Homologation and functionalization of carbon monoxide by a recyclable uranium complex

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Carbon monoxide (CO) is in principle an excellent resource from which to produce industrial hydrocarbon feedstocks as alternatives to crude oil; however, CO has proven remarkably resistant to selective homologation, and the few complexes that can effect this transformation cannot be recycled because liberation of the homologated product destroys the complexes or they are substitutionally inert. Here, we show that under mild conditions a simple triamidoamine uranium(III) complex can reductively homologate CO and be recycled for reuse. Following treatment with organosilyl halides, bis(organosiloxy)acetylenes, which readily convert to furanones, are produced, and this was confirmed by the use of isotopically ^{13}C-labeled CO. The precursor to the triamido uranium(III) complex is formed concomitantly. These findings establish that, under appropriate conditions, uranium(III) can mediate a complete synthetic cycle for the homologation of CO to higher derivatives. This work may prove useful in spurring wider efforts in CO homologation, and the simplicity of this system suggests that catalytic CO functionalization may soon be within reach.

reduction | C-C coupling | ethyne diolate | antiferromagnetic exchange coupling

The continued growth and stability of the global economy requires the ready availability of petrochemical feedstocks, but uncertainty in cost and supply, underscored by the energy crisis in the 1970s, has driven the demand for developing alternative sources (1). CO is readily produced by steam reforming reactions and is, thus, an abundant resource that can be used in the production of bulk hydrocarbon feedstocks (2). The concept of directly homologating CO is very appealing, but the triple bond in CO is very strong with a bond energy of ~257 kcal mol^{-1}, and direct dimerization of CO to O = C = C = O is highly unfavorable with $\Delta G^{\circ}_{298\ K} \approx +73$ kcal mol^{-1} (3). Although direct 1,1-migratory insertion of CO into an organometallic M-R bond to give M-C(O)R is a favorable process for many metals (4) and a key step in industrially important C-C bond formation reactions, e.g., hydroformylation (5), double insertion to give M-C(O)C(O)R is usually energetically unfeasible, but it has been documented (6–8). Thus, processes involving CO can require energy intensive reaction conditions and give varied product distributions that render them economically uncompetitive overall when crude oil remains readily available; however, combining the coupling of CO with reduction results in a thermodynamically feasible process to give a family of oxocarbon dianions $C_nO_n^{2-}$ (n = 2–6), including the reductively dimerized ethyne diolate $^{-}$O-C ≡ C-O^{-}, as building blocks for more complex and value-added organic molecules (9).

Molten potassium can effect reductive oligomerization of CO, but the resulting ill-defined salts are thermally unstable and shock-sensitive (10). CO can be electrochemically homologated, but an overpressure of 100–400 bar of CO is required (11). Very few transition metal complexes mediate the reductive coupling of CO (12–17); though, the coupled product could be hydrogenated to free alkene in 60% yield in the presence of hydrogenation cocatalysts such [Rh(PPh$_3$)$_3$Cl] or Pd/C, or under 100 psi of hydrogen, no viable metal complex could be recycled for reuse (14, 15). Conversion of CO to allene has been demonstrated, but five steps are required to close a multicomponent H_2/CO/benzyl/Me_3SiOTf/Me_3SiCl/$PhCH_2MgCl$ synthetic cycle (18). The high reduction potentials of low valent f-element complexes suggests a promising approach for the reductive activation of C_1-small molecules such as CO (19–22) and CO_2 (23); however, only a handful of f-element complexes can affect the reductive homologation of CO under ambient conditions (24, 25). Organometallic uranium complexes can effect reductive homologation of CO to C_n-oligomers (n = 2–4) (26–28), and a small number of uranium triamide and triaryloxide complexes also reductively dimerize CO (29, 30). More recently, an organometallic uranium complex was shown to effect the simultaneous reduction and hydrogenation of CO to give a coordinated methoxide that could be liberated as CH_3OSiMe_3 (31); however, there have been no reports of successful homologation, functionalization, and removal of C_n-oligomers ($n \geq 2$) under mild conditions with retention of a metal complex that may be recycled for reuse in a synthetic cycle as has been demonstrated for CO_2 (32, 33), P_4 (34), and carbodiimides (35). Thus, the direct homologation of carbon monoxide into oxycarbons in viable, simple, and straightforward synthetic cycles is yet to be accomplished (36).

