

# Synthesis of U(IV) Imidos From $\text{Tp}^*_2\text{U}(\text{CH}_2\text{Ph})$ ( $\text{Tp}^* =$ hydrotris(3,5-dimethylpyrazolyl)borate) by Extrusion of Bibenzyl

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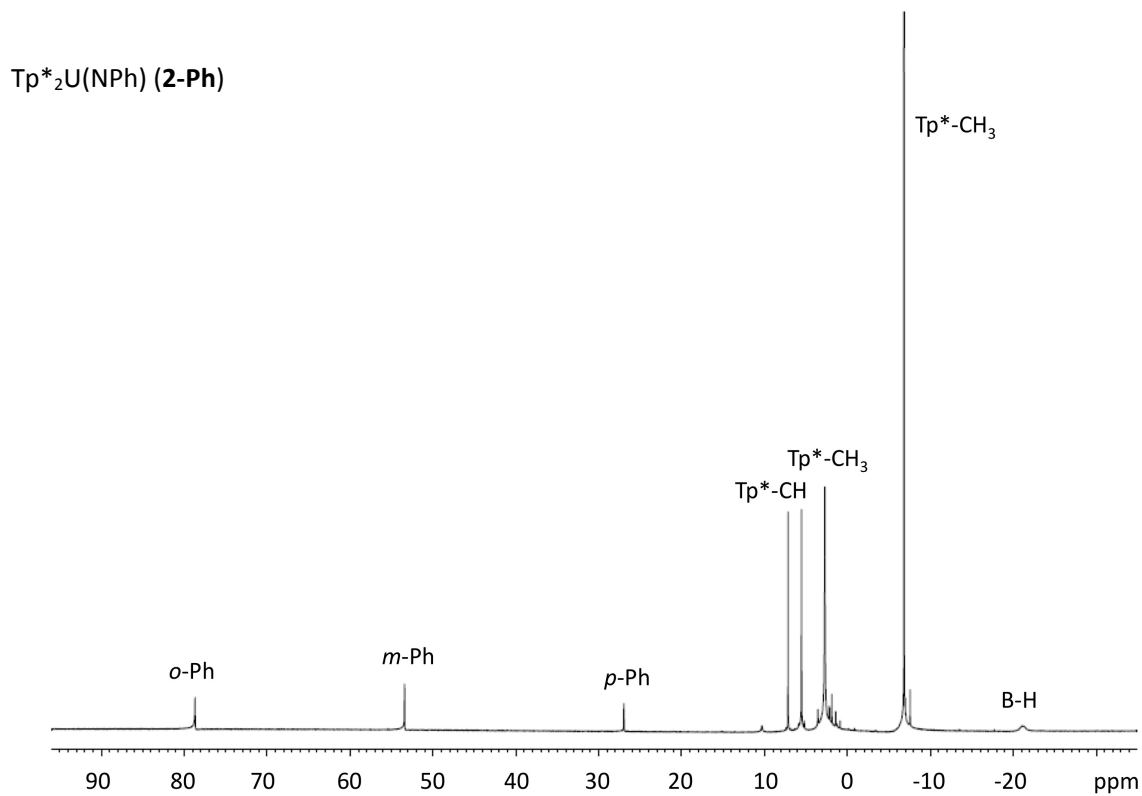
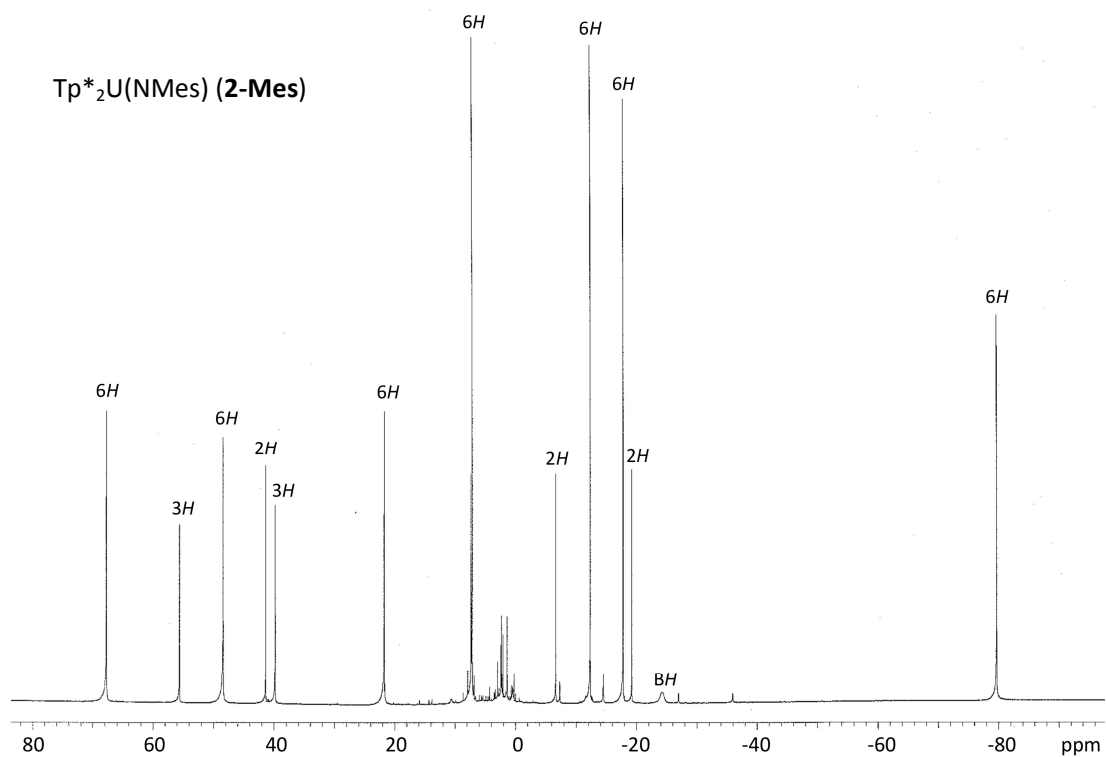
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IN, 47907

