Inorganic Chemistry

Density Functional Theory Analysis of the Importance of Coordination Geometry for $5f^3 6d^1$ versus $5f^4$ Electron Configurations in U(II) Complexes

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ABSTRACT: Density functional theory (DFT) calculations on four known and seven hypothetical U(II) complexes indicate the importance of coordination geometry in favoring $5f^3 6d^1$ versus $5f^4$ electronic ground states. The known $[Cp''_3U]^-$, $[Cp^{tet}_3U]^-$, and $[U(NR_2)_3]^-$ $[Cp'' = C_5H_3(SiMe_3)_2$, $Cp^{tet} = C_5Me_4H$, and $R = SiMe_3]$ anions were found to have $5f^3 6d^1$ ground states, while a $5f^4$ ground state was found for the known compound $(NHAr^{iPr_6})_2U$. The UV−visible spectra of the known $5f^3 6d^1$ compounds were simulated via time-dependent DFT and are in qualitative agreement with the experimental spectra. For the hypothetical U(II) compounds, the $5f^3 6d^1$ configuration is predicted for $[U(CHR_2)_3]^-$, $[U(H_3BH)_3]^-$, $[U(OAr')_4]^{2-}$, and $[(C_8H_8)U]^{2-}$ (OAr' = O-C$_6$H$_2^t$Bu$_2$-2,6-Me-4). In the case of $[U(bnz')_4]^{2-}$ (bnz' = CH$_2$-C$_6$H$_4^t$Bu-4), a $5f^3$ configuration with a ligand-based radical was found as the ground state.
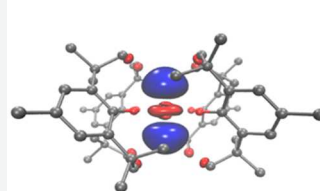
Square-planar $[U(OAr')_4]^{2-}$
$5f^3 6d^1$ configuration
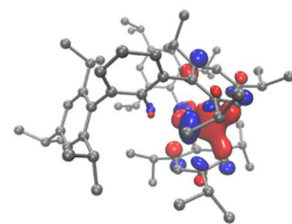
Spherical $(NHAr^{iPr6})_2U$
$5f^4$ configuration

