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A Bimetallic Uranium μ-Dicarbide Complex: Synthesis, X-ray Crystal Structure, and Bonding

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1 Synthetic Procedures

1.1 General Considerations

All manipulations were carried out at room temperature (23 °C) under an atmosphere of purified dinitrogen in a Vacuum Atmospheres MO-40M glove box or with a vacuum manifold using standard Schlenk techniques. Celite 545 (EM Science) and 4 Å molecular sieves were dried *via* storage in a 225 °C oven for 24 h followed by complete desiccation under dynamic vacuum at 210 °C for 48 h prior to use. Solvents were purified using a commercial Glass Contour solvent purification system constructed by SG Water USA (Nashua, NH USA), and were stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 and chloroform-*d* was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA USA). Prior to use, benzene-d_6 distilled from CaH_2, degassed with two freeze-pump-thaw cycles, and stored over activated 4 Å molecular sieves. Na[CCH] was obtained from Aldrich as an 18% (w/w) suspension in xylene/mineral oil. Prior to use, the Na[CCH] was washed with copious amounts of *n*-pentane and dried under reduced pressure to remove the hydrocarbon oil. The uranium(IV) iodide complex $IU(N[t\text{-}Bu]Ar)_3$ was prepared according to the literature method.[1] All glassware was oven-dried at a temperature of 225 °C prior to use.

Solution ^1H, $^{13}C\{^1H\}$, and ^{15}N NMR spectra were recorded on Varian Mercury-300 or Varian Inova-500 spectrometers at 20 °C. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to residual solvent ($C_6D_5\mathit{H}$ in C_6D_6, 7.16 ppm; C_6D_6, 128.29 ppm; $C\mathit{H}Cl_3$ in $CDCl_3$, 7.27 ppm; $\mathit{C}DCl_3$, 77.23 ppm). Raman spectra were collected at an excitation frequency of 785 nm via 180ą reflectance through the 10× objective of a Kaiser Optics Raman microscope. Infrared spectra were acquired using a Nicolet 6700 FT-IR spectrophotometer. Combustion analyses were performed by Columbia Analytical Laboratory (Santa Fe, NM USA).

1.2 Synthesis of $(\mu,\eta^1{:}\eta^1\text{-}C_2)[U(N[t\text{-}Bu]Ar)_3]_2$

A solution of $IU(N[t\text{-}Bu]Ar)_3$ (0.549 g, 0.612 mmol, 1 equiv) in THF (10 mL) was added to solid Na[CCH] (0.034 g, 0.708 mmol, 1.2 equiv). The resulting mixture was

