f-Orbital to Carbonyl 2π Back-Bonding: The Electronic Structures of $(\eta^5\text{-}C_5H_5)_3UCO$ and $(\eta^5\text{-}C_5H_5)_3UOC$

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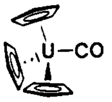
Abstract: The electronic structures of Cp_3UCO (**1**), $[Cp_3UCO]^+$ ($\mathbf{1}^+$), and Cp_3UOC (**2**) have been investigated by $X\alpha$-SW molecular orbital calculations with quasirelativistic corrections. Two major interactions of **1** are discussed. The CO 5σ lone pair interacts primarily with the empty U 6d orbitals to form the U-CO σ bond, and extensive U 5f $\rightarrow$ CO 2π back-bonding is observed. In $\mathbf{1}^+$, the σ interaction is not affected by oxidation while the π back-bonding interaction is decreased. In contrast to **1**, **2** shows no π back-bonding interaction, and the CO 4σ orbital interacts with the filled U 6p orbitals. Upon the basis of these calculations, it is believed that **2** would be unstable relative to **1**.

Since the days of the Manhattan project, chemists have been trying to synthesize uranium carbonyl compounds.[2] Discoveries of facile migratory insertion of CO into uranium bonds with various ligands in the past several years have sparked new interest in this area.[3] Until 1986, the only examples of carbon monoxide coordination to uranium have been observed in matrix isolation studies at very low temperatures.[4] Recently Andersen and coworkers have synthesized the first molecular actinide carbonyl complex that is stable at room temperature in both solution and the solid phase by exposing the organouranium(III) complex Cp'_3U ($Cp' = \eta^5\text{-}Me_3SiC_5H_4$) to carbon monoxide at 1 atm and 20 °C.[5] The infrared spectrum of the resultant complex, Cp'_3UCO (**1′**), shows a lowering of ν_{CO} by ca. 170 cm^{-1} from gaseous CO, experimental evidence for back-donation of electron density from the metal to the empty π^* antibonding orbitals of CO. This is the first time such a back-bonding interaction has been observed in a discrete actinide complex. To better understand the uranium-carbon monoxide bonding in this compound, we have undertaken quasirelativistic $X\alpha$-SW molecular orbital calculations on the model compound Cp_3UCO ($Cp = \eta^5\text{-}C_5H_5$) (**1**). Tatsumi and Hoffmann have previously reported nonrelativistic extended Hückel calculations on the hypothetical U(VI) complex Cp_3UCO^{3+} prior to the synthesis of **1′**.[6] They foresightedly concluded that there would be a good chance of making such a compound but that no strong π back-donation is expected for this formally d^0f^0 complex. We present here theoretical corroboration for extensive U 5f $\rightarrow$ CO 2π back-bonding. Further, it will be shown that the unknown isocarbonyl isomer, Cp_3UOC (**2**), should be unstable and is not expected to exist.

Computational Details

The calculations were carried out in a fashion analogous to our previous calculations on organo-f-element complexes.[7] $X\alpha$-SW calculations[8] on $Cp_3U\text{-}CO$ and $Cp_3U\text{-}OC$ were undertaken by using existing codes which incorporate the quasirelativistic corrections of Wood and Boring.[9] In order to simplify the calculations, the Cp′ ligands were replaced with Cp ligands, and the compounds were idealized to C_{3v} symmetry. Two U-C(CO) bond lengths were used for **1**, 2.29 and 2.57 Å. The first bond length was taken from $Cp_3UCHP(CH_3)_2(C_6H_5)$ in which multiple bond character is ascribed to the U-C bond,[10] and the second bond length was taken from Cp'_3UCNEt.[5] There were no significant differences between the two, and the values reported here are for the first bond length. The structural parameters, sphere radii, and α values are summarized in Table I. The initial molecular potential for each was constructed from a superposition of neutral-atom charge densities. Both calculations were performed by using a partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, $l = 1$, and $l = 0$ on the outer sphere, U, O, C, and H centers, respectively. All orbitals below the U 6s were treated as core orbitals. The converged nonrelativistic potential was used as a starting potential for the relativistic calculation. The relativistic cor-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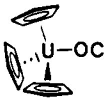
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Table I. Structural Parameters, Sphere Radii, and α Values Used in the $X\alpha$-SW Calculations on $Cp_3U\text{-}CO$ and $Cp_3U\text{-}OC$

