Table I. Sphere Radii (Å) and α Parameters for Cp_3M

	atom	sphere radius	α
	C	0.8984	0.75928
	H	0.6783	0.77725
M = Th	outer sphere	4.0788	0.75929
	Th	1.7112	0.69200
M = Pa	outer sphere	4.0700	0.75844
	Pa	1.6933	0.69200
M = U	outer sphere	4.0701	0.75762
	U	1.6879	0.69200
M = Np	outer sphere	4.0701	0.75682
	Np	1.6830	0.69200
M = Pu	outer sphere	4.0701	0.75604
	Pu	1.6659	0.69200

statistical total energies of only 100 cm^{-1}! While we are reluctant to believe the quantitative validity of the $X\alpha$ total energies,[19] we do believe the trends to be properly indicated and therefore suggest that a different ground electronic configuration might exist for **2** than for Cp_3UL complexes. The possibility of a $6d^15f^2$ ground configuration for **2** appears to be at odds with a previous calculational study on the U(IV) complex $\mathbf{2}^+$, which places the $6d_{z^2}$ orbital ca. 4 eV above the 5f orbitals.[23] We look forward to the experimental determination of the ground configuration of **2**.

Computational Details

Quasi-relativistic $X\alpha$–SW calculations were carried out in analogy to those previously reported.[1] Structural parameters for **1** and **2** were taken from the crystal structures of **1**″ and **2**′.[5a,14] The structural parameters for Cp_3Pa, Cp_3Np, and Cp_3Pu were set equal to those of **2**. Both the planar and pyramidal Cp_3M (M = Th, Pa, U, Np, Pu) calculations were performed under C_{3v} symmetry. The basis functions included all spherical harmonics through $l = 4$ on the outer sphere, $l = 3$ on M, $l = 1$ on C, and $l = 0$ on H. The starting potentials for each molecule were superpositions of neutral atomic Herman–Skillman potentials of the constituent atoms. The atomic sphere radii were chosen as 89.0% of the atomic number radii. The sphere radii and the α parameters are summarized in Table I. The calculations were first converged spin-restricted, and the converged spin-restricted potential was used as a starting potential for the spin-unrestricted calculations. Spin-restricted and spin-unrestricted total energies were calculated according to Slater's formalism.[15]

Acknowledgment. We thank Dr. C. J. Burns, Dr. D. L. Clark, and Dr. A. P. Sattelberger for stimulating discussions. We gratefully acknowledge support for this research from the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Contract DE-FG02-86ER13529), and from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(19) There have undeniably been difficulties in using the $X\alpha$–SW total energy to calculate equilibrium geometries and potential surfaces, in largest part because of the problems associated with sphere radius selection.[20] In the results reported here, we are keeping the molecular geometries and sphere radii fixed; only the orbital occupations are changed. We believe that this will achieve a reasonable separation of "geometric" and "electronic" contributions to the total energy, and we have more confidence in the latter than the former. As support for the application of $X\alpha$–SW total energies in these types of systems, we note that Edelstein et al.[21] estimate the splitting between the $5f^1$ and $6d^1$ configurations of $PaCl_6^{2-}$ to be ca. 22 000 cm^{-1}. The difference in spin-unrestricted $X\alpha$–SW statistical total energies is calculated to be 28 000 cm^{-1}, with the $5f^1$ configuration correctly predicted as the ground configuration.[22]

(20) See, for example: Weber, J.; Geoffrey, M. *J. Mol. Struct.* **1979**, *51*, 141–144.

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Bonding in Tris(η^5-cyclopentadienyl) Actinide Complexes. 3. Interaction of π-Neutral, π-Acidic, and π-Basic Ligands with $(\eta^5\text{-}C_5H_5)_3U$[1]

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Abstract: A qualitative treatment of the bonding in Cp_3M (Cp = η^5-C_5H_5) compounds under C_{3v} symmetry reveals that the Cp_3^{3-} ligand field contains a high-lying a_2 orbital which is restricted by symmetry to interact only with metals that contain f orbitals. Quantitative investigation of the electronic structure of "$5f^3$" Cp_3U via $X\alpha$-SW molecular orbital calculations with quasi-relativistic corrections reveals that the Cp ligands donate electron density primarily into the U 6d orbitals while the three principally metal-based valence electrons are housed in the 5f orbitals. Electronic structure calculations of Cl_3U show that although Cl can be considered isolobal with Cp, it is a poorer donor ligand. Calculations of Cp_3U bonded to a fourth ligand L (L = H, CO, NO, OH) indicate that the σ-bonding framework is essentially the same for π-neutral (H), π-acidic (CO, NO), or π-basic (OH) ligands: Electron density is donated from the σ orbital of the fourth ligand into a uranium orbital that is primarily $6d_{z^2}$ in character with minor contributions from the $5f_{z^3}$ orbital, the $7p_z$ orbital, and the 7s orbital. In the π-bonding framework, the U 5f orbitals are responsible for back-donation into the π^* orbitals of CO and NO, while acceptance of electron density from the π orbitals of OH involves the U 6d orbitals and, to a lesser extent, the U 5f orbitals. The bonding scheme of Cp_3UNO suggests that this molecule may prove to be a rather unusual example of a linear NO^- ligand.

Organoactinide chemistry has received considerable attention in the last two decades.[3] As was the case for organotransition-metal chemistry, the growth of this field has been intimately coupled with the use of the π-coordinating cyclopentadienyl (Cp)

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(1) (a) Part 1: Bursten, B. E.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6606–6608. (b) Part 2: Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Camille and Henry Dreyfus Foundation Teacher-Scholar (1984–1989).

or modified Cp ligands. In fact, the first well-characterized organoactinide complex, Cp_3UCl,[4] was synthesized by Reynolds and Wilkinson shortly after the synthesis of ferrocene. Since this first report, a plethora of Cp–actinide complexes have been synthesized, and it is possible to coordinate one, two, three, or four Cp ligands in an η^5 fashion.[3b] Previous studies from these laboratories have reported electronic structure calculations on a number of bis- and tetrakiscyclopentadienyl–actinide complexes, Cp_2AnX_2 and Cp_4An (An = actinide metal).[5] A consistent picture has emerged from these studies concerning the nature of the actinide–ligand bonds and, for An = U, the location of the two metal-based electrons in these formal U(IV) complexes.

The impetus for the above studies was the host of reactive molecules of formulation $Cp^*_2AnX_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) that have been synthesized in the last 10 years, primarily by Marks and co-workers.[6] The tetrakiscyclopentadienyl complexes provided a novel counterpart to these studies inasmuch as these highly symmetric molecules afforded the opportunity to investigate (i) a coordination environment that does not exist for transition elements, (ii) complexes that contain formal electron counts as high as 26, (iii) a direct comparison between Cp^- and monodentate X^- (e.g., halide or alkyl) ligands, and (iv) the correlation of calculated electronic structure with relatively simple experimental probes such as valence photoelectron spectroscopy.

