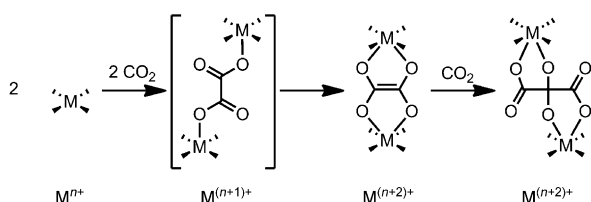


Carbon Dioxide Insertion into Uranium-Activated Dicarbonyl Complexes**

Stephan J. Zuend, Oanh P. Lam, Frank W. Heinemann, and Karsten Meyer*

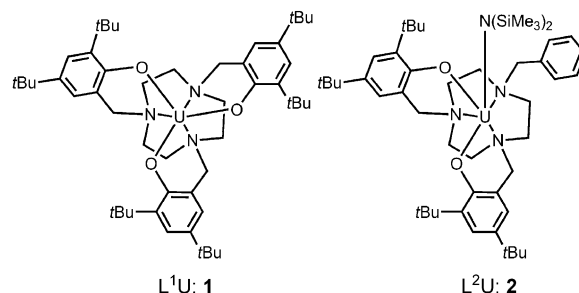
Dedicated to Professor Karl Wieghardt

The metal-mediated synthesis of complex molecules directly from CO₂ is a potentially important strategy for the preparation of fine chemicals from renewable feedstocks.^[1] The direct oligomerization of CO₂ is a conceptually simple route for C–C bond formation^[1a] that may also be relevant to the prebiotic synthesis of organic compounds.^[2] Whereas metal-catalyzed reductive dimerization of CO₂ to form oxalate has been observed,^[3] insertion of CO₂ into oxalate or oxalate equivalents, such as diketones, to form chains with three or more carbon atoms is not known. In principle, this process could proceed in two steps: metal-mediated two-electron reduction of a dicarbonyl compound to generate an enolate,^[4] followed by nucleophilic addition of the enolate to CO₂ (Scheme 1). Herein we present low-valent uranium(III) complexes that engage organic diketone ligands in both one- and two-electron reduction pathways and a dinuclear, two-electron-reduced diketone that engages CO₂ in a productive C–C bond formation reaction.



Scheme 1. A pathway for the dimerization and trimerization of CO₂ with metal complexes.

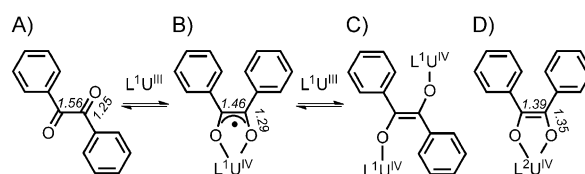
Uranium(III) (f³) ions bearing macrocyclic ligands^[5] are potent one-electron reducing agents that have been shown to stabilize bound organic radicals by generating charge-separated {U^{IV}–L[•]} species.^[6] In particular, U^{III} complex **1** (Scheme 2) reduces benzophenone and diazomethane derivatives to generate stable charge-separated radical anions, for



Scheme 2. Uranium(III) complexes used in this study.

example, the ketyl, bound to a formal U^{IV} center. Two factors are thought to be critical to this result: 1) The ability of U^{III} ions in coordination complexes to undergo selective one-electron oxidation to the corresponding U^{IV} species; and 2) the large ionic radius of uranium that allows high coordination numbers and thus the binding of additional ligands without displacement of the stabilizing macrocyclic ligand. On the basis of these results, we reasoned that **1**, or structurally related U^{III} complexes, might be capable of engaging dicarbonyl compounds in multiple one-electron reduction pathways (Scheme 3),^[7] and would thus be well-suited to test the viability of CO₂-insertion pathways into the resulting reduced dicarbonyl compounds.

We began our study by examining the reactions of various 1,2-dicarbonyl compounds with U^{III} complexes. Oxalate-derived esters, such as dimethyl oxalate, were observed to react with **1** at room temperature to provide a complex mixture of products. Although reactions under cryogenic conditions proceeded more cleanly, the resulting products underwent decomposition to provide the corresponding uranium alkoxides, precluding definitive characterization of the initial reaction products.



