

Supporting Information

Solvent-Free Organometallic Reactivity: Synthesis of Hydride and Carboxylate Complexes of Uranium and Yttrium from Gas/Solid Reactions

Christopher L. Webster, Joseph. W. Ziller and William J. Evans*

Department of Chemistry, University of California, Irvine, California 92697-2025

*To whom correspondence should be addressed, email: wevans@uci.edu

Table of Contents	Page
Experimental section	1
Infrared Spectroscopy	3
Figure S1. Infrared spectroscopic analysis of the uranium hydrides and deuterides.	4
Table S1. Crystal data and structure refinement for $(C_5Me_5)_2Y(\mu-H)YH(C_5Me_5)_2$.	4
X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Y(\mu-H)YH(C_5Me_5)_2$.	5

EXPERIMENTAL SECTION

The syntheses and manipulations described below were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves. Benzene- d_6 (Cambridge Isotope Laboratories) was dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. $(C_5Me_5)_2UMe_2$,¹ $(C_5Me_5)_2U(C_3H_5)_2$,¹⁸ $(C_5Me_5)_2U(C_3H_5)$,¹⁸ and $(C_5Me_5)_2U(C_3H_5)Cl$ ¹⁸ were prepared as previously reported. Ultra high-purity H_2 and CO_2 were purchased from Airgas and used as received. NMR experiments were conducted with a Bruker DRX 500 MHz spectrometer. Infrared spectra were collected as KBr pellets on a Varian 1000 FT-IR Scimitar Series spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer.

H₂ with (C₅Me₅)₂U(C₃H₅)₂. A solid sample of black (C₅Me₅)₂U(C₃H₅)₂ (100 mg, 0.169 mmol) was treated with H₂ (80 psi) as described above, and over 1 h, the color changed from black to dark green. After 14 h, the sample was handled as described above and the solid product (86 mg, 100%) was examined by ¹H NMR spectroscopy in C₆D₆. A 9:1 ratio of **1**: **2** was again observed with no byproducts.

The reaction of (C₅Me₅)₂U(C₃H₅)₂ with H₂ (80 psi) performed in toluene, followed by removal of solvent under vacuum, resulted in ¹H NMR spectra showing a **1**:**2** ratio of 1:1.1. However, the resonances for **1** and **2** amounted to less than 50% of the resonances assignable to (C₅Me₅)[−] ligands in uranium complexes in the spectrum.

H₂ with (C₅Me₅)₂U(C₃H₅). A solid sample of green (C₅Me₅)₂U(C₃H₅) (50 mg, 0.091 mmol) was treated with H₂ (80 psi) as described above and over 1 h, the color changed from green to dark green. After 14 h reaction time, the sample was handled as described above and the solid product (46 mg, 99%) was examined by ¹H NMR spectroscopy in C₆D₆. A 9:1 ratio of **1**:**2** was again observed with no byproducts.

The reaction of (C₅Me₅)₂U(C₃H₅) with H₂ (80 psi) performed in toluene, followed by removal of solvent under vacuum, resulted in ¹H NMR spectra with a **1**:**2** ratio of 1:1.2. The resonances for **1** and **2** amounted to less than 50% of the resonances assignable to (C₅Me₅)[−] ligands in uranium complexes in the spectrum.

CO₂ with (C₅Me₅)₂UMe₂. A sample of (C₅Me₅)₂UMe₂ (21 mg, 0.039 mmol) was reacted with CO₂ (80 psi) as described for H₂ above for 48 h to give (C₅Me₅)₂U(O₂CCH₃)₂ (24 mg, 98%) as an orange solid, identified by ¹H NMR spectroscopy.¹⁹ Reactions performed under the same conditions, but stopped after 6 h reaction time gave (C₅Me₅)₂U(O₂CCH₃)Me¹⁹ as the

major product with a small resonance for $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CCH}_3)_2$ in the ^1H NMR spectrum integrating to <1% of that for $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CCH}_3)\text{Me}$.

CO_2 with $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_3\text{H}_5)\text{Cl}$. A sample of $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_3\text{H}_5)\text{Cl}$ (10 mg, 0.017 mmol) was reacted with CO_2 (80 psi) as described above. The color changed to red-orange after 3 h. After 12 h total reaction time, a red-orange solid identified as $(\text{C}_5\text{Me}_5)_2\text{U}(\text{O}_2\text{CC}_3\text{H}_5)\text{Cl}$ by ^1H NMR spectroscopy, was isolated.

H_2 with $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{C}_3\text{H}_5)$. A solid sample of yellow $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{C}_3\text{H}_5)$ (50 mg, 0.12 mmol) was treated with H_2 (80 psi) as described above. Over 1 h, the color changed from yellow to pale orange. After 14 h, the vessel was transferred to the glovebox as described above and the solid product (45 mg, 100%) was immediately dissolved in a minimal amount of 50/50 toluene/hexane and placed in the glovebox freezer at -35°C . This yielded colorless single crystals of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-H})\text{YH}(\text{C}_5\text{Me}_5)_2$ suitable for X-ray diffraction.

