SUPPORTING INFORMATION

Insights into the mechanism of carbonate formation through reductive cleavage of carbon dioxide with low-valent uranium centers

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Abstract. Low valent U(III) complexes $[((^{t\text{-Bu}}\mathrm{ArO})_3\mathrm{mes})\mathrm{U}]$ and $[((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}]$ react with CO_2 to form bridging carbonate complexes $[\{((^{t\text{-Bu}}\mathrm{ArO})_3\mathrm{mes})\mathrm{U}\}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-CO}_3)]$ and $[\{((^{\mathrm{Ad}}\mathrm{ArO})_3\mathrm{N})\mathrm{U}\}_2(\mu\text{-}\eta^1\text{:}\kappa^2\text{-CO}_3)]$. Uranium(IV) bridging oxo complexes have been determined to be the intermediate in these transformations.

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Experimental Section

General Methods. All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. All solvents were purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA) and transferred to the glovebox without exposure to air, unless otherwise indicated.

Magnetism data of crystalline powdered samples (20 - 30 mg) were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe (5 – 300 K for **2** and **3**) and (2 – 300 K for **4**). Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment (χ_{dia} = -654.09 × 10^{-6} cm^3 mol^{-1} (**2**), -1176.94 × 10^{-6} cm^3 mol^{-1} (**3**), -1324.26 × 10^{-6} cm^3 mol^{-1} (**4**)) by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition and purity by elemental analysis (C, H, and N) and ^{1}H NMR spectroscopy. Data reproducibility was also carefully checked on independently synthesized samples. ^{1}H NMR spectra were recorded on JEOL 270 and 400 MHz instruments operating at respective frequencies of 269.714 and 400.178 MHz with a probe temperature of 23 ºC in THF-d_8. Chemical shifts were referenced to protio solvent impurities (δ 7.15 (C_6D_6)) or (δ 1.73, 1.58 (THF-d_8)) and are reported in ppm. Electronic absorption spectra were recorded from 200 to 2000 nm (Shimadzu (UV-3101PC)) in the indicated solvent. Results from elemental analysis were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nürnberg (Erlangen, Germany) on Euro EA 3000.

Starting Materials. Precursor complexes [$(THF)_4UI_3$] and [$U(N(SiMe_3)_2)_3$] were prepared as described by Clark et al.[1] The tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine ligand was synthesized from a modified literature procedure.[2] Carbon dioxide (99.8+%) and 1-propanol, anhydrous (99.7%) were purchased from Aldrich. Nitrous oxide (≥99.998%) was purchased from Fluka. All were used as received. Anhydrous 1,2-dimethoxyethane (99.5%) was purchased from Aldrich and further dried by distilling over sodium benzophenone.

[1] L. R. Avens, S. G. Bott. D. L. Clark, A. P. Sattelberger, J. G. Watkin, B. D. Zwick, *Inorg. Chem.* 1994, **33**, 2248-2256; D. L. Clark, A. P. Sattelberger, R. A. Andersen, *Inorg. Synth.* 1997, **31**, 307-315; D. L. Clark, A. P. Sattelberger, S. G. Bott, R. N. Vrtis, *Inorg. Chem.* 1989, **28**, 1771-1773.

[2] S. A. Cortes, M. A. M. Hernandez, H. Takai, I. Castro-Rodríguez, K. Meyer, A. R. Fout, D. L. Miller, J. C. Huffman, D. J. Mindiola, *Inorg. Chem. Commun.* 2005, **8**, 903-907.

Synthesis of tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine. A one-neck Schlenk vessel was charged with 2-adamantyl-4-methylphenol (15.5 g, 0.064 mol), hexamethylenetetramine (1.38 g, 0.0098 mol), and p-toluenesulfonic acid monohydrate (0.64 g, 0.0034 mol). Under an outward nitrogen flow, anhydrous 1-propanol was introduced via a syringe. A condenser was fitted and the reaction mixture was allowed to reflux at 115 °C for 1 week. A 50/50 mixture of ethanol and ether was added to the Schlenk vessel containing white precipitate in a sticky yellow mother liquor. The resulting mixture was filtered (under air) through a frit to collect the fine white precipitate. The product was washed with ethanol (3 x 10 mL) and dried in vacuo. Yield: 3.6 g (0.0046 mol, 47%).

Synthesis of $[((^{Ad}ArO)_3N)U]$ (2). A solution of $[U(N(SiMe_3)_2)_3]$ (0.600 g, 0.83 mmol) in DME (8 mL) was added dropwise to a stirring suspension of tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine (0.625 g, 0.80 mmol) in DME (8 mL). The resulting brown reaction mixture was allowed to stir at room temperature for 2 hours, after which a bronze-brown precipitate emerges. The reaction was allowed to proceed for another hour. The mixture was filtered to collect the fine bronze-brown precipitate, washed two times with cold DME (5 mL, -35 °C), and dried in vacuo. Yield: 0.625 g (0.0057 mol, 71%). Elemental analysis (%) calcd for **2**, C 63.03, H 6.93, N 1.27; found, C 62.28, H 7.04, N 1.13.

Synthesis of $[\{((^{t\text{-}Bu}ArO)_3mes)U\}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}CO_3)]$ (3). A reaction vessel containing a solution of **1** (111 mg, 0.11 mmol) in benzene (6 mL) was charged with 1 atm CO_2 (balloon). After 5 minutes, the solution color changes from dark purple to yellow with light white precipitate. The resulting yellow solution was filtered and the volatiles were removed under vacuum to afford yellow solids. Yield: 98 mg, (0.0473 mmol, 87%). Elemental analysis (%) calcd for **3**, C 62.93, H, 7.27, N, 0.00; found C, 62.63, H, 7.31, N, 0.13.

Synthesis of $[\{((^{Ad}ArO)_3N)U\}_2(\mu\text{-}\eta^1\text{:}\kappa^2\text{-}CO_3)]$ (4). A reaction vessel containing a stirring suspension of **2** (200 mg, 0.18 mmol) in DME (10 mL) was charged with 1 atm of CO_2 (balloon). The bronze-brown reaction mixture immediately de-colors, and after 5 minutes, a green precipitate starts form. The reaction was allowed to proceed for 1 hour and then filtered to collect the green precipitate. The product was washed with DME (3 x 3 mL) and dried in vacuo.