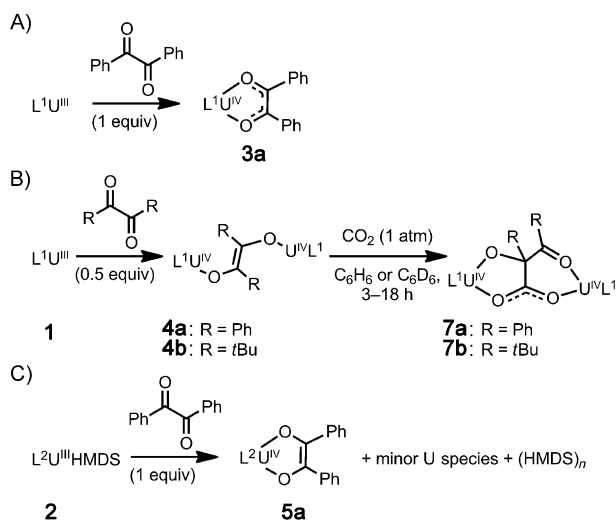
Scheme 3. The uranium(III)-mediated reduction of dicarbonyl compounds: A) Benzil; B) U^{IV} complex with benzil ketyl ligand; C) dinuclear U^{IV} complex with benzil enolate ligand; D) mononuclear U^{IV} complex with benzil enolate ligand. Expected C–C and C–O bonds [Å] (from Ref. [7a]) are indicated.

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In contrast, experiments with 1,2-diketones led to the formation of isolable products. Thus, treatment of a dark brown solution of **1** with benzil (≥ 1 equiv; Scheme 4A) in benzene or $[D_6]$ benzene resulted in the formation of a red-violet solution containing a single new species as judged by ^1H NMR spectroscopy. Slow diffusion of *n*-hexane into a concentrated benzene solution provided red-violet needles in 58% yield. Single-crystal X-ray diffraction (XRD) analysis revealed a 1:1 complex of *cis*-benzil and **1** bound through both oxygen atoms of the diketone (**3a**; Figure 1 and Table 1). In Wieghardt's recent studies of first-row transition-metal diketone-based complexes, the C–C and C–O bonds are shown to be sensitive probes of the dicarbonyl oxidation state; for example, C–C bond distances of about 1.56, 1.46, and 1.39 Å correspond to the neutral, monoanionic, and dianionic forms of the dicarbonyl ligand, respectively (Scheme 3 A,B,D).^[7] In **3a**, the observed C–C bond distance of 1.44 Å is substantially different from that expected for a neutral diketone (Table 1), but corresponds closely to that expected for the singly reduced radical form of the diketone ligand (Scheme 3 B). Similarly, the observed C–O bond distances of 1.29–1.30 Å are most consistent with the ketyl formulation.



Scheme 4. Formation of A) a mononuclear ketyl, B) a dinuclear dienolate and its CO_2 -insertion product, and C) a mononuclear enolate. $(\text{HMDS})_n$ = uncharacterized by-product derived from hexamethyldisilazane.

In analogous experiments, treatment of **1** with approximately 0.5 equiv of benzil (Scheme 4B) resulted in the formation of a yellow-orange solution and a new species distinct from either **1** or **3a**, as judged by ^1H NMR spectroscopy.^[8] Orange crystals suitable for XRD analysis were obtained by slow diffusion of hexane into a saturated benzene solution. The resulting molecular structure consists of *trans*-benzil bridging two uranium centers, with a crystallographic inversion center at the central C–C bond (**4a**; Figure 1 and Table 1). The substantially shorter C–C and longer C–O bond in this structure relative to **3a** are consistent with an enolate rather than a ketyl formulation (Table 1 and Scheme 3 C).^[9]

