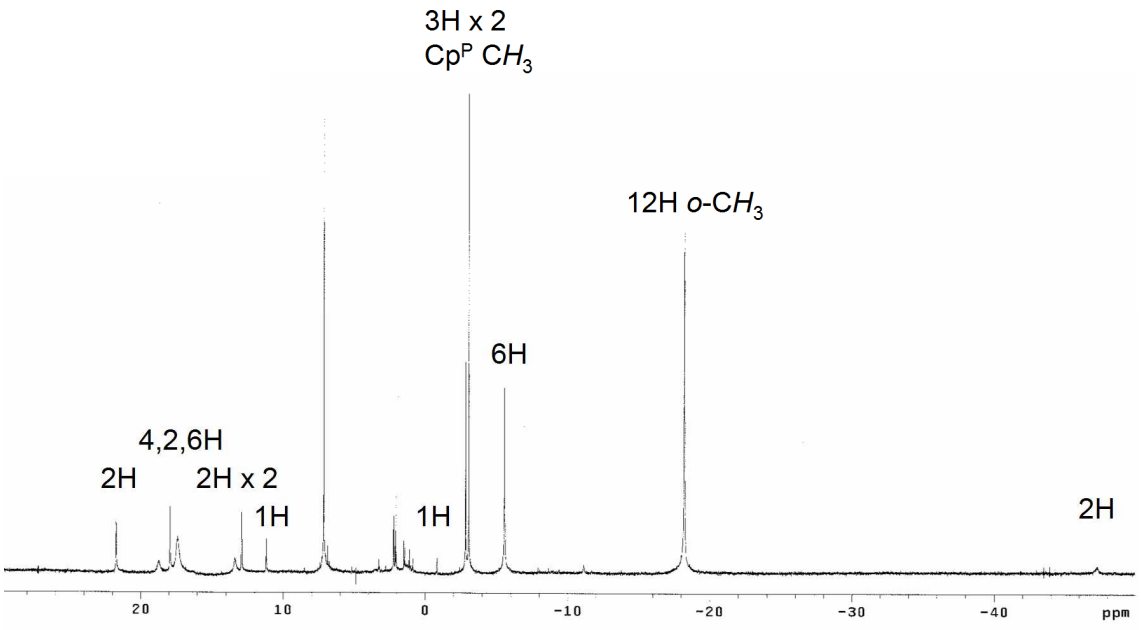


Figure S8 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}UI_2(^{Mes}PDI^{Me})$ in $C_6D_6$

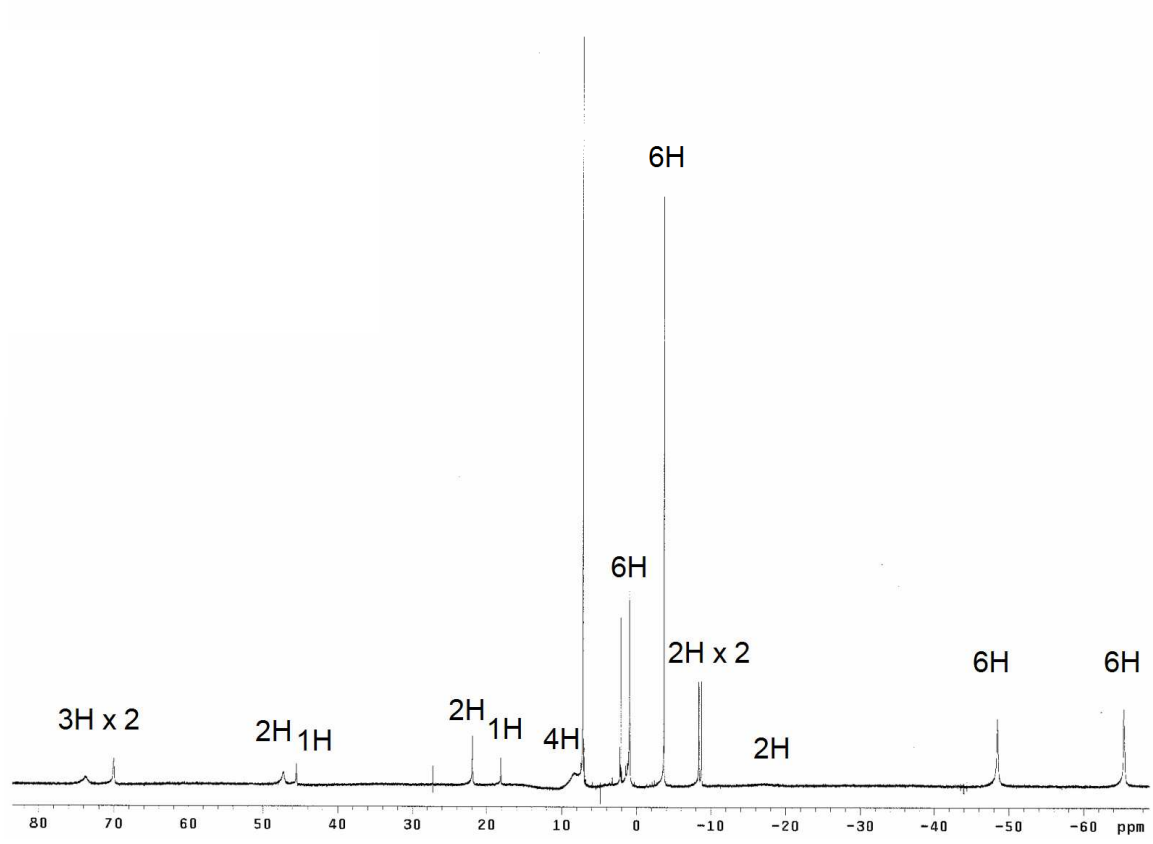


Figure S9 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}UI(^{Mes}PDI^{Me})$ in $C_6D_6$