Yield: 163 mg, (0.0718 mmol, 80%). Alternatively, complex **4** can be synthesized from treating an orange solution of **5** (150 mg, 0.067 mmol) in DME (10 mL) with excess CO_2. The resulting green precipitate is filtered and worked up as previously described. Yield: 108 mg, (0.0476 mmol, 71%). Elemental analysis (%) calcd for **4**, C 61.89, H 6.75, N 1.23; found, C 61.36, H 6.98, N 1.09.

Synthesis of [{((${}^{t\text{-Bu}}$ArO)$_3$mes)U}$_2$(*μ*-O)] (5). A 50 mL Schlenk tube containing a benzene solution of [((${}^{t\text{-Bu}}$ArO)$_3$mes)U] (121 mg, 0.120 mmol) in benzene (6 mL) was charged with N_2O gas while stirring at room temperature. Within 5 minutes, the dark purple solution turns brown. The resulting brown solution was filtered and the volatiles were removed under vacuum to afford a dark green solid, which was washed with cold Et_2O to obtain pale green solids. Yield: 51 mg, (0.0250 mmol, 42%). Elemental analysis (%) calcd for **5**, C 63.70, H 7.42, N 0.00; found, C 63.65, H 7.24, N 0.00.

Synthesis of [{((^{Ad}ArO)$_3$N)U}$_2$(*μ*-O)] (6). A reaction vessel containing a stirring suspension of **2** (200 mg, 0.18 mmol) in DME (10 mL) was charged with 1 atm of N_2O (balloon). The reaction solution immediately turns orange, with light white precipitate. The reaction was allowed to proceed for 1 hour. The resulting mixture was filtered to remove the white precipitate. The mother liquor was concentrated and over a few days, crystals of **6** can be collected. Yield: 157 mg, (0.0705 mmol, 78%). Elemental analysis (%) calcd for **6**, C 62.58, H 6.88, N 1.26; found, C 62.82, H 6.93, N 1.28.

X-Ray Crystal Structure Data

Table S1. Selected bond distances for molecular structures of **2**, **3**, **4**, and **6**.

Compounds	**2**	**3**	**4**	**6**
U1—N1	2.622(4) Å	-	2.586(6) Å	2.550(4) Å
U2—N2	-	-	2.561(6) Å	2.550(4) Å
U1—arene$_{\text{cntr}}$	-	2.594 Å	-	-
U2—arene$_{\text{cntr}}$	-	2.608 Å	-	-
U1—O$_{\text{Ar avg.}}$	2.222(4) Å	2.146(3) Å	2.178(6) Å	2.206(3) Å
U2—O$_{\text{Ar avg.}}$	-	2.146(4) Å	2.162(6) Å	2.206(3) Å
U1—O$_{\text{DME}}$	2.656(3) Å	-	2.706(6) Å	2.667(13) Å
U1—O$_{\text{DME}}$	2.621(3) Å	-	2.592(6) Å	2.945(5) Å
U2—O$_{\text{DME}}$	-	-	2.613(6) Å	2.404(18) Å
U2—O$_{\text{DME}}$	-	-	2.668(6) Å	-
U1—O$_{\mu}$	-	-	-	2.1036(2) Å
U2—O$_{\eta}$	-	-	2.210(6) Å	-
U1—C$_{\text{CO3}}$	-	-	2.801(9) Å	-
C—O$_{\text{CO3}}$	-	1.285(6) Å	1.263(10) Å	-
C— O$_{\text{CO3}}$	-	1.279(7) Å	1.281(10) Å	-
C— O$_{\text{CO3}}$	-	1.305(6) Å	1.305(11) Å	-
U1—O$_{\kappa}$	-	2.332(3) Å	2.414(6) Å	-
U1—O$_{\kappa}$	-	2.659(4) Å	2.439(6) Å	-
U2—O$_{\kappa}$	-	2.603(4) Å	-	-
U2—O$_{\kappa}$	-	2.333(4) Å	-	-

Crystallographic Details for 2. Brown plates of **2**, grown from a concentrated solution of DME at room temperature, were coated with isobutylene oil on a microscope slide. Intensity data were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects, semi-empirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[1] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using *SHELXTL NT* 6.12.[2] The $(^{Ad}ArO)_3N$ ligand is subjected to rotational disorder around the central U-N axis. Two preferred orientations were refined resulting in occupancies of 83.9(9) % for the major component and 16.1(3) % for the minor component (denoted by an additional A). SIMU, ISOR, SADI and FLAT restraints were applied in the refinement of the disordered structure parts. All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5.

Crystallographic Details for 3. Yellow needles of **3**, grown from layering ether on top of a toluene solution at room temperature, were coated with isobutylene oil on a microscope slide. Intensity data were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[1] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using *SHELXTL NT* 6.12.[2] The compound crystallizes with one molecule of toluene and 1.5 molecules of diethylether per formula unit. SIMU restraints were applied in the refinement of the solvent molecules and of two of the *t*-Bu groups of the ligand (C51 – C54 and C105 – C108). All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5.

Crystallographic Details for 4. Green blocks of **4**, grown from a concentrated solution of DME at room temperature, were coated with isobutylene oil on a microscope slide. Intensity data were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[1] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using *SHELXTL NT* 6.12.[2] The compound crystallizes with a total of three molecules of DME, one of which is disordered over two independent sites that are occupied by approximately 50 % each. SAME, SIMU and ISOR restraints were applied in the refinement of the solvent molecules. All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5.

Crystallographic Details for 6. Yellow-orange blocks of **6**, grown from a concentrated solution of DME at room temperature, were coated with isobutylene oil on a microscope slide. Intensity data were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[1] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using *SHELXTL NT* 6.12.[2] The complex molecule is situated on a crystallographic twofold rotation axis. Disorder is observed for the DME co-ligand that is coordinating one of the two uranium centers with two and the other uranium center with only one oxygen donor atom. One of the adamantyl groups is disordered. Two alternative orientations were refined resulting in occupancies of 76.6(4) % for C34 – C42 and 23.4(4) % for C34A – C42A. SIMU and SADI restraints were applied in the refinement of this disorder. The compound crystallizes with a total of three molecules of DME per formula unit one of which is situated on crystallographic twofold rotation axis. All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5.

Crystal data and structure refinement for 2.

