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Communication

Organometallic Uranyl Complexes Featuring a Carbodicarbene Ligand

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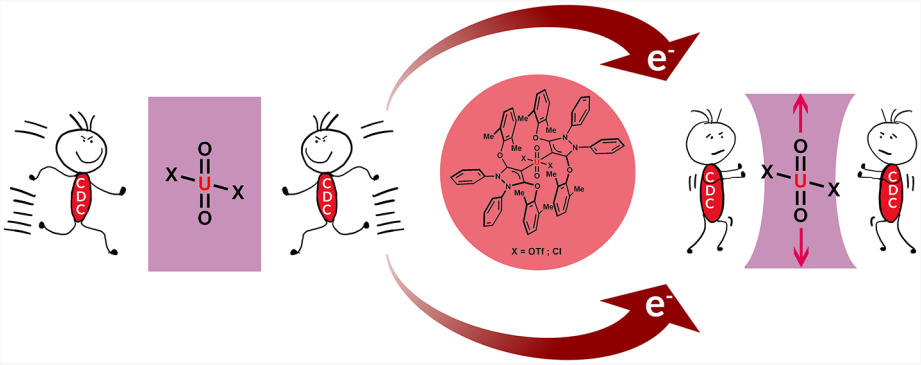
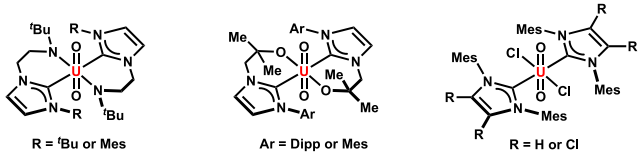


ABSTRACT: Uranyl−carbon bonds are rare due to the limited numbers of synthetic routes. The synthesis of carbodicarbene uranyl complexes is reported, along with complete spectroscopic and structural characterization. These data along with a computational analysis confirm strong electron donation by the carbodicarbene ligand, as well as a single-bond order between the uranium(VI) ion and the carbon.

The uranyl ion, $[UO_2]^{2+}$, characterized by its hexavalent ion and *trans*-$[O{=}U{=}O]^{2+}$ unit, predominantly accommodates hard donor ligands (N, O, F, or Cl) in its orthogonal plane. More rare are organometallic uranyl complexes that feature direct uranium−carbon bonds in this plane. In organometallic chemistry, metal−carbon bonds are commonly installed using alkali-metal alkylating reagents in salt metathesis reactions. These reagents are also strongly reducing and in certain instances cause reduction of the metal rather than alkylation. This is the cause for the rarity of uranyl−carbon bonds, as reduction to pentavalent uranyl derivatives, $[UO_2]^{+}$, can occur.[1,2] Uranium(V) disproportionation readily ensues, generating U(VI), U(IV), and organic products.

Despite these challenges, reports of anionic carbon-based ligands on uranyl have become increasingly more common in recent years.[3−11] Specific systems have been developed that feature this type of linkage. For example, Sarsfield and later Liddle utilized a tridentate bis(iminophosphorano)methane-based ligand around uranyl to force a uranyl−carbon bond.[3,4] Hayton reported an example of a fleeting homoleptic uranyl alkyl complex, $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$, which was found to be thermally unstable.[5]

Coordination of neutral carbon (or carbene) to uranyl is even more challenging, as the interaction between a soft donor carbon and the hard $[UO_2]^{2+}$ ion is an unstable match. This issue has been circumvented by judiciously designing chelating ligands where neutral N-heterocyclic carbenes (NHCs) are tethered with anionic amides or alkoxides to serve as an anchor to uranium. For example, Arnold reported the synthesis of uranyl carbene complexes using amido-NHCs or alkoxy-NHCs where two of these chelating ligands coordinate to uranyl in the equatorial plane (Figure 1).[12,13] Costa has reported the only examples of isolated uranyl complexes stabilized by nontethered NHC ligands. Two complexes, synthesized using 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-dimesityl-4,5-



P. Arnold, 2004 | P. Arnold, 2008 | D. Costa, 2001

Figure 1. Examples of uranyl complexes bound to neutral carbon.