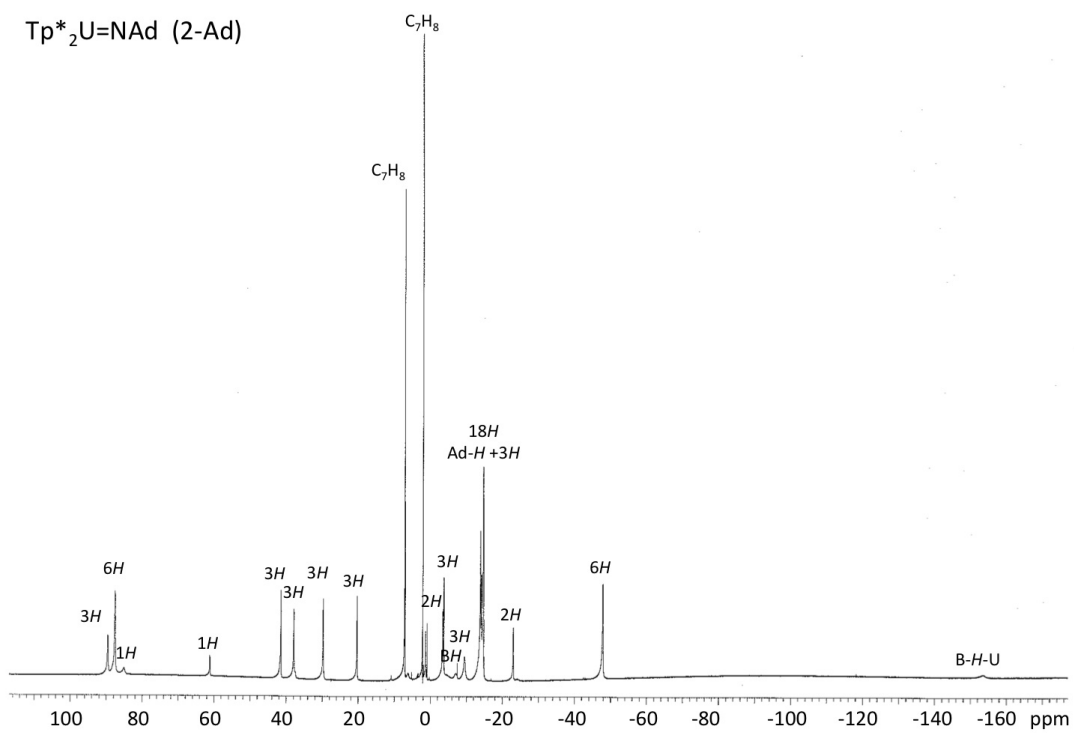
[sbart@purdue.edu](mailto:sbart@purdue.edu)