Here, we show that a simple, preorganized triamidoamine uranium(III) complex can reductively homologate CO to give selectively the ethyne diolate unit. This valuable C_2 building block can be functionalized and liberated as bis(organosiloxy)acetylenes following straightforward treatment with organosilylhalides, and these acetylenes readily convert to furanones. A triamidoamine uranium(IV) iodide complex, which is the precursor to the triamido uranium(III) complex, is formed concomitantly, thus, the uranium(III) complex can be recycled. Therefore, using only three steps and four components, all the required transformations to close the synthetic cycle for the homologation of carbon monoxide to higher order derivatives in high yields are now established.

Results and Discussion

Reductive Homologation of CO. As part of our work examining the chemistry of triamido uranium complexes (37–40), we studied the reaction of [U(Tren^{DMSB})] [1, ref. 41, Tren^{DMSB} = N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_3$] with excess CO at ambient pressure (1 bar) in pentane. This resulted in a rapid fading of the purple colored solution of 1 to brown to give the dimeric complex [{U(Tren^{DMSB})}$_2$(μ-η^1 : η^1-OCCO)] (2) in up to 62% isolated

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Data deposition: The atomic coordinates have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, United Kingdom (CCDC 854138 and 854139). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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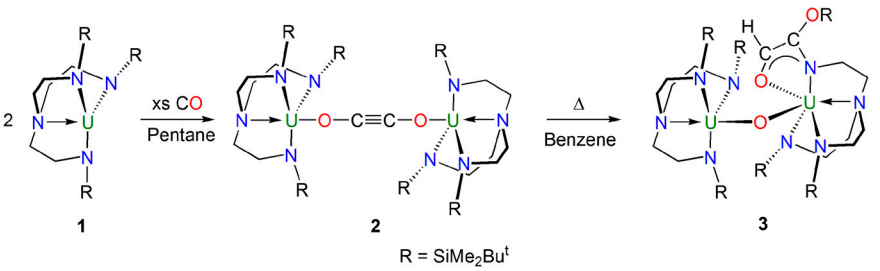


Scheme 1. Synthesis of 2 and 3.

yield (Scheme 1). The reaction is quantitative as indicated by ^{1}H NMR spectroscopy, and the yield of 2 reflects its high solubility in hydrocarbons. Crystallization from pentane at −30 °C afforded pale green plates suitable for X-ray diffraction studies, which revealed a reductively homologated CO dimer, bridging two uranium(IV) centers that are related by a crystallographic inversion center.

The structure of 2 (Fig. 1) shows an almost linear $^-$O-C ≡ C-O$^-$ unit that exhibits a O1-C25-C25A angle of 173.8(6)°. The U-N_{amide} and U-N_{amine} bond lengths are unremarkable, but the U-O bond distances of 2.156(3) Å are notably longer than in $[(UN''_3)_2(\mu\text{-}\eta^1:\eta^1\text{-OCCO})]$ $[N'' = N(SiMe_3)_2$, U-O av. = 2.102(2) Å] (29) reflecting the sterically highly congested uranium centers in 2. The C25-C25A bond length of 1.187(8) Å confirms the presence of a C ≡ C triple bond in the ethyne diolate fragment. When the preparation of 2 is repeated with isotope ^{13}C-enriched ^{13}CO, the ^{13}C NMR spectrum of ^{13}C-2 exhibits a resonance at 236 ppm, that corresponds to the ethyne diolate carbon nuclei, and this resonance is not observed in the absence of ^{13}C labeling. The FTIR spectrum of 2 exhibits a band at 1,341 cm^{-1} assigned as a C-O stretch. This band is shifted to 1,316 cm^{-1} in ^{13}C-2, which compares well to the calculated isotopomer shift of 1,311 cm^{-1} from reduced mass considerations. The oxidation of uranium(III) to uranium(IV) during the conversion of 1 to 2 is supported by the UV/visible(vis)/NIR electronic absorption spectrum and variable-temperature superconducting quantum interference device (SQUID) magnetization data for 2. Complex 2 exhibits strong ligand to metal charge transfer absorptions in the region 25,000 – 15,000 cm^{-1} and weak ($\varepsilon \sim 20$ M^{-1} cm^{-1}) bands in the 15,000 – 9,000 cm^{-1} region that are characteristic of Laporte forbidden f → f transitions for uranium(IV). The magnetic moment of powdered 2 is 4.00 μ_B at 300 K. This value declines smoothly until ∼50 K after which it decreases more sharply so that at 1.8 K the magnetic moment is 0.69 μ_B. The SQUID magnetization trace tends to zero, which is consistent with a f^2 ($^3H_4$) electronic configuration that at low temperature has a magnetic singlet state (42).

