

## Electronic Supporting Information

### Molybdenum Sulphide Clusters as Redox Active Supports for Low-Valent Uranium

Kamaless Patra, William W. Brennessel, and Ellen M. Matson\*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

\* Corresponding author

#### Supporting Information Table of Contents

<b>Experimental</b> .....	2
<b>Table S1.</b> Crystallographic parameters for molecular structures of complexes for $[(Cp^*_3Mo_3S_4)Cp^*UI_2] \cdot (C_6D_6)_2$ , $[(Cp^*_3Mo_3S_4)Cp^*UI]$ and $[(Cp^*_3Mo_3S_4)Cp^*U(=NPh)_2] \cdot (C_7H_8)$ ...	5
<b>Table S2.</b> Selected bond distances from the X-ray crystal structures of $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$ , $[(Cp^*_3Mo_3S_4)Cp^*UI]$ , and $[(Cp^*_3Mo_3S_4)Cp^*U(=NPh)_2]$ .....	6
<b>Figures S1 and S2.</b> $^1H$ NMR spectra of $[(Cp^*_3Mo_3S_4)]$ and stacked with $[(Cp^*_3Mo_3S_4)PF_6]$ .....	7
<b>Figures S3 and S4.</b> $^1H$ NMR spectra of $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$ in THF- $d_8$ and benzene- $d_6$ .....	8
<b>Figure S5.</b> Stacked $^1H$ NMR spectra of $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$ with starting materials in THF- $d_8$ ..	9
<b>Figure S6.</b> $^1H$ NMR spectrum of $[(Cp^*_3Mo_3S_4)Cp^*UI]$ in benzene- $d_6$ .....	10
<b>Figure S7.</b> $^1H$ NMR spectrum of $[(Cp^*_3Mo_3S_4)Cp^*U]$ in benzene- $d_6$ .....	10
<b>Figure S8.</b> Stacked $^1H$ NMR spectra of $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$ , $[(Cp^*_3Mo_3S_4)Cp^*UI]$ , $[(Cp^*_3Mo_3S_4)Cp^*U]$ in benzene- $d_6$ .....	11
<b>Figure S9.</b> $^1H$ NMR spectrum of $[(Cp^*_3Mo_3S_4)Cp^*U(=NPh)_2]$ in benzene- $d_6$ .....	12
<b>References.</b> .....	12

## EXPERIMENTAL.

**General Considerations.** All air- and moisture sensitive manipulations were carried out using standard high vacuum line, Schlenk, or cannula techniques, or in an MBraun inert atmosphere drybox containing and atmosphere of purified dinitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System (Pure Process Technology, LLC) and stored over activated 4 Å molecular sieves (Fisher Scientific) prior to use. Deuterated solvents for  $^1\text{H}$  NMR spectroscopy were purchased from Cambridge Isotope Laboratories and stored in the glovebox over activated 3 Å molecular sieves after three freeze-pump-thaw cycles. Chemicals were purchased from commercial sources and used without further purification. Azobenzene was purchased from Sigma Aldrich and recrystallized from a concentrated solution of pentane at  $-30\text{ }^\circ\text{C}$ .  $[\text{Cp}^*\text{Mo}_3\text{S}_4]$ ,<sup>1</sup>  $[\text{Cp}^*\text{UI}_2(\text{THF})_3]$ ,<sup>2</sup>  $\text{KCp}^*$ ,<sup>3</sup> and  $\text{KC}_8$ <sup>4</sup> were synthesized following established procedures.

**Safety Considerations.** Caution! Depleted uranium (primary isotope  $^{238}\text{U}$ ) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of  $4.47 \times 10^9$  years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.

**Synthesis of  $[(\text{Cp}^*\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}_2]$ .** A 20 mL scintillation vial was charged with  $(\text{Cp}^*\text{Mo})_3\text{S}_4$  (0.050 g, 0.061 mmol) dissolved in a minimal amount of toluene ( $\sim 8$  mL), affording a green-colored, homogenous solution. An equivalent of  $[\text{Cp}^*\text{UI}_2(\text{THF})_3]$  (0.051 g, 0.061 mmol) was added as a solid to the original vial without stirring. The reaction mixture was swirled gently, affording a color change to dark green-brown. The solvent was concentrated immediately under reduced pressure, resulting in the formation of brown crystals at the bottom of the scintillation vial. After decanting the mother liquor, the product,  $[(\text{Cp}^*\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}_2]$ , can be further purified by washing the brown crystals with pentane. Yield = 0.072 g, 0.049 mmol, 81%.  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ )  $\delta = 7.02$  (58, 15H), 4.52 (61, 45 H);  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta = 7.39$  (59, 15H), 4.45 (65, 45 H). Brown crystals suitable for single-crystal X-ray diffraction

were grown from a concentrated solution of the product in benzene. Anal Calcd for  $C_{40}H_{60}Mo_3S_4UI_2 \cdot C_6H_6$  (mol. Wt.  $1526.96 \text{ g mol}^{-1}$ ): C, 36.18; H 4.36; Found: C, 36.04; H, 4.36.