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### $^1\text{H}$ NMR Data: benzene- $d_6$ , 25° C





## Crystallographic Experimental Data:

**Structural Report:**  $\text{Tp}^*_2\text{U}(\text{NMes})$  (2-Mes)  
 $\text{C}_{39}\text{H}_{55}\text{B}_2\text{N}_{13}\text{U}$

### DATA COLLECTION

A red needle of  $\text{C}_{39}\text{H}_{55}\text{B}_2\text{N}_{13}\text{U}$  having approximate dimensions of 0.20 x 0.10 x 0.05 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu  $K_\alpha$  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 49215 reflections in the range  $2 < \theta < 72^\circ$ . The monoclinic cell parameters and calculated volume are:  $a = 15.3252(5)$ ,  $b = 14.1075(4)$ ,  $c = 19.9873(4)$   $\text{\AA}$ ,  $\beta = 106.487(2)^\circ$ ,  $V = 4143.6(2)\text{\AA}^3$ . For  $Z = 4$  and F.W. = 965.61 the calculated density is  $1.55\text{ g/cm}^3$ . The refined mosaicity from DENZO/SCALEPACK<sup>1</sup> was  $0.44^\circ$  indicating good crystal quality. The space group was determined by the program ABSEN<sup>2</sup>. From the systematic presences of:

$$h0l \quad h+l=2n, \quad 0k0 \quad k=2n$$

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  $2\theta$  of  $144.4^\circ$ .

### DATA REDUCTION

A total of 49215 reflections were collected, of which 7883 were unique. Frames were integrated with DENZO-SMN.<sup>1</sup>

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $122.1\text{ /mm}$  for Cu  $K_\alpha$  radiation. An empirical absorption correction using SCALEPACK<sup>1</sup> was applied. Transmission coefficients ranged from 0.187 to 0.543. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 3.6% based on intensity.

### STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99<sup>3</sup>. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement. Some were restrained to ride on the atom to which they are bonded, while other hydrogen atoms were resolved from crystallographic data. The structure was refined in full-matrix least-squares where the function minimized was  $S w(|F_o|^2 - |F_c|^2)^2$  and the weight  $w$  is defined as  $1/[s^2(F_o^2) + (0.0566P)^2 + 6.9090P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Scattering factors were taken from the "International Tables for Crystallography".<sup>4</sup> 7883 reflections were used in the refinements. However, only the 7558 reflections with  $F_o^2 > 2s(F_o^2)$  were used in, calculating R1. The final cycle of refinement included 518 variable parameters and converged (largest parameter shift was  $< 0.01$  times its su) with unweighted and weighted agreement factors of:

$$R1 = \sum |F_o - F_c| / \sum F_o = 0.030$$
$$R2 = \text{SQRT} \left( \sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2 \right) = 0.081$$

The goodness-of-fit parameter was 1.07. The highest peak in the final difference Fourier had a height of  $1.49\text{ e/\AA}^3$ . The minimum negative peak had a height of  $-1.53\text{ e/\AA}^3$ . Refinement was performed on a LINUX PC using SHELX-97<sup>5</sup>. Crystallographic drawings were done using programs ORTEP<sup>6</sup>, and PLUTON<sup>7</sup>.