Infrared Spectroscopy

Infrared spectral data from four different reactions are presented below and an overlay of the spectra is shown in Figure S1. A mixture of the uranium hydrides, $[(\text{C}_5\text{Me}_5)_2\text{UH}_2]_2$ and $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$, made from the reaction of $(\text{C}_5\text{Me}_5)_2\text{UMe}_2$ in the solid state with H_2 under solvent-free conditions is labeled SS H_2 . This sample after dissolving in toluene and removing solvent is labeled Sol H_2 . A gas solid reaction using D_2 under solvent-free condition is labelled SS D_2 and this sample after being dissolved in toluene and the solvent removed is called Sol D_2 .

SS H_2 : IR: 2964m, 2903s, 2856s, 2723w, 1436m, 1377m, 1328w, 1258w, 1192bs, 1070w, 1019m, 802w cm^{-1} .

Sol H₂: IR: 2964m, 2903s, 2856s, 2723w, 1437m, 1377m, 1334w, 1261w, 1165w, 1103w, 1019m, 801m cm⁻¹.

SS D₂: IR: 2967m, 2901s, 2855s, 2722w, 1491w, 1437m, 1377m, 1261w, 1063w, 1019wm, 949m, 803w cm⁻¹.

Sol D₂: IR: 2967m, 2902s, 2857s, 2724w, 1437m, 1373m, 1274w, 1192m, 1018m, 956w, 730w

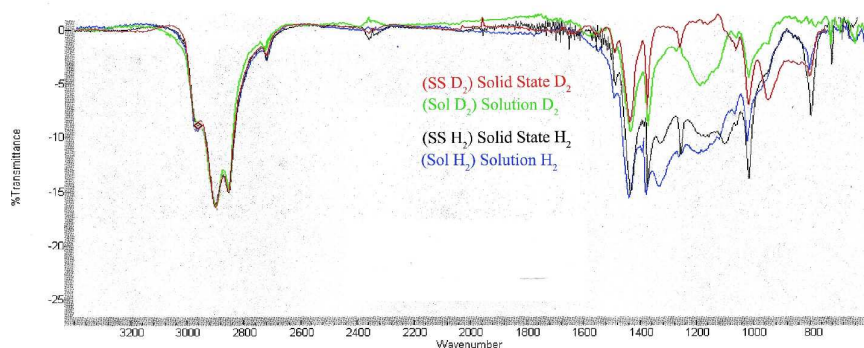


Figure S1. Infrared spectroscopic analysis of the uranium hydrides made as described above.

Table S1. Crystal data and structure refinement for (C₅Me₅)₂Y(μ -H)YH(C₅Me₅)₂.

Identification code	clw45	
Empirical formula	C ₄₀ H ₆₂ Y ₂ •C ₇ H ₈	
Formula weight	812.85	
Temperature	83(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 10.9754(15) Å	$\alpha = 90^\circ$.
	b = 31.177(4) Å	$\beta = 99.6476(18)^\circ$.
	c = 12.5004(17) Å	$\gamma = 90^\circ$.
Volume	4216.9(10) Å ³	
Z	4	
Density (calculated)	1.280 Mg/m ³	
Absorption coefficient	2.768 mm ⁻¹	

F(000)	1720
Crystal color	yellow
Crystal size	0.826 x 0.191 x 0.115 mm ³
Theta range for data collection	1.777 to 28.368°
Index ranges	-14 ≤ <i>h</i> ≤ 14, -41 ≤ <i>k</i> ≤ 41, -16 ≤ <i>l</i> ≤ 16
Reflections collected	49412
Independent reflections	10238 [R(int) = 0.0654]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.8455 and 0.2027
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10238 / 0 / 471
Goodness-of-fit on F ²	1.027
Final R indices [I > 2σ(I) = 7627 data]	R1 = 0.0350, wR2 = 0.0748
R indices (all data, 0.75 Å)	R1 = 0.0646, wR2 = 0.0840
Largest diff. peak and hole	0.512 and -0.683 e.Å ⁻³

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₅)₂Y(μ-H)YH(C₅Me₅)₂.

A yellow crystal of approximate dimensions 0.115 x 9.191 x 0.826 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group *P*2₁/*n* that was later determined to be correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques⁵. The analytical scattering factors⁶ for neutral atoms were used throughout the analysis. The hydride atoms were located from a difference-Fourier map and refined (*x*,*y*,*z* and *U*_{iso}). The remaining hydrogen atoms were included using a riding model. There was one molecule of toluene solvent present per formula-unit.

At convergence, wR2 = 0.0840 and Goof = 1.027 for 471 variables refined against 10238 data (0.75 Å), R1 = 0.0350 for those data with I > 2.0σ(I).

References.

1. APEX2 Version 2012.4.-0. Bruker AXS, Inc.; Madison, WI 2012.
 2. SAINT Version 7.68a, Bruker AXS, Inc.; Madison, WI 2009.
 3. Sheldrick, G. M. SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2008.
 4. Sheldrick, G. M. SHELXTL, Version 2008/4, Bruker AXS, Inc.; Madison, WI 2008.
 5. Sheldrick, G. M. SHELXL-2013/3.
 6. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
-

Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.