molecule	bond length or angle	value
	Structural Parameters	
$Cp_3U\text{-}L$ (L = CO or OC)	U-C(Cp)	2.79 Å
	C-O	1.15 Å
	C-C	1.39 Å
	C-H	1.00 Å
	Cp(centroid)-U-L	100.0°
L = CO	U-C(CO)	2.29 Å
L = OC	U-O	2.29 Å

molecule	atom	sphere radius (Å)	α value
	Calculational Parameters		
$Cp_3U\text{-}CO$	outer sphere	4.32	0.75683
	U	1.63	0.69200
	O	0.88	0.74447
	C(CO)	0.87	0.75928
	C(Cp)	0.89	0.75928
	H	0.64	0.77725
$Cp_3U\text{-}OC$	outer sphere	4.32	0.75683
	U	1.63	0.69200
	O	0.86	0.74447
	C(CO)	0.88	0.75928
	C(Cp)	0.89	0.75928
	H	0.64	0.77725

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[1] Camille and Henry Dreyfus Foundation Teacher-Scholar (1984-1989) and Fellow of the Alfred P. Sloan Foundation (1985-1987).

[2] Gilman, H.; Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Nobis, J. F.; Thirtle, J. R.; Yale, H. L.; Yeoman, F. A. *J. Am. Chem. Soc.* **1956**, *78*, 2790-2792.

[3] See, for example: (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J. In *Organometallics of the f-Elements*: Marks, T. J., Fischer, R. D., Eds.; Reidel Publishing Co.: Dordrecht, Holland, 1979; Chapter 4. (b) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford: England, 1982. (c) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206-2220. (d) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869-871. (e) Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 5393-5396. (f) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063-4066.

[4] (a) Roberts, L. E. J. *J. Chem. Soc.* **1955**, 3939-3946. (b) Slater, J. L.; Sheline, R. K.; Lin, K. C.; Weltner, W., Jr. *J. Chem. Phys.* **1971**, *55*, 5129-5130. (c) Kunze, K. R.; Hauge, R. H.; Hamill, D.; Margrave, J. L. *J. Phys. Chem.* **1977**, *81*, 1664-1667. (d) Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 309-316.

[5] Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335-336.

[6] Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1984**, *23*, 1633-1634.

[7] (a) Bursten, B. E.; Fang, A. *J. Am. Chem. Soc.* **1983**, *105*, 6495-6496. (b) Bursten, B. E.; Fang, A. *Inorg. Chim. Acta* **1985**, *110*, 153-160. (c) Bursten, B. E.; Novo-Gradac, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 904-905.

[8] Case, D. A. *Ann. Rev. Phys. Chem.* **1982**, *33*, 151-171.

[9] Wood, J. H.; Boring, A. M. *Phys. Rev. B* **1978**, *18*, 2701-2711.

[10] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589-3590.