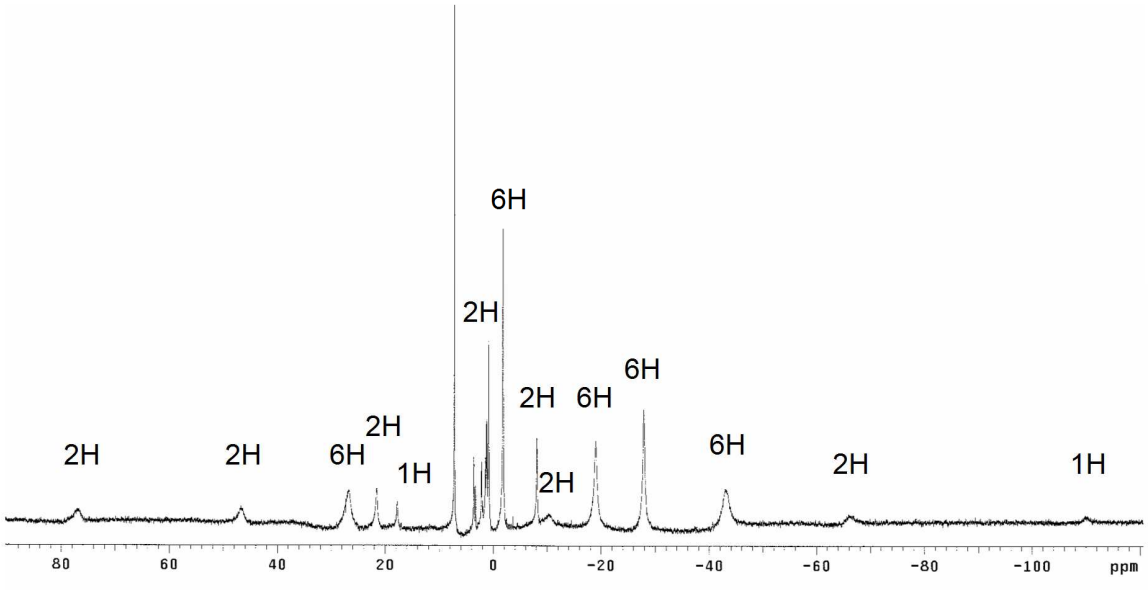


Figure S10 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}U(^{Mes}PDI^{Me})$ in $C_6D_6$

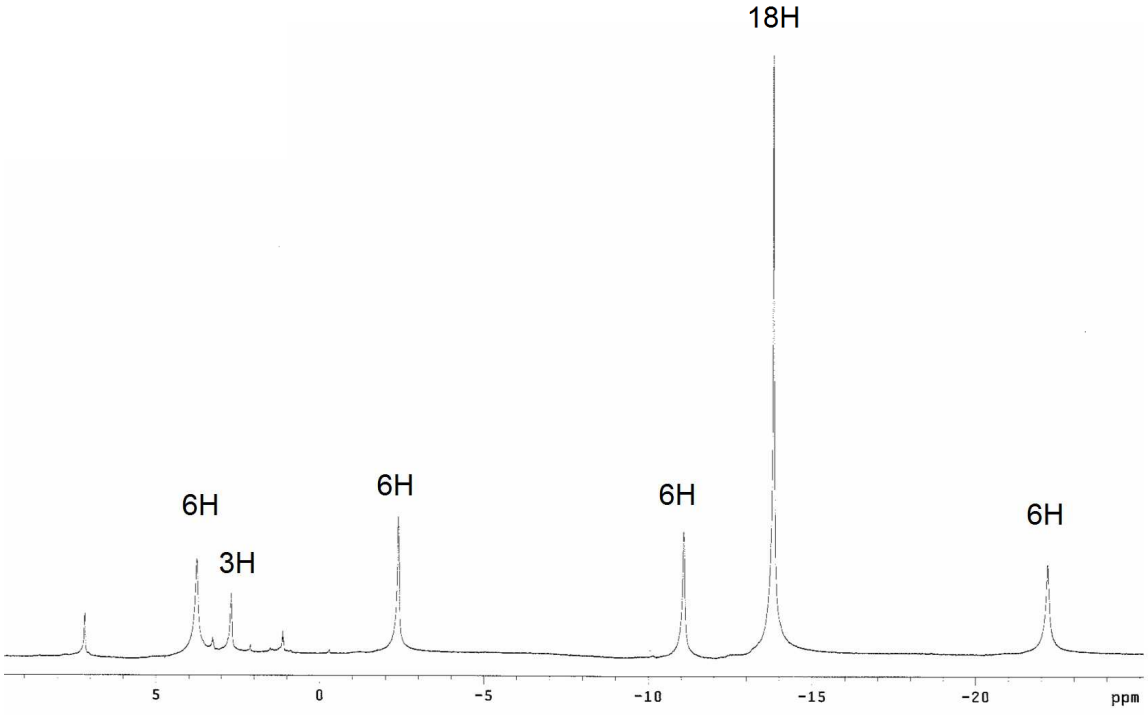


Figure S11 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}{}_{3}U$ in $C_6D_6$