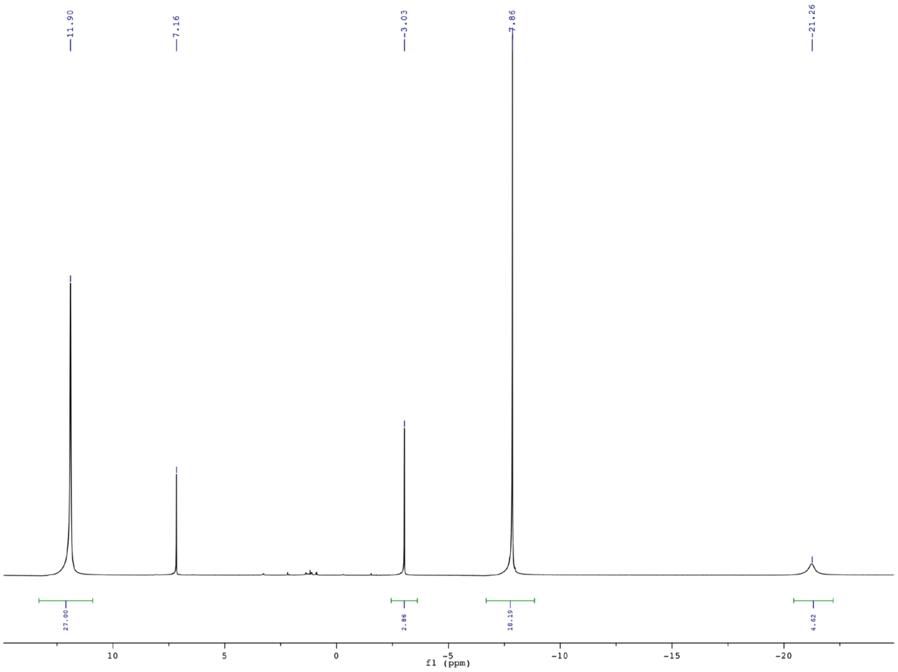

Figure 1: ^{1}H NMR spectrum (300 MHz, benzene-d_6)of (μ,η^1:η^1-C_2)[U(N[*t*-Bu]Ar)$_3$]$_2$.

allowed to stir overnight at ambient temperature. The mixture was then filtered through a plug of Celite and volatile materials were removed from the filtrate under reduced pressure. *n*-Hexane (5 mL) was added to and subsequently removed under reduced pressure from the residue that remained. Toluene (10 mL) was added and the resulting solution was filtered through a plug of Celite. Volatile materials were removed from the filtrate under reduced pressure. *n*-Pentane (5 mL) was added to the resulting residue, creating a suspension of the product (μ,η^1:η^1-C_2)(U(N[*t*-Bu]Ar)$_3$)$_2$. The suspension was cooled to -35 °C and the product was isolated by filtering the suspension through a medium frit. The isolated red-brown solids were washed with *n*-pentane (3 mL) and dried under reduced pressure (0.125 g, 26%). ^{1}H NMR (300 MHz, benzene-d_6): δ = 11.90 (s, 27H, NC(CH_3)$_3$), -3.03 (s, 3H, *p*-Ar*H*), -7.86 (s, 18H, *m*-ArCH_3), -21.26 (s, 6H, *o*-Ar*H*) ppm. Anal. calcd. for $C_{74}H_{108}N_6U_2$: C, 57.06; H, 6.99; N, 5.39%. Found: C, 56.92; H, 6.84; N, 5.13%. Single crystals of (μ,η^1:η^1-C_2)(U(N[*t*-Bu]Ar)$_3$)$_2$ were grown from a Et$_2$O/THF solution at -35 °C.

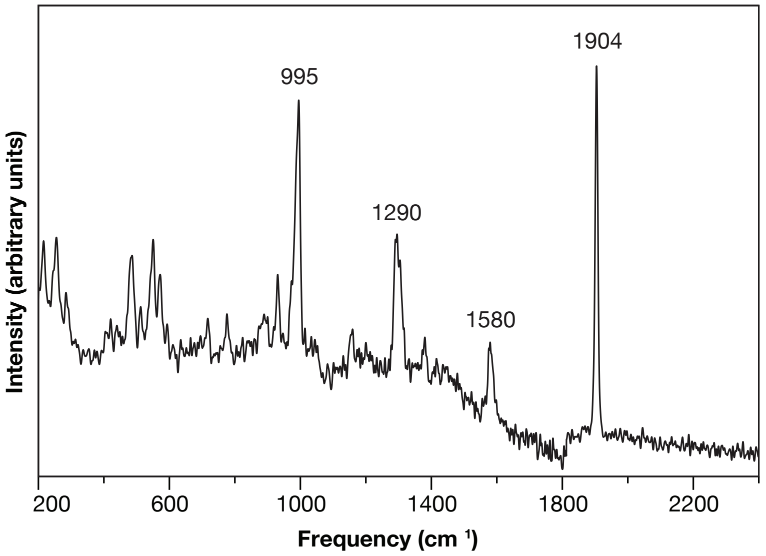

Figure 2: Raman spectrum of $(\mu,\eta^1{:}\eta^1\text{-}C_2)[U(N[t\text{-}Bu]Ar)_3]_2$.