Thermolysis of the Homologated Complex. Thermolysis of 2 at 80 °C in benzene for 48 h afforded its quantitative conversion to complex 3 as determined by ^{1}H NMR spectroscopy (Scheme 1). Intermediates were not observed under the experimental conditions, and the relatively simple ^{1}H NMR spectrum of 2, which exhibits four resonances, converts to a more complex spectrum containing fourteen resonances. Although the proton, which most likely originates from solvent, on the newly formed alkene unit in 3 was not observed, the complex nature of the ^{1}H NMR spectrum of 3 is consistent with its dinuclear formulation. Complex 3 was isolated in 60% yield as green plates suitable for X-ray diffraction studies, which revealed insertion of the ethyne diolate group into one of the N-Si bonds of the Tren^{DMSB} ligand (Fig. 2). This reaction is accompanied by protonation of the ethyne diolate and insertion of an oxo-bridge, which most likely derives from the glass reaction vessel, between the two uranium(IV) centers. The reduction of the C ≡ C triple bond in the ethyne diolate group is confirmed by the C43-C44 bond length of 1.478(7) Å, and the

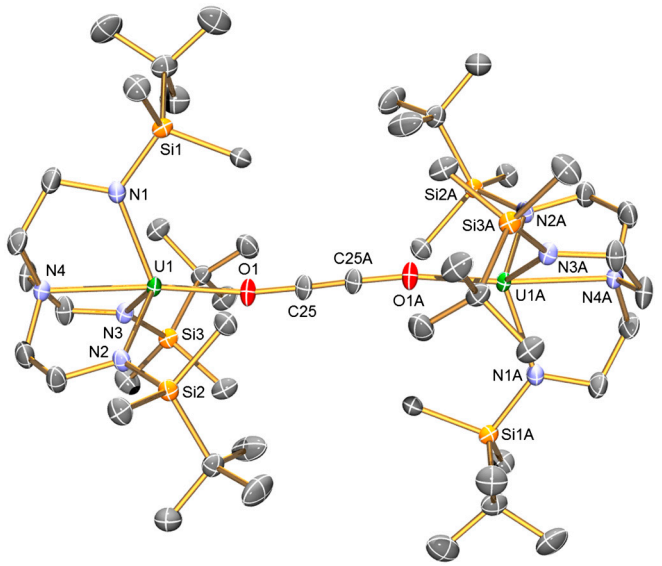


Fig. 1. Molecular structure of 2 with displacement ellipsoids at 50% and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for 2:U1-N1, 2.265(4); U1-N2, 2.246(4); U1-N3, 2.263(3); U1-N4, 2.534(3); U1-O1, 2.156(3); O1-C25, 1.302(5); C25-C25A, 1.187(8); U1-O1-C25, 158.8(3); O1-C25-C25A, 173.8(6).

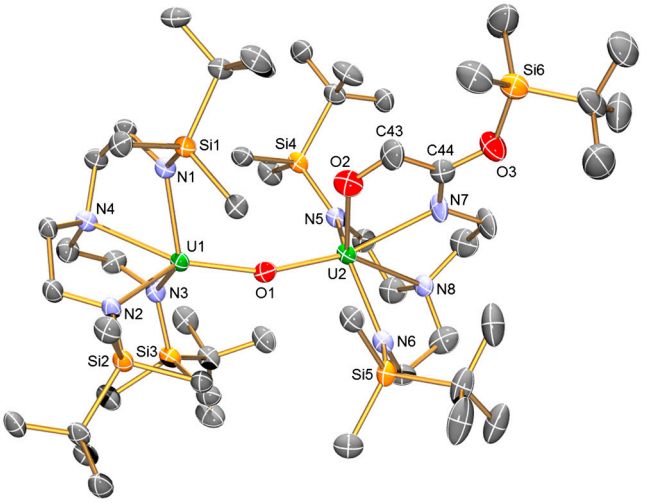


Fig. 2. Molecular structure of 3 with displacement ellipsoids at 50% and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for 3:U1-N1, 2.300(4); U1-N2, 2.316(4); U1-N3, 2.284(4); U1-N4, 2.580(4); U1-O1, 2.116(3); U2-O1, 2.138(3); U2-O2, 2.186(4); U2-N5, 2.322(4); U2-N6, 2.289(4); U2-N7, 2.541(4); U2-N8, 2.691(4); N7-C44, 1.254(6); C44-O3, 1.372(6); C43-C44, 1.478(7); C43-O2, 1.343(7); U1-O1-U2, 160.87(16); O2-U2-N7, 65.06(14); O2-C43-C44, 109.8(5); C43-C44-N7, 119.6(5).