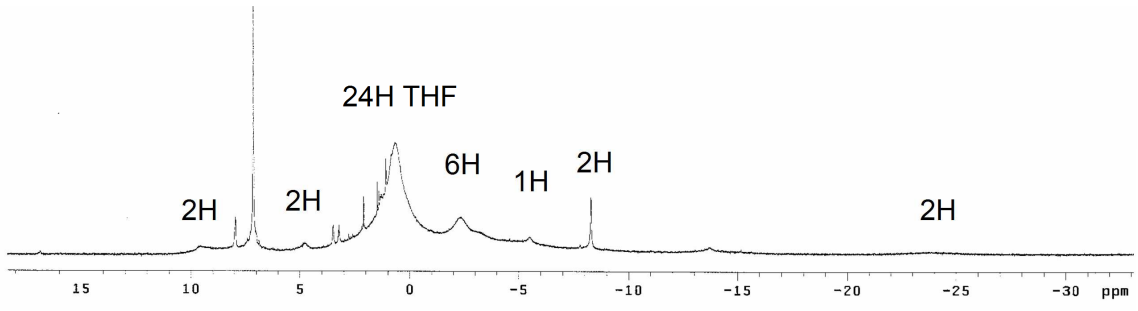


Figure S12 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}UI_2(THF)_3$ in $C_6D_6$

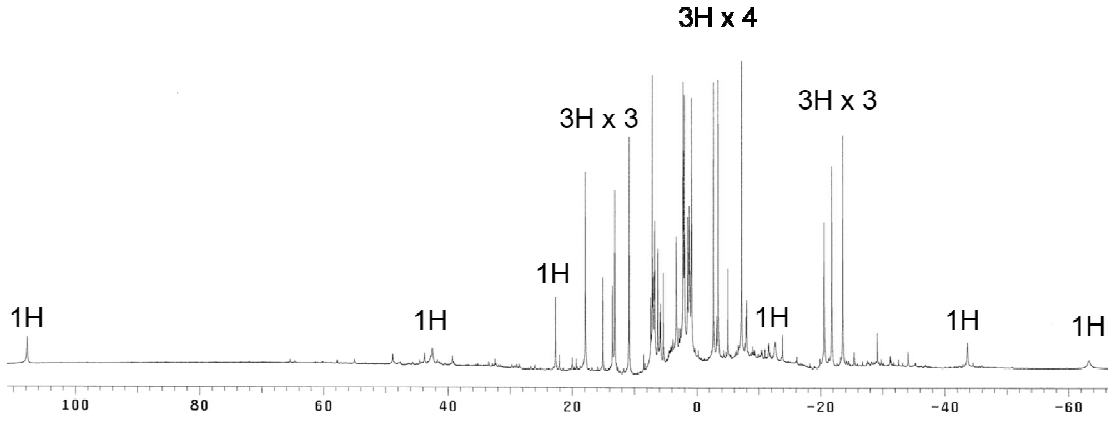


Figure S13 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}UI(Furf)(^{Mes}PDI^{Me})$ in $C_6D_6$

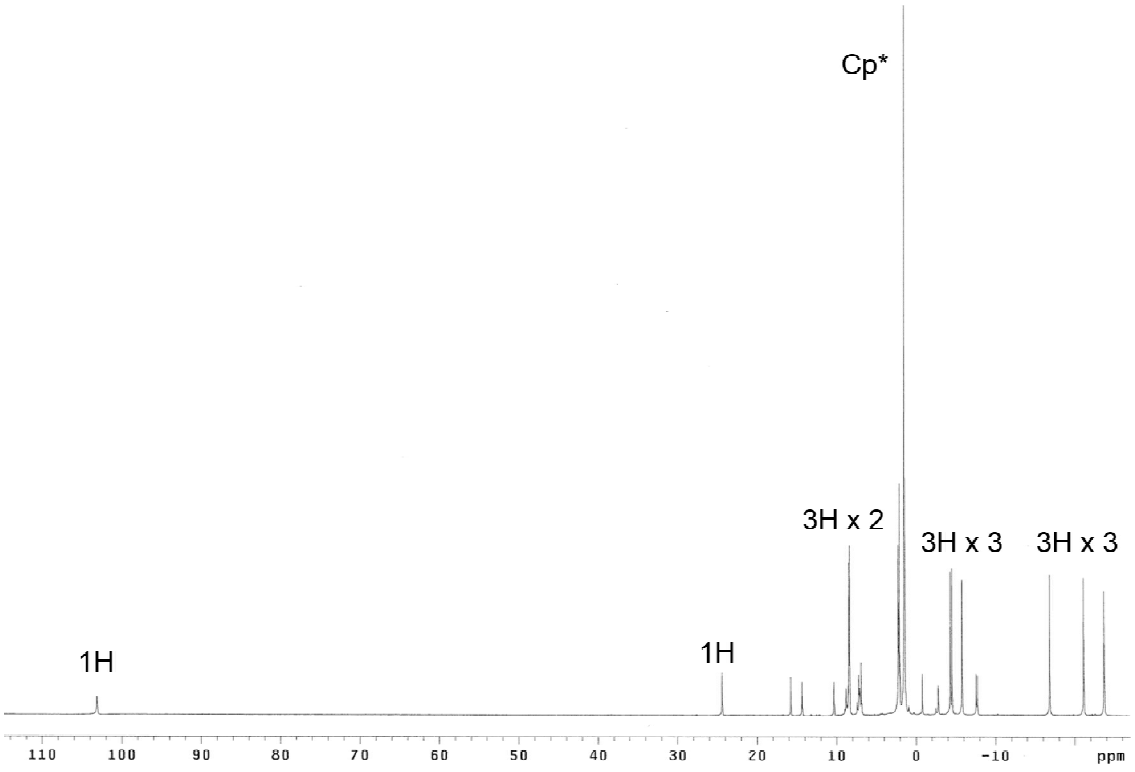


Figure S14 $^{1}$H NMR spectrum (23 °C) of Cp*UI(Furf)($^{Mes}$PDI$^{Me}$) in $C_6D_6$