Identification code	opl0911
Empirical formula	$C_{62}H_{86}NO_7U$
Formula weight	1195.35
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.672(2) Å alpha = 90°
	b = 11.219(2) Å beta = 94.067(8)°
	c = 38.622(3) Å gamma = 90°
Volume	5477.0(14) Å^3
Z, Calculated density	4, 1.450 Mg/m^3
Absorption coefficient	3.017 mm^{-1}
F(000)	2452
Crystal size	0.31 x 0.18 x 0.08 mm^3
Theta range for data collection	3.14° to 27.10°
Limiting indices	-16<=h<=16, -14<=k<=14, -49<=l<=48
Reflections collected / unique	57996 / 11997 [R(int) = 0.0860]
Completeness to theta = 27.10°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.790 and 0.581
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11997 / 394 / 834
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.0816
R indices (all data)	R1 = 0.0809, wR2 = 0.0911
Largest diff. peak and hole	1.189 and -1.153 e.Å^{-3}

Crystal data and structure refinement for 3.

Identification code	sd0803	
Empirical formula	$C_{122}H_{173}O_{10.5}U_2$	
Formula weight	2283.66	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)	
Unit cell dimensions	a = 17.4828(18) Å	alpha = 90°
	b = 25.766(2) Å	beta = 90°
	c = 25.784(2) Å	gamma = 90°
Volume	11614.7(17) $Å^3$	
Z, Calculated density	4, 1.306 Mg/m^3	
Absorption coefficient	2.840 mm^{-1}	
F(000)	4692	
Crystal size	0.30 x 0.07 x 0.06 mm^3	
Theta range for data collection	3.16° to 27.10°	
Limiting indices	-22<=h<=21, -30<=k<=32, -32<=l<=32	
Reflections collected / unique	116536 / 25130 [R(int) = 0.0818]	
Completeness to theta = 27.10°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.843 and 0.572	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25130 / 193 / 1278	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0706	
R indices (all data)	R1 = 0.0824, wR2 = 0.0798	
Absolute structure parameter	0.011(4)	
Largest diff. peak and hole	1.339 and -0.764 e.$Å^{-3}$	

Crystal data and structure refinement for 4.

Identification code	opl0917
Empirical formula	$C_{129}H_{182}N_2O_{19}U_2$
Formula weight	2540.83
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 22.680(3) Å alpha = 90° b = 24.539(4) Å beta = 116.041(9)° c = 25.430(8) Å gamma = 90°
Volume	12716(5) Å ^{3}
Z, Calculated density	4, 1.327 Mg/m^3
Absorption coefficient	2.606 mm^{-1}
F(000)	5224
Crystal size	0.28 x 0.24 x 0.20 mm^3
Theta range for data collection	3.32° to 26.37°
Limiting indices	-28<=h<=28, -30<=k<=30, -31<=l<=31
Reflections collected / unique	152032 / 25808 [R(int) = 0.0655]
Completeness to theta = 26.37°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0 and 0.691
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	25808 / 261 / 1439
Goodness-of-fit on F^2	1.245
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1245
R indices (all data)	R1 = 0.1143, wR2 = 0.1619
Largest diff. peak and hole	3.990 and -2.498 e.Å $^{-3}$

Crystal data and structure refinement for 6.

Identification code	opl0941
Empirical formula	$C_{128}H_{182}N_2O_{17}U_2$
Formula weight	2496.82
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 32.734(2) Å alpha = 90° b = 15.847(2) Å beta = 92.575(8)° c = 22.159(3) Å gamma = 90°
Volume	11483(2) Å^3
Z, Calculated density	4, 1.444 Mg/m^3
Absorption coefficient	2.883 mm^{-1}
F(000)	5136
Crystal size	0.32 x 0.28 x 0.20 mm^3
Theta range for data collection	3.37° to 27.10°
Limiting indices	-41<=h<=41, -19<=k<=20, -28<=l<=28
Reflections collected / unique	78453 / 12648 [R(int) = 0.0721]
Completeness to theta = 27.10°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.562 and 0.461
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12648 / 290 / 822
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0590
R indices (all data)	R1 = 0.0924, wR2 = 0.0746
Largest diff. peak and hole	2.413 and -1.596 e.Å^{-3}

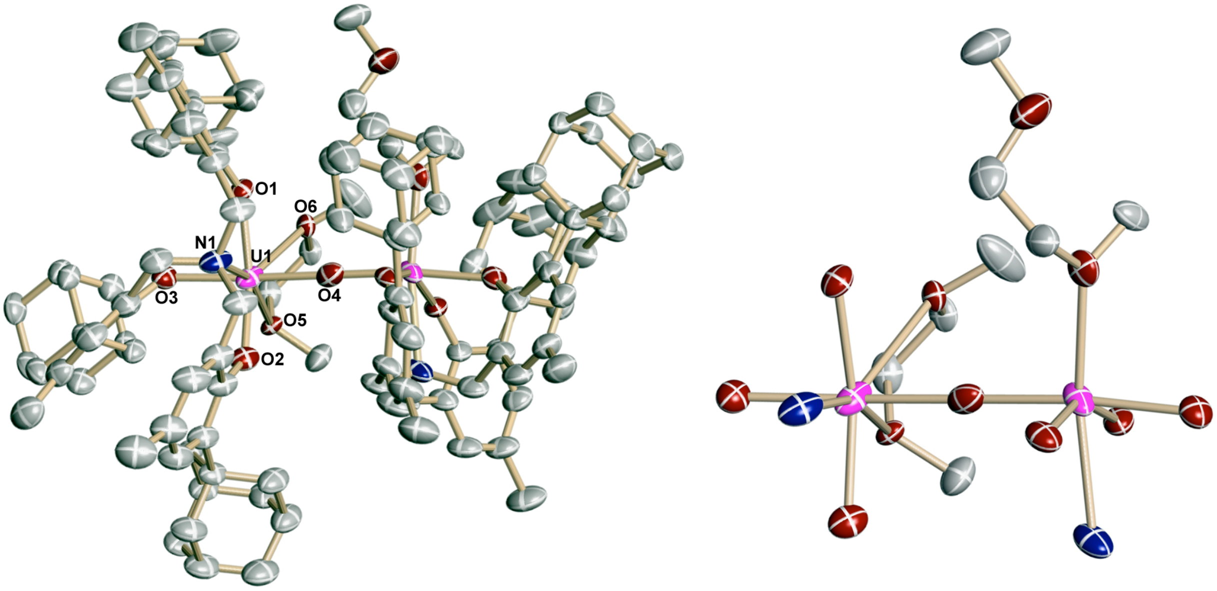


Figure S1. Molecular structure of complex **6** and core. Thermal ellipsoids are drawn at 50% probability.

References

[1] *SADABS 2.06*, Bruker AXS, Inc., **2002**, Madison WI., U.S.A.
[2] *SHELXTL NT 6.12*, Bruker AXS, Inc., **2002**, Madison WI., U.S.A.