In comparison to the bis-Cp* and tetrakis-Cp complexes, the chemistry of actinide complexes containing three Cp (or modified Cp) ligands has been, until recent years, rather scant. There was a spurt of activity in the late 1960s to the early 1970s, concerned primarily with investigations into trivalent organoactinides. The reaction of UCl_3 with Cp^-, or the reduction of Cp_3UX in the presence of neutral Lewis bases L, was shown to produce a variety of U(III) complexes Cp_3UL.[7,8] Nearly concurrently, the coordination of three Cp ligands to trans-plutonium elements was explored, leading to the syntheses of a number of Cp_3An (An = Pu, Am, Cm, Bk, Cf) complexes,[9] some of which represent the only known organometallic complex for the given element. Following nearly 10 years of dormancy after this, the chemistry of tris(cyclopentadienyl)–actinide complexes (especially those of uranium) took off once again, largely through the pioneering efforts of two research groups. First, Cramer, Gilje, and co-workers uncovered a rich chemistry in the reactions of Cp_3UCl with lithiated phosphoylides and related molecules.[10] The complexes they have synthesized exhibit a wide variety of novel structures and reactivities, including uranium–carbon multiple bonding, and have been the subject of relativistically parameterized extended Hückel MO calculations by Tatsumi and co-workers.[11] More recently, Andersen and co-workers have probed the reactions of the Cp_3U fragment with a variety of simple ligands to produce a wide spectrum of extremely interesting U(III) and U(IV) complexes;[12] among these is Cp'_3UCO ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$), the first example of a discrete actinide–carbonyl complex.[12a] We have recently reported a preliminary account of the electronic structure of this complex.[1a]

Table I. Structural Parameters, Sphere Radii, and α Values Used in the Xα-SW Calculations on Cp_3U, Cl_3U, Cp_3UH, Cp_3UNO, and Cp_3UOH

	structural parameters	
molecule	bond length or angle	value
Cp_3U	U–C	2.79 Å
	C–C	1.39 Å
	C–H	1.00 Å
	Cp(centroid)–U–Cp(centroid)	117.0°
Cp_3U–L	Cp–U–L	100.0°
L = H	U–H	2.00 Å
L = NO	U–N	2.29 Å
	N–O	1.15 Å
L = OH	U–O	2.06 Å
	O–H	1.00 Å
Cl_3U	U–Cl	2.53 Å
	Cl–U–Cl	117.0°

	calculational parameters		
molecule	atom	sphere radius, Å	α value
Cp_3U	outer sphere	3.87	0.75762
	U	1.69	0.69200
	C	0.89	0.75928
	H	0.65	0.77725
Cl_3U	outer sphere	5.65	0.71631
	U	1.70	0.69200
	Cl	1.42	0.72325
Cp_3UH^a	outer sphere	3.99	0.75786
	U	1.66	0.69200
	H (hydride)	0.90	0.77725
Cp_3UNO^a	outer sphere	5.14	0.75646
	U	1.63	0.69200
	O	0.85	0.74447
	N	0.85	0.75197
Cp_3UOH^a	outer sphere	4.06	0.75695
	U	1.57	0.69200
	O	0.95	0.74447
	H (OH)	0.61	0.77725

[a] The calculational parameters for the C(Cp) and H(Cp) atoms are the same as in the Cp_3U calculation.

In this report, we will extend our applications of the quasi-relativistic Xα-SW molecular orbital method to encompass several tris(cyclopentadienyl)–uranium complexes. It was not obvious to us whether or not the Cp_3U fragment could be considered as merely an extension of our previous studies on bis and tetrakis complexes, especially since the C_{3v} geometry of the fragment could force quantization of the U orbitals about a threefold axis, as compared to the twofold axis quantization that we observed for the C_{2v} Cp_2AnX_2 and D_{2d} Cp_4An systems. We will begin with a qualitative analysis of the bonding of three Cp rings to either a transition element or an actinide element, followed by a discussion of the quantitative results for the C_{3v} U(III) molecule Cp_3U. The role of the Cp ligands in this molecule will be discussed by comparing Cp_3U with Cl_3U. The Cp_3U fragment will be allowed to interact with H, OH, and CO to form models of the known complexes Cp_3UH,[13] Cp_3UOR, and Cp'_3UCO. Finally,

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(3) See, for example: (a) *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1985. (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) *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1979.

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(13) Cp_3UH has not been isolated to our knowledge. It has been observed as part of the fragmentation pattern of an electron impact mass spectrometry study on $Cp_3U[\eta^2\text{-}C(CH_3){=}N(R)]$ ($R = C_6H_{11}$, $n\text{-}C_4H_9$).[14] It has also been tentatively identified as an intermediate in the reduction of Cp_3UCH_3 by $LiCH_3$.[15] Cp_3ThH is believed to be an intermediate in a photoinduced β-hydride elimination reaction of Cp_3ThR ($R = i\text{-}C_3H_7$, $n\text{-}C_4H_9$).[16]

in view of the formation of the carbonyl complex and the presence of fπ → pπ back-bonding, we will report calculations on the as yet unknown complex Cp_3UNO and will comment on the prospects for its existence.

Computational Details

All of the calculations reported here employ the Xα-SW molecular orbital method[17] and were undertaken with existing codes that incorporate the quasi-relativistic corrections of Wood and Boring.[18] The calculations were carried out in a fashion analogous to our previous calculations on organo-f-element complexes.[1,5,19] The structural parameters, sphere radii, and α values are summarized in Table I. The initial molecular potentials were constructed from a superposition of neutral-atom charge densities. Convergence was assumed when the maximum shift in the potential from one iteration to the next was less than 0.0010 Ry. The fragment orbital energies were obtained in a manner analogous to previous studies.[1a]

Cp_3U. The structural parameters for this compound were taken from the X-ray crystal structures of Cp_3U–THF[20] and Cp_4U[21] and are consistent with most Cp_3U-containing compounds. The compound was idealized to C_{3v} symmetry. A partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, and $l = 0$ on the outer sphere, U, C, and H centers, respectively, was used. All orbitals below the U 6p were treated as unfrozen core orbitals. The relativistic corrections were incorporated from the beginning of the SCF procedure; it was not necessary to first converge the molecule nonrelativistically. The calculation was converged with three unpaired electrons occupying the 15e and 11a$_1$ orbitals.

Cl_3U. The structural parameters for this molecule were chosen to closely resemble those used for Cp_3U. The U–Cl bond length was taken from the known compound UCl_4.[22] A partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$ on the outer sphere, U, and Cl centers, respectively, was used. All orbitals below the U 6s were treated as unfrozen core orbitals. The relativistic corrections were mixed over 10 iterations. The calculation was converged with one electron occupying the 6a$_1$ orbital and two electrons occupying the 6e (HOMO) orbital.

Cp_3UH. The structural parameters for the Cp_3U portion of Cp_3UH are identical with those used in the Cp_3U calculation. Two different U–H distances were used (see discussion). A partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, $l = 0$ on the outer sphere, U, C, and H centers, respectively, was used. All orbitals below the U 6p were treated as unfrozen core orbitals. The relativistic corrections were incorporated from the beginning of the SCF procedure. For the Cp_3U portion of the molecule, the previously converged potentials from the Cp_3U calculation were used as a starting point in order to facilitate convergence.

Cp_3UNO. The structural parameters for this unknown molecule were chosen to be identical with those used in a previous molecular orbital calculation of Cp_3UCO.[1] A partial wave basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, $l = 1$, $l = 1$, and $l = 0$ on the outer sphere, U, O, N, C, and H centers, respectively, was used. All orbitals below U 6s were treated as unfrozen core orbitals. The relativistic corrections were incorporated from the beginning of the SCF procedure. The calculation was converged with four electrons, spin paired, occupying the 16e (HOMO) orbital.

Cp_3UOH. The structural parameters for the Cp_3U portion of Cp_3UOH are identical with those used in the Cp_3U calculation. To our knowledge there are no structurally characterized Cp_3UOR complexes; therefore, a reasonable U–O bond length was estimated from structural data on other uranium(IV) alkoxide complexes.[23] The compound was first studied in idealized C_{3v} symmetry, i.e., with a linear U–O–H linkage. 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, was used. All orbitals below the U 6s were treated as unfrozen core orbitals. The converged nonrelativistic potential was used as a starting potential for the relativistic calculation. The relativistic corrections were mixed in over 10 iterations. A second calculation was performed with a U–O–H angle of 153.7°.[38] The converged potential of the first calculation was used as a starting point for this low-symmetry (C_s) calculation. Other than showing an increase in mixing between MO's, the results of the C_s calculation are not significantly different from those of the higher symmetry C_{3v} calculation, and the results presented here are those of the latter.