C-H proton was located in the Fourier difference map. The O2-C43 and N7-C44 bond distances of 1.343(7) and 1.254(6) Å, respectively, are suggestive of significant C = O and N = C double bond character. Taken together with the C43-C44 bond, which is intermediate to single and double C-C bonds, these metrical parameters suggest delocalization around the OCCN fragment. In support of this, the U2-N7 bond length of 2.541(4) Å is closer to the dative U-N_{amine} distances (average 2.636 Å) than the polarized-covalent U-N_{amide} distances (average 2.302 Å) reflecting its dative nature resulting from the strong imino character of N7. Complex 3 has been fully characterized and exhibits a solid state magnetic moment of 4.28 μ_B at 298 K that decreases to 0.87 μ_B at 1.8 K consistent with the uranium(IV) formulation. Complex 3 is notable because magnetometric measurements reveal a maximum in a plot of χ_M vs. T at 3 K (Fig. 3) that suggests weak antiferromagnetic exchange coupling between the two uranium cations through the oxo-bridge. Magnetic exchange coupling between uranium(IV) centers is very rare (43), and, more generally, clear-cut exchange between uranium ions is uncommon because it is often masked by other phenomena (44).

The observed insertion that produces 3 contrasts to the only other example of linear ethyne diolate reactivity where a silylmethyl C-H bond in a uranium amide coordination environment was reported to add across the C ≡ C triple bond (29); however, the straightforward and clean formation of 3 suggested that the ethyne diolate unit in 2 is unusually silicophilic (32, 45, 46) and, therefore, amenable to reaction with organosilyl reagents that could be exploited to close the synthetic cycle.

Liberation Studies and Closing the Synthetic Cycle. Treatment of a pentane solution of 2 or ^{13}C-2 with Me_3SiI or $PhMe_2SiI$ quantitatively afforded a mixture of [U($Tren^{DMSB}$)I] (4) (47), which is the precursor to 1, and the oils $Me_3SiOC \equiv COSiMe_3$ (5a and ^{13}C-5a) or $PhMe_2SiOC \equiv COSiMe_2Ph$ (5b or ^{13}C-5b) (Scheme 2). In contrast, 3 does not appear to react with Me_3SiI or $PhMe_2SiI$. The formation of 4 was confirmed by comparison of its ^{1}H NMR spectrum with that of an authentic, independently prepared sample and also by an X-ray crystallographic unit cell determination. Complex 4 can easily be separated from 5a/5b in essentially quantitative yield and be converted back to 1 in essentially quantitative yield by stirring over a potassium mirror. Compound 1 can be recycled for subsequent reuse over at least four cycles in yields of 80–90% of 4 for each step before separation of 4 from 5 becomes impractical on the scales employed in this study (details are given in the *SI Appendix*). Addition of Ph_2MeSiI or Ph_3SiI to 2 or ^{13}C-2 did not liberate the corresponding bis(organosiloxy)acetylenes. Although we cannot rule out electronic effects, these observations suggest that $PhMe_2SiI$ represents the optimum steric compromise between the functionalization and liberation reaction proceeding and isolating a well-defined homologated product. The reductive homologation of CO to 5 and 6 affords a route to organic bis(ether)acetylenes and furanones that are precursors to important diols and furans that are produced on industrial scales

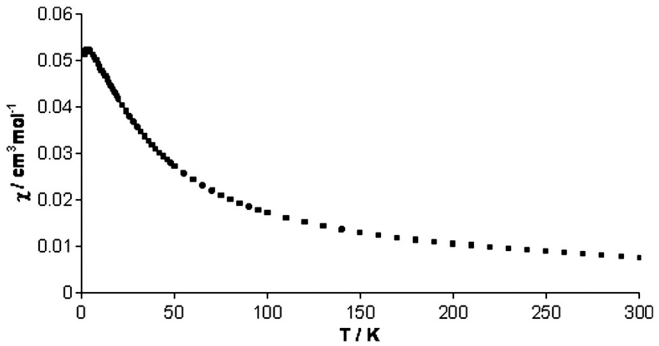
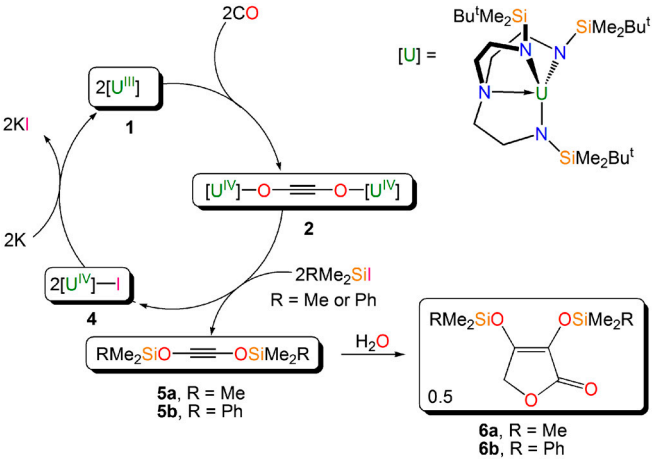


Fig. 3. Plot of χ_M versus T for 3.