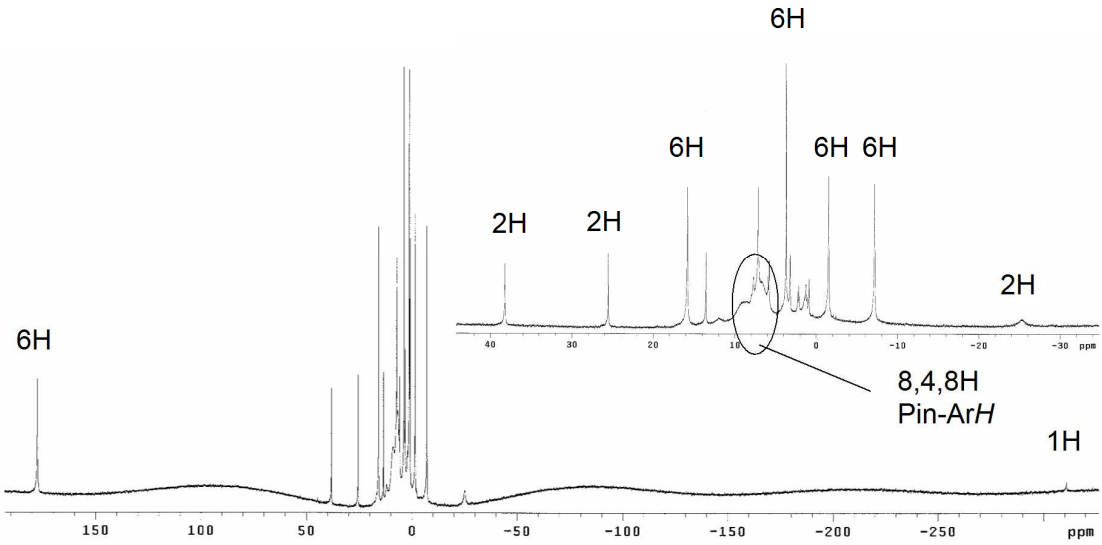


Figure S15 $^{1}$H NMR spectrum (23 °C) of Cp$^{P}$U($O_2C_2Ph_4$)($^{Mes}$PDI$^{Me}$) in $C_6D_6$

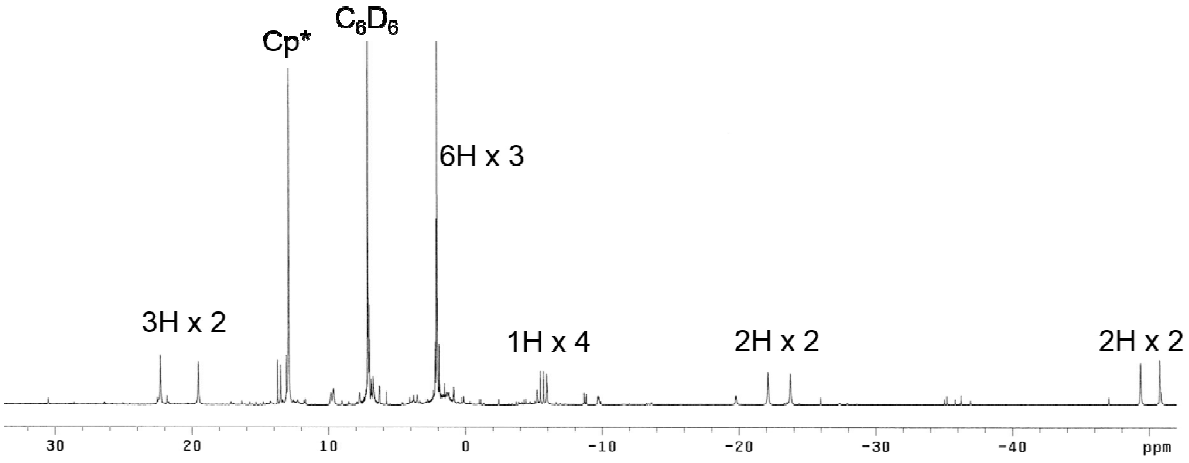


Figure S16 $^{1}$H NMR spectrum (23 °C) of $Cp^{P}U(O_2C_2Ph_2H_2)(^{Mes}PDI^{Me})$ in $C_6D_6$