2 X-Ray Structure Determination

2.1 General Considerations

Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex charge-coupled device (CCD) and a graphite-monochromated Mo Kα radiation beam (0.71073 Å). Diffraction data were collected by performing ϕ- and ω-scans. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SAINT+ (v6.45) and SHELXTL (v6.14) program suites.[2–5] The structure was solved by either direct methods or Patterson methods, in conjunction with standard Fourier difference techniques, and refined on F^2 by full-matrix least-squares procedures. A semi-empirical absorption correction was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed at calculated positions refined isotropically using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). Complete crystallographic data for $(\mu,\eta^1{:}\eta^1\text{-}C_2)[U(N[t\text{-}Bu]Ar)_3]_2\cdot\{(THF)_{0.5}(Et_2O)_{0.5}\}$ may be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC deposition number 770238) *via* the Internet at `http://www.ccdc.cam.ac.uk.data_request/cif` (or directly: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033).

The X-ray diffraction experiment was executed as follows: inside the glove box, crystals of **1** were removed from the mother liquor, then placed on a microscope slide and covered in a heavy hydrocarbon oil. The slide was removed from the glove box and placed within the optical field of a stereomicroscope. A suitable crystal was then selected and mounted on a nylon loop. The loop was then mounted on the goniometer under a flow of cold nitrogen gas. The crystal was centered in the X-ray beam and the crystal dimension were recorded. A frame exposure duration that maximized the observed signal-to-noise ratio was selected and data collection was initiated.

2.2 Details Regarding Structure Refinement

The crystal structure of (μ,η^1:η^1-C_2)[U(N[*t*-Bu]Ar)$_3$]$_2$ contains a molecule of THF and a molecule of Et_2O that were both placed in a PART-1 function and were both modeled at 25% occupancy. Strong rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances applied to both solvent molecules during the refinment process.[6,7]

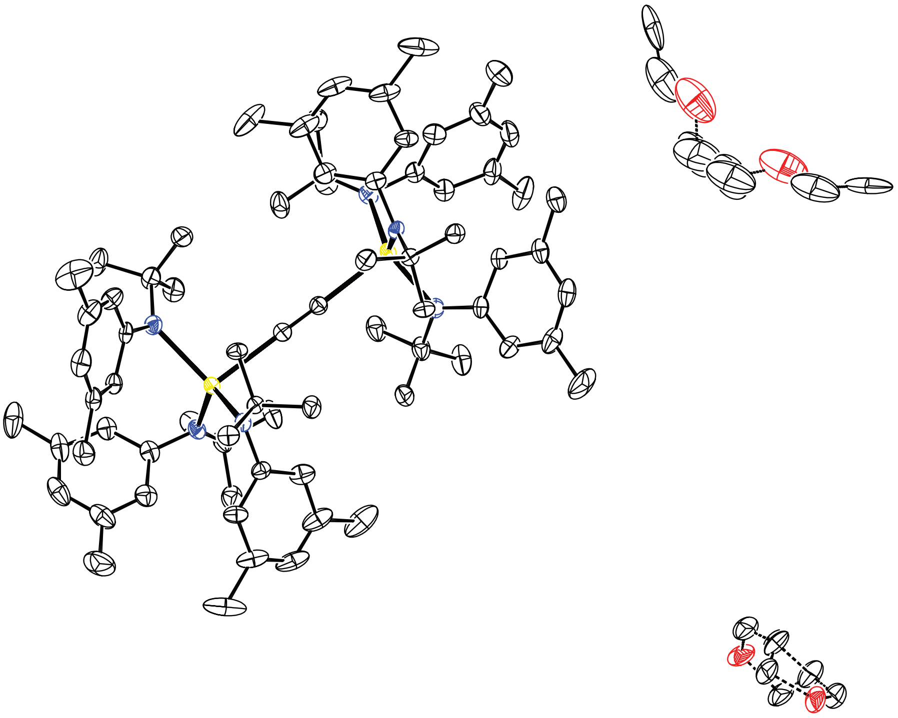

Figure 3: Structure of $(\mu,\eta^1{:}\eta^1\text{-C}_2)[\text{U(N}[t\text{-Bu]Ar)}_3]_2\cdot\{(\text{THF})_{0.5}(\text{Et}_2\text{O})_{0.5}\}$ with co-crystallized solvent shown. Thermal ellipsoids at 50% probability; hydrogen atoms have been omitted.