Spectroscopic Data

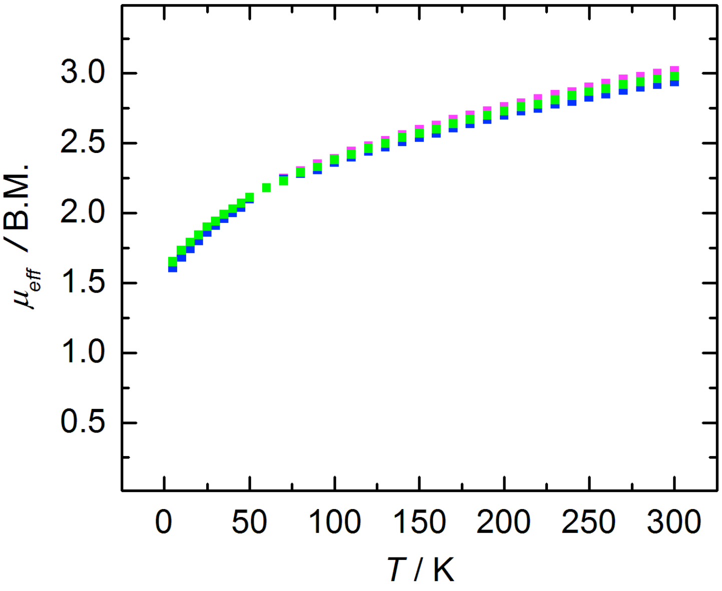


Figure S2. Temperature-dependent SQUID magnetization data (at 1 T) of U(III) complex $[((^{Ad}ArO)_3N)U]$ (**2**) plotted as a function of magnetic moment (μ_{eff}) vs. temperature (T). The plot shows three data sets measured on three independently synthesized samples. Data were corrected for underlying diamagnetism.

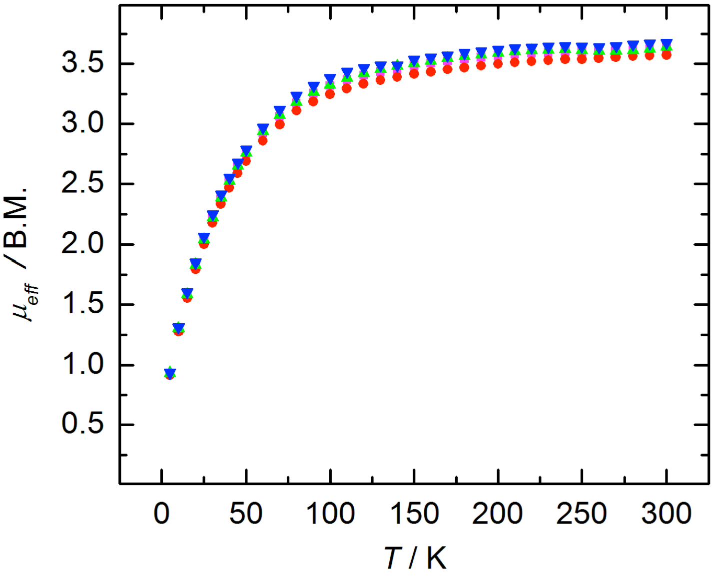


Figure S3. Temperature-dependent SQUID magnetization data (at 1 T) of U(IV)/U(IV) dinuclear complex $[\{((^{t\text{-}Bu}ArO)_3mes)U\}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}CO_3)]$ (**3**) plotted as a function of magnetic moment (μ_{eff}) vs. temperature (T). The plot shows three data sets measured on three independently synthesized samples. Data were corrected for underlying diamagnetism.

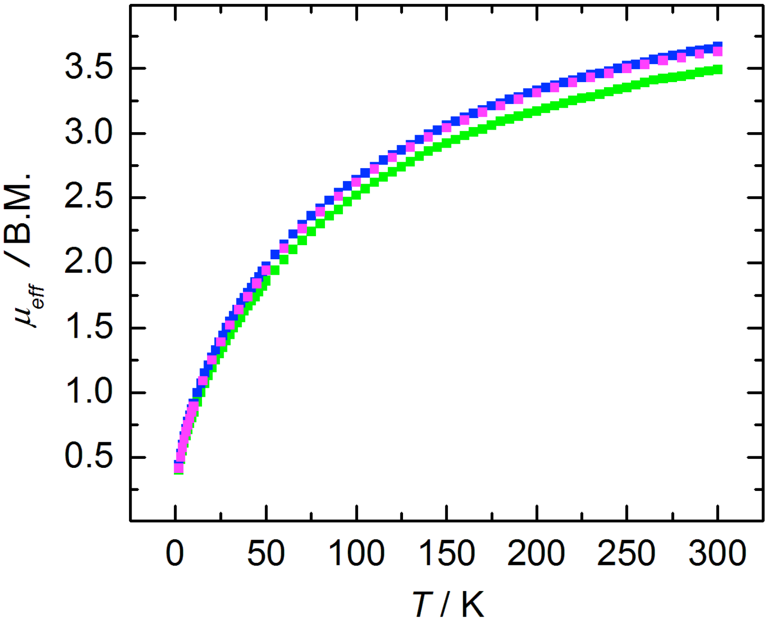


Figure S4. Temperature-dependent SQUID magnetization data (at 1 T) of U(IV)/U(IV) dinuclear complex [{((^{Ad}ArO)$_3$N)U}$_2$(μ-η^1:κ^2-CO$_3$)] (**4**) plotted as a function of magnetic moment (μ_{eff}) vs. temperature (T). The plot shows three data sets measured on three independently synthesized samples. Data were corrected for underlying diamagnetism.