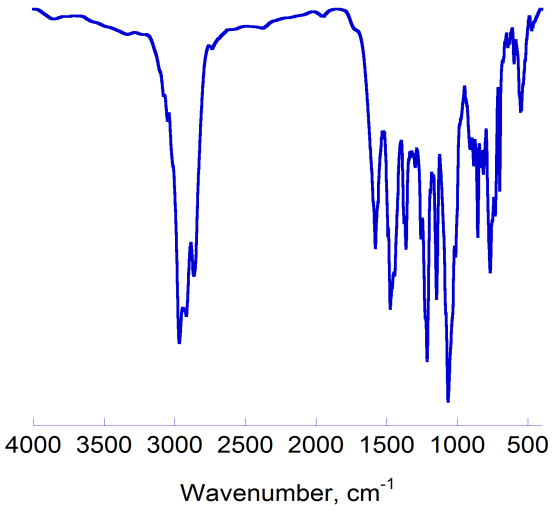


Figure S17 IR spectrum (Film) of $Cp^{P}UI(Furf)(^{Mes}PDI^{Me})$

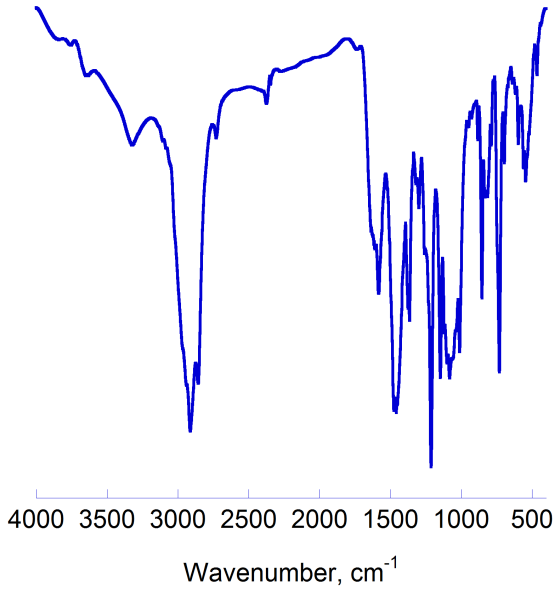


Figure S18 IR spectrum (Film) of Cp*UI(Furf)($^{Mes}$PDI$^{Me}$)

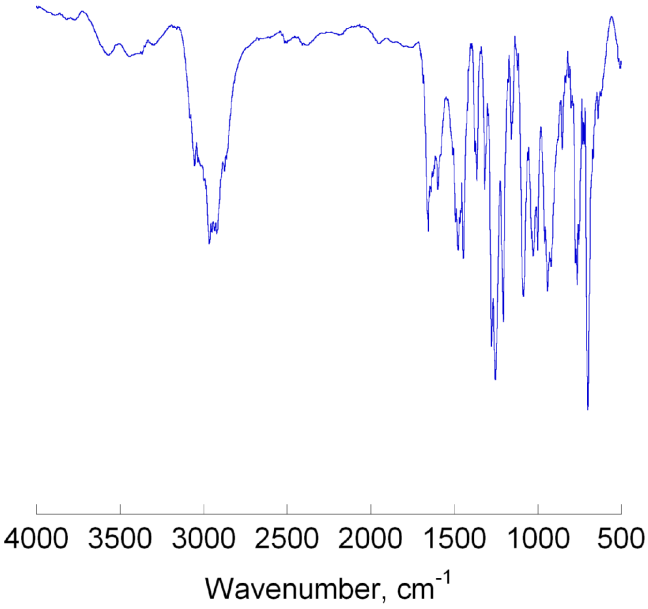


Figure S19 IR spectrum (KBr Pellet) of Cp$^{P}$U($O_2C_2Ph_4$)($^{Mes}$PDI$^{Me}$)

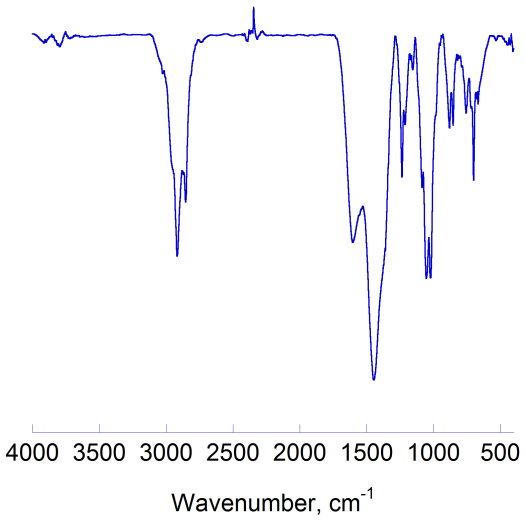


Figure S20 IR spectrum (Film) of Cp*U($O_2C_2Ph_2H_2$)($^{Mes}$PDI$^{Me}$)

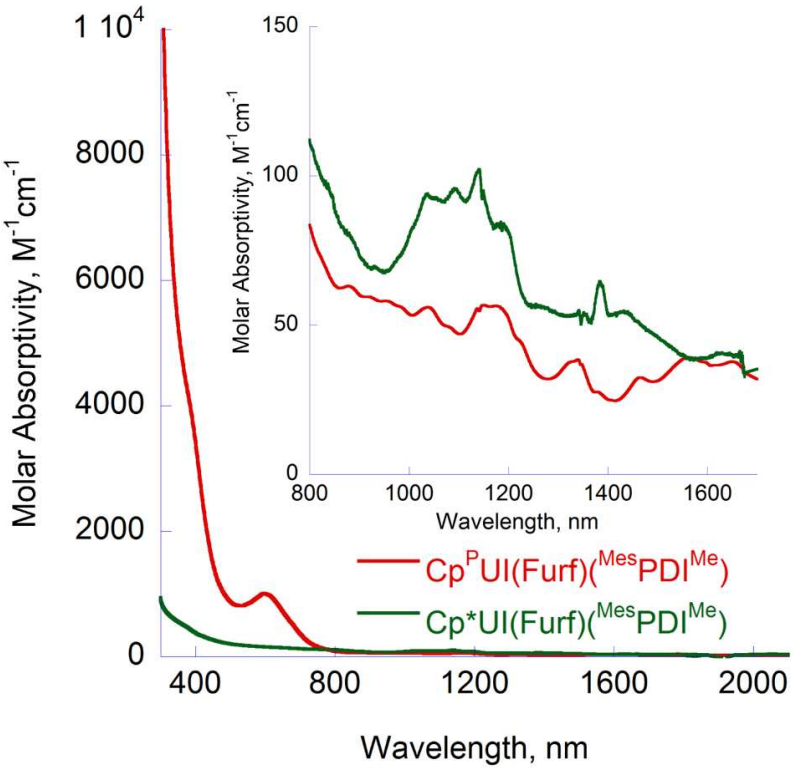


Figure S21 Electronic Absorption Spectrum of **4-Cp$^P$** (red) and **5-Cp$^P$** (green) recorded from 300-2100 nm in tetrahydrofuran at room temperature. Solvent overtones between 1650 and 1800 nm have been removed for clarity.