Scheme 2. The synthetic cycle for the reductive homologation and functionalization of carbon monoxide to 5a/5b and ultimately to 6a/6b.

(8, 48). This method is also a convenient route for incorporating ^{13}C-labeled organic molecules into a synthetic cycle and utilizes organosilyl halides that are industrially produced on a large scale. These findings establish that, under the appropriate conditions, uranium(III) can mediate a complete and straightforward synthetic cycle for the homologation of CO to higher derivatives as illustrated in Scheme 2.

Postliberation Chemistry of the Bis(organosiloxy)acetylenes. Following functionalization and liberation of the ethyne diolate group the viscous oils $RMe_2SiOC \equiv COSiMe_2R$ (R = Me, 5a or ^{13}C-5a; R = Ph, 5b or ^{13}C-5b) are liberated in nonoptimized yields of 90% for 5b/^{13}C-5b and estimated yields of 90% for 5a/^{13}C-5a; however, the stability of these compounds appears to be dependent on the nature of the silyl substituents. Compounds 5b or ^{13}C-5b appear to be more stable than 5a or ^{13}C-5a in neat form possibly due to the extra steric protection afforded by the phenyl substituent. The identities of 5b and ^{13}C-5b (R = Ph) were confirmed by CHN combustion analyses, FTIR spectroscopy, and the presence of the molecular ions $[5b - Ph]^+$ and $[^{13}C\text{-}5b - Ph]^+$ at $m/z = 249$ and 251, respectively, in electrospray ionization (MS-ESI) mass spectra; however, NMR spectra of 5b and ^{13}C-5b could not be obtained because in solution they react further to afford quantitatively the furanones 6b and ^{13}C-6b (Scheme 2) as evidenced by multinuclear NMR and IR spectroscopies and mass spectrometry (see *SI Appendix*).

For 5a and ^{13}C-5a (R = Me), the resulting bis(trimethylsiloxy) acetylene is unstable and rapidly undergoes subsequent reaction neat or in solution. For example, molecular ions were not observed and instead only the dimerized squarate ions $[(Me_3SiOCCOSiMe_3)_2]^+$ and $[(Me_3SiO^{13}C^{13}COSiMe_3)_2]^+$ were observed at $m/z = 404$ and 408, respectively, in MS electron impact ionization (EI) experiments. This is consistent with the literature where $Bu^tOCCOBu^t$ is the only known stable bis (oxy)acetylene (49). All other derivatives react further at room temperature to give ill-defined mixtures of products (50), and $Bu^tOCCOBu^t$ can be converted to a squarate derivative by thermolysis (51). This generates a ketene through isobutene elimination and hydrogen migration to give $Bu^tOC(H) = C = O$ that undergoes a [2 + 2]-cycloaddition with the parent $Bu^tOCCOBu^t$ (52). Although trimethylsilyl is larger than *tert*-butyl, the Si-O bond is longer than the corresponding C-O bond, which affords less steric protection of the OCCO linkage for the silyl derivative. Thus, although we could record FTIR spectra in Nujol mulls, definitive NMR spectra of 5a or ^{13}C-5a could not be obtained. Whereas the CHN data for 5b or ^{13}C-5b are consistent with the proposed formulations, the CHN data for 5a or ^{13}C-5a con-

sistently deviate from anticipated values and repeatedly return the same elemental composition data showing that subsequent reaction is already and repeatedly occurring at this stage.