INTRODUCTION

One of the recent developments in actinide chemistry was the discovery that the 2+ oxidation state is accessible to uranium.[1−8] The initial discovery was made by reduction of the $5f^3$ uranium(III) tris(silylcyclopentadienyl) complex Cp′$_3$U (Cp′ = C$_5$H$_4$SiMe$_3$; eq 1).[1] Surprisingly, the [K(crypt)]-[Cp′$_3$U] (crypt = 2.2.2-cryptand) product was found to have a $5f^3 6d^1$ ground state instead of the traditional $5f^4$ configuration.[1] The unique mixed principal quantum number electron configuration was rationalized for this complex by the pseudo-D_3 symmetry of the tris(cyclopentadienyl) ligand environment. In this geometry, a nonbonding $6d_{z^2}$ orbital is evidently close enough in energy to the 5f manifold to be populated upon reduction.[9−12] Density functional theory (DFT) calculations were consistent with this view, and time-dependent DFT (TDDFT) calculations successfully predicted the UV−visible spectrum of [K(crypt)][Cp′$_3$U]. Subsequently, [K(crypt)]{[(^{Ad,Me}ArO)$_3$mes]U} was reported and assigned a $5f^4$ electron configuration based on spectroscopic, crystallographic, and theoretical analysis.[2] Although several other U(II) complexes have been reported,[3−6] DFT studies have not always accompanied the synthetic studies. Structural and spectroscopic data can be used to make tentative assignments, but magnetic analysis of U(II) compounds is complicated because the expected room temperature magnetic moment for an $f^3 d^1$ electron configuration is 2.68 or 4.02 μ_B, depending on the coupling scheme used,[13,14] and the moment of a f^4 configuration, 2.68 μ_B, is identical with one of these values.
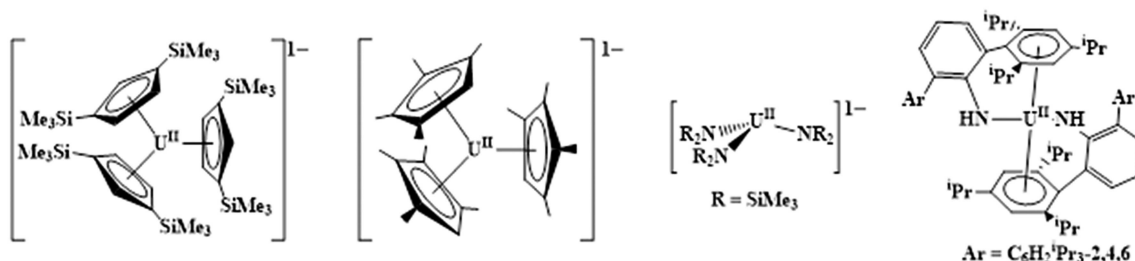
(1)
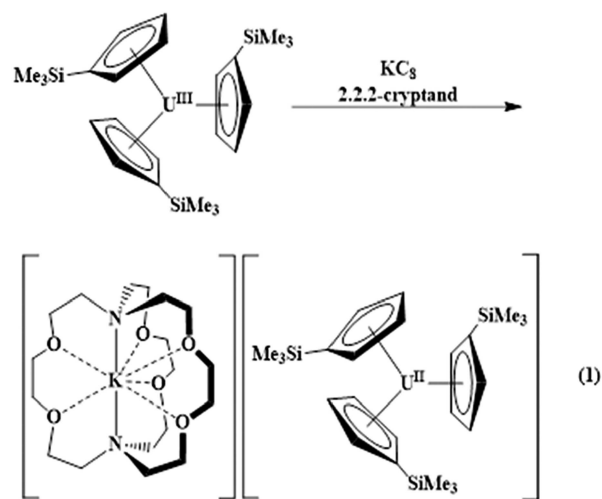
A recent study on the heteroleptic uranium complexes $[(C_5Me_5)_nU^{II}(NR_2)_{3-n}]^-$ (R = SiMe$_3$; n = 1, 2)[15] showed that these complexes also possess a $5f^3 6d^1$ electronic configuration,
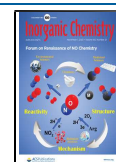
Scheme 1. Molecular Structures of $[Cp''_3U]^-$, $[Cp^{tet}_3U]^-$, $[U(NR_2)_3]^-$, and $(NHAr^{iPr_6})_2U$

despite the deviation from the idealized D_3 geometry. These reduction studies suggested that there could be a more general trend and that the $5f^36d^1$ electron configuration is optimal if there is a planar arrangement of ligands around the U(II) center. This present study was initiated to better understand how the electronic structure of U(II) complexes is affected by the ligand geometries. Four previously synthesized U(II) compounds and seven hypothetical U(II) compounds with various coordination geometries including trigonal planar, square planar, linear, tetrahedral, and octahedral were analyzed. The results are compared with known U(II) complexes[1,2,15] and related Ln(II) compounds.[10,20−22,24,25,47] Note that within this study the term "planar" refers to the primary coordination sphere of the uranium complex, considering the donor atom of a monohaptic ligand or the centroid of a ring system.

The DFT methods used in this study have been shown to accurately predict the electronic structure for U(II) complexes $[Cp'_3U]^-$,[1] $[(C_5Me_5)_2U(NR_2)]^-$,[15] $[(C_5Me_5)U(NR_2)_2]^-$,[15] and $(C_5^iPr_5)_2U$,[52] related thorium complexes Cp'_3Th,[17] $[Cp''_3Th]^-$,[18] and $[Cp''_2Th(H)(\mu\text{-}H)_3ThCp''_2]^-$,[19] and Ln(II) (Ln = rare-earth metal) complexes in various ligand environments such as $[Cp'_3Ln]^-$,[10,20−22] $[Cp''_3Ln]^-$,[23] $[Cp^{tet}_3Ln]^-$,[24] $[Ln(NR_2)_3]^-$,[25] $\{[(^{Ad,Me}ArO)_3mes]Ln\}^-$,[26,27] and $(C_5^iPr_5)_2Ln$[16] $[Cp'' = C_5H_3(SiMe_3)_2$; $Cp^{tet} = C_5Me_4H]$. The theoretical compounds chosen for this study were selected because they are derived from known U(IV) or U(III) compounds that could serve as reasonable precursors for the theoretical U(II) complexes. Hence, there is a realistic possibility that the results reported here could be verified experimentally. This study should be considered a targeted screening effort aiming to guide future synthetic and more refined theoretical efforts to probe how the ligand geometry affects the electronic structure of low-valent f-block complexes.