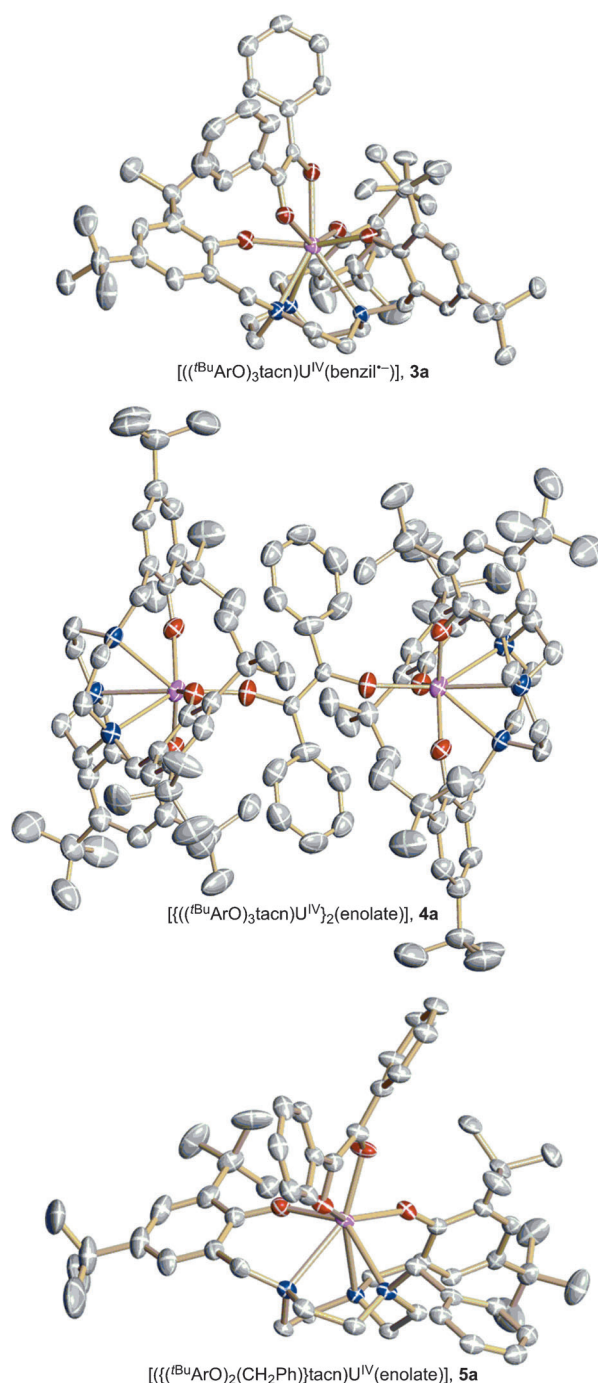


Figure 1. Molecular structures of the monomeric one-electron reduced form of benzil (**3a**), the dimeric two-electron reduced form (**4a**), and the monomeric two-electron reduced form (**5a**) bound to uranium(IV). U pink, C gray, O red, N blue. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

Table 1: Selected bond lengths in complexes **3a**, **4a**, and **5a**.

Complex	C–C [Å] ^[a]	C–O [Å] ^[a]	U–O [Å] ^[a]
3a	1.440(8)	1.286(7), 1.301(7)	2.404(4), 2.463(4)
4a	1.36(3)	1.393(12)	2.117(3)
5a	1.366(8)	1.367(7), 1.369(7)	2.182(4), 2.247(4)

[a] Determined by X-ray diffraction analysis.

We sought to prepare a complex containing a monometallic two-electron-reduced diketone, both to determine accurately the bond lengths in such a species and to allow comparison with **3a** and **4a** in its reaction chemistry. To accomplish this, pentadentate triazacyclononane-derived ligands were prepared (analogues of the hexadentate (ArO)₃-(tacn)³⁻ ligand, as in **1**) with the general structure (ArO)₂(R)tacn²⁻.^[10] The uranium complex derived from the ligand in which R = CH₂Ph (**2**) emerged as a promising candidate for further study: treatment of **2** with benzil (1 equiv; Scheme 4C) yielded a dark orange solution containing a mixture of compounds, as judged by ¹H NMR spectroscopic analysis.^[11] The major species could be isolated as a yellow–orange powder in 44% yield by selective crystallization.^[12] Crystals suitable for XRD analysis were grown by slow diffusion of hexane into a concentrated benzene solution, revealing the monometallic complex **5a** (Figure 1 and Table 1). The observed C–C (1.37 Å) and C–O (1.37 Å) bonds are consistent with a doubly reduced enolate (Scheme 3D) rather than a singly reduced ketyl complex. Interestingly, the most pronounced effect of the diketone oxidation state on the structure is observed in the U–O distances, which are about 0.2 Å shorter in enolate **5a** compared with ketyl **3a**; this effect can be ascribed to the greater negative charge density on oxygen in **5a**. Thus, comparison of the U–O bonds in **4a** and **5a** indicates that the diketone ligand in dinuclear complex **4a** also has a somewhat greater negative charge density than in its mononuclear counterpart, indicating a cooperative role of the two uranium ions in ligand reduction.

