Supporting information

Reactivity of U^{3+} Metallocene Allyl Complexes Leads to a Nanometer-Sized Uranium Carbonate, $[(C_5Me_5)_2U]_6(\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)_6$

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X-ray Data Collection, Structure Solution and Refinement for $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)U[\eta^3\text{-}CH_2C(Me)CH_2]$, 6.

A brown crystal of approximate dimensions 0.04 x 0.25 x 0.44 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] 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 SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

At convergence, wR2 = 0.0395 and Goof = 1.020 for 655 variables refined against 9062 data (0.74 Å), R1 = 0.0178 for those 7753 data with I > 2.0σ(I).

Table S2. Crystal data and structure refinement for (η^5-C_5Me_5)(η^8-C_8H_8)U[η^3-$CH_2C(Me)CH_2$], 6.

Identification code	clw53 (Chris Webster)
Empirical formula	C_{22} H_{30} U
Formula weight	532.49
Temperature	83(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.8131(4) Å α= 106.6569(5)°.
	b = 14.2385(6) Å β= 98.8404(5)°.
	c = 16.0147(6) Å γ = 90.4651(5)°.
Volume	1899.52(14) Å^3
Z	4
Density (calculated)	1.862 Mg/m^3
Absorption coefficient	8.544 mm^{-1}
F(000)	1016
Crystal color	brown

Crystal size	0.44 x 0.25 x 0.04 mm^3
Theta range for data collection	1.69 to 28.77°
Index ranges	$-11 \leq h \leq 11$, $-18 \leq k \leq 19$, $-21 \leq l \leq 21$
Reflections collected	22727
Independent reflections	9062 [R(int) = 0.0198]
Completeness to theta = 25.50°	99.7 %
Absorption correction	Numerical
Max. and min. transmission	0.7542 and 0.1173
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9062 / 0 / 655
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I) = 7753 data]	R1 = 0.0178, wR2 = 0.0375
R indices (all data, 0.74Å)	R1 = 0.0257, wR2 = 0.0396
Largest diff. peak and hole	1.217 and -0.840 $e.Å^{-3}$

X-ray Data Collection, Structure Solution and Refinement for $\{[(C_5Me_5)_2U](\mu\text{-}\kappa^1\text{:}\kappa^2\text{-}CO_3)\}_6$, 7.

An orange crystal of approximate dimensions 0.136 x 0.218 x 0.373 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (35 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. Thee

systematic absences were consistent with the trigonal space groups $R3$ and $R\bar{3}$. The centrosymmetric space group $R\bar{3}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques[5]. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There was one molecule of benzene solvent present. The molecule and solvent were located about sites of $\bar{3}$ symmetry.

At convergence, wR2 = 0.0818 and Goof = 1.096 for 245 variables refined against 3759 data (0.83Å), R1 = 0.0292 for those 3355 data with I > 2.0σ(I).

Table S4. Crystal data and structure refinement for {[$(C_5Me_5)_2U$](μ-κ^1:κ^2-CO_3)}$_6$, 7.

Identification code	clw40 (Chris Webster)	
Empirical formula	C_{126} H_{180} O_{18} U_6 • C_6H_6	
Formula weight	3488.98	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	$R\bar{3}$	
Unit cell dimensions	a = 31.339(2) Å	α= 90°.
	b = 31.339(2) Å	β= 90°.
	c = 10.9920(8) Å	γ = 120°.
Volume	9349.4(15) Å^3	

Z	3
Density (calculated)	1.859 Mg/m^3
Absorption coefficient	7.830 mm^{-1}
F(000)	5022
Crystal color	orange
Crystal size	0.373 x 0.218 x 0.136 mm^3
Theta range for data collection	1.999 to 25.249°
Index ranges	$-37 \leq h \leq 37$, $-37 \leq k \leq 37$, $-13 \leq l \leq 13$
Reflections collected	30788
Independent reflections	3759 [R(int) = 0.0278]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2791 and 0.1612
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3759 / 0 / 245
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I) = 3355 data]	R1 = 0.0292, wR2 = 0.0765
R indices (all data, 0.83Å)	R1 = 0.0346, wR2 = 0.0818
Largest diff. peak and hole	4.202 and -0.609 $e.Å^{-3}$

X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_5)_2U]_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}O,O'\text{-}O_2CCH_2CH{=}CH_2)_2$, **10**.

A green crystal of approximate dimensions 0.20 x 0.24 x 0.31 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data

collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques[5]. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center.

At convergence, wR2 = 0.0332 and Goof = 1.097 for 254 variables refined against 5542 data (0.74Å), R1 = 0.0145 for those 5271 data with I > 2.0σ(I).

Table S3. Crystal data and structure refinement for $[(C_5Me_5)_2U]_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{-}O,O'\text{-}O_2CCH_2CH{=}CH_2)_2$, 10.

Identification code	clw44 (Chris Webster)	
Empirical formula	$C_{48}\ H_{70}\ O_4\ U_2$	
Formula weight	1187.10	
Temperature	83(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.7800(5) Å	α= 90°.
	b = 15.6266(9) Å	β=

102.8544(6)°.

	c = 15.0373(8) Å γ = 90°.
Volume	2240.5(2) $Å^3$
Z	2
Density (calculated)	1.760 Mg/m^3
Absorption coefficient	7.260 mm^{-1}
F(000)	1148
Crystal color	green
Crystal size	0.309 x 0.240 x 0.200 mm^3
Theta range for data collection	1.905 to 28.864°
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 21$, $-20 \le l \le 19$
Reflections collected	26491
Independent reflections	5542 [R(int) = 0.0159]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.3900 and 0.2249
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5542 / 0 / 254
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I) = 5271 data]	R1 = 0.0145, wR2 = 0.0328
R indices (all data, 0.74Å)	R1 = 0.0159, wR2 = 0.0332
Largest diff. peak and hole	0.589 and -0.563 $e.Å^{-3}$

References.

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