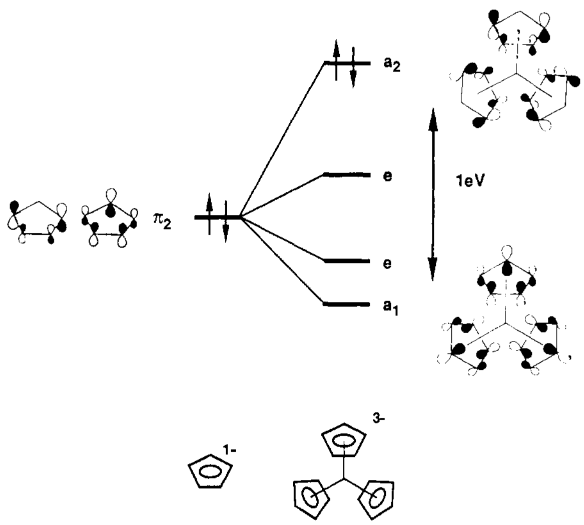

Figure 1. Splitting of the π_2 orbitals of three cyclopentadienyl ligands under C_{3v} symmetry. The relative energy splittings were calculated by the Fenske–Hall molecular orbital method.

Table II. Metal Orbital Interactions with Cp_3^{3-} Under C_{3v} Symmetry

Cp_3^{3-} orbital	transition metal	f orbitals
a$_1$	s p_z d_{z^2} (dσ)	f_{z^3} (fσ) $f_{x(x^2-3y^2)}$ (fϕ)
e	p_x,p_y d_{xz},d_{yz} (dπ) $d_{x^2-y^2}$,d_{xy} (dδ)	f_{xz^2},f_{yz^2} (fπ) f_{xyz},$f_{z(x^2-y^2)}$ (fδ)
a$_2$	none	$f_{y(3x^2-y^2)}$ (fϕ)

Results and Discussion

Cp_3M Compounds: Symmetry Considerations. The bonding interactions of a metal center with the π orbitals of a D_{5h} cyclopentadienyl ligand take place between the valence orbitals of the metal and the Cp e$_1''$ (π_2) orbital and, to a lesser extent, the Cp a$_2''$ (π_1) orbital.[24] When three Cp ligands are distributed in threefold fashion about a central point, as in Figure 1, their π orbitals are split due to ligand–ligand interactions. Under C_{3v} symmetry, the three π_1 orbitals generate group orbitals of a$_1$ and e symmetry. When the angle between the centroids of the Cp ligands and the z axis is 100°, as typically will be assumed here, neither of these group orbitals is significantly stabilized or destabilized with respect to the π_1 orbital of the free ligand. The doubly degenerate π_2 orbitals transform as a$_1$ + a$_2$ + 2e representations. As can be seen in Figure 1, the a$_1$ representation contains constructive interactions between the π orbitals of the

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(24) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742. Interestingly, the first group theoretical treatment of the interaction of three η^5-Cp ligands with an actinide element was given by Moffitt as part of the paper reporting the original synthesis of Cp_3UCl by Reynolds and Wilkinson. We are grateful to Professor R. A. Andersen for pointing this out to us.

three ligands and is strongly stabilized with respect to the π_2 orbital of the free ligand. One of the e representations is slightly stabilized with respect to the free ligand, while the other e representation is slightly destabilized. The remaining a_2 representation, which is pictured in Figure 1, contains strongly antibonding interligand interactions and is thus strongly destabilized with respect to the π_2 orbital of the free ligand. Obviously, a key role that a metal center could play in the stabilization of this geometry would be the stabilization of this high energy, ligand-based orbital via the acceptance of charge from it. We will now look at how d- and f-block metals compare in their ability to achieve this.

Lauher and Hoffmann[24] have previously presented a brief but lucid discussion of the interactions that occur when a transition metal is placed at the focus of the set of three Cp ligands. Each of the nine metal valence atomic orbitals can interact with the π_2 group orbitals of the Cp_3^{3-} unit. As can be seen in Table II, the metal s, p_z, and d_{z^2} orbitals each are of the proper symmetry to interact with the a_1 orbital of Cp_3^{3-}. In each case, the overlap of the metal and ligand a_1 orbitals is poor; hence, the metal orbitals are unable to interact with (and thus stabilize) the ligand a_1 orbital to a great extent. Such stabilization is not necessary for the Cp_3^{3-} a_1 orbital, however, since it is comprised of intra- and interligand bonding interactions. The metal (p_x,p_y), (d_{xz},d_{yz}), and $(d_{x^2-y^2},d_{xy})$ orbitals can interact with the e combinations of Cp_3^{3-}. The lobes of the two d orbital sets are directed toward the lobes of the π orbitals of the cyclopentadienyl rings, thus resulting in good overlap of the metal and ligand orbitals. As a result, a transition metal with suitable empty orbitals is able to stabilize the e orbitals of Cp_3^{3-} quite well.

What about the Cp_3^{3-} a_2 orbital, which, as noted above, is greatly destabilized relative to a single Cp ligand? A transition metal contains no orbitals of a_2 symmetry under C_{3v} symmetry, and hence the ligand a_2 orbital cannot interact with the metal atom and must remain highly destabilized. It is interesting to note that the suitability of a ligand for a given metal atom is often judged on the basis of the ligand's ability to stabilize the orbitals of the metal, as in the case of the preference of zero-valent metals for π-acidic ligands. In this case, we will turn this argument around: *It appears that a transition metal should be an inappropriate template about which to place three Cp ligands because of the inability of the metal atom to stabilize a high-energy orbital of the ligand set.* In fact, to our knowledge only one transition metal, zirconium, has (in two instances[25]) been shown unequivocally to adopt this geometry. One of these complexes, Cp_4Zr, the static structure of which contains three η^5 and one η^1 cyclopentadienyl ligands, has long M–C(η^5-Cp) bond lengths which helps to minimize the unfavorable a_2 interaction. Lauher and Hoffmann[24] have pointed out that $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$, which appears to be a 20-electron complex, is in actuality an 18-electron species since the ligand-based a_2 orbital is incapable of donation to the metal.

If, instead of a transition metal, an actinide metal is placed in the center of the three cyclopentadienyl rings, the situation changes markedly. An actinide metal has 16 valence orbitals available to interact with the π orbitals of Cp_3^{3-}. Nine of the 16 are the same as those in the transition-metal case and will interact in the same manner as discussed above. The 5f orbitals comprise the remaining seven orbitals and are responsible for the observed differences. As can be seen in Table II, two of these seven transform as a_1 representations under C_{3v} symmetry. The f_{z^3} orbital is directed along the threefold axis and, like the p_z and d_{z^2} orbitals, is not expected to overlap significantly with the π orbitals of the cyclopentadienyl rings. The lobes of the $f_{x(x^2-3y^2)}$ orbital are directed at the lobes of the π orbitals of Cp_3^{3-}, so this orbital might have the ability to interact with the a_1 representation to a much greater extent than any of the other a_1 metal valence orbitals. Four of the 5f orbitals transform as two sets of e orbitals. Since the lobes of these orbitals are directed only somewhat toward the Cp π orbitals, the overlap is rather small and the participation of these orbitals in metal–Cp bonding is not expected to be great. This leaves one metal orbital, the $5f_{y(3x^2-y^2)}$, which is of a_2 symmetry under C_{3v}. The lobes of this orbital point directly at those of the Cp_3^{3-} a_2 orbital, which results in sizable metal–ligand overlap. Thus, this metal atomic orbital strongly interacts with, and stabilizes, the ligand a_2 orbital, relieving the unfavorable electronic situation within the Cp_3^{3-} ligand set. It is this electronic interaction, in conjunction with (as Lauher and Hoffmann[24] have noted) the larger size of the actinide atoms, that we believe is largely responsible for the abundance of Cp_3M derivatives for the actinide elements compared to the scarcity of such for the transition elements. We will now proceed to describe the interactions in Cp_3An complexes more quantitatively.