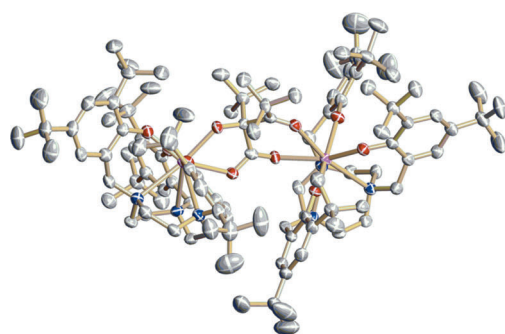
We used a combination of experimental (SQUID magnetization) and DFT-based computational analyses to assess the validity of the structural assignments and to help probe the electronic structure of the prepared species. Structures of model complexes were fully optimized using the B3LYP level of theory, with the Stuttgart–Dresden 60-electron pseudopotential used on the uranium atom (Supporting Information).^[13] Computed mononuclear complexes (models of **3a** and **5a**) have structures that are almost identical to those of their experimental counterparts. The triplet state corresponding to **5a**, having two unpaired f electrons, is substantially more stable than the corresponding singlet state, as has generally been observed with analogous U^{IV} complexes. In contrast, the doublet and quartet states corresponding to **3a**, corresponding to species in which the spin of the ligand-centered electron is orthogonal and aligned with those of the f electrons, respectively, are isoenergetic. This result indicates that the electronic system of the one-electron reduced diketone ligand and the uranium metal are essentially completely decoupled from each other.

Variable-temperature SQUID magnetization data of **5a** reveal magnetic moments of 3.00 B.M. at 300 K and 0.47 B.M. at 3.5 K, consistent with a $\text{U}^{\text{IV}} f^2$ ion with a singlet ground state in the $[\{(\text{R}^{\text{ArO}})_3\text{tacn}\}\text{U}(\text{L})]$ system in which L is an axially coordinated closed-shell ligand (Supporting Information). In contrast, complex **3a** exhibits a similar magnetic moment of 3.19 B.M. at 300 K; however, the magnetic moment at 2 K of 1.59 B.M. is significantly higher than that of **5a** (0.47 B.M. at 5 K). Increased low-temperature magnetic moments have

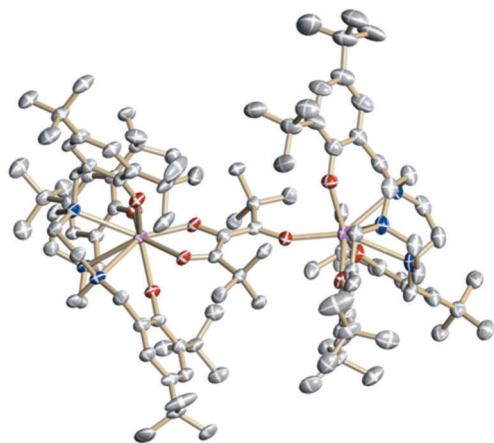
been identified previously in $\{\text{U}^{\text{IV}}\text{-L}^{\cdot-}\}$ systems,^[6b-d] and have been ascribed to magnetic contributions arising from the one unpaired electron residing on the reduced ligand. Consequently, the variable-temperature magnetic behavior of **3a** is related to complexes possessing open-shell radical anionic ligands. The SQUID data for complexes **3a** and **5a** are thus consistent with both the computational analysis and with magnetization data collected on other U^{IV} complexes with coordinated (open-shell) radical anionic ligands.