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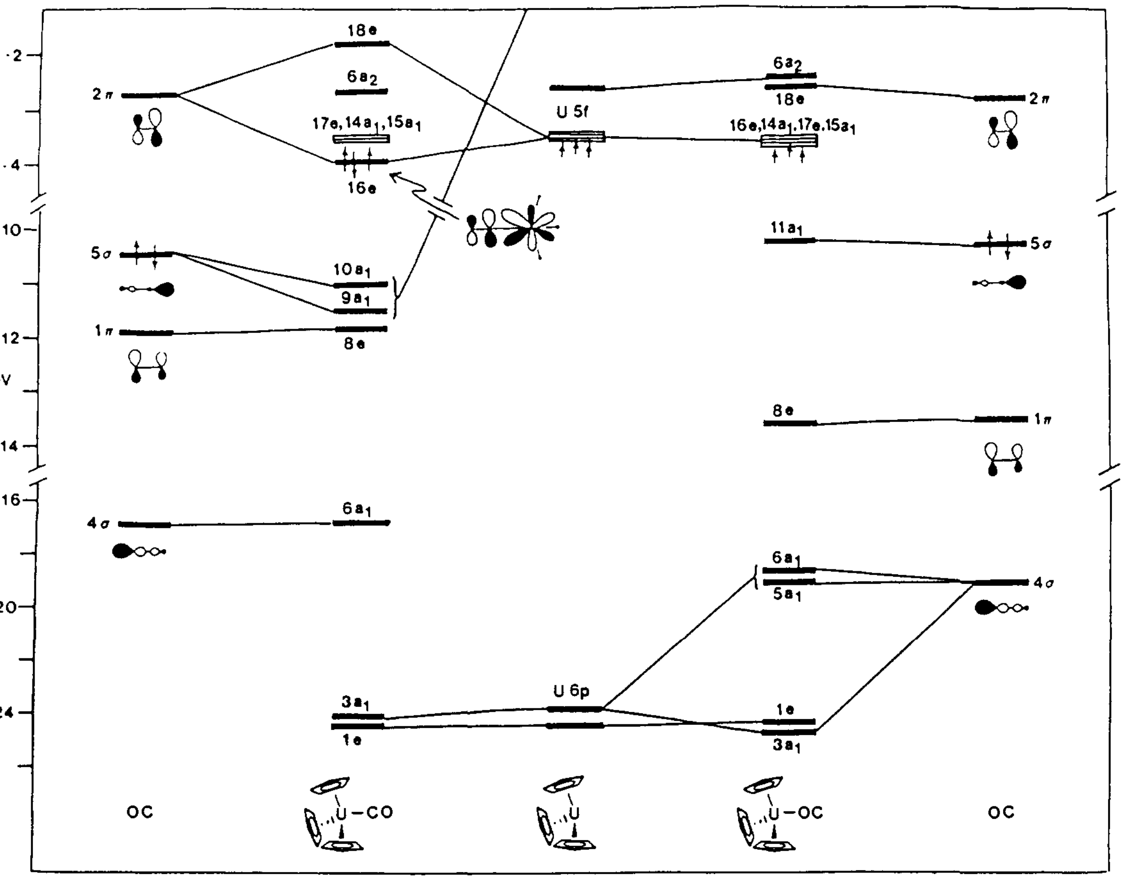

Figure 1. Molecular orbital diagram showing the interaction of a CO ligand and an OC ligand with the Cp_3U fragment to form **1** and **2**, respectively. For clarity, the orbitals which are primarily Cp in character have been omitted.

Table II. Energies and Compositions of Selected Molecular Orbitals of **1**, **1**$^+$, and **2** Which Are Involved in U-CO or U-OC Interactions

					% uranium contributions			
MO	ε (eV)	%C	%O	%U	s	p	d	f
				Cp_3U-CO				
18e[a]	-1.85	16.4	11.2	48.4	0	0	19	81
16e[b]	-3.87	7.0	6.8	84.0	0	0	4	96
10a$_1$	-11.02	20.0	1.8	9.5	24	24	40	13
9a$_1$	-11.45	35.3	3.4	17.6	18	17	44	21
				$[Cp_3U\text{-}CO]^+$				
18e[a]	-6.07	22.9	12.7	38.8	0	0	23	77
16e[c]	-8.29	5.9	5.7	86.5	0	0	3	97
9a$_1$	-15.84	56.3	4.9	27.0	17	19	44	20
				Cp_3U-OC				
6a$_1$	-18.58	4.3	22.2	12.1	4	85	9	3
5a$_1$	-19.09	8.2	43.9	13.0	7	56	24	13
3a$_1$	-24.48	2.9	13.2	81.7	0	99	0	0

[a] Unoccupied orbital. [b] HOMO, occupied with three electrons. [c] HOMO, occupied with two electrons.

rections were mixed in over 10 iterations. Convergence was assumed when the maximum shift in the potential from one iteration to the next was less than 0.0010 Ry. Due to its vanishingly small HOMO-LUMO gap, **2** had to be converged with three unpaired electrons.

The calculation on the cation, **1**$^+$, was performed by taking the converged potential of **1**, removing one electron from the HOMO, and reconverging the calculation.