Cp_3U. Our prior calculations on organoactinide complexes have demonstrated a dichotomy in the roles of the actinide valence 5f and 6d orbitals. The latter are the most important with regard to the acceptance of electron density from ligands; typically, the An 6d contribution to the metal–ligand bonding orbitals is about twice as great as that of the 5f orbitals. In the case of complexes wherein the metal atom is not in its highest possible oxidation state ("non-f^0" complexes), the 5f orbitals are used exclusively to house the metal-based electrons. Clearly, in view of the above discussion, this situation must change somewhat for a Cp_3An complex, inasmuch as the Cp_3^{3-} a_2 orbital can only interact with the 5f orbitals of the metal. We have chosen to investigate the quantitative bonding effects in Cp_3An complexes by looking at the known U(III) complex Cp_3U. It is clear that two reasonable choices could be made for the assumed Cp(centroid)–U–Cp(centroid) angles. The first, which is based on the known structures of Cp_3U derivatives, would have the angle <120°, i.e., a pyramidal C_{3v} structure. The second, which is based on the recent structures of the Th(III) complex Cp''_3Th [Cp'' = 1,3-bis(trimethylsilyl)-cyclopentadienyl],[26] or the U(III) complex Cp'_3U,[12f,g] would require setting the angle equal to 120°, giving a trigonal-planar, pseudo-D_{3h} structure. We are not certain to what extent the bulky $SiMe_3$ groups govern the observed geometry of these complexes, and furthermore, we are interested in extending the calculation on Cp_3U to its adducts with a fourth ligand. For these reasons, we have assumed here a pyramidal structure for Cp_3U, with a centroid–U–centroid angle = 117°.

An additional assumption must be made regarding the ground electron configuration of the Cp_3U fragment. Recent experimental studies on Cp''_3Th[27] and theoretical studies on trigonal-planar Cp_3Th and Cp_3U[1b] indicate that, in the absence of a fourth ligand, it is possible to occupy an actinide 6d orbital preferentially over the 5f's. This situation does not exist in complexes that contain a fourth ligand, wherein the metal-based electrons occupy 5f orbitals exclusively. Since we are primarily interested here in Cp_3U as a fragment (as opposed to a molecule in its own right), the calculations reported for Cp_3U and Cl_3U are those with a $5f^3$ (rather than $6d^15f^2$) metal configuration.

The molecular orbital diagram of Cp_3U is shown in Figure 2. The metal–ligand bonding orbitals can be grouped into two distinct manifolds, namely, one involving donation from the three Cp π_1 orbitals to U and one representing the donation from the degenerate Cp π_2 orbitals to the metal. As would be expected from energetic considerations, there is less ligand-to-metal donation in the former set of orbitals than in the latter. As can be seen in Table III, the MO's of Cp_3U that are derived from the Cp π_1 orbitals contain 10–14% U character. In the $8a_1$ MO,[28] the donation is almost entirely into the U 7s orbital, analogous to the

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[25] (a) Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985–990. (b) Rogers, R. D.; Vann Bynum, R.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238–5239. (c) Kulishov, V. I.; Brainina, E. M.; Bokiy, N. G.; Struchkov, Yu. T. *J. Chem. Soc. D* **1970**, 475.

[26] Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148–1149.

[27] Kot, W. K.; Shalimoff, G. F.; Edelstein, N. M.; Edelman, M. A.; Lappert, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 986–987.

[28] For Cp_3U, molecular orbital levels $1a_1$–$7a_1$, $1a_2$–$4a_2$, and 1e–11e consist of U 6p orbitals and Cp C–H and C–C σ-bonding orbitals. This will be the numbering scheme used throughout this discussion. In ref 1a the U 6s orbital is counted as the $1a_1$ orbital, hence the $(n)a_1$ orbital of ref 1 corresponds to the $(n-1)a_1$ orbital of this paper.

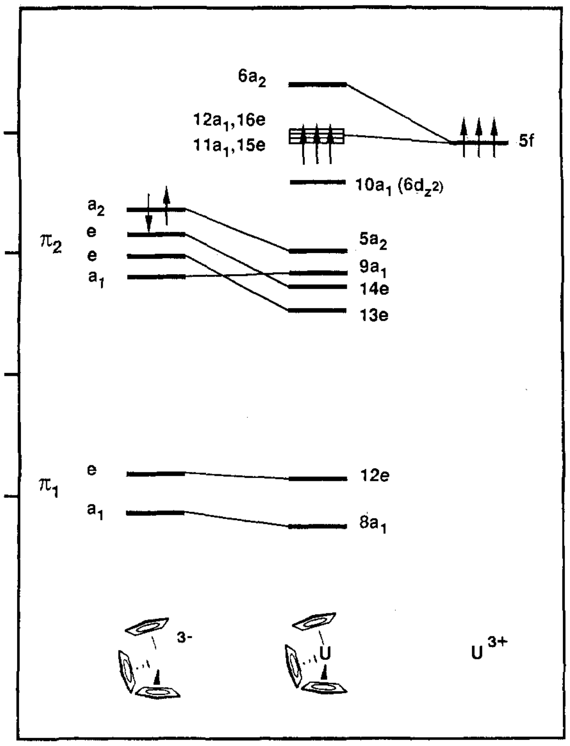

Figure 2. Molecular orbital diagram showing the interaction of Cp_3^{3-} with U^{3+} to form Cp_3U. The $10a_1$ MO is unoccupied (see text).

Table III. Highest Occupied and Lowest Unoccupied Molecular Orbitals of Cp_3U and Cl_3U

MO	orbital type	ε, eV	uranium contribns, % s	p	d	f	ligand contribns, %
			Cp_3U				
$6a_2$[a]	(U 5f)	−1.26				84	16
$12a_1$[a]	(U 5f)	−2.10	1			98	1
$16e$[a]	(U 5f)	−2.12			4	94	2
$11a_1$[b]	(U 5f)	−2.14			4	93	3
$15e$[c]	(U 5f)	−2.18			3	94	3
$10a_1$[a]	(U $6d_{z^2}$)	−3.00	14	4	66		16
$5a_2$	(Cp π_2)	−4.04				29	71
$9a_1$	(Cp π_2)	−4.35		4	7	7	82
14e	(Cp π_2)	−4.51		2	14	7	77
13e	(Cp π_2)	−4.88		1	24		75
12e	(Cp π_1)	−7.69		4	6		90
$8a_1$	(Cp π_1)	−8.54	12		2		86
			Cl_3U				
$8a_1$[a]	(U $6d_{z^2}$)	−2.05	21		69	7	3
$2a_2$[a]	(U 5f)	−3.05				97	3
$7a_1$[a]	(U 5f)	−3.15	4		1	94	1
$7e$[a]	(U 5f)	−3.19			1	98	1
$6e$[d]	(U 5f)	−3.24			2	98	0
$6a_1$[e]	(U 5f)	−3.24				99	1
5e	(Cl pπ)	−8.26		3		2	95
$5a_1$	(Cl pπ)	−8.34		1		2	97
$1a_2$	(Cl pπ)	−8.43				5	95
4e	(Cl pπ)	−8.54			4	1	94
3e	(Cl pσ)	−9.52		4	16	2	78
$4a_1$	(Cl pσ)	−10.27	8		6	7	78

[a] Unoccupied orbital. [b] HOMO, singly occupied orbital. [c] Occupied with two electrons. [d] HOMO, occupied with two electrons. [e] Singly occupied orbital.

donation seen from the a_1 Cp π_1 orbital in the pseudotetrahedral molecule Cp_4U,[5a] wherein the U s orbital is the only one of a_1 symmetry. The 12e MO's represent donation principally into the U 6d orbitals.

Immediately above the $8a_1$ and 12e MO's is the set of four orbitals (13e, 14e, $9a_1$, and $5a_2$) that comprise the donation from the Cp π_2 orbitals to the U center. The two doubly degenerate orbitals both involve donation primarily into the U 6d orbitals, consistent with our previous observations. The $9a_1$ MO, interestingly, contains nearly equal contributions from the U 6d and 5f orbitals. This is due in largest part to the poor orientation of the U $6d_{z^2}$ orbital for overlap with the pπ orbitals of the Cp rings, the same factor that led to such a small 6d contribution to the $8a_1$ MO and that leads to the prediction of a different electron configuration for "base-free" Cp_3U complexes as compared to Cp_3UL complexes.[1b] It is noted that the $9a_1$ MO correspondingly contains the smallest U contribution of this set of MO's and, as a result, is stabilized less than the orbitals of e symmetry. The final member of this set is the $5a_2$ MO (Figure 3), in which, as discussed above, the Cp to U donation is symmetry-restricted to use only the U $5f_{y(3x^2-y^2)}$ orbital as an acceptor. The ligand-to-metal donation is largest (29% U contribution) in this orbital and leads to considerable stabilization of the a_2 orbital relative to Cp_3^{3-}. A relativistically parameterized extended Hückel calculation on Cp_3U[11a] showed a similar interaction, although the U 5f contribution to the a_2 MO was found to be only 8%.