## Crystallographic Details

## Experimental: $^{Mes}$PDI$^{Me}$

DATA COLLECTION

A yellow needle of $C_{27}H_{31}N_3$ having approximate dimensions of 0.25 x 0.10 x 0.10 mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed Cu $K_\alpha$ radiation ($\lambda$ = 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 24853 reflections in the range $4 < \theta < 66°$. The triclinic cell parameters and calculated volume are: a = 8.2054(2), b = 11.4190(2), c = 13.0767(9) Å, $\alpha$ = 79.305(6), $\beta$ =77.099(5), $\gamma$ = 76.629(5)°, V = 1150.30(9)Å$^3$. For Z = 2 and F.W. = 397.57 the calculated density is 1.15 g/cm$^3$. The refined mosaicity from CrystalClear[1] was 0.87° indicating moderate crystal quality. The space group was determined by the program XPREP.[2] 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 2$\theta$ of 133.2°.

DATA REDUCTION

A total of 24853 reflections were collected, of which 4023 were unique. Frames were integrated using program CrystalClear.[1]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 5.2 /mm for Cu $K_\alpha$ radiation. An empirical absorption correction using CrystalClear[1] was applied. Transmission coefficients ranged from 0.862 to 0.950. A secondary extinction correction was applied (ref 2). The final coefficient, refined in least-squares, was 0.0094000 (in absolute units). Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 5.3% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXT.[4] 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/[$\sigma$. Scattering factors were taken from the "International Tables for Crystallography".[5] 4023 reflections were used in the refinements. However, only the 2835 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 280 variable parameters and converged (largest parameter shift was 0.06 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.046$$

$$R2 = SQRT ( \Sigma w ( Fo^2 - Fc^2 )^2 / \Sigma w (Fo^2)^2 ) = 0.119$$

The goodness-of-fit parameter was 1.18. The highest peak in the final difference Fourier had a height of 0.25 e/A$^3$. The minimum negative peak had a height of -0.25 e/A$^3$.

Refinement was performed on a LINUX PC using SHELX2013.[2] Crystallographic drawings were done using programs ORTEP,[8] and PLUTON.[9]

## Experimental: Cp$^P$UI$_2$($^{Mes}$PDI$^{Me}$)

DATA COLLECTION

An orange needle of $C_{41}H_{46}I_2N_3U$ having approximate dimensions of 0.20 x 0.06 x 0.05

mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu $K_a$ radiation (l = 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 36985 reflections in the range $3 < q < 66°$. The monoclinic cell parameters and calculated volume are: a = 8.4353(7), b = 23.8206(18) c = 20.8500(15) Å, b = 94.155(6)°, V = 4178.5(6) $Å^3$. For Z = 4 and F.W. = 1072.68 the calculated density is 1.71 $g/cm^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.83° indicating moderate crystal quality. The space group was determined by the program XPREP[2]. 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 2q of 133.7°.

DATA REDUCTION

A total of 36985 reflections were collected, of which 6114 were unique. Frames were integrated with DENZO-SMN[1]. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 227.5 /mm for Cu $K_a$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.049 to 0.321. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 9.1% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99[3]. 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 $1/[s^2(Fo^2)+(0.1409P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 6114 reflections were used in the refinements. However, only the 4730 reflections with $F_o^2>2s(F_o^2)$ were used in calculating R1. The final cycle of refinement included 434 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\ |Fo - Fc| / S\ Fo = 0.067$$

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2 / S\ w\ (Fo^2)^2\ ) = 0.184$$

The goodness-of-fit parameter was 1.05. The highest peak in the final difference Fourier had a height of 2.46 $e/A^3$. The minimum negative peak had a height of -0.87 $e/A^3$.

Residual electron density was adjusted using the SQUEEZE option in PLATON[5]. Refinement was performed on a LINUX PC using SHELX-97[2]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental: $Cp^{P}UI(^{Mes}PDI^{Me})$**

DATA COLLECTION

A brown plate of $C_{41}H_{46}IN_3U$, $2(C_7H_8)$ having approximate dimensions of 0.66 x 0.45 x 0.36 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Mo $K_a$ radiation (l = 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 24061 reflections in the range $1 < q < 27°$. The triclinic cell parameters and calculated volume are: a = 11.6038(6), b = 14.5150(5), c = 15.5767(7) Å, a = 75.149(3), b =77.997(2), g = 73.826(3)°, V = 2409.06(18) $Å^3$. For Z = 2 and F.W. = 130.06 the calculated density is 1.56 $g/cm^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.67° indicating moderate crystal quality. The space group was determined by the program XPREP[2]. 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 55.6°.

DATA REDUCTION

A total of 24061 reflections were collected, of which 10954 were unique. Frames were integrated with DENZO-SMN[1]. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 40.5 /mm for Mo $K_a$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.193 to 0.233. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 2.9% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99[3]. 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 $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.0240P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 10954 reflections were used in the refinements. However, only the 8998 reflections with $F_o^2 > 2s(F_o^2)$ were used in calculating R1. The final cycle of refinement included 553 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\,|Fo - Fc| / S\,Fo = 0.030$$

$$R2 = SQRT\left( S\,w\,( Fo^2 - Fc^2 )^2 / S\,w\,(Fo^2)^2 \right) = 0.059$$

The goodness-of-fit parameter was 0.99. The highest peak in the final difference Fourier had a height of 1.10 e/$A^3$. The minimum negative peak had a height of -1.07 e/$A^3$. Refinement was performed on a LINUX PC using SHELX-97[2]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental: $Cp^{P}U(O_2C_2Ph_4)(^{Mes}PDI^{Me})$**