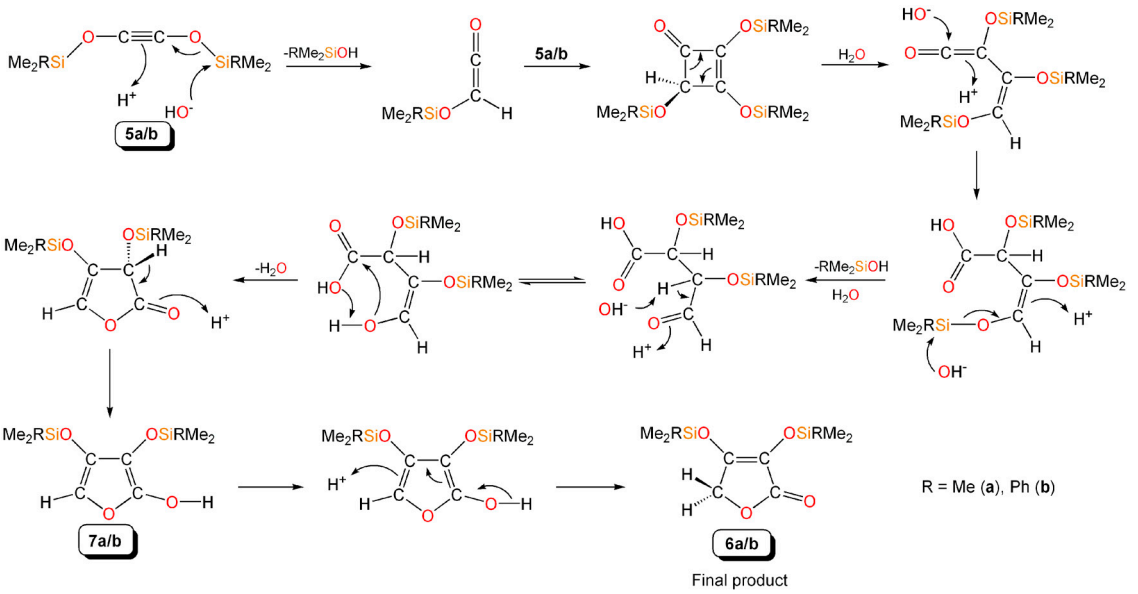
The FTIR data for 5a and 5b are consistent with the proposed formulations, but we could not unambiguously identify any isotopomer effects as the bands that are anticipated to be affected are in the fingerprint regions that contain overlapping band structures; however, over time the FTIR spectra of neat 5a, ^{13}C-5a, 5b, and ^{13}C-5b change and carbonyl bands are observed to grow in intensity. For 5a and 5b, carbonyl stretches at 1,780 and 1,764 cm^{-1}, respectively, are observed. For ^{13}C-5a and ^{13}C-5b the corresponding stretches are observed at 1,753 and 1,719 cm^{-1}, respectively, which corresponds to isotope shifts of 27 and 45 cm^{-1}, respectively. This compares well to ^{12}C/^{13}C isotopomer shifts expected from reduced mass considerations (usually ~40 cm^{-1}). Initial ^{13}C NMR spectra (see *SI Appendix*, Figs. S11–S18) of 5a or 5b show the presence of two organic products. Monitoring over time shows that 5a/5b each convert into a mixture of the corresponding furanones 6a/b with another species tentatively assigned as the tautomeric hydroxyfurans 7a/b. Resonances attributable to 7a/b decay over time to give only 6a/b, which is consistent with the relative acid dissociation constants (pK_a) of the C-H and O-H bonds involved in this tautomeric equilibrium. In dry benzene, the conversion of 5b and ^{13}C-5b into 6b or ^{13}C-6b is ~40% complete after 18 h, and full conversion is achieved within 2 wks, but reaction times can be reduced to within 2 h by the addition of water or heating. The final chemical shifts compare very well to the related furanones 2,3,5,6-tetrakis-O-(trimethylsilyl) ascorbate and 3,4-dimethoxy-5-(hydroxymethyl)-5-methyl-2(5H)-furanone (53, 54).

The proposed mechanism for the conversion of 5a/b to 6a/b is illustrated in Scheme 3. Conversion of bis(oxy)acetylenes to ketenes is well known as are [2 + 2]-cycloadditions of ketenes with alkynes to give squarate derivatives. A π-cycloreversion reaction produces a transient ketene that is converted to a carboxylate. Base-induced elimination of a silyl group opens the way for a subsequent tautomerization that is followed by ring closure. A formal overall sigmatropic rearrangement, which in a concerted mechanism would be symmetry forbidden, can proceed in a stepwise mechanism that may involve ring opening and subsequent reclosure and affords the hydroxyfurans 7a/b that subsequently tautomerize to the furanones 6a/b. This mechanism is supported by the extensive literature precedents for the individual reaction steps (55) and also by the tentative observation of 7a/b as well as 6a/b in NMR spectra recorded promptly after the aqueous washing step, the decay of resonances attributable to 7a/b, and the growth of resonances assigned to 6a/b over time to finally give 6a/b only. The presence of water accelerates these reactions, but it should be noted that trace H^+ and hydroxyl groups on the surface of glass flasks can promote this reaction (55).

