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Electronic Structure and Photoelectron Spectroscopy of the Monomeric Uranium(III) Alkyl $[\eta^5\text{-}(CH_3)_5C_5]_2UCH[Si(CH_3)_3]_2$[†,‡]

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The ground state configuration and the electronic structure of the title compound have been investigated by relativistic effective core potential configuration interaction ab initio calculations and He I/He II UV photoelectron spectroscopy. It has been found that the $^4A''$ $[(a')^1\,(a'')^1\,(a')^1]$ state, associated with the $5f^3$ uranium configuration, represents the molecular ground state and is close in energy to the higher-lying $^4A''$ ($5f^2\,6d^1$) state. The comparison of the present photoelectron data and theoretical results with those reported for analogous lanthanide complexes indicates close similarities in metal−ligand bonding between the 4f and 5f M(III) organometallics. The relative stability of the $5f^3$ versus $5f^2\,6d^1$ uranium ion configuration correlates with the inherent chemical stability of U(III) organometallics, compared to that of the Th(III) ($6d^1$) analogues. The easier M(IV) → M(III) reduction for U(IV) relative to Th(IV), the numerous examples of reductive elimination processes in U(IV) organometallic chemistry, and the greater Th−R versus U−R experimental homolytic bond disruption energies in cyclopentadienylactinide(IV) alkyls can all be rationalized in terms of the differing electronic stabilities of the U(III) and Th(III) ground states.

Introduction

A rich and diverse chemistry has been developed for organouranium complexes of the tetravalent metal ion.[1] In contrast, there is a paucity of information on trivalent uranium organometallics.[1] Generally, they possess a tendency toward higher coordination numbers and, therefore, consist either of UL_3 units coordinated to additional neutral ligands[2] such as THF, nitrile, CO, alkylphosphine, *etc*., or of oligomeric/polymeric structures.[2i,3,4] The use of sterically encumbered ancillary ligands such as C_5Me_5 (Cp′), $CH(SiMe_3)_2$, and $N(SiMe_3)_2$ has allowed isolation of the first monomeric “base free” organo−U(III) complexes.[2h,3c,5] These compounds offer the rare opportunity for comparative experimental and theoretical investigations of the electronic structure of genuine trivalent organouranium complexes. Moreover, they facilitate useful comparisons with related U(IV) species[6] and with homologous lanthanide(III)[7] complexes. To date, such investigations have been limited to experiment-only gas-phase UV photoelectron (PE) studies of homoleptic $U[N(SiMe_3)_2]_3$[8] and to ab initio[9]

[†] Part 13 of the series Photoelectron Spectroscopy of f-Element Organometallic Complexes. For part 12, see ref 7.

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Table 1. Total and Relative Energies (SCF and CI) of Low-Lying Electronic States for the Neutral (η^5-C_5H_5)$_2$UCH(SiH_3)$_2$ Model Complex

			tot. energy (hartree)		rel energy (eV)	
state	confign	metal confign	SCF	CI	SCF	CI
$^4A''$	$38(a')^1\ 25(a'')^1\ 39(a')^1$	$5f^3$	−1054.631 42	−1054.641 93	0.00	0.00
$^4A''$	$38(a')^1\ 25(a'')^1\ 39(a')^1$	$5f^2\ 6d^1$	−1054.603 81	−1054.621 56	0.75	0.55
$^2A'$	$38(a')^2\ 25(a'')^1$	$5f^3$	−1054.546 53		2.31	

and Xα−SW[10] theoretical calculations on homoleptic (fictitious) UMe_3 and Cp_3U (Cp = C_5H_5) model compounds.[11]

In this contribution, we report a comparative study by relativistic effective core potential (RECP) configuration interaction ab initio calculations and He I/He II PE spectroscopy of the electronic structure of the alkyl complex $Cp'_2UCH(SiMe_3)_2$[2h,3c] (**1**). This complex represents one of the few known[5] trivalent "base free" organouranium complexes. A detailed analysis of the bonding features, including an investigation of the ground state electronic configuration, is reported as well.