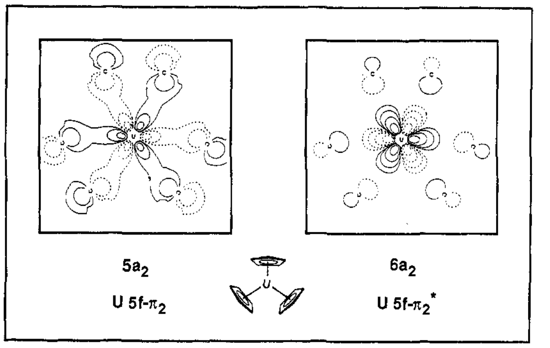

Figure 3. Contour plots of the $5a_2$ and $6a_2$ MO's of Cp_3U in a plane that contains the U atom and is perpendicular to the threefold axis. Contour values: ±4, ±3, ±2, ±1 = ±0.32, ±0.16, ±0.08, ±0.04.

Immediately above the Cp-based orbitals is a single 6d-based orbital, the $10a_1$. As alluded to above, and detailed elsewhere,[1b] this orbital is the one that leads to electron configurational differences between Cp_3U and Cp_3UL complexes, the $10a_1$ orbital will be energetically raised above the 5f orbitals through interaction with a fourth ligand (vide infra). Thus, for consistency between the Cp_3U fragment and Cp_3UL complexes, the $10a_1$ orbital is kept unoccupied here in spite of its low energy.

Finally, there is the set of U 5f orbitals that comprises the highest occupied orbitals of Cp_3U. Under C_{3v} symmetry, the f orbitals split as $2a_1 + a_2 + 2e$, and with one exception, these are clustered in a very narrow (<0.1 eV) energetic band. This is due to the rather small role that the U 5f orbitals play in metal–ligand bonding; the orbitals are nearly pure U 5f and are scarcely split by the Cp_3 "ligand field". Two orbitals of a_1 symmetry ($11a_1$ and $12a_1$), which are mixtures of the $5f_{z^3}$ orbital (the fσ orbital) and the $5f_{x(3y^2-x^2)}$ orbital (one of the fϕ orbitals), and two orbitals of e symmetry (15e and 16e), which are mixtures of the ($5f_{xz^2}$,$5f_{yz^2}$) set of orbitals (the fπ orbitals) and the [$5f_{xyz}$,$5f_{z(x^2-y^2)}$] set of orbitals (the fδ orbitals), lie in this band of orbitals. Since this band is only partially filled, it is possible for the aforementioned orbitals to act as donor orbitals or as acceptor orbitals to a fourth ligand. It will be of great interest to see whether or not these U 5f orbitals play a significant role in the bonding of a fourth ligand, and if so, to what extent do they participate. The only U 5f-based MO that lies outside of this band is, of course, the $6a_2$ MO of Cp_3U, which is the antibonding counterpart of the $5a_2$ MO and contains a 15% contribution from the Cp ligands (Figure 3). This orbital is correspondingly destabilized relative to the other U 5f-based MO's.

Cp_3U vs Cl_3U: The Role of the Cp Ligands. Although not many molecular compounds containing the Cl_3U fragment are known,[29] it is nevertheless instructive to compare the electronic structures of Cp_3U with this fragment. The valence p orbitals of a Cl[30] ligand

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(29) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979**, *41*, 533, and references therein.

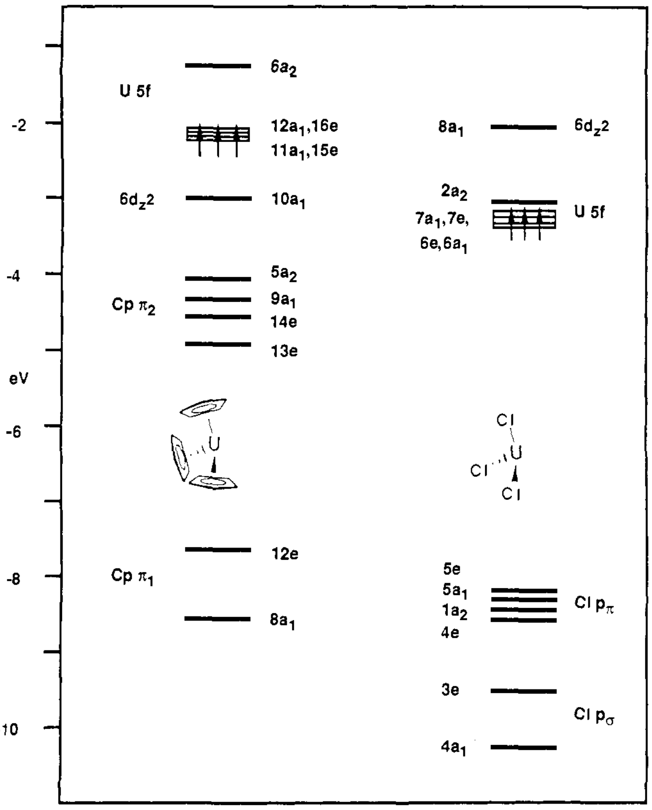
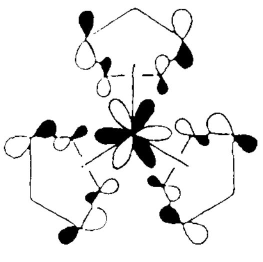
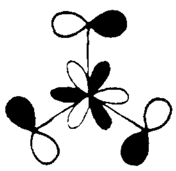


Figure 4. Comparison of the orbital energies of Cp_3U and Cl_3U. The $10a_1$ MO of Cp_3U and $8a_1$ MO of Cl_3U are unoccupied (see text).

are isolobal to the filled π orbitals of a Cp ligand, the major difference being one of effectiveness of overlap with the orbitals of a metal atom. Whereas the Cp π_2 orbitals are directed toward the metal center, the p_x and p_y orbitals of Cl are perpendicular to the metal–Cl bond, rendering them less effective π donors to the metal. This is readily apparent in a comparison of the molecular orbital diagrams of these two fragments, as shown in Figure 4. The ligand- and metal-based MO's in Cl_3U are lower in energy than the corresponding ones in Cp_3U. A similar trend was previously noted for Cl_4U and Cp_4U and was attributed to the stronger donor ability of Cp as compared to Cl.[5b] Another consequence of replacing Cl with Cp in the X_4U (X = Cp or Cl) complexes is a greater splitting of the 5f orbitals. This, not surprisingly, is also seen in the case of the X_3U fragments. While the highest lying 5f orbital in Cp_3U, the $6a_2$, is ca. 0.84 eV above its nearest neighboring 5f orbital ($12a_1$), the corresponding orbitals in Cl_3U ($2a_2$ and $6a_1$) are split by only 0.10 eV. As shown below, this is a consequence of the poorer overlap of the Cl pπ orbitals with the U $5f_{y(3x^2-y^2)}$ orbitals than was seen in Cp_3U (cf. Figure 3).





Population analysis of the upper valence levels of Cp_3U and Cl_3U is presented in Table III. In agreement with the notion that Cp is a better donor ligand than Cl, the uranium atom contributions are considerably greater in the Cp π_2 bonding orbitals (from 18 to 29%) than they are in the corresponding Cl_3U bonding orbitals (from 3 to 5%). Again, this reflects the favorable directional properties of the π_2 orbitals of Cp relative to the $3p_x$ and $3p_y$ orbitals of Cl.