Electronic Structure of 2 and Thermodynamic Considerations. The facile liberation of bis(organosiloxy)acetylenes from 2 and ^{13}C-2 in yields of *ca.* 90% contrasts with previous reports where coordinated ethyne diolates were reported as impervious to release (29) and forcing conditions resulted in decomposition of the metal complexes (14) that would be highly deleterious to synthetic or catalytic cycles (15). In order to investigate the liberation chemistry of 2, we carried out Density Functional Theory calculations on the whole molecule of 2. The calculated bond lengths and angles are reproduced to within 0.05 Å and 2°, respectively; so, we conclude that the calculations provide a qualitative model of the electronic structure of 2. The HOMO and HOMOs −1, −2, and −3 of 2 are singly occupied and of essentially exclusive 5f character and are delocalized across both uranium centers (Fig. 4). This supports the uranium(IV) formulation suggested by the structural, spectroscopic, and magnetic characterization of 2. HOMO–4 and HOMO–5 describe the principal U-O interactions in the frontier orbital region and represent a quasidegenerate pair of π-donor interactions from oxygen to uranium that approximate to a_{1u} symmetry if the molecule is considered to possess C_i point symmetry. These interactions are polarized towards the oxygen centers as expected for such polar bonds. The calculated spin densities at the uranium, oxygen, amide, and amine centers in 2 are calculated to be 2.33, −0.07, −0.07, and −0.01, respectively, and the U-O, U-N_{amide}, and U-N_{amine}, C-O, and C ≡ C Nalewajski-Mrozek bond indices are 1.25, 1.44, 0.52, 1.49, and 2.54, respectively. These values reflect weak U-O π-donation, stronger, but still relatively modest U-N π-donation, the dative amine donation to uranium, and also the formation of a C ≡ C triple bond.

In order to calculate the bond enthalpy change for the reactions

$$[\{U(Tren^{DMSB})\}_2(\mu\text{-}\eta^1 : \eta^1\text{-}OCCO)](\mathbf{2}) + 2R_3SiI \rightarrow R_3SiOCCOSiR_3(\mathbf{5}) + 2[U(Tren^{DMSB})I](4), \quad [1]$$



Scheme 3. Proposed mechanism for the conversion of the bis(siloxy)acetylenes 5a/5b to the furanones 6a/6b.

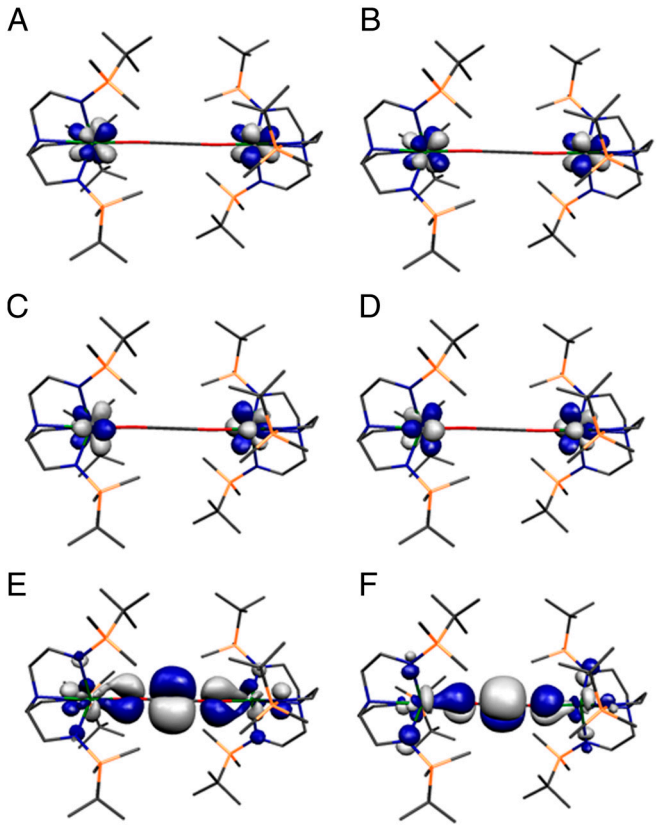


Fig. 4. The top six occupied α-spin Kohn–Sham molecular orbitals of 2. Hydrogen atoms are omitted for clarity. (*A*) HOMO (379*a*, −2.743 eV); (*B*) HOMO–1 (378*a*, −2.745 eV; (*C*) HOMO–2 (377*a*, −2.778); (*D*) HOMO–3 (376*a*, −2.781); (*E*) HOMO–4 (375*a*, −4.399); (*F*) HOMO–5 (374*a*, −4.449 eV).