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dichloroimidazol-2-ylidene ($IMesCl_2$) ligands, were crystallographically characterized to reveal a near-perfect octahedral geometry around uranium (Figure 1).[14]

Related to N-heterocyclic carbenes are "carbodicarbenes", originally predicted to be synthetically viable by Frenking in 2007, which contain divalent carbon(0) flanked between two NHCs.[15] In the very next year, Bertrand isolated such species, demonstrating that they both are stable at room temperature and could also act as ligands.[16,17] Computational and experimental data suggest that these carbodicarbenes (CDCs) are dibasic and behave as four-electron donors to metals.[18] These CDCs are attractive as ligands because they are predicted to be stronger ligands in comparison to NHCs due to their possible σ- and π-donation capabilities (Figure 2).[17] The superior donor strength of CDCs is reflected in the

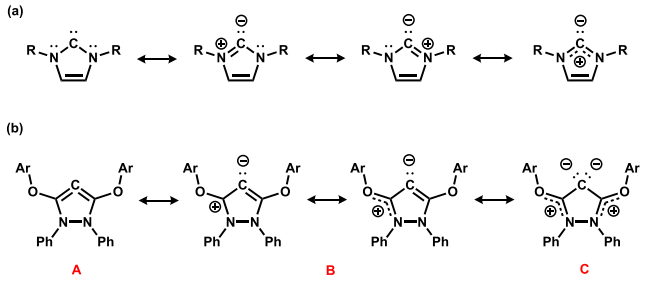
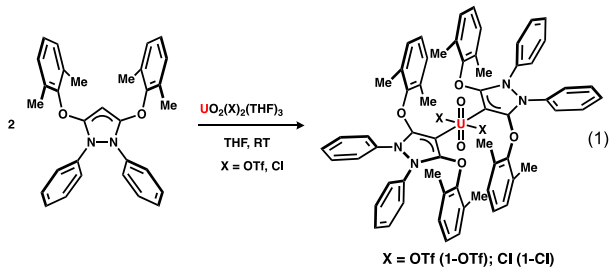


Figure 2. Resonating structures of (a) NHC showing only σ donation and (b) carbodicarbene showing the possibility of σ and π donation.

average ν_{CO} value of $[(CDC)RhCl(CO)_2]$ (2018 cm^{-1}), in comparison to the NHC congener $[(NHC)RhCl(CO)_2]$ (2038 cm^{-1}).[19] Despite the unique properties of CDCs, few reports can be found in the literature describing the coordination chemistry of these molecules.[20−27]

Recent work from our laboratory[11,28−30] has demonstrated that strong π-donor ligands weaken and activate the $[O{=}U{=}O]^{2+}$ unit, as well as bis(imido) analogues, $[RN{=}U{=}NR]^{2+}$. We hypothesized that the strong, neutral σ donation of the CDC ligand could also serve to activate the $[UO_2]^{2+}$ unit, while also creating a new family of organouranyl species. Herein, we present the synthesis of carbodicarbene complexes of uranyl. Full characterization using spectroscopic and crystallographic methods is reported, as well as a computational analysis to explore the electronic structure of these derivatives.