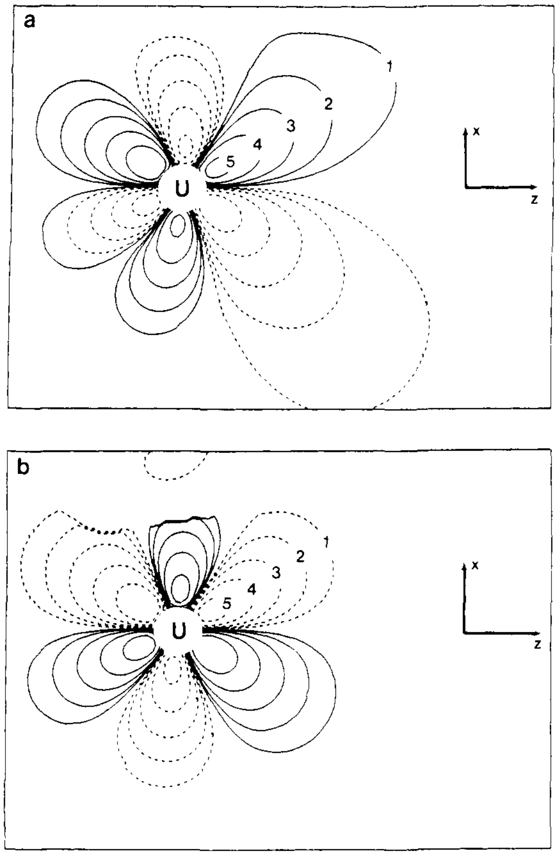


Figure 5. Contour plots of the fπ orbitals of (a) Cp_3U and (b) Cl_3U, in a plane containing U and one of the mirror planes. Contour values: ±5, ±4, ±3, ±2, ±1 = ±0.32, ±0.16, ±0.08, ±0.04, ±0.02.

The superior donor ability of Cp also manifests itself in the electron richness of the uranium center, as can be seen in a comparison of the contour plots of an analogous pair of f orbitals for Cp_3U (16e) and Cl_3U (7e) (Figure 5). It is noted that the radial extension of these f orbitals (which in this case would interact in a π fashion with a fourth ligand) is considerably greater for the former than for the latter. It is thus reasonable to expect that, all else being equal, the overlap between a fourth ligand and a UX_3 fragment should be better for X = Cp than for X = Cl. We will now discuss the interactions of the Cp_3U fragment with σ-only, π-acceptor, and π-donor ligands.

Interaction of Cp_3U with σ-Only Ligands. Before looking at the interaction of Cp_3U with more complicated ligands, it will be instructive to consider its interaction with ligands that can only interact in a σ fashion. To do this we will allow Cp_3U to interact with the simplest of all ligands, a hydrogen atom, to yield the formally U(IV) hydride complex Cp_3UH. A judicious choice of the U–H bond distance is not obvious since there are no reports in which a U–H bond length has been determined structurally. Marks and co-workers[31] have reported a neutron diffraction study on $[Cp^*_2ThH(\mu\text{-}H)]_2$ in which the Th–H distances were determined for the bridging and terminal hydrides. The mean Th–H terminal bond distance is 2.03 Å, which is, as the authors note, close to the sum of the covalent radii for hydrogen and thorium. The mean Th–C(ring) distance in this dimer is 2.83 Å which is 0.04 Å longer than the "typical" U(IV)–C(ring) bond length of 2.79 Å that we use in our studies of Cp_3U complexes. On the basis of these observations, we performed our calculations using

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(30) Throughout the discussion ligands are denoted as neutral (e.g., anionic ligands, X^-, are denoted as neutral ligands, X). This is done merely for consistency in the text and does not have any implications on the calculational method used nor does it have any effect on interpretation of the results.

[31] Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* **1979**, *203*, 172–174.

Table IV. Energies and Compositions of Selected Molecular Orbitals in Cp_3UL Complexes (L = H, CO, NO, OH)

MO	orbital type	ϵ, eV	uranium contribns, %				% L
			s	p	d	f	
		Cp_3UH					
$9a_1$	(σ)	−6.32	3	3	24	8	56
		Cp_3UCO[a]					
18e[b]	($M \rightarrow L\pi^*$)*	−1.85			9	39	28
16e[c]	($M \rightarrow L\pi^*$)	−3.87			3	81	14
$9a_1$[d]	(σ)	−11.02	2	2	4	1	22
$8a_1$[d]	(σ)	−11.45	3	3	8	4	39
		Cp_3UNO					
18e[b]	($M \rightarrow L\pi^*$)*	−3.58				52	35
16e[e]	($M \rightarrow L\pi^*$)	−5.25			2	59	35
$8a_1$	(σ)	−15.30	2	5	7	3	80
		Cp_3UOH					
17e[b]	($L \rightarrow M\pi^*$)	−2.37				88	4
12e	($L \rightarrow M\pi$)	−8.67		1	6	4	86
$7a_1$	(σ)	−12.67	2	7	10	6	73

[a] From ref 1a. [b] Unoccupied orbital. [c] HOMO, occupied with three electrons. [d] Orbital contains significant Cp contribution. [e] HOMO, occupied with four electrons.

two different U–H bond distances: 1.8 Å (based on the covalent radius of U being approximately 0.2 Å smaller than that of Th[32]) and 2.0 Å (based on the typical difference of the M–C(ring) bond length for Cp derivatives of Th and U, which is also close to the difference in the +4 ionic radii of the elements[32]). The two calculations are qualitatively similar and the results reported here are for the latter choice.

We will be primarily interested in two aspects of the results for Cp_3UH: the nature of the U–H bond, and the effect the hydride ligand has on the f orbitals. The U–H σ-bonding interaction is contained nearly entirely in one molecular orbital ($9a_1$), which lies in energy between the two manifolds of U–Cp π-bonding orbitals (vide supra). This orbital is 56% hydride in character, with the majority of the uranium contribution deriving from the $6d_{z^2}$ orbital (24%; Table IV). Only minor contributions are observed from the $5f_{z^3}$ orbital (8%), the 7s orbital (3%), and the $7p_z$ orbital (3%). Thus, the $9a_1$ MO of Cp_3UH is best considered as the bonding MO formed between the H 1s orbital and the $10a_1$ orbital of the Cp_3U fragment. The corresponding antibonding MO could not be located in the energy search and likely has a positive orbital energy. Therefore, this predominantly U $6d_{z^2}$ MO resides *above* the 5f block in Cp_3UH, whereas the $10a_1$ orbital of Cp_3U was *below* the 5f block (vide supra). The dominance of the $6d_{z^2}$ orbital in this interaction is completely in accord with our general observations for An–L σ-bonding interactions: The ligand-to-actinide σ donation is primarily into the 6d orbitals of the actinide atom.[1,5b,19] It is noteworthy that the highest lying Cp π a_1 orbital in Cp_3UH ($10a_1$) contains considerably less U 6d character (2%) than the corresponding orbital ($9a_1$) in Cp_3U (7%; Table III). This is consistent with the U $6d_{z^2}$ being "tied-up" in the U–H σ bond in the former, whereas it is more available to accept electron density in the latter. There is a slight quantitative difference between the calculations on the two different U–H bond lengths that should be mentioned here. At the shorter bond distance there is greater participation of the U 5f orbitals relative to the U 6d orbitals in the U–H σ bond than in the calculation with the longer bond. We believe that this is a direct reflection of the greater radial extension of the $6d_{z^2}$ orbital over the $5f_{z^3}$ orbital. Nevertheless, both calculations show U $6d_{z^2}$ dominance in the U–H σ bond.

Turning our attention to the f block of orbitals, we see that, as was the case when no fourth ligand was bound to Cp_3U, these orbitals are clustered in a narrow (0.13-eV) energy band (with the exception of the $6a_2$ orbital). This lack of orbital splitting is further evidence of the minor contribution of these 5f orbitals in metal–ligand σ bonding. However, when the Cp_3U fragment interacts with a fourth ligand containing π orbitals, we will see that f-orbital splittings become significant.