**Synthesis of  $[(Cp^*_3Mo_3S_4)Cp^*UI]$ .** A 20 mL scintillation vial equipped with a magnetic stir bar was charged with  $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$  (0.050 g, 0.034 mmol) and 8 mL of toluene. Potassium graphite ( $KC_8$ , 0.010 g, 0.075 mmol, 2.2 eq) was weighed by difference and added as uranium-containing solution with vigorous stirring. The reaction mixture was stirred for ~1 h. The toluene solution was filtered through celite and evaporated under reduced pressure. The resultant brown residue was washed twice with pentane to afford the title compound as a brown solid. Yield: 0.029 g, 0.022 mmol, 65%.  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta = 8.05$  (68, 15H), 4.88 (53, 45 H). Brown crystals suitable for single crystal X-ray diffraction were grown from a concentrated toluene solution of the product at  $-30 \text{ }^\circ\text{C}$ . Anal. Calcd for  $C_{40}H_{60}Mo_3S_4UI \cdot 0.6(C_7H_8)$  (mol. Wt.  $1377.23 \text{ g mol}^{-1}$ ): C, 38.55; 4.74. Found: C, 38.64; H, 4.65.

**Synthesis of  $[(Cp^*_3Mo_3S_4)Cp^*U]$ .** A 20 mL scintillation vial equipped with a magnetic stir bar was charged with  $[(Cp^*_3Mo_3S_4)Cp^*UI_2]$  (0.050 g, 0.034 mmol) and 10 mL of toluene. Potassium graphite ( $KC_8$ , 0.019 g, 0.138 mmol, 4.0 eq) was weighed by difference and added as a solid to the uranium-containing solution. The color of the solution turned darker, and the reaction mixture was stirred for 16 hr. After this time, the solution was filtered over Celite, and residual solvent was evaporated under reduced pressure. The residue was dissolved in cold pentane, filtered through Celite, and pumped dry to afford the title compound as a black powder. Yield: 0.025 g, 0.021 mmol, 61 %.  $^1H$  NMR (400 MHz,  $C_6D_6$ )  $\delta = -0.44$  (47, 45H), -7.89 (57, 15H). Anal. Calcd for  $C_{40}H_{60}Mo_3S_4U \cdot (KI)_{0.2}$  (mol. Wt.  $1228.24 \text{ g mol}^{-1}$ ): C, 39.12; H, 4.92. Found: C, 38.83; H, 4.98.

**Synthesis of  $[(Cp^*_3Mo_3S_4)Cp^*U(NPh)_2]$ .** A 20 mL scintillation vial was charged with  $[(Cp^*_3Mo_3S_4)Cp^*U]$  (0.020 g, 0.017 mmol) and 5 mL of toluene. In a separate vial, azobenzene (0.003 g, 0.017 mmol, 1.0 eq) was dissolved in 2 mL of toluene. The azobenzene solution was added dropwise to the solution of  $[(Cp^*_3Mo_3S_4)Cp^*U]$ , with swirling of the solution gently after each addition. Solvent was subsequently

removed under reduced pressure, affording the title compound as a black crystalline solid. Yield = 0.021 g, 0.015 mmol, 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 9.77 (43, 45H), 6.63 (37, 5H), 6.46 (32, 3H), 5.91 (31, 2H), 3.63 (33, 15H). Brown crystals suitable for single crystal X-ray diffraction were grown from the concentrated toluene solution of the title compound at  $-30\text{ }^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{52}\text{H}_{70}\text{Mo}_3\text{S}_4\text{N}_2\text{U} \cdot (\text{KI})_{0.2}$  (mol. Wt.  $1410.46\text{ g mol}^{-1}$ ): C, 44.28; H, 5.00; N, 1.99. Found: C, 44.24; H, 4.80; N, 1.94.

**Physical Measurements.**  $^1\text{H}$  NMR spectra were recorded at room temperature on a 400 MHz Bruker AVANCE spectrometer locked on the signal of deuterated solvents. All the chemical shifts are reported relative to the chosen deuterated solvent as a standard. Elemental analysis data were obtained from the Elemental Analysis Facility at the University of Rochester. Microanalysis samples were weighed with a PerkinElmer model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