**Structural Report:**  $\text{Tp}^*_2\text{U}(\text{NAd})$  (2-Ad)  
 $\text{C}_{40}\text{H}_{59}\text{B}_2\text{N}_{13}\text{U} \cdot 2(\text{C}_7\text{H}_8)$

## Experimental

### DATA COLLECTION

A orange chunk of  $C_{40}H_{59}B_2N_{13}U_2(C_7H_8)_2$  having approximate dimensions of 0.20 x 0.18 x 0.15 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu  $K_\alpha$  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 50971 reflections in the range  $2 < \theta < 70^\circ$ . The triclinic cell parameters and calculated volume are:  $a = 9.1993(4)$ ,  $b = 14.0954(6)$ ,  $c = 22.3766(7)\text{\AA}$ ,  $\alpha = 97.930(3)$ ,  $\beta = 101.255(3)$ ,  $\gamma = 106.142(3)^\circ$ ,  $V = 2676.03(18)\text{\AA}^3$ . For  $Z = 2$  and F.W. = 1165.94 the calculated density is 1.45  $\text{g/cm}^3$ . The refined mosaicity from DENZO/SCALEPACK<sup>1</sup> was  $0.51^\circ$  indicating moderate crystal quality. The space group was determined by the program XPREP.<sup>5</sup> 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  $140.3^\circ$ .

### DATA REDUCTION

A total of 50971 reflections were collected, of which 9387 were unique. Frames were integrated with DENZO-SMN.<sup>1</sup>

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 89.1 /mm for Cu  $K_\alpha$  radiation. An empirical absorption correction using SCALEPACK<sup>1</sup> was applied. Transmission coefficients ranged from 0.176 to 0.263. 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<sup>3</sup>. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement. Some were restrained to ride on the atom to which they are bonded, while other hydrogen atoms were resolved from crystallographic data. 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  $1/[s^2(F_o^2) + (0.0702P)^2 + 4.3016P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Scattering factors were taken from the "International Tables for Crystallography".<sup>4</sup> 9387 reflections were used in the refinements. However, only the 9373 reflections with  $F_o^2 > 2s(F_o^2)$  were used in calculating R1. The final cycle of refinement included 652 variable parameters and converged (largest parameter shift was  $< 0.01$  times its su) with unweighted and weighted agreement factors of:

$$R1 = \sum |F_o - F_c| / \sum F_o = 0.036$$
$$R2 = \text{SQRT} \left( \sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2 \right) = 0.096$$

The goodness-of-fit parameter was 1.06. The highest peak in the final difference Fourier had a height of  $2.39 \text{ e/\AA}^3$ . The minimum negative peak had a height of  $-1.46 \text{ e/\AA}^3$ .

Refinement was performed on a LINUX PC using SHELX-97<sup>5</sup>. Crystallographic drawings were done using programs ORTEP<sup>6</sup>, and PLUTON<sup>7</sup>.

### References:

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- <sup>2</sup> P. C. McArdle, *J. Appl. Cryst.*, 1996, **29**, 306.
- <sup>3</sup> P. T. Beurskens, G. Beurskens, R. deGelder, S. Garcia-Granda, R. O. Gould, and J. M. M. Smits, "The DIRDIF2008 Program System." *Crystallography Laboratory*, Univ. of Nijmegen, The Netherlands, 2008.
- <sup>4</sup> "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4
- <sup>5</sup> G.M. Sheldrick, *Acta Cryst.*, 2008, **112**, A64.
- <sup>6</sup> C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA 1976.
- <sup>7</sup> A. L. Spek, PLUTON. Molecular Graphics Program, Univ. of Utrecht, The Netherlands, 1991.