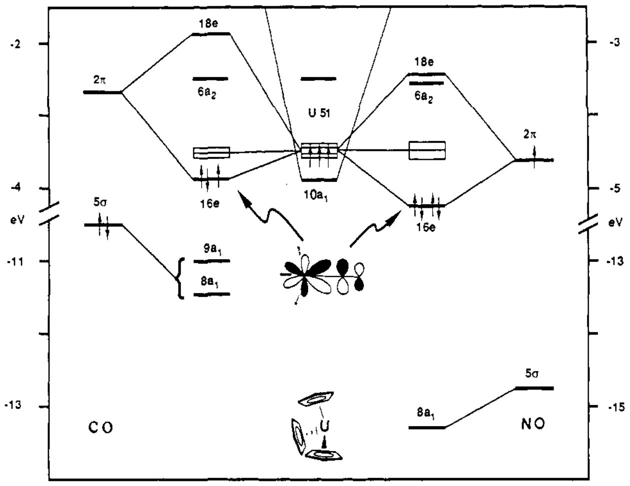

Figure 6. Molecular orbital diagram showing the interaction of CO and NO with Cp_3U to form Cp_3UCO and Cp_3UNO, respectively. The orbital energies of the Cp_3U fragment, which are relatively the same for both molecules, are ca. 1 eV lower in Cp_3UNO than in Cp_3UCO.

Interaction of Cp_3U with π-Acceptor Ligands. Andersen and Brennan have shown that the reaction of a pentane or hexane solution of Cp'_3U ($Cp' = \eta^5\text{-}Me_3SiC_5H_4$) with CO results in a carbon monoxide containing compound in which ν_{CO} is lowered by 170 cm^{-1} from the free ligand, consistent with the formulation of the product as the carbonyl adduct Cp'_3UCO.[12a] This is the first molecular actinide carbonyl complex to be synthesized. We have previously reported the results of an Xα-SW molecular orbital investigation of Cp_3UCO,[1a] as a model of the isolated Cp′ derivative, and we will briefly reiterate the major features of this prior study here.

There are two major interactions of Cp_3U with the carbonyl ligand. First, the CO 5σ MO, which is a lone-pair orbital localized on the carbon atom, interacts with the $10a_1$ orbital of Cp_3U to form the U–C σ bond. This interaction is similar to the σ donation reported above for Cp_3UH, and consistent with this, the interaction primarily involves the U $6d_{z^2}$ orbital. Second, it is found that the unoccupied, doubly degenerate CO 2π antibonding orbitals can act as acceptors of electron density from the U $5f\pi$ orbitals, which subsequently become the 16e HOMO of the complex (Figure 6). The uranium character of this U–C π-bonding orbital is almost entirely U 5f, and thus truly represents an example of U 5f → CO 2π backbonding (Table IV).

In our low-spin calculations on Cp_3UCO, it is seen that three electrons reside in the U–CO π-bonding 16e orbital. Maximum U–L π back-bonding would be achieved by complete occupation of this orbital; therefore, we have chosen to extend our studies of the interaction of the Cp_3U fragment with π-acceptor ligands by investigating the electronic structure of the unknown nitrosyl adduct Cp_3UNO, in which we have assumed a linear U–N–O linkage.[33] To our knowledge, the reactivity of organoactinide complexes toward nitric oxide has not been explored. In transition-metal systems, however, nitrosyl is generally a stronger π acid than carbonyl,[35] and it is of interest to us to see whether this trend is followed in the actinide systems. Additionally, NO is an effective electron-transfer reagent,[34] able to act in principle as

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(32) Bagnall, K. W. *The Actinide Elements*; Elsevier: Amsterdam, 1972; Chapters 2 and 4.

(33) The possibility must be recognized that NO might bind to actinide centers in a bent fashion, as it often does to transition-metal centers.[34] This coordination mode is not parallel to that observed for CO, however, and it will not be investigated here.

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either an oxidant (giving formally NO^+) or as a reductant (giving NO^-). Given the relatively higher energy of the actinide 5f orbitals compared to the d orbitals of transition metals, it is of interest to explore whether charge transfer between the actinide fragment and the NO ligand would occur from metal-to-ligand or ligand-to-metal.

The results of the calculation on Cp_3UNO are presented in the molecular orbital diagram in Figure 6, and in Table IV. In the MO diagram, fragment analysis has been used in order to envision the molecule as arising from the interaction of a Cp_3U fragment with a neutral NO molecule. It is seen that the resultant bonding picture for NO as a ligand is qualitatively similar to that for CO, although there are some differences. Because of the greater electronegativity of N than C, the MO's of NO are at lower energy than the corresponding ones in CO; it is this effect that makes NO a superior π acceptor and poorer σ donor than CO in transition-metal systems. As is evident in Figure 6 and Table IV, this also occurs in the actinide system. It is seen that the NO 5σ orbital resides well below that of CO, and as a result, the U–NO σ-bonding orbital ($8a_1$) contains approximately 10% less uranium character relative to that in Cp_3UCO (wherein the U–CO σ bonding is split between the $8a_1$ and $9a_1$[28] MO's). Interestingly, the p character of the uranium contribution to the $8a_1$ orbital increases substantially in Cp_3UNO, a consequence of the increased importance of the filled U 6p orbitals as the energy of the 5σ lone pair is lowered.

An even more dramatic difference between Cp_3UCO and Cp_3UNO is seen in the U–L π bonding. The energy of the NO 2π orbital is lowered sufficiently relative to that of CO to make it nearly isoenergetic with the U 5f levels. As a result, the NO contribution to the 16e HOMO of Cp_3UNO is ca. 2.5 times greater than the CO contribution to the 16e HOMO of Cp_3UCO, i.e., NO is acting as a far superior back-bonding ligand. In both cases, the U contribution is nearly pure 5f and hence only the extent, and not the nature, of the U $\rightarrow$ L back-bonding is affected by the change in L.

The other major difference between CO and NO as ligands, of course, is the presence of one more electron in the 2π orbital of the latter. In reactions with mononuclear transition-metal systems, this electron is generally transferred to the lower lying metal d orbitals, resulting formally in the reduction of the metal atom and oxidation of the ligand to NO^+.[36] The much higher energy of the U 5f orbitals alters this picture substantially. The 16e HOMO of Cp_3UNO is fully occupied with four electrons (as compared to three electrons in the 16e orbital of Cp_3UCO). If the 16e orbital is crudely regarded as 50% Cp_3U and 50% NO in character, then population analysis would "give" two electrons to the Cp_3U fragment and two to the NO ligand. Thus, the description that results is one of a U(IV) Cp_3U^+ fragment interacting with NO^-, and it is seen that NO is formally acting as an oxidant of the metal rather than a reductant. While this picture is certainly oversimplified, we believe that it is qualitatively correct: The high energy of the U 5f orbitals will facilitate a net transfer of charge from the metal to the NO ligand upon the formation of the U–NO bond. For transition metals a similar reversal of the role of NO was predicted when the energy of the NO 2π orbital falls below that of the metal d_{z^2} orbital.[37] It is worth noting that, within the guidelines established by Hoffmann et al.,[37] the U–N–O linkage is expected to be linear since σ donation by the nitrosyl ligand is into an empty orbital of Cp_3U. Also noteworthy is the possibility that Cp_3UNO will be a diamagnetic molecule, as we have constrained it to be in our calculation. If the U $5f\pi$–NO 2π interaction is strong enough to stabilize the 16e HOMO well below the nonbonding f band, it is not inconceivable that this would be the first example of a diamagnetic U(IV) complex.

To summarize the differences between the uranium carbonyl and uranium nitrosyl systems, we find decreased σ bonding and increased π bonding between the metal and ligand in the latter than in the former. The question of whether Cp_3UNO is stable can not be answered directly from our calculations; however, the existence of Cp'_3UCO certainly portends the possibility of other π-acid derivatives of the Cp_3U unit, and we see no reason why the analogous nitrosyl complex should not exist.

Interaction of Cp_3U with π-Donor Ligands. In the previous section, we have investigated the capability of the U 5f orbitals to act as donors to vacant ligand π orbitals. Here we will look at the converse interaction, wherein the Cp_3U fragment is acting as an acceptor of electron density from the filled π orbitals of a fourth ligand. We will focus on oxygen donor ligands because of the high oxophilicity of high-valent uranium, and because nearly all oxygen donors contain filled π orbitals that are capable of donating to the actinide center.