Our studies were initiated by pursuing the synthesis of a stable carbodicarbene complex of either uranyl triflate or uranyl chloride. Slow addition of 2 equiv of 1,2-diphenoxy-3,5-bis(2,6-dimethylphenyl)pyrazolin-4-ylidene (CDC′) to a THF solution of 1 equiv $UO_2(OTf)_2(THF)_3$ or $UO_2Cl_2(THF)_3$ produced off-white solutions (eq 1). Following workups, pale



yellow microcrystalline solids were isolated in each case and assigned as **1-OTf** and **1-Cl**. The ^1H NMR (THF-d_8, 25 °C) spectrum of **1-OTf** showed characteristic resonances for a diamagnetic compound, including one at 2.16 ppm for the methyl protons of the aryloxide fragments. One signal at −79 ppm was observed in the $^{19}F\{^1H\}$ NMR (THF-d_8, 25 °C) spectrum for **1-OTf**, suggesting C_{2v} symmetry in solution. Furthermore, two distinctive signals were located in the $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C) spectrum at 125.7 and 186.5 ppm, likely assignable to two ring carbon atoms, CCC and NCO, respectively. Interestingly, these resonances are shifted significantly downfield in comparison to the free CDC (115.5 and 174.8 ppm for CCC and NCO, respectively), corroborating a ligation to the Lewis acidic uranyl ion.

The product of the carbodicarbene reaction with $UO_2Cl_2(THF)_3$, **1-Cl**, was largely insoluble in common NMR solvents, except for acetonitrile-d_3. In this case, the resonance assignable to the methyl protons of the aryloxide groups appeared at 2.20 ppm, which was expected on the basis of the location of the resonance for **1-OTf**.

To confirm the exact composition of this yellow precipitate assigned as **1-OTf**, X-ray-quality single crystals were grown from a concentrated THF solution stored at −35 °C for 1 week. Refinement of the data showed the bis(ligand) derivative $[(CDC')_2UO_2][OTf]_2$ (**1-OTf**). The molecular structure of **1-OTf** features an octahedral uranium with two *trans* oxos, two *trans* CDC′ ligands, and two *trans* OTf anions (Figure 3). The

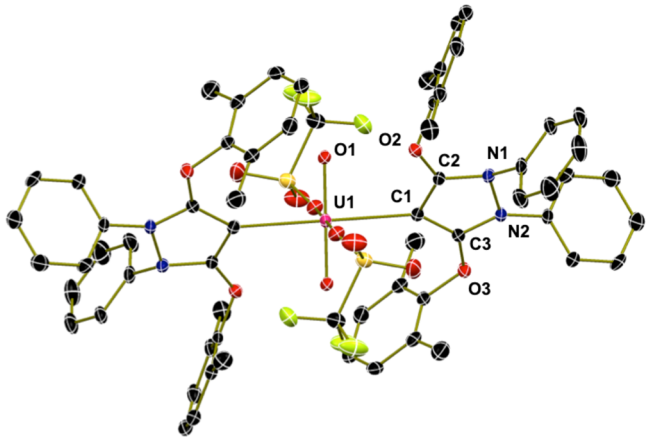


Figure 3. Solid-state structure of **1-OTf** shown with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U1−O1 = 1.753(3), U1−C1 = 2.541(4), C1−C2 = 1.389(6), C1−C3 = 1.378(6), C2−N1 = 1.353(5), C3−N2 = 1.372(6), C1−U1−O1 = 92.6, C2−C1−C3 = 100.3, U−O(OTf) = 2.370(3); ∑N1 = 358.3, ∑N2 = 356.3.

uranyl U−O bond distance of 1.753(3) Å is comparable to that observed in the analogous $UO_2Cl_2(NHC)_2$ complexes.[14] The O−U−C and O−U−O_{OTf} angles are 92.6 and 87.3°, respectively. The two CDC′ ligands are coordinated 180° with respect to each other. The U−C distance of 2.541(4) Å is shorter than that in the NHC complex (2.626(7) Å) reported by Costa and co-workers.[14] This U−C distance is significantly longer than those reported for uranyl methanediide complexes, including $[UO_2(BIPM^{TMS})(DMAP)_2]$ (2.383(3) Å) and $[UO_2(SCS)(Py)_2]$ (2.430(6) Å), where the authors suggest multiple-bond character between uranium and carbon.[8,10] Interestingly, the steric environment around the uranium center causes one of the aryloxide substituents to point toward