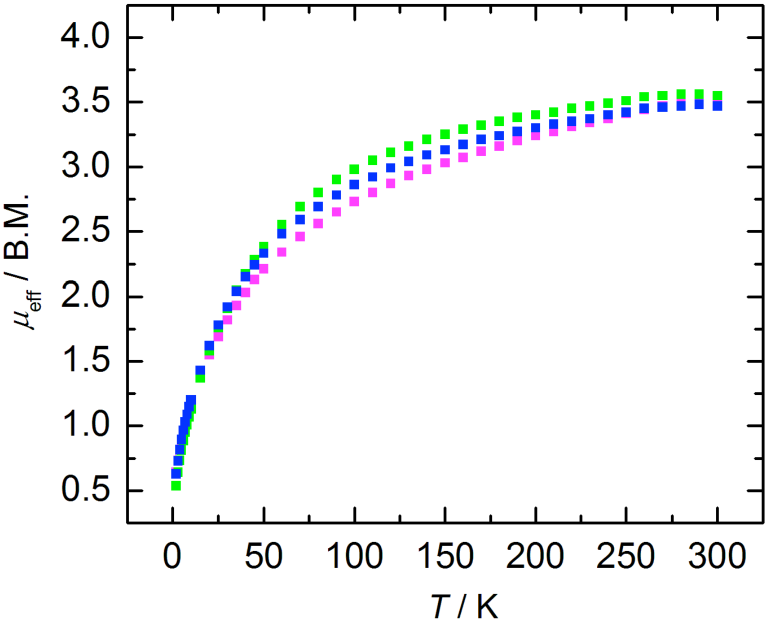


Figure S5. Temperature-dependent SQUID magnetization data (at 1 T) of U(IV)/U(IV) dinuclear complex [{((^{Ad}ArO)$_3$N)U}$_2$(μ-O)] (**6**) plotted as a function of magnetic moment (μ_{eff}) vs. temperature (T). The plot shows three data sets measured on three independently synthesized samples. Data were corrected for underlying diamagnetism.

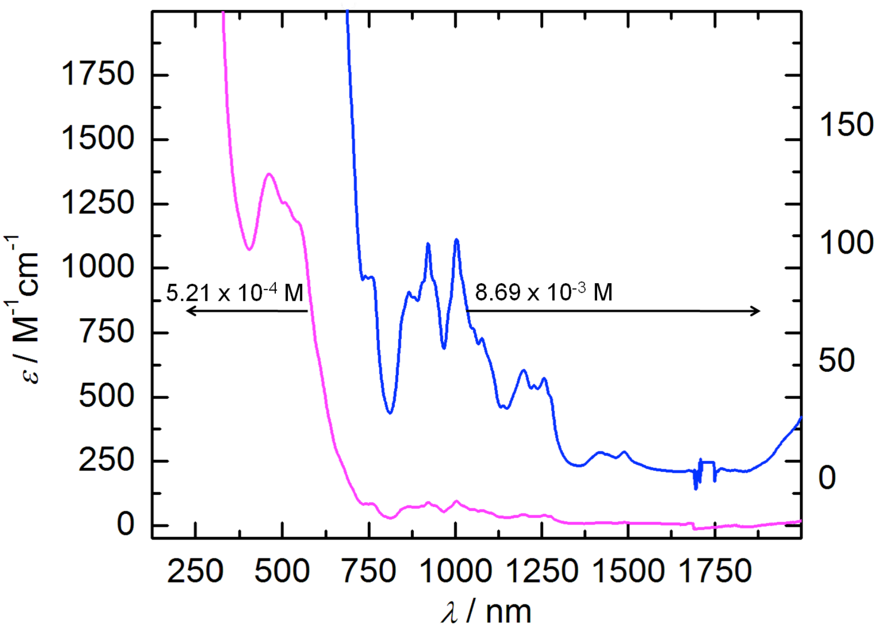


Figure S6. Electronic absorption spectrum of U(III) complex [((^{Ad}ArO)$_3$N)U] (**2**) recorded at two different concentrations, (5.21 x 10^{-4} M, magenta; 8.69 x 10^{-3} M, blue) in tetrahydrofuran from 200 to 2000 nm.

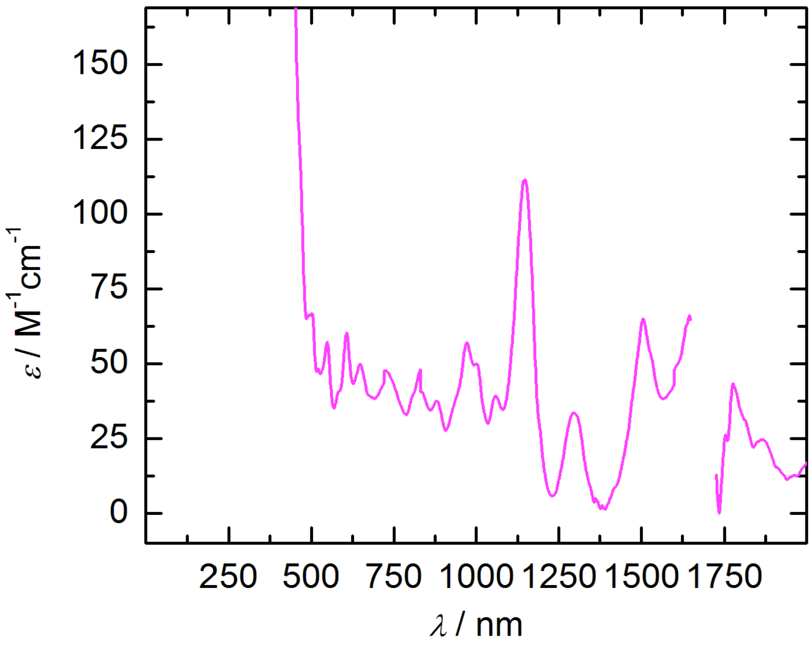


Figure S7. Electronic absorption spectrum of U(IV)/U(IV) dinuclear complex [{((${}^{t\text{-}Bu}$ArO)$_3$mes)U}$_2$(μ-κ^2:κ^2-CO$_3$)] (**3**) recorded in toluene from 200 to 2000 nm.

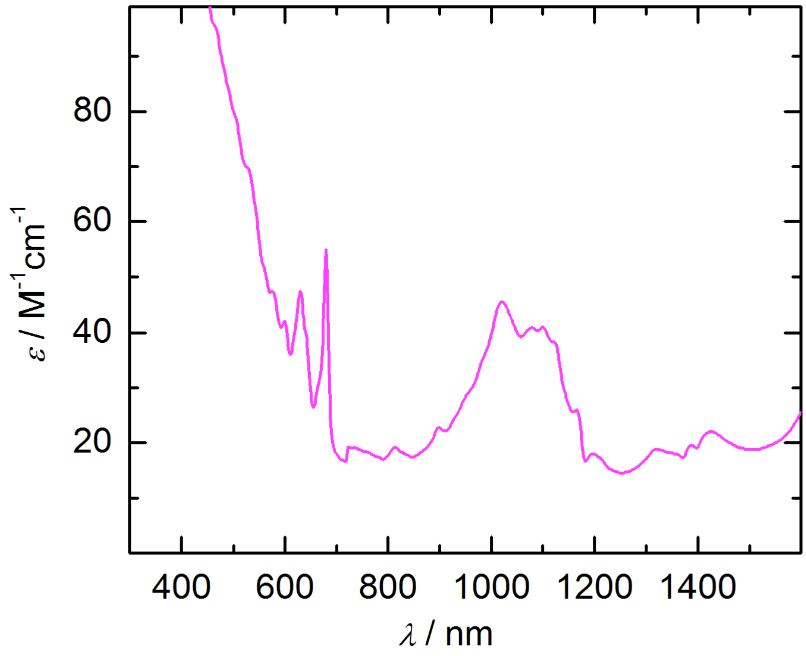


Figure S8. Electronic absorption spectrum of U(IV)/U(IV) dinuclear complex [{((^{Ad}ArO)$_3$N)U}$_2$(μ-η^1:κ^2-CO$_3$)] (**4**) recorded in tetrahydrofuran from 300 to 2000 nm.