Table 1: Crystallographic data for **1**.

	$(\mu,\eta^1{:}\eta^1\text{-C}_2)[\text{U(N[}t\text{-Bu]Ar)}_3]_2\cdot\{(\text{Et}_2\text{O})_{0.5}(\text{THF})_{0.5}\}$
CCDC Deposition Number	770238
Empirical formula	$C_{78}H_{117}N_6OU_2$
Formula weight (g mol^{-1})	1630.84
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$C222_1$
Unit cell dimensions (Å, deg)	$a = 17.1923(13),\ \alpha = 90$
	$b = 124.0034(19),\ \beta = 90$
	$c = 20.6647(16),\ \gamma = 90$
Volume (Å^3)	8527.8(11)
Z	4
Density (calculated) (Mg m^{-3})	1.27
Absorption coefficient (mm^{-1})	3.833
$F(000)$	3276
Crystal size (mm^3)	$0.23 \times 0.21 \times 0.20$
Theta range for collection (deg)	1.76 to 26.97
Index ranges	$-23 \leq h \leq 33$
	$-33 \leq k \leq 33$
	$-29 \leq l \leq 28$
Reflections collected	84322
Independent reflections	11996 [$R_{int} = 0.0650$]
Completeness to $\theta_{\max}$ (%)	99.4
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5144 and 0.4726
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11996/523/448
Goodness-of-fit[a]	1.202
Final R indices [$I > 2\sigma(I)$[b]	$R_1 = 0.0411, wR_2 = 0.0954$
R indices (all data)[b]	$R_1 = 0.0497, wR_2 = 0.0982$
Largest diff. peak and hole (e Å^{-3})	1.733 and -2.081

[a] GooF = $\left[\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)}\right]^{\frac{1}{2}}$ [b] $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$; $wR_2 = \left[\frac{\Sigma[w(F_o^2-F_c^2)^2}{\Sigma[w(F_o^2)^2]}\right]^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(F_o^2)+(aP)^2+bP}$; $P = \frac{2F_c^2+\max(F_o^2,0)}{3}$

3 Computational Details

3.1 General Considerations

All calculations were performed using the ADF release 2009.01 program suite.[8] The relativistic ZORA option was employed. ZORA basis sets of triple zeta quality with two added polarization functions (TZ2P) in conjunction with large frozen core approximations were used for all atoms. The core electrons were modeled by invoking the “`core large`” keyword in the ADF input file. Geometry optimizations were carried out and energy differences determined using the local density approximation of Vosko, Wilk, and Nusair (LDA VWN)[9] together with the nonlocal gradient corrections of Becke and Perdew (GGA BP86)[10] for exchange and correlation respectively. No molecular symmetry constraints were applied to the model systems. The geometry optimization procedure was based on the method of Versluis and Ziegler.[11]

3.2 DFT Optimized Atomic Coordinates

3.2.1 $(\mu,\eta^1:\eta^1\text{-C}_2)[U(N[Me]Ph)_3]_2$

Table 2: Optimized atomic coordinates (Å) of $(\mu,\eta^1:\eta^1\text{-C}_2)(U(N[Me]Ph)_3)_2$.

