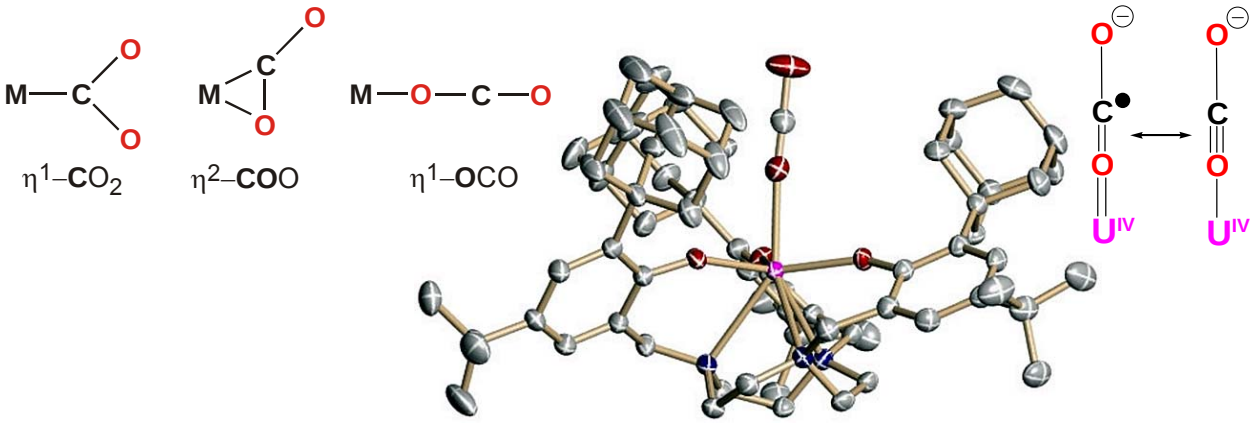
A Linear, O-Coordinated η^1-CO_2 Bound to Uranium

Ingrid Castro-Rodriguez, Hidetaka Nakai, Lev N. Zakharov, Arnold L. Rheingold and Karsten Meyer*

Department of Chemistry and Biochemistry, University of California, San Diego
9500 Gilman Drive, MC 0358, La Jolla, CA 92093-0358, USA
Phone: 858 822 4247 E-mail: kmeyer@ucsd.edu



A new coordination mode of carbon dioxide has been structurally characterized. The electron-rich, six-coordinate tris-aryloxide uranium(III) species, [((^{Ad}ArO)$_3$tacn)U] (**1**) reacts rapidly with CO_2. It yields a rare example of a metal-CO_2 complex, namely [((^{Ad}ArO)$_3$tacn)U(η^1-**O**CO)] (**2**), in which the CO_2 ligand is linearly coordinated through its oxygen atom (η^1-**O**CO). Complex **2** has been crystallographically and spectroscopically characterized. The metric parameters within the U-OCO entity ($d_{U—O}$ = 2.351 Å, $d_{O—C}$ = 1.122 Å, $d_{C—O}$ = 1.277 Å), vibrational data (ν_3: $\nu_O{}^{12}{}_{CO}$ = 2188 cm^{-1}, $\nu_O{}^{13}{}_{CO}$ = 2128 cm^{-1}), SQUID magnetization and electronic absorption spectroscopy data suggest that the electronic structure of **2** can be best described with charge-separated resonance structures: U(IV)=O=C$^{\bullet}$—O^{-} ↔ U(IV)—O≡C—O^{-}, in which the uranium center is oxidized to U(IV) and the CO_2 ligand reduced by one electron.