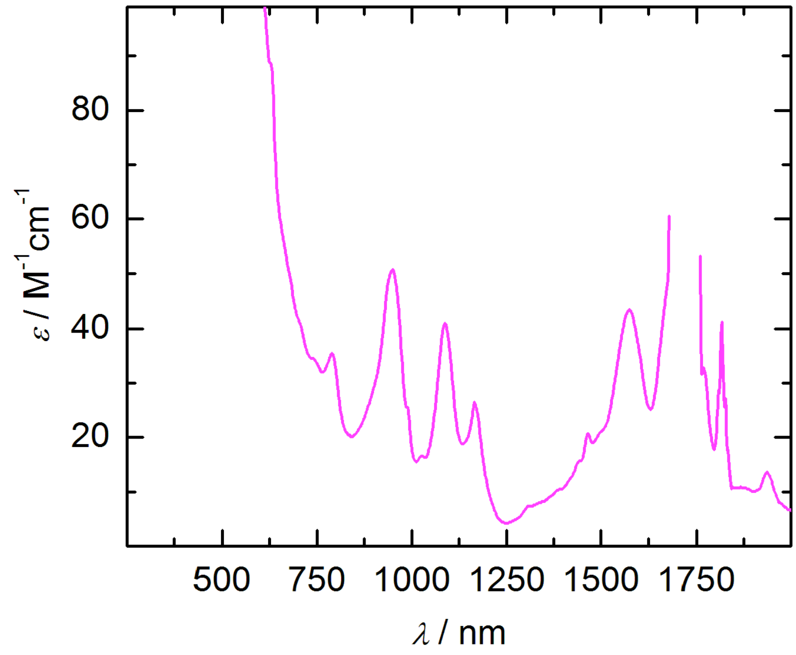


Figure S9. Electronic absorption spectrum of U(IV)/U(IV) dinuclear complex [{((^{Ad}ArO)$_3$N)U}$_2$(μ-O)] (**6**) recorded in tetrahydrofuran from 250 to 2000 nm.

Carbon Monoxide Detection

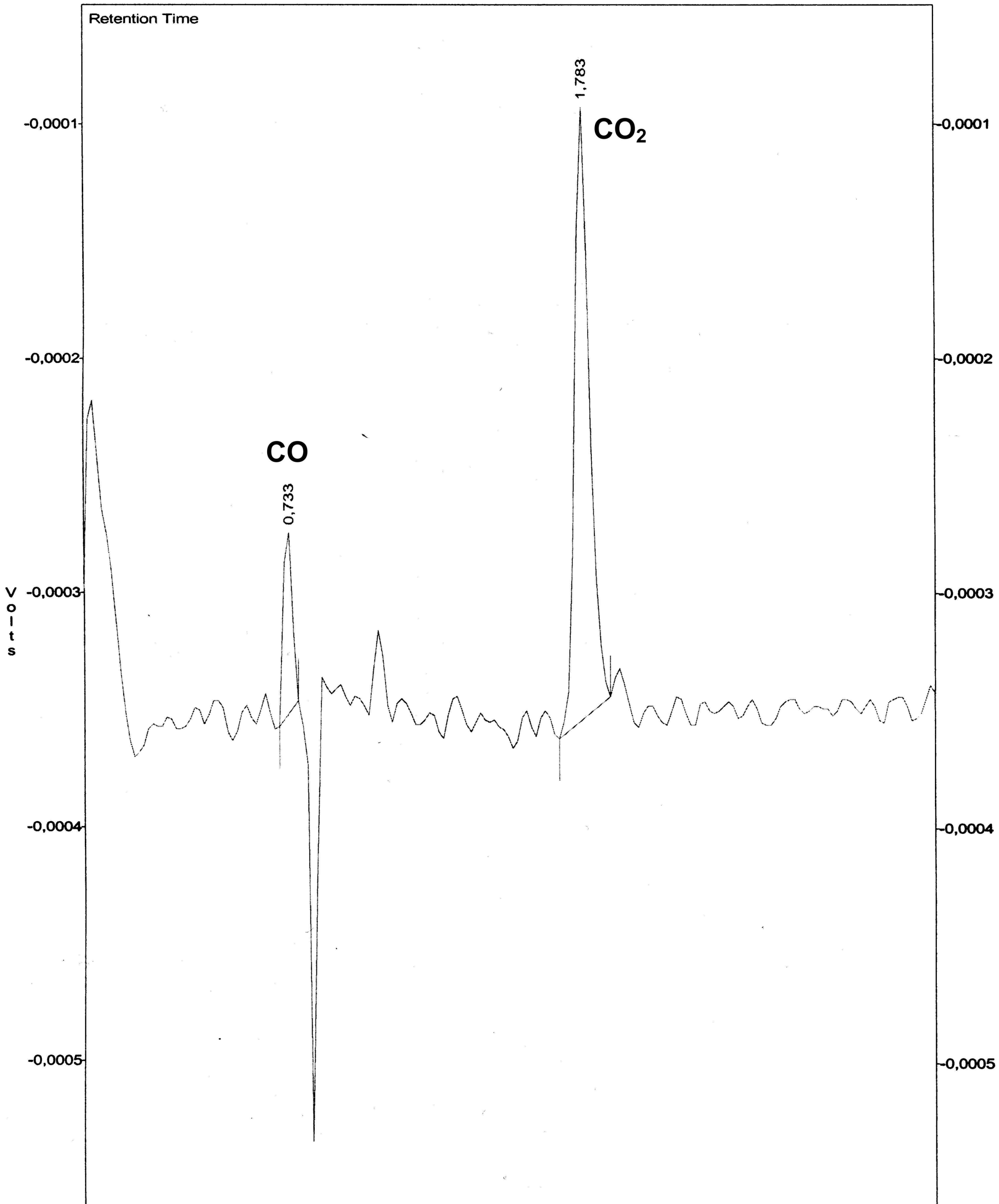


Figure S10. GC-TCD chromatogram of the head space from the reaction of **2** with CO_2 to form **4** with liberation of CO (retention time = 0.733 min (peak), 0.815 min (trough)) at 70 °C. The reaction was done on a 400 mg scale of **2**, with an injection volume of 250 µL. Excess carbon dioxide is detected (retention time = 1.783 min) along with carbon monoxide.