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and the other to point away from the $UO_2(OTf)_2$ fragment, as previously observed in RuHCl(CO)(CBA)(SIMes) reported by Stephan.[21] This "semiopen" alignment is rare, as these substituents usually either both bend toward or away from the ligated metal fragment.[17,20,21,31] The backbone nitrogen atoms of CDC are nearly planar ($\sum_{N1}$ = 358.3° and $\sum_{N2}$ = 356.3°). The average N−C distance (1.362(7) Å) is within error of that of a free CDC (1.387(4) Å).[17] These metrical parameters in combination with a significantly shorter U−C distance do not suggest multiple-bond character between uranium and carbon. Additionally, these metrics are most consistent with the CDC resonance structure indicated as C (Figure 2). Due to the poor solubility of **1-Cl**, crystallization and X-ray diffraction analysis was not possible.

Vibrational spectroscopy was also used to assess the electronics of the uranyl species, as the O═U═O stretch is inversely proportional to the donor strength of the ligand in the equatorial plane. The infrared spectrum of **1-OTf** shows an intense absorbance at 907 cm^{-1} (KBr pellet) assignable to the asymmetric O═U═O stretch. This signal shifted to 862 cm^{-1} for the ^{18}O-labeled uranyl carbodicarbene complex $(CDC')_2U^{18}O_2(OTf)_2$ (**1-OTf-^{18}O**) (Figure 4). Raman spectroscopy showed a symmetric stretch at 864 cm^{-1} (Figure S8). The infrared spectrum for the chloride analogue, $(CDC')_2UO_2Cl_2$ (**1-Cl**), showed an asymmetric O═U═O stretch at 901 cm^{-1} (Figure S7), while the Raman spectrum showed a value of 827 cm^{-1} for the symmetric stretch (Figure S9). The values obtained for the asymmetric stretches for both **1-OTf** and **1-Cl** are significantly lower than the 938 or 942 cm^{-1} observed in similar NHC complexes of uranyl reported by Costa,[14] consistent with further activation of the uranyl moiety from the more strongly donating carbodicarbene ligand. The Raman stretches are slightly shifted from the values of uranyl salts (~840 s cm^{-1}).

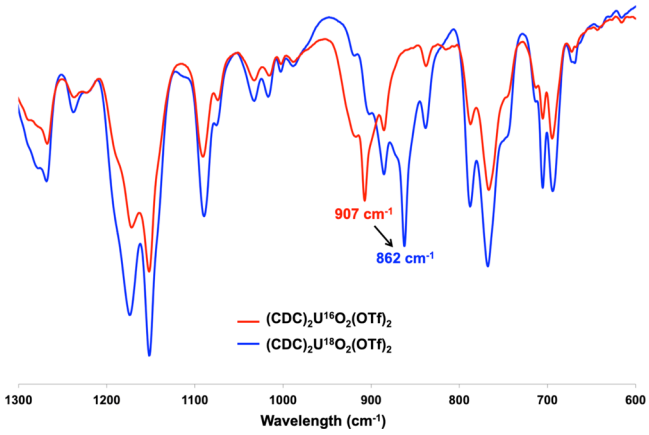

Figure 4. Overlay of solid-state infrared (IR) spectra of $(CDC')_2U^{16}O_2(OTf)_2$ (**1-OTf**) and $(CDC')_2U^{18}O_2(OTf)_2$ (**1-OTf-^{18}O**).

The electronic structure of **1-OTf** was then interrogated using density functional theory (DFT) calculations at the B3PW91-GD3BJ level of theory. B3PW91 is a well-established functional for actinide-containing systems,[32−36] but in this case, it was necessary to also consider dispersion effects in the system.[37] While the calculated U−O(triflate) and U−O(oxo) bond distances were in agreement (~0.02 Å) with experimentally determined values, the U−C bond was calculated to be 2.613 Å, or ~0.07 Å longer (Figure 5) than the experimentally determined value. When dispersion effects were included in the analysis, the calculated U−C(carbene), U−O(oxo), and U−O(triflate) bond distances of 2.538, 1.741, and 2.347 Å, respectively, were all in excellent agreement with the crystallographically determined values of 2.541(4), 1.753(3), and 2.370(3) Å, respectively (Table 1).