DATA COLLECTION

A brown plate of $C_{67}H_{66}N_3O_2U$, $C_4H_8O$ having approximate dimensions of 0.20 x 0.15 x 0.08 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu $K_a$ radiation (l = 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 55030 reflections in the range 2 < q < 72°. The triclinic cell parameters and calculated volume are: a = 12.5568(5), b = 13.1001(4), c = 18.1409(6) Å, a = 78.949(2), b =88.801(3), g = 84.910(3)°, V = 2917.19(18) $Å^3$. For Z = 2 and F.W. = 1255.43 the calculated density is 1.43 g/$cm^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.49° indicating good crystal quality. The space group was determined by the program XPREP[2]. 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 145.4°.

DATA REDUCTION

A total of 55030 reflections were collected, of which 10826 were unique. Frames were integrated with DENZO-SMN[1]. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 82.2 /mm for Cu $K_a$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.448 to 0.518. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 6.9% 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. 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 $1/[s^2(Fo^2)+(0.0699P)^2+5.7064P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 10826 reflections were used in the refinements. However, only the 10610 reflections with $F_o^2>2s(F_o^2)$ were used in calculating R1. The final cycle of refinement included 713 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\ |Fo - Fc| / S\ Fo = 0.039$$

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2 / S\ w\ (Fo^2)^2\ ) = 0.103$$

The goodness-of-fit parameter was 1.05. The highest peak in the final difference Fourier had a height of 2.29 e/$A^3$. The minimum negative peak had a height of -1.14 e/$A^3$. Refinement was performed on a LINUX PC using SHELX-97[2]. Crystallographic drawings were done using programs ORTEP[8] and PLUTON[9].

**Experimental: $Cp^P_3U$**

DATA COLLECTION

A yellow plate of $C_{42}H_{45}U$ having approximate dimensions of 0.20 x 0.14 x 0.02 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu $K_a$ radiation (l = 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 14825 reflections in the range $3 < q < 66°$. The monoclinic cell parameters and calculated volume are: a = 33.2510(16), b = 8.3849(4) c = 27.5427(11) Å, b = 114.731(3)°, V = 6974.8(5)Å$^3$. For Z = 8 and F.W. = 787.86 the calculated density is 1.50 g/cm$^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.77° indicating moderate crystal quality. The space group was determined by the program XPREP[2]. 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 260(1) K. Data were collected to a maximum 2q of 133.5°.

DATA REDUCTION

A total of 14825 reflections were collected, of which 5451 were unique. Frames were integrated with DENZO-SMN[1]. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 132.8 /mm for Cu $K_a$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.612 to 0.767. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 8.5% 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. 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 $1/[s^2(Fo^2)+(0.1328P)^2+70.4248P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 5451 reflections were used in the refinements. However, only the 4733 reflections with $F_o^2>2s(F_o^2)$ were used in calculating R1. The final cycle of refinement included 394 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted

agreement factors of:

$$R1 = S |Fo - Fc| / S Fo = 0.066$$

$$R2 = SQRT ( S w ( Fo^2 - Fc^2 )^2 / S w (Fo^2)^2 ) = 0.179$$

The goodness-of-fit parameter was 1.05. The highest peak in the final difference Fourier had a height of 4.40 e/A$^3$. The minimum negative peak had a height of -1.83 e/A$^3$. Residual electron density was adjusted using the SQUEEZE option in PLATON[5]. Refinement was performed on a LINUX PC using SHELX-97[2]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental: $Cp^PUI_2(THF)_3$**

DATA COLLECTION

A blue needle of $C_{26}H_{39}I_2O_3U$ having approximate dimensions of 0.20 x 0.12 x 0.06 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu $K_a$ radiation (l = 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 13343 reflections in the range 3 < q < 72°. The orthorombic cell parameters and calculated volume are: a = 22.2642(12), b = 24.4304(10), c = 12.2650(6)Å, V = 6671.2(6)Å$^3$. For Z = 8 and F.W. = 891.44 and the calculated density is 1.77 g/cm$^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.69° indicating moderate crystal quality. The space group was determined by the program XPREP[2]. From the systematic presences of:

hkl h+k+l=2n

h0l h=2n

0kl k=2n

and from subsequent least-squares refinement, the space group was determined to be I b a 2(# 45). The data were collected at a temperature of 150(1) K. Data were collected to a maximum 2q of 144.6°.

DATA REDUCTION

A total of 13343 reflections were collected, of which 4664 were unique. Frames were integrated with DENZO-SMN (ref 1). Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 283.8 /mm for Cu $K_a$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.182 to 0.182. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 10.6% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99[3]. 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 $1/[s^2(Fo^2)+(0.1217P)^2+46.1951P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 4664 reflections were used in the refinements. However, only the 4425 reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 291 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

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

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2 / S\ w\ (Fo^2)^2\ ) = 0.192$$

The goodness-of-fit parameter was 1.15. The highest peak in the final difference Fourier had a height of 1.97 e/A$^3$. The minimum negative peak had a height of -2.41 e/A$^3$. Residual electron density was adjusted using the SQUEEZE option in PLATON[5]. The factor for the determination of the absolute structure[6] refined to 0.02. Refinement was performed on a LINUX PC using SHELX-97[2]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental Cp*U($O_2C_2Ph_2H_2$)($^{Mes}$PDI$^{Me}$):**

DATA COLLECTION

A green plate of $C_{51}H_{58}N_3O_2U$ having approximate dimensions of 0.10 x 0.10 x 0.06 mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed Cu $K_\alpha$ radiation ($\lambda$ = 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 37135 reflections in the range $2 < \theta < 72°$. The monoclinic cell parameters and calculated volume are: a = 11.5323(3), b = 12.9693(3) c = 29.1811(6) Å, $\beta$ = 94.776(2)°, V = 4349.34(18)Å$^3$. For Z = 4 and F.W. = 983.08 the calculated density is 1.50 g/cm$^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.25° indicating good crystal quality. The space group was determined by the program XPREP[2]. 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 200(1) K. Data were collected to a maximum $2\theta$ of 144.5°.