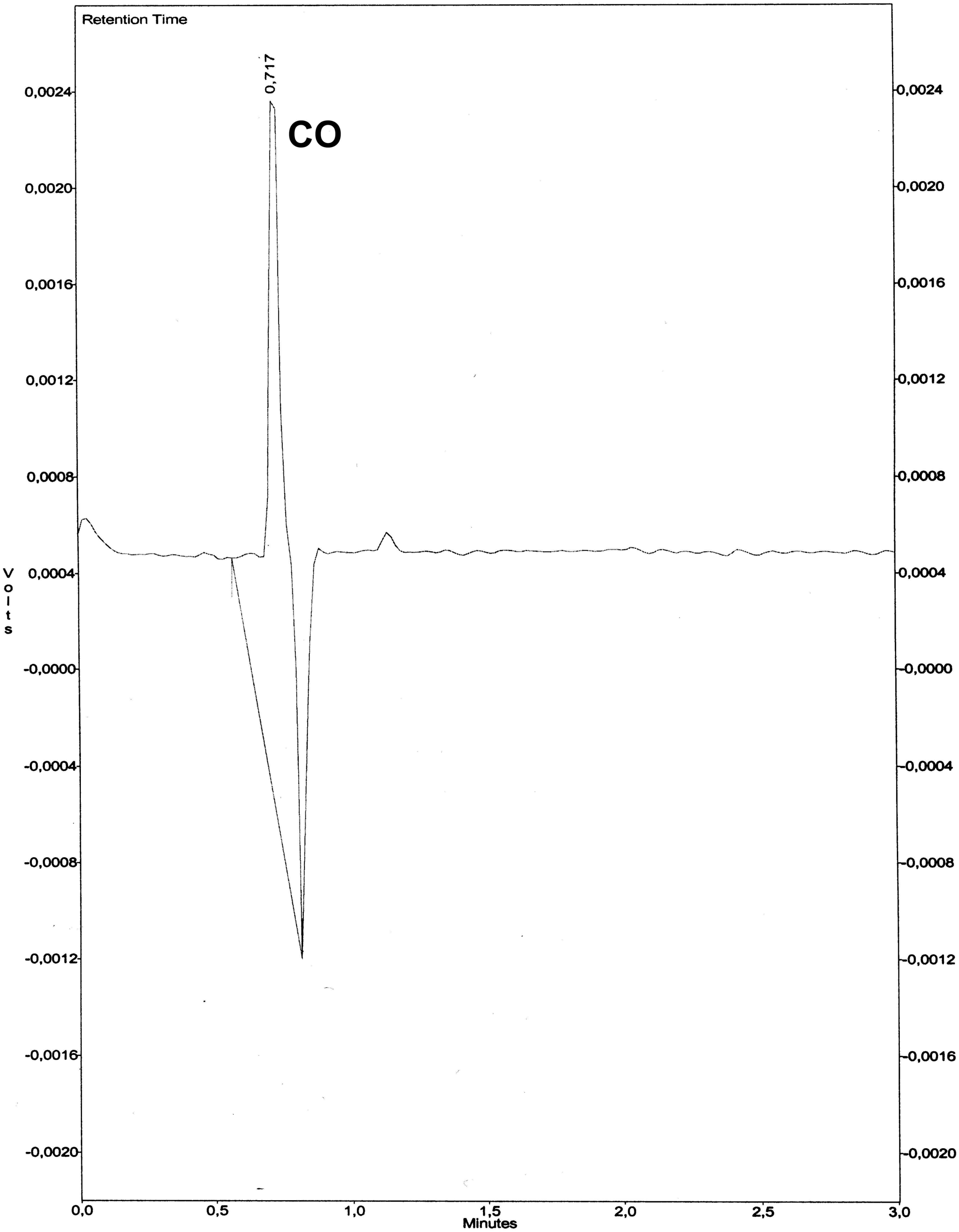


Figure S11. Control experiment: GC-TCD chromatogram of carbon monoxide (>99.99%, 10 vol% in dinitrogen) at 70 °C with an injection volume of 250 µL (retention time = 0.717 min).