The fragment orbital energies of **1** and **2** were obtained by taking the converged potential of the compound in question, "removing" the atoms that are not present in the fragment, and performing one iteration with use of 0.2% mixing of the new potential into the old. Since these fragment energies are not converged potentials, they are not good representations of the fragments as separate entities, but they do provide a means of showing the amount of stabilization (or destabilization) that the orbitals undergo upon "in situ" interaction of the two fragments.

Discussion

The molecular orbital diagram of **1** (left side of Figure 1), constructed by allowing the orbitals of CO to interact with those of Cp_3U,[11] shows that there are two major interactions between the orbitals of these two fragments. The first of these is the formation of the U-CO σ bond, a bond which is derived from donation of the carbonyl 5σ lone pair into an empty orbital of Cp_3U. This interaction is contained primarily in the 9a$_1$ MO with a smaller portion in the 10a$_1$ MO, an orbital which is primarily Cp in character. As can be seen in Table II, the overall uranium contribution to the σ bond is 27% with the carbonyl portion amounting to 60%. Consistent with our prior molecular orbital studies of ligand-to-actinide σ donation,[7] the major contributor to the uranium portion of the σ bond is a 6d orbital (in this instance, the $6d_{z^2}$), with approximately equal, but minor, contributions from the $5f_{z^3}$ orbital, the $7p_z$ orbital, and the 7s orbital. Thus, the σ interaction of CO with the actinide fragment is

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[11] For a discussion of the frontier orbitals in Cp_3U, see: Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* **1984**, *272*, 141-154.

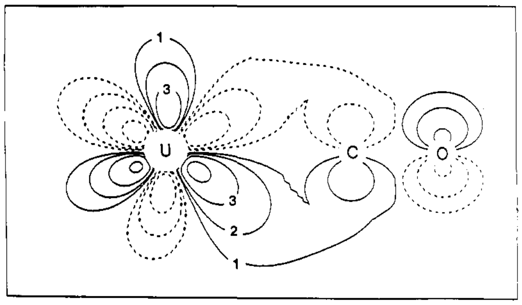

Figure 2. Contour plot of the 16e MO of **1** in a plane containing the U, C, and O atoms. Contour values are as follows: ±4, ±3, ±2, ±1 = ±0.40, ±0.20, ±0.10, ±0.05.

qualitatively the same as that found for other σ donor ligands such as halides, alkyls, or even anionic organometallic fragments.

In contrast to the σ bonding, the second major interaction between the uranium atom and CO nearly exclusively involves the U 5f orbitals. In our previous studies we have found a dichotomy in the roles of the actinide 5f and 6d orbitals: While the latter are principally involved in the σ-binding of ligands, the former contain the highest energy metal-based valence electrons apropos of the particular oxidation state of the metal atom. Thus, in our studies of "f^2" U(IV) complexes with σ-only ligands, the two metal-based electrons reside in essentially pure U 5f orbitals and are nonbonding with respect to the ligands. In the case of **1**, the three metal-based electrons of Cp_3U indeed reside in the U 5f orbitals, but, in this instance, these now have the proper symmetry to interact with the 2π orbitals of the CO ligand. We find a strong interaction between the carbonyl 2π orbitals and the U 5f orbitals, creating bonding (16e) and antibonding (18e) sets of orbitals. The bonding orbital, which is the HOMO of **1**, is 14% carbonyl and 84% uranium in character with the uranium portion consisting of 96% 5f character. This interaction, depicted in Figure 2, represents donation of electron density from the degenerate set of $f\pi$ orbitals on uranium ($5f_{xz^2}$ and $5f_{yz^2}$) to the carbonyl 2π orbital. As is the case in transition-metal-to-carbonyl back-bonding, the donation of electron density into the C–O antibonding 2π orbital would result in a lowering of ν_{CO} from free CO, consistent with the experimental data.

To investigate the effects of oxidation of **1** to U(IV), calculations were performed on the $[Cp_3UCO]^+$ cation, $\mathbf{1}^+$. The orbital energies for all the MO's were lowered over 4 eV from the neutral compound. The σ interaction, which is now contained entirely in one MO (the $9a_1$, Figure 3), is not affected by oxidation since it consists mostly of U 6d character, while the π back-bonding interaction (16e, 18e), which is dominated by U 5f orbitals, is decreased. This reduction of back-bonding capability can be explained in view of the following observations: (1) In $\mathbf{1}^+$ only two electrons are able to backbond as opposed to three electrons in **1**. (2) The 5f orbitals in $\mathbf{1}^+$ are contracted relative to **1** as a result of the increased effective nuclear charge. (3) The lower orbital energies of the U 5f orbitals leads to an increase in energetic separation from the CO 2π orbital, hence a less favorable interaction.