Experimental Section

The complex $Cp'_2UCH(SiMe_3)_2$ was synthesized according to the published procedure.[2h,3c] It was purified by sublimation in vacuo. PE spectra were recorded as described elsewhere.[6a−c] Resolution measured on the He ($1s^{-1}$) line was always around 25 meV. The spectra were run in the 110−130 °C range without any evidence of thermal decomposition.

Computational Methods

The calculations were performed by using the restricted open Hartree−Fock (ROHF) method. The RECPs and the [3s,2p,2d,2f] contracted basis set of Hay *et al.*[12] were used for the uranium atom. Pople's 6-31G basis sets[13] were adopted for the C, Si, and H atoms. The ionization energy of the lower lying ionic states and the relative stability of the low-lying excited states of the neutral molecule were evaluated using the ΔSCF procedure, which accounts for the relaxation energy upon different occupation of the molecular orbitals (MOs).[14] For the two most stable states of the neutral molecule, the $5f^3$ and $6d^15f^2$ metal configurations, correlation effects were included using the configuration interaction procedure including all single and double excitations (CISD) from the single Hartree−Fock reference. The three partially filled MOs, the 37a′ (formally representing the σ U−C bond), and the lowest 64 virtual MOs were used as active space in the CISD procedure. The choice of this active space does not account, of course, for the total correlation energy. It allows, however, a good description of correlation effects associated with the unpaired electrons and, hence, a valuable estimation of differential electron correlation energy for the two states.

Because of the computational effort required for calculations on the entire $Cp'_2UCH(SiMe_3)_2$ molecule, the simpler $Cp_2UCH(SiH_3)_2$ model molecule was adopted for theoretical studies. The geometrical parameters of the UCp_2 fragment were fixed with a 134° Cp(centroid)−U−Cp(centroid) angle[15] and 2.47 Å U−Cp(centroid) distance.[5c] The U−C and C−Si bond distances and U−C−Si bond angle were fixed at 2.52 Å, 1.90 Å, and 114°,[7,9] respectively, assuming C_s symmetry.

All of the calculations were performed using the HONDO8 code[16] on IBM ES/9000 and IBM SP2 systems.

Results and Discussion

Two different metal ion configurations, $5f^3$ and $5f^2d^1$, may be expected[10] in "base free" U(III) complexes. Earlier experimental data indicated that the gaseous U^{3+} free ion possesses a $5f^3$ ground state configuration.[17] No experimental studies have, however, been reported to date on the ground state electronic configuration in U(III) complexes. In the case of Th(III), EPR measurements on Th[η^5-$C_5H_3(SiMe_3)_2$]$_3$ have indicated a $6d^1$ ground state configuration[18] despite the established $5f^1$ configuration of the free ion.[17]

For the present $Cp_2UCH(SiH_3)_2$ model structure, several doublet and quadruplet states associated with both the $5f^3$ and $5f^26d^1$ metal ion configurations have been considered. The calculations indicate that the lowest lying state is the $^4A''$ [$(38a')^1\ (25a'')^1\ (39a')^1$] state, which is associated with the $5f^3$ configuration, while the $^4A''$ [$(38a')^1\ (25a'')^1\ (39a')^1$] state, related to the $5f^26d^1$ configuration, lies 0.75 eV higher in energy (Table 1). The most stable doublet state is the $^2A''$ [$(38a')^2\ (25a'')^1$] state, which is associated with the $5f^3$ configuration and lies 2.31 eV higher in energy relative to the $^4A''$ ground state. Within the context of a ligand field theory description, this is indicative of a small orbital splitting compared to the spin-pairing energy.[1c]

In order to evaluate more quantitatively the relative energy of the most stable quadruplet states, CISD calculations have also been performed. The inclusion of correlation effects still results in a $^4A''$ ($5f^3$ metal ion configuration) ground state, which is 0.55 eV more stable than the lowest lying excited state associated with the $5f^26d^1$ metal ion configuration (Table 1). This result is in good agreement with the ROHF energetic sequence and total energy difference. The influence of spin−orbit coupling, which in principle could play some role, certainly cannot represent a major factor as far as the relative stabilities of these two states are concerned. In fact, there is no direct spin−orbit interaction in the double-spinor C_s* group, since there are no degenerate