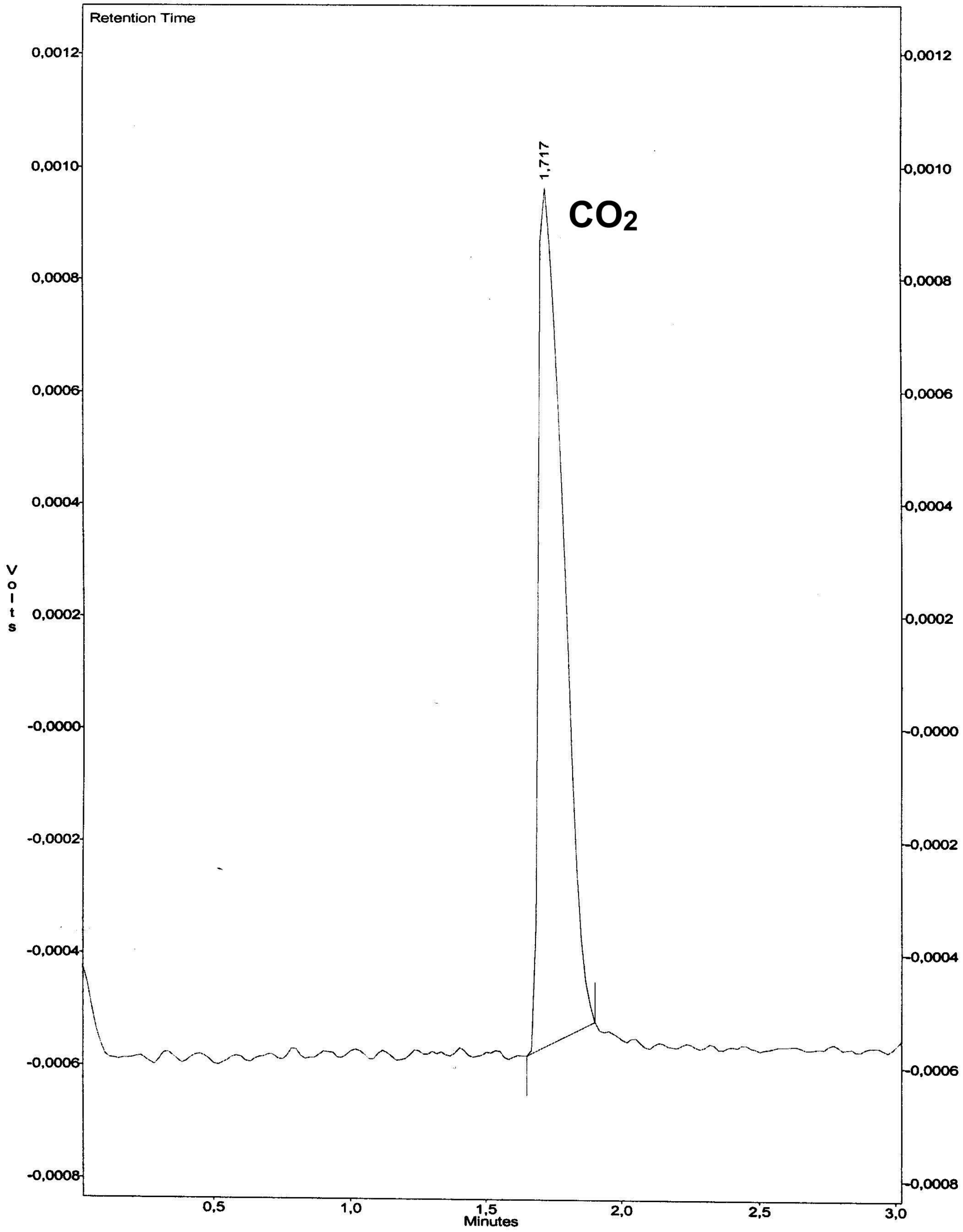
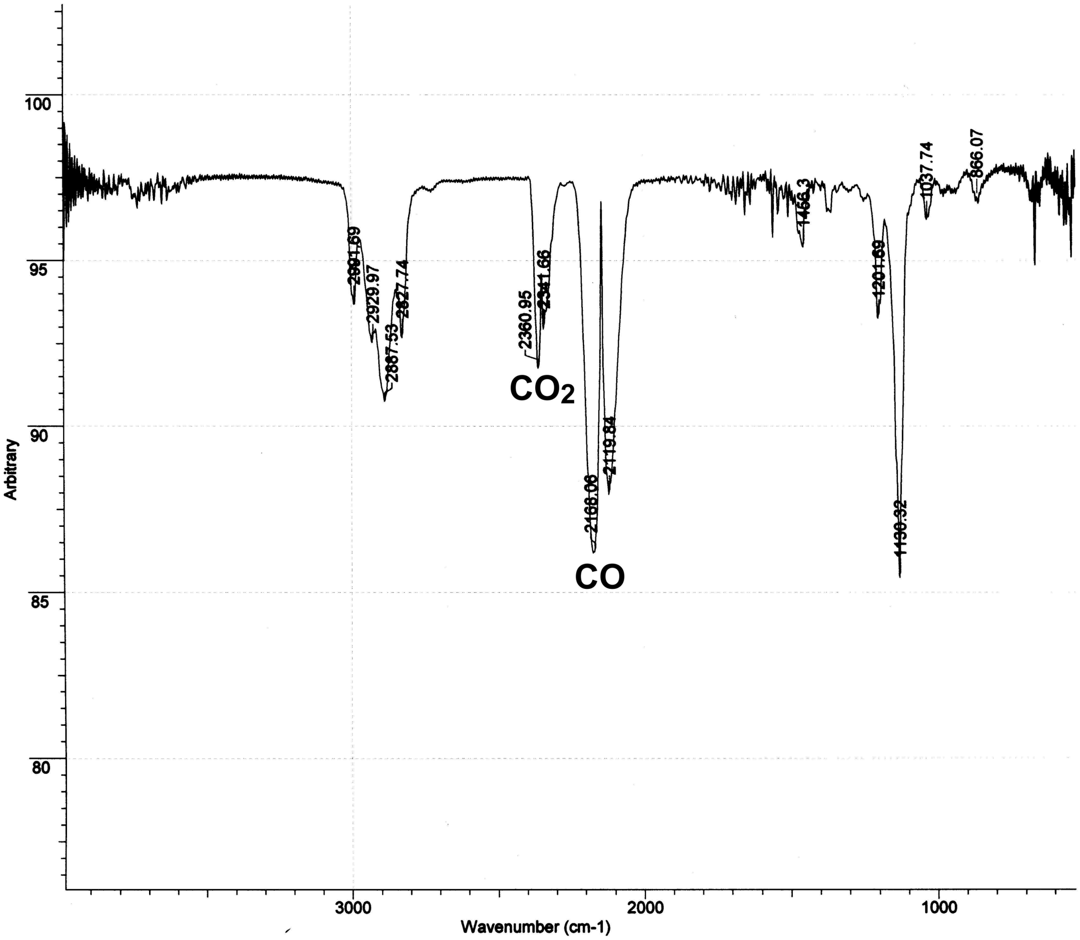


Figure S12. Control experiment: GC-TCD chromatogram of carbon dioxide (99.8+%, 10 vol% in dinitrogen) used in syntheses of **3** and **4** at 70 °C with an injection volume of 250 μL (1.717 min); no CO is present.

4594-LKT

22 Dec 2009

File Name	J:\UCO3U-OANH-2009.TXT			**Date**	22 Dec 2009 18:05:00
Technique	Infrared	**Spectral Region**	IR	**X Axis**	Wavenumber (cm-1)
Y Axis	Arbitrary	**Spectrum Range**	399.2782 - 4000.4972	**Points Count**	1868
Data Spacing	1.9289				



No	cm-1	Arbitrary	Intensity
1	866.07	96.916	W
2	1037.74	96.260	W
3	1130.32	85.458	W
4	1201.69	93.270	W
5	1456.30	95.408	W
6	2119.84	87.976	W
7	2168.06	86.220	W
8	2341.66	92.975	W
9	2360.95	91.759	W
10	2827.74	92.692	W
11	2887.53	90.754	W
12	2929.97	92.538	W
13	2991.69	93.683	W

Figure S13. Gas phase IR spectrum of the head space from the reaction of **2** with CO_2 to form **4** with liberation of CO (2168.06 cm^{-1}, 2119.84 cm^{-1}) taken with dinitrogen as the background. Excess carbon dioxide stretches are also observed (2360.95 cm^{-1}, 2341.66 cm^{-1}).