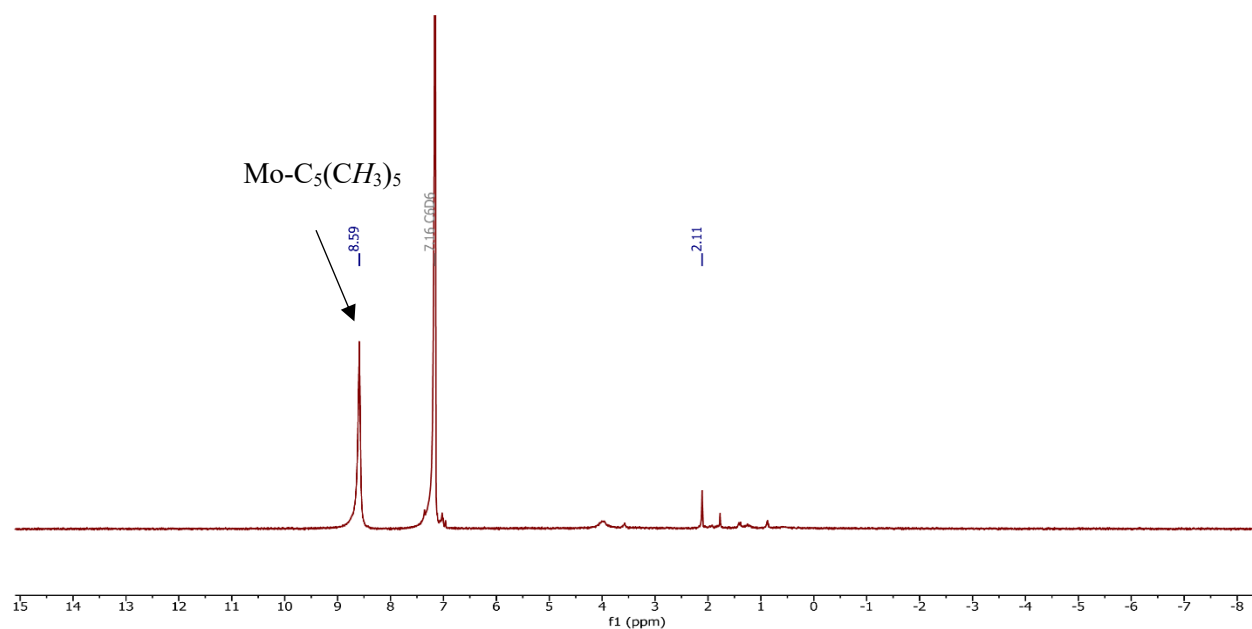
**Single Crystal X-ray Crystallography.** The single crystals of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}_2]$ ,  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}]$ , and  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}(\text{NPh})_2]$  were collected on a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at  $100.00(10)\text{ K}$ . A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections. A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection for all four complexes was carried out using a PhotonJet (Cu) X-ray source. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of the strong reflections from the actual data collections after integration. The structure was solved using SHELXT and refined using SHELXL. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares/difference Fourier cycles were performed, which located any remaining non-hydrogen atoms. All the non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

**Table S1:** Crystallographic parameters for molecular structures of complexes for [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*UI<sub>2</sub>].(C<sub>6</sub>D<sub>6</sub>)<sub>2</sub>, [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*UI] and [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*U(=NPh)<sub>2</sub>].(C<sub>7</sub>H<sub>8</sub>).

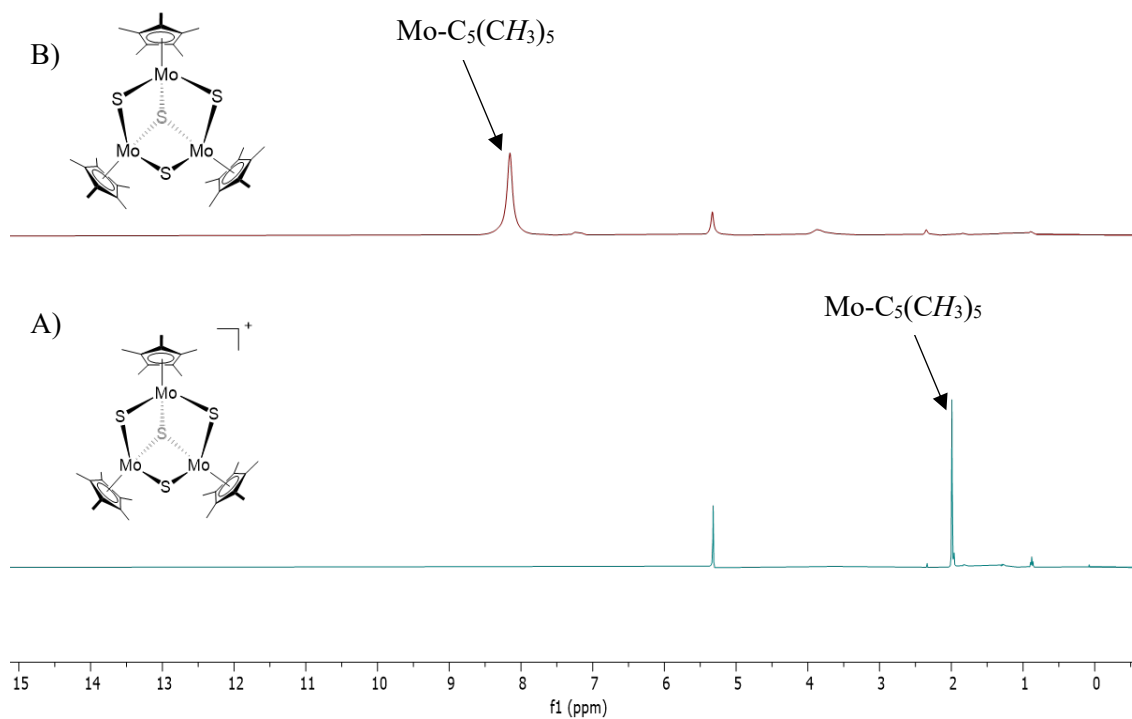
Compound	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*UI <sub>2</sub> ].(C <sub>6</sub> D <sub>6</sub> ) <sub>2</sub>	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*UI]	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*U(=NPh) <sub>2</sub> ].(C <sub>7</sub> H <sub>8</sub> )
Empirical formula	C <sub>52</sub> H <sub>60</sub> D <sub>12</sub> I <sub>2</sub> Mo <sub>3</sub> S <sub>4</sub> U	C <sub>40</sub> H <sub>60</sub> IMo <sub>3</sub> S <sub>4</sub> U	C <sub>59</sub> H <sub>78</sub> Mo <sub>3</sub> N <sub>2</sub> S <sub>4</sub> U
Formula weight	1617.06	1321.87	1469.32
Temperature / K	100.00(10)	100.00(10)	100.00(10)
Wavelength / Å	1.54184	1.54184	1.54184
Crystal group	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions	<i>a</i> = 13.30840(10) Å <i>b</i> = 13.3384(3) Å <i>c</i> = 17.3783(3) Å <i>α</i> = 90.0360(1)° <i>β</i> = 109.1620(10)° <i>γ</i> = 110.9690(10)°	<i>a</i> = 11.22430(9) Å <i>b</i> = 20.51803(14) Å <i>c</i> = 21.54896(19) Å <i>α</i> = 79.9966(7)° <i>β</i> = 75.1189(7)° <i>γ</i> = 87.6951(6)°	<i>a</i> = 11.01510(10) Å <i>b</i> = 20.26860(10) Å <i>c</i> = 24.4744(2) Å <i>α</i> = 90° <i>β</i> = 90° <i>γ</i> = 90°
Volume / Å <sup>3</sup>	2696.47(8)	4723.32(7)	5509.31(7)
<i>Z</i>	2	4	4
Reflections collected	91758	260733	70003
Independent reflections	11563	47571	11882
Completeness (theta)	99.7% (74.504°)	99.9% (67.684°)	100.0% (74.504°)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.086	1.039	1.110
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0284	<i>R</i> 1 = 0.0445	<i>R</i> 1 = 0.0379
Largest diff. peak and hole	1.796 and -1.502 e.Å <sup>-3</sup>	2.942 and -3.500 e.Å <sup>-3</sup>	1.269 and -1.472 e.Å <sup>-3</sup>