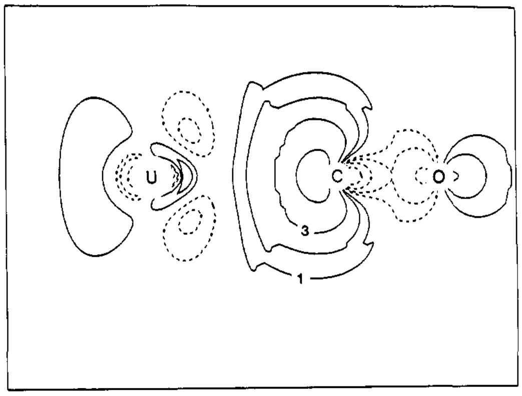

Figure 3. Contour plot of the $9a_1$ MO of $\mathbf{1}^+$ in a plane containing the U, C, and O atoms. Contour values are as follows: ±4, ±3, ±2, ±1 = ±0.32, ±0.16, ±0.08, ±0.04.

The formation of a carbon-bound organouranium complex of CO is quite remarkable in view of the high affinity for oxygen that these systems exhibit. This high oxophilicity, even for the oxygen atoms of free[3] or coordinated[12] CO, has been well-documented both experimentally[3,12] and theoretically.[13] The apparent facile formation of **1′** prompted us to investigate the unknown isocarbonyl complex **2**. A comparison of the two major interactions between the Cp_3U fragment and an O-bound isocarbonyl ligand with those observed for **1** shows significant differences between the two isomers (Figure 1). Although the CO 2π orbital and the U 5f orbitals have identical energy separation in the two complexes, the CO 2π is primarily localized on the carbon atom, away from the U 5f orbitals in **2**. Thus, no stabilization of the U 5f orbitals as a result of π interaction with the isocarbonyl is observed. Second, and more important, is the realization that the σ interaction now involves the oxygen "lone pair" orbital, the CO 4σ, which is a rather strongly C–O bonding orbital. As such, it is at a much lower energy than the CO 5σ orbital and, for that matter, the oxygen lone pair orbitals of other oxygen donors such as alkoxides[14] or phosphine oxides.[15] Because of its low energy, the CO 4σ orbital has a stronger tendency to interact with the filled U 6p orbitals rather than the empty U 6d orbitals, creating a "filled–filled" interaction which results in no net U–O bonding. The mixing in of some U 6d and 5f character, particularly in the $5a_1$ MO, can be viewed as an attempt on the part of the molecule to alleviate some of the U 6p-oxygen antibonding; such an explanation has recently been advanced by Larsson and Pyykkö in the discussion of their relativistic extended Hückel results for UO_2^{2+}.[16] Nevertheless, a comparison of the bonding in Cp_3U–CO and Cp_3U–OC leads to the expectation that the isocarbonyl complex should not be stable relative to the carbonyl complex. The bonding of other oxygen-containing ligands to the Cp_3U fragment will be detailed in a later publication.

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[12] (a) Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6749–6750. (b) Cramer, R. E.; Higa, K. T.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 7245–7247. (c) Cramer, R. E.; Jeong, J. H.; Gilje, J. W. *Organometallics* **1986**, *5*, 2555–2557.

[13] (a) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451. (b) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467–4476.

[14] (a) Ter Haar, G. L.; Dubeck, M. *Inorg. Chem.* **1964**, *3*, 1648–1650. (b) Ammon, R. v.; Kanellakopulos, B. *Radiochim. Acta* **1969**, *11*, 162–168. (c) Ammon, R. v.; Fischer, R. D.; Kanellakopulos, B. *Chem. Ber.* **1972**, *105*, 45–62.

[15] Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761–1765.

[16] Larsson, S.; Pyykkö, P. *Chem. Phys.* **1986**, *101*, 355–369. We are grateful to a referee for bringing this reference to our attention.