we calculated the gas phase geometry optimized structures of 2, Me_3SiI, $PhMe_2SiI$, Ph_2MeSiI, Ph_3SiI, $Me_3SiOCCOSiMe_3$ (5a), $PhMe_2SiOCCOSiMe_2Ph$ (5b), $Ph_2MeSiOCCOSiMePh_2$, $Ph_3SiOCCOSiPh_3$, and 4 to estimate the heats of formation (ΔH_{for}) for these species. ΔH_{rxn} for the above reaction is

$$\Delta H_{rxn} = [\Delta H_{for}(ROCCOR) + 2\Delta H_{for}(\mathbf{4})] - [\Delta H_{for}(\mathbf{2}) + 2\Delta H_{for}(RI)], \quad [2]$$

which reveals that the enthalpy change of the gas phase reaction is exergonic overall at -15.9 kcal mol^{-1} (R = Me_3Si), -15.4 kcal mol^{-1} (R = $PhMe_2Si$), -13.1 kcal mol^{-1} (R = Ph_2MeSi), and -9.5 kcal mol^{-1} (R = Ph_3Si). Experimentally, the latter two silyl iodides did not affect liberation of the ethyne diolate fragment that we attribute to steric effects that may kinetically block the reaction. Interestingly, the corresponding enthalpies when $[(UN_3'')_2(\mu\text{-}\eta^1 : \eta^1\text{-OCCO})]$ (29), which was reported to be inert to liberation using silyl reagents (29), and $[UN_3''I]$ are substituted for 2 and 4, respectively, in Eq. **2** are -2.8 kcal mol^{-1} (R = Me_3Si), -2.4 kcal mol^{-1} (R = $PhMe_2Si$), -0.1 kcal mol^{-1} (R = Ph_2MeSi), and $+3.5$ kcal mol^{-1} (R = Ph_3Si). The ∼12 kcal mol^{-1} disparity between these two sets of calculated data may reflect a smaller ligand reorganization energy for preorganized $[U(Tren^{DMSB})]$ (56) compared to $[UN''_3]$ that, for the former, is calculated to be 10.8 kcal mol^{-1} per uranium center. It is interesting to note that the U-O-C angle in 2 is 158.8(3)°; whereas, in $[(UN_3'')_2(\mu\text{-}\eta^1 : \eta^1\text{-OCCO}))]$, the corresponding angle is 177.5°. Although care must be taken when correlating M-O-R bond angles to bond strength (57, 58), it may be that the rigid and steric demands of the $Tren^{DMSB}$ ligand weakens the U-OR linkage in 2 and perhaps opens up the sterically crowded environment to kinetically feasible substitution and product liberation. The solvent and entropy of the reaction are clearly important reaction parameters that are not considered in these gas phase calculations; however it would appear that the steric demands of rigid, preorganized (56) ancillary ligands may play a key role.

Summary and Outlook. To summarize, we have shown that under mild conditions complex 1 can reductively homologate CO to selectively give 2. Following treatment with organosilyl halides, 5 is liberated, and this occurs with concomitant formation of 4, which is the direct precursor to 1. Thus, 1 can be recycled and reused, thereby closing the synthetic cycle with only three steps. We suggest that the unusually facile liberation of 5 may be attributable to the sterically demanding nature of 1 coupled with its rigidity, and this may be an important consideration to apply more generally to the challenge of designing selective catalytic cycles for the reductive homologation and functionalization of CO. The elaboration of 5 into 6 holds promise for the catalytic homologation of CO into more complex and value-added organic molecules. Detailed chemical and engineering studies are currently underway to ameliorate reagent incompatibilities (59), and the simplicity of this system suggests that catalytic CO functionalization may soon be within reach.

Materials and Methods

All operations involving 1–4 were carried out under pure nitrogen or carbon monoxide using Schlenk or glovebox techniques. All reagents and solvents were rigorously dried and degassed prior to use. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, and 79.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to tetramethylsilane. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. UV/vis/NIR spectra were recorded on a Perkin Elmer Lambda 750 spectrometer. Variable-temperature magnetic moment data were recorded in an applied DC field of 0.1 T on a Quantum Design MPMS XL5 SQUID magnetometer using doubly recrystallized powdered samples. Mass Spectrometry was carried out using Bruker Apex IV Fourier transform ion cyclotron resonance (MS-EI) and Bruker MicroTOF (MS-ESI) instruments. Elemental microanalyses were carried out at the University of Nottingham and by Stephen Boyer at the London Metropolitan University (UK). Density Functional Theory calculations were carried out with Amsterdam Density Functional program version 2010.01 (60). X-ray crystallographic files are available in Datasets 1 and 2 and full details of this and experimental procedures are published in the *SI Appendix*.

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