**Table S2:** Selected bond distances from the X-ray crystal structures of [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*UI<sub>2</sub>], [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*UI], and [(Cp\*<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>)Cp\*U(=NPh)<sub>2</sub>].

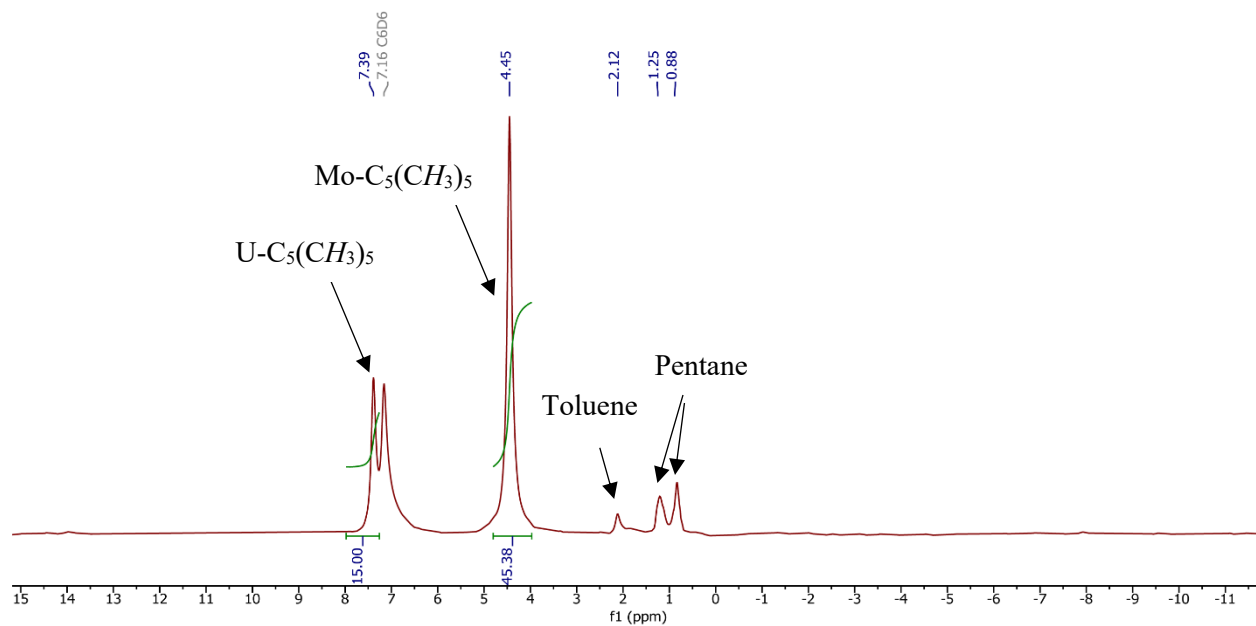
Bond	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*UI <sub>2</sub> ]	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*UI]	[(Cp* <sub>3</sub> Mo <sub>3</sub> S <sub>4</sub> )Cp*U(=NPh) <sub>2</sub> ]
U-C <sub>Cp*</sub>	2.774(5)-2.802(6) Å	2.754(7)-2.813(6) Å	2.775(11) – 2.812(10) Å
U-Cp* <sub>cent</sub>	2.512(2) Å	2.513(3) Å	2.511(5) Å
U-I	3.0681(3), 3.0825(3) Å	3.1169 Å	--
U-N <sub>imido</sub>	--	--	2.015(9), 2.024(8) Å
N <sub>imido</sub> -U-N <sub>imido</sub>	--	--	99.1(4) <sup>o</sup>
U-S	2.7724(11)-2.7770(11) Å	2.6299(15)-2.7011(15) Å	2.771(2) – 2.989(3) Å
Mo-S <sub>U</sub> (avg)	2.3644 Å	2.4032 Å	2.337 Å
Mo-S <sub>Mo</sub> (avg)	2.3262 Å	2.3281 Å	2.346 Å
Mo-Mo (Å)	2.8648(5)-2.8975(5) Å	2.6657(6)-2.9096(6) Å	2.7714(11)-2.9323(11) Å
U-S <sub>surf</sub>	1.8554(6) Å	1.6623(9) Å	2.0187(15) Å