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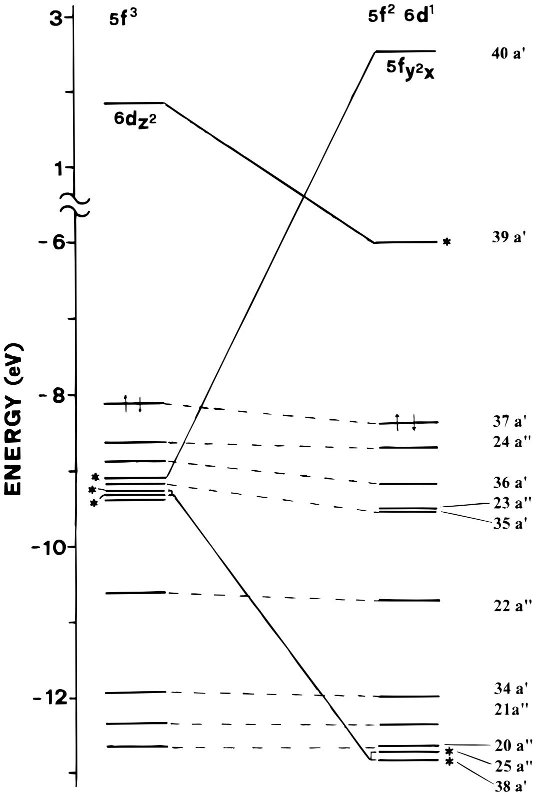

Figure 1. Orbital correlation energy diagram for the $5f^3$ and the $5f^26d^1$ metal ion configurations of the $Cp_2UCH(SiH_3)_2$ model structure. The stars indicate the partially filled orbitals.

orbitals. In addition, all of the MOs are of the same symmetry ($e_{1/2}$) in the C_s* group and only a small, indirect spin−orbit interaction can be active.[19] This interaction should not significantly influence the overall results.[20]

In Figure 1, the energy sequences of the uppermost valence molecular orbitals of $Cp_2UCH(SiH_3)_2$ are compared for the $^4A''$ ($5f^3$) and $^4A''$ ($5f^26d^1$) states. Almost identical energies and sequences of ligand-based MOs are noted. In contrast, notable differences are evident as far as the energies of MOs involving unpaired metal electrons are concerned. In the $5f^3$ configuration, the three partially filled orbitals lie below the HOMO[21] and are close in energy. In the $5f^26d^1$ configuration, the 5f-based orbitals are more stabilized and are buried among ligand-based orbitals, while the 6d-based orbital lies higher in energy and thus represents the HOMO. It therefore turns out that the greater stability of the $5f^3$ configuration found in the present U(III) complex accounts well for the facile reductive elimination, with formation of stable U(III) species,[2gh,22] observed in U(IV) organometallics. Conversely, favorable one-electron oxidative addition processes are expected for the U(III) $5f^26d^1$ configuration, as found in analogous Th(III) ($5f^0$, $6d^1$ configuration) organometallics.[22]

The present results are in agreement with earlier Xα−SW calculations on Cp_3U,[10] in which almost isoenergetic states have been estimated for the $5f^3$ and $5f^26d^1$ configurations, as well as with recent ab initio CAS−MCSCF calculations on the model UMe_3 molecule,[9] which indicate a number of lower-lying states associated with the $5f^3$ configuration. Population data for the uppermost filled MOs of $Cp_2UCH(SiH_3)_2$ (Table 2) provide useful insights into the metal−ligand bonding. The 5f electrons are marginally involved in the bonding and remain localized on the metal center. The U−Cp bonding principally involves MOs (23a″−24a″) which are combination of the uppermost filled π_2 orbitals of the Cp anion and of the metal 6d subshells. The major metal-6d contribution is found in the more internal 23a″ and 35a′ MOs. The interaction of the U metal center with the $-CH(SiH_3)_2$ hydrocarbyl group (37a′) is σ-only in nature and involves the 6p, 7p, and 6d metal orbitals. The remaining MOs largely represent the Si-C bonds and are essentially ligand-centered. These results closely resemble those already reported for the homologous $Cp_2LaCH(SiH_3)_2$ model complex.[7]