Atom	*x*	*y*	*z*
U	−0.749795	2.841759	−12.492007
C	−0.141105	0.615172	−12.335090
N	0.071266	3.930594	−10.755267
C	−0.475921	5.239906	−10.671876
C	−1.622364	5.487601	−9.8921480
C	−2.218056	6.748171	−9.8820080
H	−3.109706	6.919642	−9.2797640
C	−1.683204	7.785548	−10.652270
C	−0.546726	7.555234	−11.430644
H	−0.129546	8.357378	−12.039481
C	0.057677	6.295602	−11.439131
C	1.219943	3.609963	−9.9139760
H	1.574834	2.596730	−10.153357
H	0.958150	3.626171	−8.8421300
H	2.056383	4.311887	−10.073200
N	0.063347	3.223731	−14.536065
C	1.280946	3.913639	−14.483060
C	2.334560	3.359067	−13.721629
C	3.540719	4.046761	−13.557905
H	4.346097	3.588419	−12.983931
C	3.737421	5.283396	−14.172474
C	2.706531	5.835483	−14.947043
H	2.851700	6.799906	−15.434766
C	1.495585	5.169110	−15.099922
H	0.129546	−8.357378	−12.039481
C	−0.057677	−6.295602	−11.439131
C	−1.219943	−3.609963	−9.9139760
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C	−3.540719	−4.046761	−13.557905
H	−4.346097	−3.588419	−12.983931
C	−3.737421	−5.283396	−14.172474
C	−2.706531	−5.835483	−14.947043
H	−2.851700	−6.799906	−15.434766
C	−1.495585	−5.169110	−15.099922
C	0.636028	−3.118638	−15.811447
H	1.611262	−2.636122	−15.655471
H	0.831288	−4.093131	−16.285347
H	0.064042	−2.497017	−16.519879
N	3.004770	−2.673953	−12.268100
C	3.712987	−3.354513	−13.251222
C	4.857739	−2.849493	−13.914363
C	5.450862	−3.565670	−14.951490
H	6.332235	−3.153932	−15.444210

Table 2: Optimized atomic coordinates (Å) of $(\mu,\eta^1:\eta^1\text{-C}_2)(\text{U(N[Me]Ph)}_3)_2$, continued.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C	−0.636028	3.118638	−15.811447	C	4.935136	−4.798472	−15.368750
H	−1.611262	2.636122	−15.655471	C	3.822748	−5.324534	−14.707313
H	−0.831288	4.093131	−16.285347	H	3.432965	−6.304310	−14.983136
H	−0.064042	2.497017	−16.519879	C	3.232750	−4.626649	−13.654918
N	−3.004770	2.673953	−12.268100	C	3.663176	−1.594810	−11.544448
C	−3.712987	3.354513	−13.251222	H	4.548587	−1.960363	−10.996913
C	−4.857739	2.849493	−13.914363	H	3.981884	−0.762785	−12.194080
C	−5.450862	3.565670	−14.951490	H	2.963049	−1.174089	−10.808386
H	−6.332235	3.153932	−15.444210	H	−2.040393	4.668804	−9.3070550
C	−4.935136	4.798472	−15.368750	H	−2.155468	8.767572	−10.649640
C	−3.822748	5.324534	−14.707313	H	0.945301	6.110688	−12.046361
H	−3.432965	6.304310	−14.983136	H	2.211597	2.346025	−13.329724
C	−3.232750	4.626649	−13.654918	H	4.688973	5.804200	−14.074579
C	−3.663176	1.594810	−11.544448	H	0.696873	5.620018	−15.688735
H	−4.548587	1.960363	−10.996913	H	−5.275805	1.889671	−13.615436
H	−3.981884	0.762785	−12.194080	H	−5.411427	5.351594	−16.177109
H	−2.963049	1.174089	−10.808386	H	−2.442183	5.112833	−13.074219
C	0.141105	−0.615172	−12.335090	H	2.040393	−4.668804	−9.3070550
U	0.749795	−2.841759	−12.492007	H	2.155468	−8.767572	−10.649640
N	−0.071266	−3.930594	−10.755267	H	−0.945301	−6.110688	−12.046361
C	0.475921	−5.239906	−10.671876	H	−2.211597	−2.346025	−13.329724
C	1.622364	−5.487601	−9.8921480	H	−4.688973	−5.804200	−14.074579
C	2.218056	−6.748171	−9.8820080	H	−0.696873	−5.620018	−15.688735
H	3.109706	−6.919642	−9.2797640	H	5.275805	−1.889671	−13.615436
C	1.683204	−7.785548	−10.652270	H	5.411427	−5.351594	−16.177109
C	0.546726	−7.555234	−11.430644	H	2.442183	−5.112833	−13.074219

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