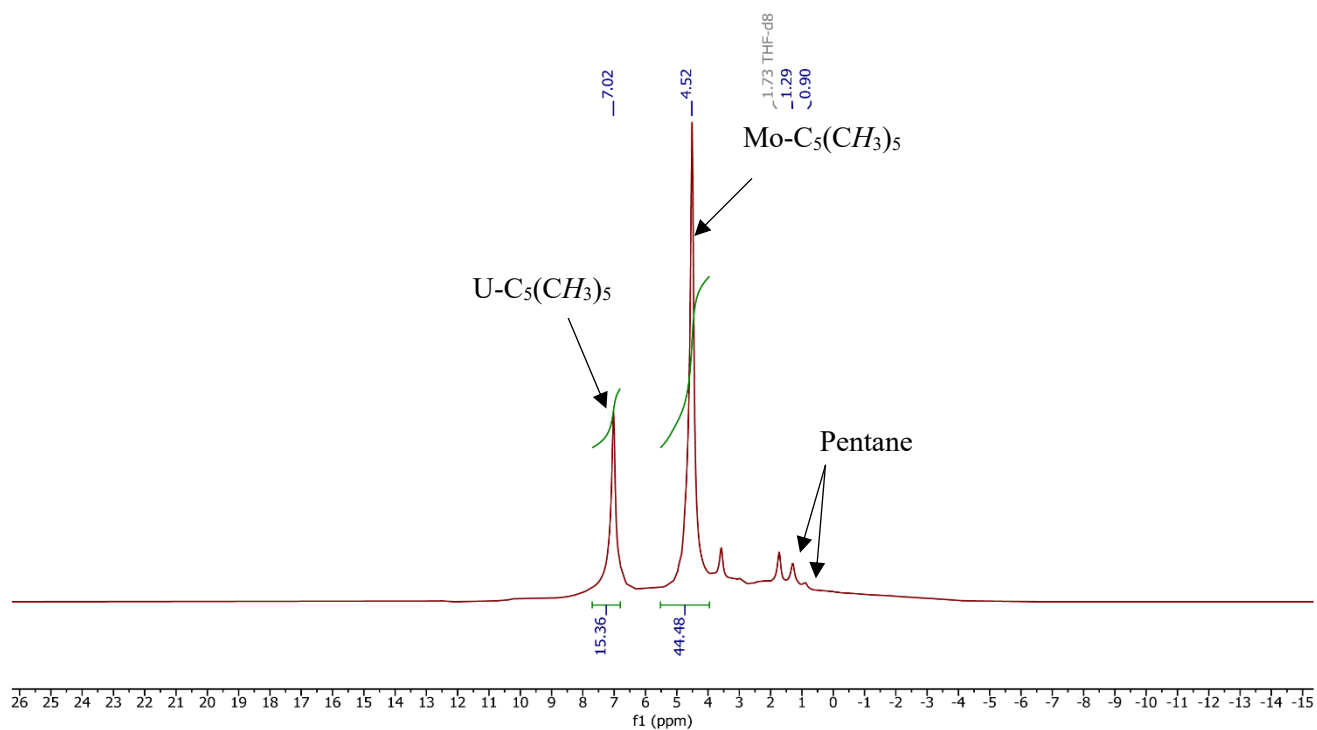
**Figure S1.**  $^1\text{H}$  NMR spectrum (400 MHz) of neutral metalloligand  $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$  in  $\text{C}_6\text{D}_6$ .



**Figure S2.** Stacked  $^1\text{H}$  NMR spectra (400 MHz) of **A)** Cationic metalloligand  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)(\text{PF}_6)]$  and **B)** neutral metalloligand  $[\text{Cp}^*_3\text{Mo}_3\text{S}_4]$  in  $\text{CD}_2\text{Cl}_2$ .