DATA REDUCTION

A total of 37135 reflections were collected, of which 8221 were unique. Frames were

integrated with HKL3000[1].

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 108.3 /mm for Cu $K_\alpha$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.189 to 0.522. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 5.0% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXT[3]. 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"[4]. 8221 reflections were used in the refinements. However, only the 7617 reflections with $F_o^2>2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 527 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.032$$

$$R2 = SQRT ( \Sigma w ( Fo^2 - Fc^2 )^2 / \Sigma w (Fo^2)^2 ) = 0.086$$

The goodness-of-fit parameter was 1.06. The highest peak in the final difference Fourier had a height of 0.81 e/$A^3$. The minimum negative peak had a height of -1.19 e/$A^3$.

Refinement was performed on a LINUX PC using SHELX 2013[7]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental Cp*UI($^{Mes}$PDI$^{Me}$)**

DATA COLLECTION

A brown needle of $C_{37}H_{46}IN_3U$ having approximate dimensions of 0.50 x 0.20 x 0.08 mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed Mo $K_\alpha$ 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 21292 reflections in the range 1 < θ < 29°. The orthorombic cell parameters and calculated volume are: a = 26.9579(7), b = 12.3690(3), c = 11.8789(2) Å, V = 3960.93(16)Å$^3$. For Z = 4 and F.W. = 897.73 the calculated density is 1.51 g/cm$^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 0.56° indicating moderate crystal quality. The space group was determined by the program ABSEN[2]. From the systematic presences of:

h0l h=2n

0kl k+l=2n

and from subsequent least-squares refinement, the space group was determined to be P n a 21(# 33).

The data were collected at a temperature of 200(1) K. Data were collected to a maximum 2θ of 58.0°.

DATA REDUCTION

A total of 21292 reflections were collected, of which 7807 were unique. Frames were integrated with HKL3000[1].

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 49.0 /mm for Mo $K_\alpha$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.069 to 0.676. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 7.7% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXT[3]. 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 $w=1/[\sigma^2(Fo^2)+(0.0055P)^2]$ where $P=(Fo^2+2\,Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 7807 reflections were used in the refinements. However, only the 4886 reflections with $F_o^2>2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 392 variable parameters and converged (largest parameter shift was 0.07 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma\,|Fo - Fc| / \Sigma\,Fo = 0.040$$
$$R2 = SQRT\,(\,\Sigma\,w\,(\,Fo^2 - Fc^2\,)^2 / \Sigma\,w\,(Fo^2)^2\,) = 0.061$$

The goodness-of-fit parameter was 1.01. The highest peak in the final difference Fourier had a height of 1.60 e/$A^3$. The minimum negative peak had a height of -1.84 e/$A^3$. Residual electron density was adjusted using the SQUEEZE option in PLATON[5]. The factor for the determination of the absolute structure[6] refined to 0.08.

Refinement was performed on a LINUX PC using SHELX 2013[7]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

**Experimental Cp*UI(Furf)($^{Mes}$PDI$^{Me}$)**

DATA COLLECTION

A green plate of $C_{58.5}H_{68.5}IN_3O_2U$ having approximate dimensions of 0.70 x 0.60 x 0.50

mm was mounted on a nylon loop in a random orientation. Preliminary examination and data collection were performed Cu $K_\alpha$ radiation ($\lambda$ = 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 36605 reflections in the range $2 < \theta < 72°$. The monoclinic cell parameters and calculated volume are: a = 12.8518(3), b = 15.4726(5) c = 15.6750(6) Å, $\beta$ = 73.288 °, V = 2664.29(15) Å$^3$. For Z = 4 and F.W. = 1210.59 the calculated density is 1.509 g/cm$^3$. The refined mosaicity from DENZO/SCALEPACK[1] was 1.72 ° indicating moderate crystal quality. The space group was determined by the program XPREP[2]. 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(# 2).

The data were collected at a temperature of 200(1) K. Data were collected to a maximum 2$\theta$ of 144.5°.

DATA REDUCTION

A total of 36605 reflections were collected, of which 16047 were unique. Frames were integrated with HKL3000[1].

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 108.3 /mm for Cu $K_\alpha$ radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.189 to 0.522. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 5.0% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SHELXT[3]. 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/[$\sigma$. Scattering factors were taken from the "International Tables for Crystallography"[4]. 16047 reflections were used in the refinements. However, only the 7617 reflections with $F_o^2 > 2\sigma(F_o^2)$ were used in calculating R1. The final cycle of refinement included 577 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \Sigma |Fo - Fc| / \Sigma Fo = 0.054$$

$$R2 = SQRT ( \Sigma w ( Fo^2 - Fc^2 )^2 / \Sigma w (Fo^2)^2 ) = 0.079$$

The goodness-of-fit parameter was 1.06. The highest peak in the final difference Fourier

had a height of 0.81 e/$A^3$. The minimum negative peak had a height of -1.19 e/$A^3$.

Refinement was performed on a LINUX PC using SHELX 2013[7]. Crystallographic drawings were done using programs ORTEP[8], and PLUTON[9].

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