The He I PE spectrum of **1** (Figure 2) consists, in the low ionization energy (IE) region (<12.5 eV), of four resolved bands (**a-d**) and of a low-intensity onset structure (**x**). The spectrum is remarkably similar to those of the previously studied lanthanide homologues.[7] Therefore, the assignments can be safely based on the present ab initio calculations as well as comparisons with the previous PE data for the homologous lanthanide compounds. Envelope **a** can be associated with ionization from the σ(U−C) (37a′) MO and with the four π_2-Cp MOs (Table 2). Bands **b-d** represent ionizations of more internal σ(Si−CH) and σ(Si−Me) orbitals[7] localized on the $-CH(SiMe_3)_2$ moiety. Because of the model structure used, a full comparison between calculations and PE data is not possible in the energy region higher than 8.5 eV. Nevertheless, the present calculations predict the first σ(Si−CH) ionizations 1.2 eV below the lowest π_2 Cp ionizations, in agreement with PE data.

Finally, a broad, low IE onset structure, **x**, is observed at 5.75 eV, the relative intensity of which increases in the He II spectrum (Figure 2). An analogous onset feature has been observed in the PE spectra of "base free" $U[N(SiMe_3)_2]_3$ (5.96 eV)[8] as well as in the spectrum of $Cp_3U{\cdot}THF$ (6.43 eV).[11b] These features have been assigned to $5f^{-1}$ ionizations. Therefore, a similar assignment can be confidently proposed for the present $Cp'_2UCH(SiMe_3)_2$ complex. We note, on passing, that relaxation effects in the $5f^{-1}$ ion states are clearly responsible for the disruption of the ground state MO sequence and that the ΔSCF values (Table 2) favorably reproduce the absolute experimental IEs.

In the present context, it is of interest to note that the energy separation (0.2 eV) between the triplet states produced upon ionization of the $5f^3$ ground configuration agrees (Table 2) well with the appearance of a single, unresolved band associated with the $5f^{-1}$ ionizations (band **x**, Figure 2). In contrast, any ionization pattern arising from metal-based orbitals of the alternative $5f^26d^1$ configuration would necessarily result in two well-separated PE bands.[23] Band **x** is shifted to a

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(21) (a) This is a common feature of ground state ab initio calculations involving partially filled metal "d" and "f" orbitals.[6a,21b−d] (b) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A. *Inorg. Chem.* **1981**, *20*, 1962. (c) Doran, M.; Hillier, I. H.; Seddon, E. A.; Seddon, K. R.; Thomas V. H. *Chem. Phys. Lett.* **1979**, *63*, 612. (d) Ferreira, R. *Struct. Bonding (Berlin)* **1976**, *31*, 1.

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Table 2. Ab Initio Eigenvalues, Ionization Energies, and Mulliken Population Analysis[a] for the $^4A''$ Ground State ($5f^3$ Configuration) of $(\eta^5\text{-}C_5H_5)_2UCH(SiH_3)_2$

	energies (eV)			U							
MO	$-\epsilon$	ΔSCF	exptl IE[b]	s[c]	p[d]	6d	5f	CH	2Cp	$2SiH_3$	character
39a′	9.17	5.38	5.75 (**x**)	−1	0	4	97	0	0	0	$f_{x^3} + f_{y^2x} + f_{z^2x}$
25a″	9.26	5.43		0	0	0	98	0	2	0	$f_{z^3} + f_{x^2z} + f_{y^2z}$
38a′	9.38	5.57		0	0	0	99	0	1	0	$f_{y^3} + f_{x^2y} + f_{z^2y}$
37a′	8.12	6.27	7.47 (**a**)	−1	7	3	−1	43	39	10	σ U−C + π_2 + p_x
24a″	8.64	7.68		0	6	2	1	0	91	0	$\pi_2 + d_{xz} + p_z$
36a′	8.89			0	0	9	2	1	88	0	$\pi_2 + d_{xy}$
35a′	9.20			−4	0	16	1	26	53	8	$\pi_2 + d_{x^2}$
23a″	9.40			0	0	13	1	0	86	0	$\pi_2 + d_{yz}$
22a″	10.63			0	0	1	0	49	0	50	σ Si−C
34a′	11.93			0	0	1	0	33	0	66	σ Si−C