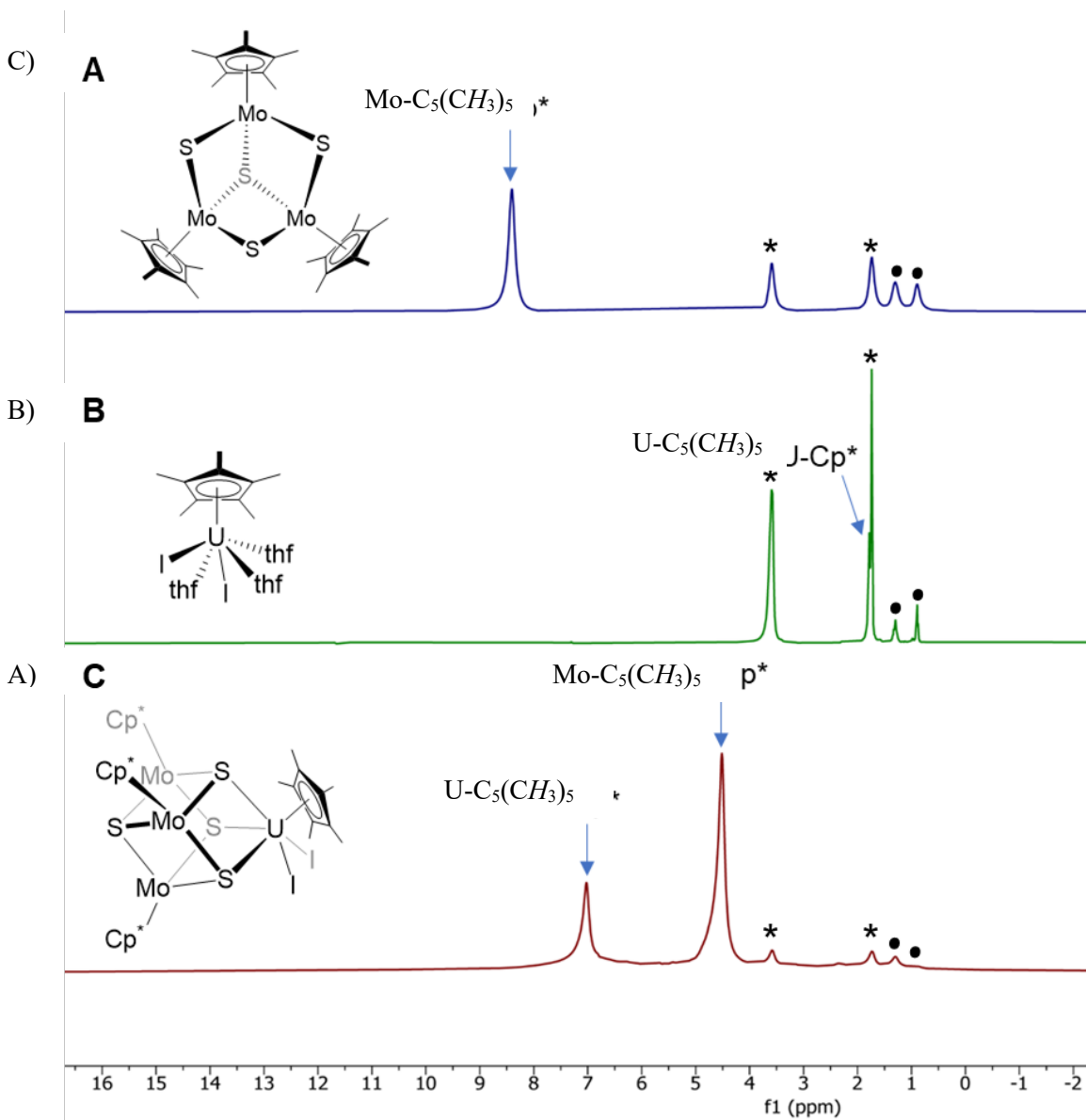


**Figure S3.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}]_2$  in  $\text{C}_6\text{D}_6$ .

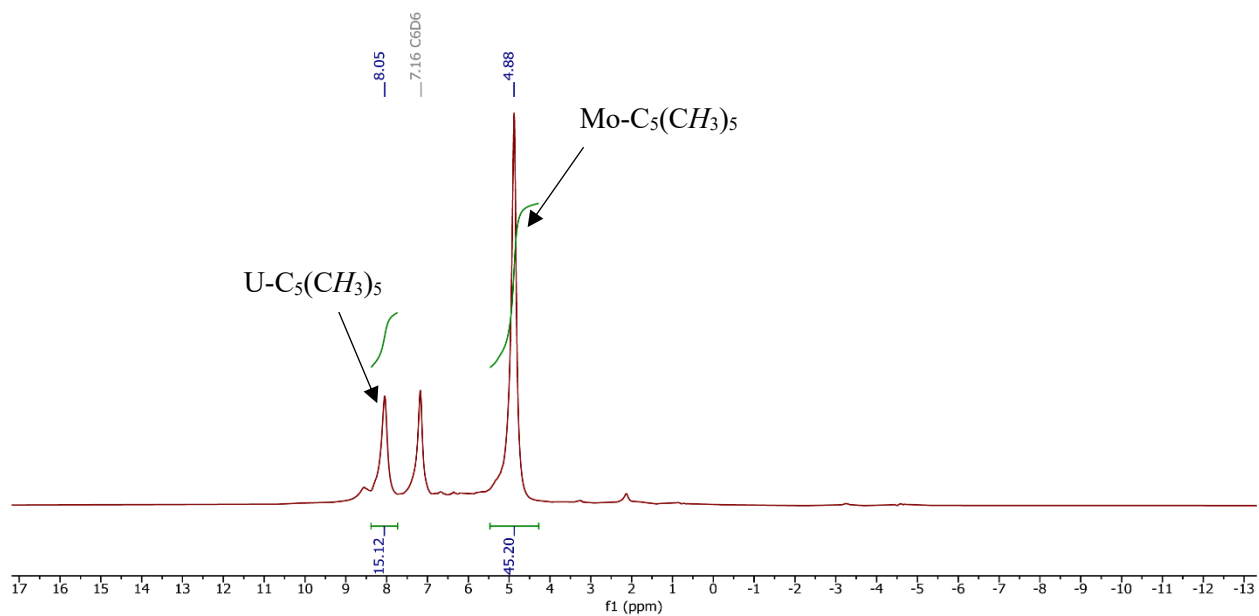


**Figure S4.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}]_2$  in  $\text{THF-}d_8$ .

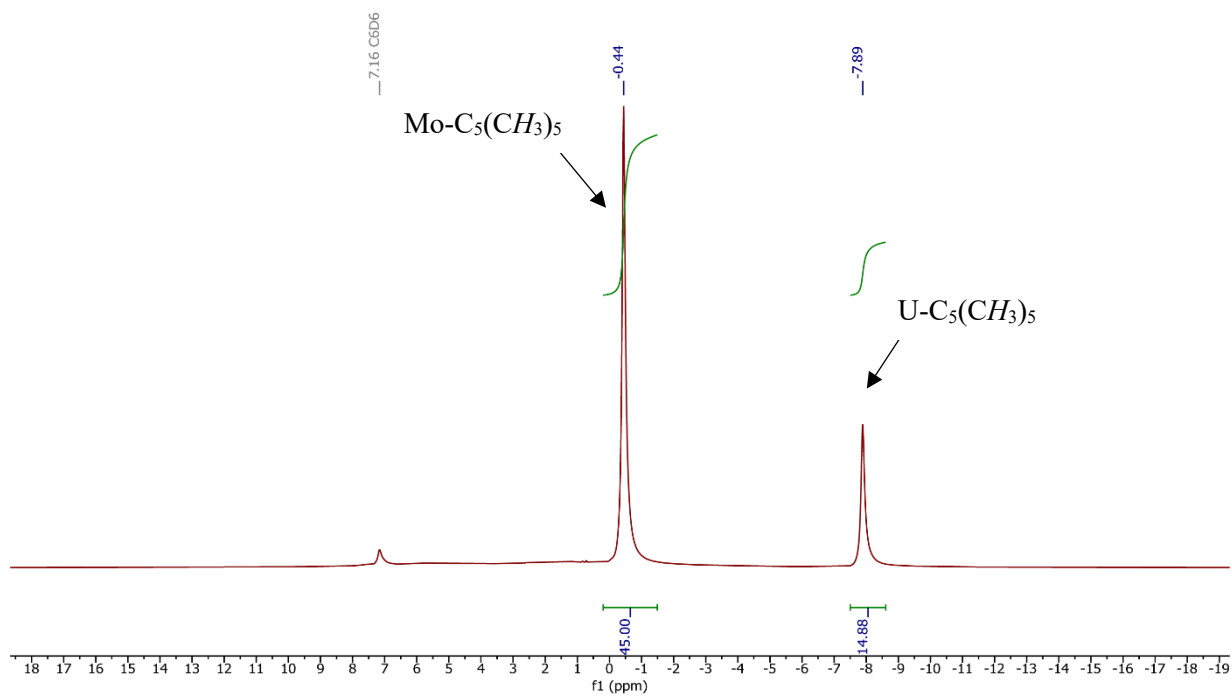




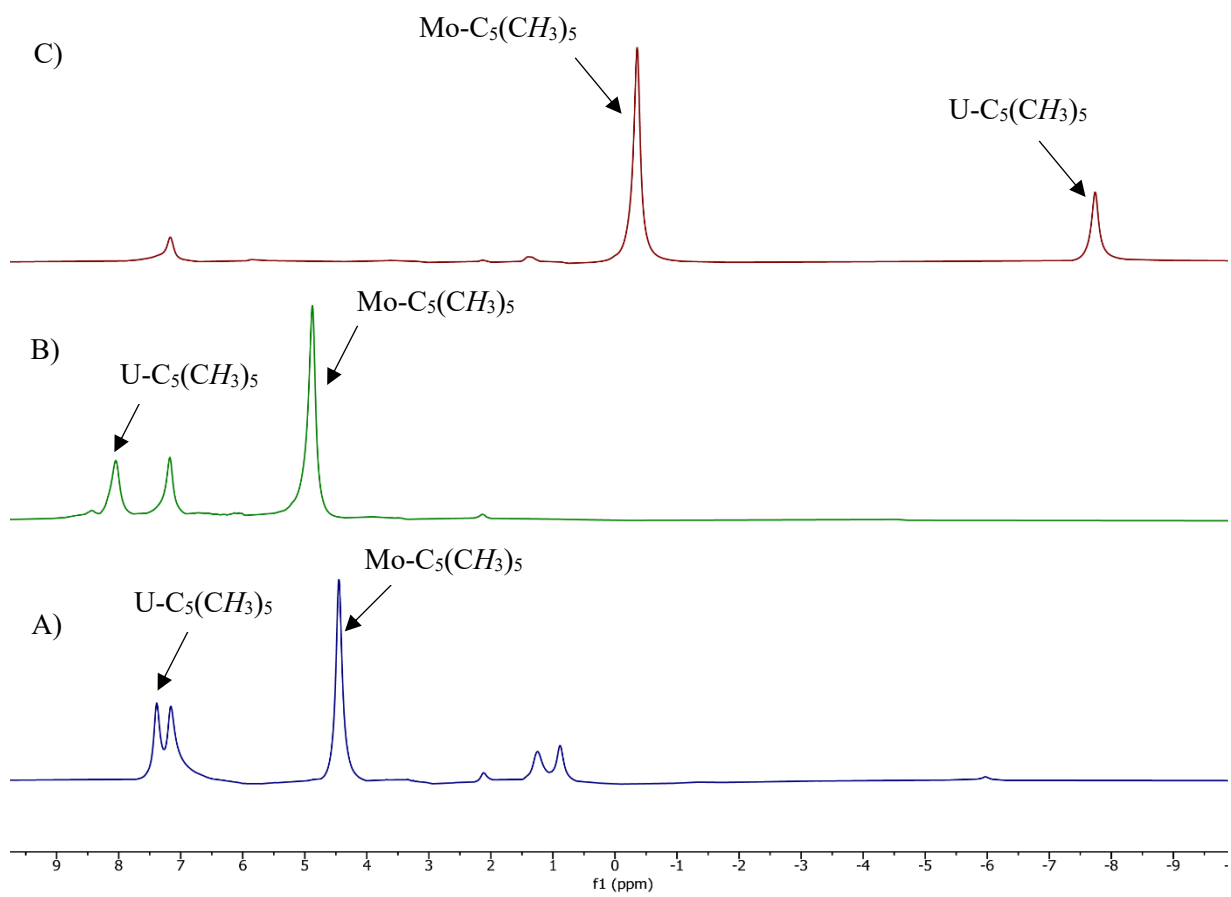
**Figure S5.** Stacked  $^1\text{H}$  NMR spectra of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}]_2$  (A);  $[\text{Cp}^*\text{U}_2(\text{thf})_3]$  (B);  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)]$  (C) in  $\text{THF-}d_8$ ; (\* indicates residual signals of  $\text{THF-}d_8$ ; • indicates solvent impurities (pentane) and grease).