In our earlier study[1a] of the bonding in Cp_3UCO, we also presented the results of a MO investigation of the hypothetical isocarbonyl complex Cp_3UOC. Given the high oxophilicity of uranium, it did not seem reasonable to rule out this isomer as the product of reaction between Cp'_3U and CO.[12a] Our calculation showed that the low energy of the C–O bonding 4σ orbital of CO (the oxygen "lone pair") prevented a favorable interaction with the uranium 5f or 6d orbitals. The same effect was noted for the CO 1π orbital; the stabilization of the oxygen π orbitals through the formation of C–O π bonds prevented their effective interaction with the much higher lying acceptor orbitals on U. Thus, it was the lower energy of these orbitals, resulting from their intraligand bonding character, that rendered the isocarbonyl isomer unfavorable relative to the carbonyl. These results suggested that both the σ and π bonding between an oxygen donor ligand and Cp_3U could be improved by raising the energies of the filled σ and π orbitals on oxygen. These criteria are both satisfied by alkoxide ligands, for which both the σ and π orbitals on O are available for bonding.

There are a host of alkoxide derivatives for high-valent uranium[23] Structural studies on these complexes show rather short U–O bond lengths, and very obtuse U–O–R angles, on the order of 160°. Both of these features have been considered to be indicators of extensive O π donation to U, and we have reaffirmed this by calculation for the homoleptic U(VI) alkoxide $U(OMe)_6$.[38] With regard to alkoxide adducts of Cp_3U, the first such complex was discovered serendipitously by Ter Haar and Dubeck.[39] In an attempt to synthesize Cp_3U, they treated UCl_3 with Cp^- in THF, and observed the formation of Cp_3UOBu from the apparent ring opening of the solvent. Since this first report, several more Cp_3UOR complexes have been reported,[40] demonstrating the inherent affinity of the Cp_3U^+ fragment for OR^-. We have chosen to model such interactions via calculations on the model hydroxide complex Cp_3UOH. In order to preserve the highest possible symmetry, we report here the results of a calculation with a linear U–O–H linkage; we have also performed the calculations with an angle of 154° and find only small differences between this C_s molecule and the more easily analyzed C_{3v} model. The bending of the U–O–H linkage can be treated as a perturbation from the linear case as we have shown previously for $U(OMe)_6$.[38]

The molecular orbital diagram of Cp_3UOH is depicted in Figure 7, and the composition of the MO's is given in Table IV. As was the case with Cp_3UCO (and Cp_3UNO), there are two major interactions between the uranium fragment and the fourth ligand, in this case OH.[30] As anticipated, the oxygen σ-donor orbital of hydroxide is both more localized on the oxygen atom and lies at a much higher energy (3σ, ca. −12 eV) then the analogous orbital in the isocarbonyl case (4σ, ca. −19 eV).[1a] This allows for a strong bonding interaction between uranium and oxygen, creating the

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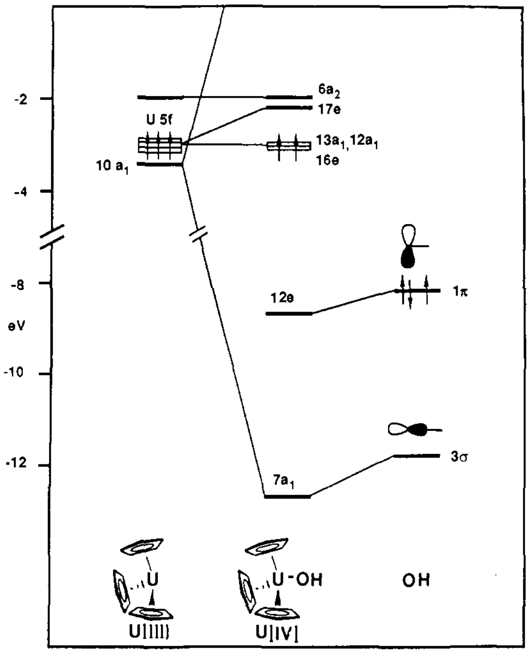

Figure 7. Molecular orbital diagram showing the interaction of Cp_3U with OH to form Cp_3UOH.

$7a_1$ bonding MO. This U–O σ bond, to which uranium contributes nearly 26%, principally involves the $10a_1$ MO of Cp_3U, with smaller contributions coming from the empty 7p and the partially filled 5f orbitals. This σ interaction is similar to that observed for the hydride, carbonyl, and nitrosyl cases discussed previously as well as for σ-donor ligands such as halides, alkyls, or even anionic organometallic fragments.[5,19]

In Cp_3UL (L = CO, NO), the second interaction between the Cp_3U fragment and the π-acid ligand is the back-bonding from the primarily U 5f orbitals of the fragment to the unoccupied 2π orbitals of L. In the case of the hydroxide complex, the fourth ligand has occupied π orbitals that are lower in energy than the U 5f orbitals (and, a fortiori, the 6d orbitals) and are capable of acting as electron donors to the metal. It is indeed seen that the 1π orbitals of the OH ligand are donating significantly to the uranium atom; the 12e orbital of Cp_3UOH contains nearly 12% U character. Interestingly, the donation is primarily into the U 6d orbitals (6%), as was the case for σ donation, but also contains a significant contribution from the 5f orbitals (4%). The 17e MO of Cp_3UOH, which is derived from the U 5fπ orbitals, is now destabilized relative to the others and, in contrast to the π-acid systems, is unoccupied. The uranium contribution to this orbital is still pure 5f, and the OH contribution is rather small. There is presumably a high-lying, principally U 6d MO that is U–OH π*, but we have been unable to locate it.

Conclusion

A qualitative investigation of the electronic structures of Cp_3M complexes in a trigonal-pyramidal geometry indicated that actinides possess f orbitals of appropriate symmetry to interact with all the symmetry-adapted linear combinations of three Cp ligand orbitals under C_{3v} symmetry, thus accounting for the ubiquitous nature of Cp_3An complexes as compared to the dearth of transition-metal complexes with the same ligand set. A quantitative study of Cp_3U using the Xα-SW molecular orbital method with quasi-relativistic corrections showed that Cp–U bonding is dominated by the Cp π_2 set of orbitals donating electron density into the U 6d orbitals and into the U $5f_{y(3x^2-y^2)}$ (a_2 under C_{3v} symmetry) orbital. The 5f orbitals of Cp_3U, with the exception of $5f_{y(3x^2-y^2)}$, are clustered in a narrow energy band. A comparison of Cp_3U and Cl_3U revealed that Cp is a better donor than Cl as witnessed by the overall higher energies of the metal-based orbitals and greater splitting of the U 5f a_2 orbital of Cp_3U from the remaining 5f orbitals. Bonding of σ-only ligands to Cp_3U is dominated by the U $6d_{z^2}$ orbital and causes no additional splitting of the 5f orbitals relative to those of Cp_3U. Cp_3U can act as a π donor to or a π acceptor from a fourth ligand. Interaction of Cp_3U with π-acceptor ligands shows significant U 5f $\rightarrow$ L (L = CO, NO) π back-bonding and causes stabilization of the U fπ set of orbitals. Conversely, interaction of Cp_3U with OH reveals that Cp_3U accepts π electron density from the hydroxide ligand into primarily the U 6d orbitals with a significant contribution from the U 5f orbitals, which causes a slight destabilization of the U fπ set. In the case of Cp_3UNO, we see that NO is formally acting as an oxidant to the metal and the compound can be best described as a linear U(IV) complex of NO^-. The attempted synthesis of this new complex, and experimental verification of its electronic structure, is currently under investigation.[41]

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Registry No. Cp_3U, 54007-00-0; Cp_3UH, 55411-31-9; Cp_3UNO, 118017-98-4; Cp_3UOH, 96427-65-5; Cl_3U, 10025-93-1.

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(41) In a preliminary study of the reactivity of Cp'_3U with NO(g), we have found only U(IV) products with no evidence for a stable NO adduct: Burns, C. J.; Bursten, B. E.; Sattelberger, A. P., unpublished results.