Overall Charge

$U = s^{1.91}\,p^{6.30}\,5f^{3.11}\,6d^{1.29} = +\,1.39$; $[CH(SiH_3)_2] = -0.68$; $2Cp = -0.71$

[a] Negative metal s and p populations have been reported for many transition metal complexes. See for example: Ammeter, J. H.; Burgi, H. B.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. [b] See Figure 2. [c] Values refer to 6s and 7s orbital populations. [d] Values refer to 6p and 7p orbital populations.

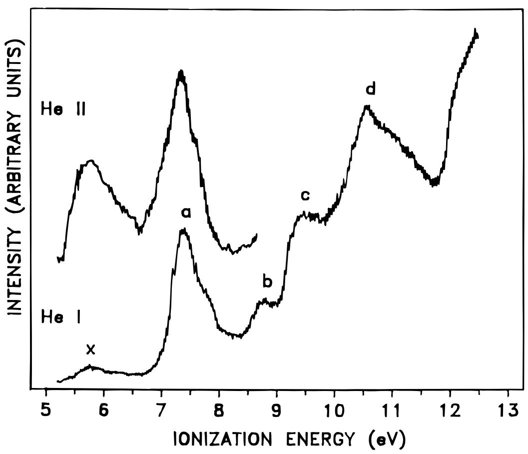

Figure 2. Gas-phase He I and He II PE spectra of $Cp_2'UCH(SiMe_3)_2$ in the low-IE region.

somewhat lower IE value than found for the $5f^{-1}$ ionization in typical U(IV) complexes,[6] as a consequence of the lower formal oxidation state of uranium center. In the case of the neodymium homologue, the $4f^{-1}$ ionizations lie higher in energy.[7] This is consistent with the more pronounced "corelike" character of 4f orbitals versus 5f.[10b]

Conclusions

The results of this study provide the first experimental and theoretical evidence to date for close similarities in bonding between isoleptic 4f and 5f M(III) bis(cyclopentadienyl) complexes. Consistent with the experimental PE spectra, the RECP ab initio calculations indicate a ground state $5f^3$ configuration associated with the uranium metal ion. The theoretical analysis of the energetics and molecular orbital evolution on passing from the $5f^3$ to the $5f^26d^1$ uranium ion configuration underscores the inherent stability of U(III) organometallics vis-à-vis the Th(III) ($6d^1$) analogues.[22] Thus the different metal ion configuration ($5f^3$) of the U(III) organometallics, compared to that encountered ($6d^1$) in the Th(III) complexes studied to date,[18] correlates well with the smaller homolytic U−R bond disruption energies, relative to Th homologues, found in cyclopentadienylactinide(IV) alkyl complexes,[24] as well as for the more facile An(IV) → An(III) (An = Th, U) reductive processes in U(IV) species.[25] These observations support our earlier contention[6a] that the peculiarities of the aforementioned processes are not entirely governed by the electronic properties of An(IV) ground states but that they also depend upon the energetics associated with the variation of the formal metal oxidation state, i.e., upon the stability of the An(III) final states.

Research is now in progress to better define the role of the $5f^2\,6d^1$ metal configuration in the reaction profiles associated with U(III) oxidative additions.

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(23) The calculated ΔSCF value for the $6d^{-1}$ ionization ($5f^26d^1$ configuration) is 4.62 eV. This value is surprisingly close to that observed for the $6d^{-1}$ ionization (4.87 eV) in the $Th[\eta^5\text{-}C_5H_3(SiMe_3)_2]_3$ parent complex.[18] In contrast, the calculated average f^{-1} IE ($5f^3$-configuration) is 5.46 eV (Table 2) and compares well with the experimental (5.75 eV) IE value.

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