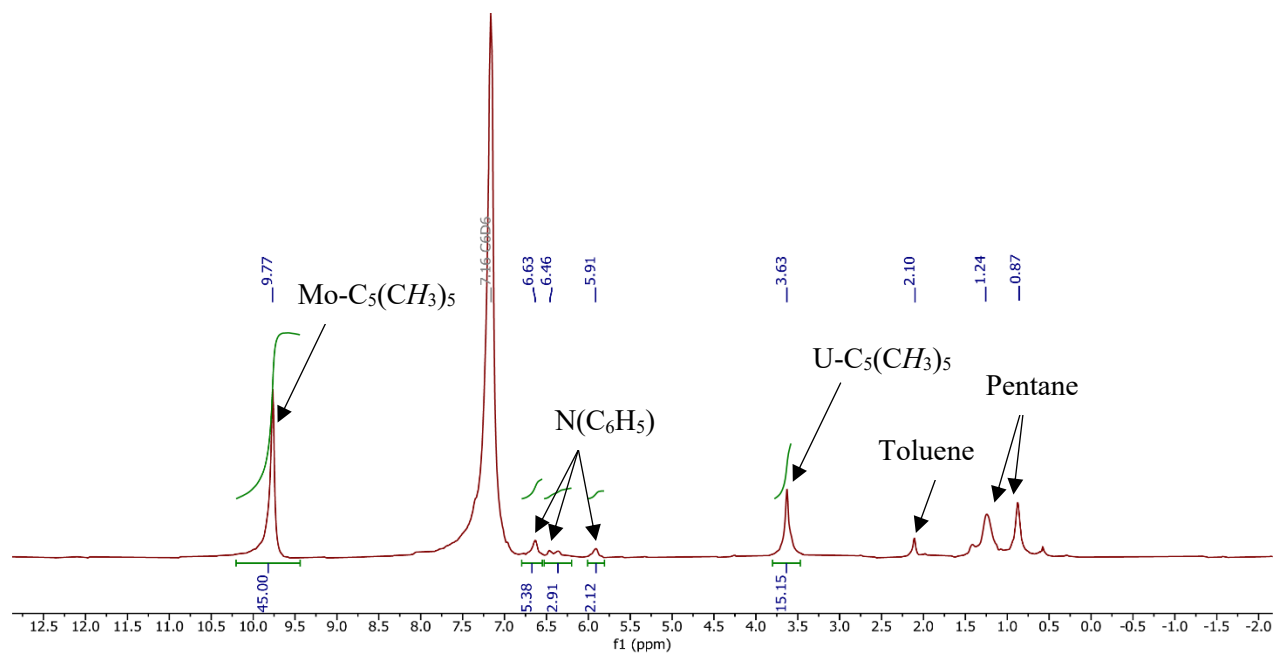
**Figure S6.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}]$  in  $\text{C}_6\text{D}_6$ .



**Figure S7.**  $^1\text{H}$  NMR spectrum (500 MHz) of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}]$  in  $\text{C}_6\text{D}_6$ .



**Figure S8.** Stacked  $^1\text{H}$  NMR spectra of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}_2]$  (A);  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{UI}]$  (B);  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}]$  (C) in  $\text{C}_6\text{D}_6$ .



**Figure S9.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[(\text{Cp}^*_3\text{Mo}_3\text{S}_4)\text{Cp}^*\text{U}(=\text{NPh})_2]$  in  $\text{C}_6\text{D}_6$ .

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