To determine their reactivity properties and to test the viability of the proposed C–C bond formation pathway, complexes **3a**, **4a**, and **5a** were each exposed to CO₂ (1 atm) under a variety of conditions. Benzil ketyl complex **3a** proved unreactive towards CO₂, as might be expected because of the reluctance of the CO₂ molecule to engage in one-electron reduction pathways.^[6b] In contrast, dinuclear enolate **4a** underwent complete reaction with CO₂ to form a new product within 3 h at room temperature (Scheme 4B). The ¹H NMR spectrum was consistent with that of a dinuclear species of low symmetry. Definitive characterization of the reaction product was achieved using an analogous complex: a solution of **1** in benzene was treated with di-*tert*-butyl diketone^[14] followed immediately by CO₂. Single crystals suitable for XRD analysis could be grown by slow evaporation of a concentrated solution of the reaction product from *n*-hexane, and revealed a highly unsymmetrical dinuclear complex in which a CO₂ molecule had inserted into the enolate and formed a new C–C bond (Figure 2).^[15] The molecular structure reveals that the CO₂ unit is coordinated in an η² fashion, with U–O_{CO₂} bond lengths of 2.36 and 2.52 Å. Accordingly, the two C–O bond lengths corresponding to the diketone show distinct single- and double-bond character (1.22 and 1.39 Å), whereas the two C–O bond lengths within the CO₂ unit are essentially identical, suggesting almost complete charge delocalization (1.25–1.26 Å). Finally, in contrast to the dinuclear enolate, mononuclear enolate **5a** proved to be unreactive towards CO₂ under identical reaction conditions. These results are in accord with the analysis described above, which suggested a somewhat greater negative charge density than on the enolate in **4a** compared with **5a**.^[16]

To extend the process depicted in Scheme 1 to generate extended carbon chains, the reduction and chain extension of tricarbonyl (and greater) compounds must be achieved. In efforts to test the viability of such processes, **1** was treated with *t*BuCOCOCOtBu,^[17] resulting in the formation of a dinuclear complex **8b**, in which the triketone has undergone two-electron reduction, as judged by x-ray crystallography (Figure 2). The C–C bonds of the tricarbonyl moiety of this complex measure 1.45 and 1.39 Å, indicating that the two C–C bonds are inequivalent and that one of the two has almost complete double-bond character. Reactivity studies of **8b** (generated in situ) with CO₂ demonstrate that this complex is reactive: for example, under conditions similar to those used for the synthesis of **7b**, a new product of low symmetry is formed within about 1 h, as revealed by ¹H NMR spectroscopy. However, this initial product appears to be unstable and it reacts further to generate a complex mixture of products, as judged by ¹H NMR spectroscopy. In one case, we were able to characterize the connectivity of one of these species by XRD



$[[((tBuArO)_3tacn)U^{IV}]_2(CO_2tBuCOCOtBu)], 7b$



$[[((tBuArO)_3tacn)U^{IV}]_2(tBuCOCOCOCOtBu)], 8b$

Figure 2. Molecular structure of CO₂-insertion product (**7b**) and reduced triketone (**8b**). U pink, C gray, O red, N blue. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

analysis of a crystal grown at -40°C , which revealed that a CO₂ unit had undergone insertion into one of the U–O bonds of the enolate.^[18] Although it has also not been possible to isolate the initially formed species observed by ¹H NMR spectroscopy, our experiments demonstrate that CO₂ insertion into the triketone enolate is a viable process that is accompanied by complex reorganization under all conditions examined

This work demonstrates that metal-mediated CO₂ insertion into di- and triketone-derived enolates (Scheme 1) is a productive process in the context of diketones, and initial data indicate that this process is available to triketones as well. Substrate activation by a two-metal, two-electron mechanism appears to play a role in this process, as neither the corresponding singly or doubly reduced mononuclear species are observed to form stable CO₂ insertion products. The insertion reaction does not require a net change in metal oxidation state or cleavage of a metal–carbon bond. We thus expect that this work will lead to the development of productive reaction sequences for the reductive coupling of multiple CO₂ units to generate small organic molecules.

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- [14] Complex **4b**, which is presumably formed initially, appears to decompose rapidly, and it has not been possible to isolate and characterize **4b**. Attempts to obtain single crystals suitable for XRD analysis at ambient or low temperatures resulted in the isolation of decomposition products, including $U_2\text{-}\mu\text{-O}$ species or complexes in which the macrocyclic ligand has undergone decomposition.
- [15] ^1H NMR spectroscopic analysis of the reaction mixture indicates the initial formation of an intermediate species within about 5 min, which subsequently reacts to form **7b** over the course of 18 h. The ^1H NMR spectrum of **7b** and the complex formed from **4a** are analogous, suggesting that the latter complex is **7a**. Details are included in the Supporting Information.
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