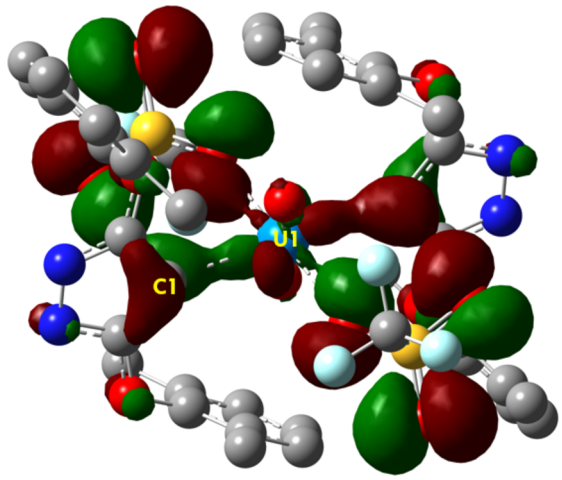

Figure 5. σ bond, HOMO-12, between U−C(carbene) in **1-OTf** (isolevel 0.02).

Table 1. Experimental and Calculated Data of Uranium−Carbon (NHC Carbon) in 1-OTf

complex	U−C exptl	U−C calcd	ρ	H
1-OTf	2.541(4) Å	2.538 Å	0.069	0.0171

Next, the quantum theory of atoms in molecules (QTAIM) level of theory was used to examine the electron density, ρ, and the total energy density, H, at the bond critical point of the U−C bond in **1-OTf** (Table 1). These parameters afford a measure of covalency with $\rho > 0.2$ and $H < 0$, indicating higher degrees of covalent character. For **1-OTf**, the calculated values of 0.069 and −0.0171 for ρ and H, respectively, are indicative of an M−C σ bond (Figure 5). For comparison, the U(IV)-NHC complexes $U(L)[N(SiMe_3)]_2X$ (L = OC-Me_2CH_2(CNCH$_2$N-2,6-^{i}Pr$_2$C$_6$H$_3$), where X = F, has ρ = 0.055 and H = −0.007. Substituting the halogen causes a slight change, as X = Cl shows values of 0.053 (ρ) and −0.007 (H).[38] Given that the effective charge of uranyl is less than that of U(IV),[39] this would indicate that the CDC ligand is more strongly donating than an NHC ligand. However, with a contribution only from σ bonding, these CDC ligands are two-electron donors, not four-electron donors, which has been observed recently with U(IV).[40]

In summary, examples of organoactinide complexes bearing a carbodicarbene ligand have been synthesized and isolated in this work. Spectroscopic characterization shows these species are stable in both solution and the solid state. Structural information highlights uranium−carbon bond distances that are similar to those for uranium-NHC complexes, consistent with a single bond. A theoretical analysis confirms that the correct formulation for these species are as those containing uranium−carbon single bonds, where the bonding is largely ionic. Although no U−C multiple-bond character is present in these molecules, the uranyl moiety is still activated, as indicated by vibrational spectroscopy. This is likely due to

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the superior electron-donating ability of the carbodicarbene, which surpasses that of the N-heterocyclic carbene. Future work will be aimed at understanding how CDC ligands support uranyl redox chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. Computational details. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00860.

Cartesian coordinates for the calculated structure (XYZ)

Experimental procedures and characterization data, ^{1}H, ^{13}C, and ^{19}F NMR, Raman, and IR spectra for all compounds, and crystallographic data for **1-OTf** (PDF)

Accession Codes

CCDC 1969836 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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