■ COMPUTATIONAL DETAILS

All calculations were completed at the density functional level of theory using the TPSSh hybrid meta-generalized gradient density functional[28] with Grimme's D3 dispersion correction[29,30] and the resolution of the identity (RI-J) approximation.[31] Scalar relativistic small-core effective core potentials[32] with the def-TZVP basis set[33] were used for uranium, while the polarized split-valence basis set def2-SV(P)[33] was used for the other atoms. Quadrature grids of size m4 were used.[34] Structure optimizations were initiated from the crystal-structure or DFT-optimized coordinates of $[Li(THF)_4][Cp''_3U]$ (THF = tetrahydrofuran),[5] $[K(crypt)][Cp^{tet}_3U]$,[4] $[K(crypt)][U(NR_2)_3]$,[4] $U(NHAr^{iPr_6})_2$,[6] $U(CHR_2)_3$,[35] $[Th(OAr')_4]^-$,[36] $(C_8H_8)_2U$,[37] $U(\eta^4\text{-}bnz')_4$ (bnz' = $CH_2\text{-}C_6H_4^tBu$-4),[38] and $U(H_3BH)_3(THF)_3$[39] at a convergence threshold of 10^{-4} atomic units (au) and an energy convergence of at least 10^{-7} au. No point-group symmetry constraints were applied. The continuum solvation model COSMO[40] was used for anionic species with a dielectric constant $\varepsilon = 7.52$ for THF,[41] except for the bis(cyclooctatetraenyl)uranium

compound, in which a dielectric constant of $\varepsilon = \infty$ was employed to guarantee a bound ground state. Ground-state geometries were confirmed by the lack of imaginary frequencies in the vibrational spectrum.[42] Various spin states were analyzed for these U(II) compounds, and the highest spin value ($S = 2$, quintet state) was always energetically favored. Representative energies for the singlet, triplet, and quintet states of $[Cp''_3U]^-$ and $[Cp^{tet}_3U]^-$ are given in Table S1. The $\langle S^2 \rangle$ values for all U(II) compounds in this study were between 6.006 and 6.024, indicating a negligible amount of spin contamination in the quintet ground states [expected $S(S + 1) = 6$ for the $S = 2$ system; Table S2].

TDDFT calculations[43] were carried out on the optimized structures with the same functional and basis sets described above. An additional diffuse p primitive was added to the def-TZVP basis set for uranium by downward extrapolation. This addition to the basis set has been shown to be essential for accurate simulation of d-to-p transitions in similar U(II) and Ln(II) compounds.[15,24,25] TDDFT calculations on $[U(NR_2)_3]^-$ and $[Cp^{tet}_3U]^-$ without this basis set extrapolation lacked transitions at lower energy that were seen in the experimental spectra (Figures S1 and S2). Electronic absorption spectra were simulated using Gaussian line profiles centered on the oscillator energy. The transitions are summarized and complete details can be found in the Supporting Information (SI). Electronic configurations were assigned by inspection of the molecular orbitals using VMD[44] and Mulliken population analysis. All calculations were performed with *TURBOMOLE*, version 7.4.1.[45,46]

One main goal of this study was to analyze changes in the electronic structure as a function of the ligand geometry. Further computational studies, such as multiconfigurational character, inclusion of spin−orbit coupling, and larger basis sets, could certainly be performed. We chose the present methods because they have been shown to accurately predict the electronic structure for many low-valent f-element compounds[1,10,15−27,36,50,52,54] and are a compromise between accuracy and computational cost.

■ RESULTS

Previously Synthesized U(II) Compounds. Initially, the electronic structures of known U(II) complexes were investigated, including three trigonal U(II) compounds, $[Cp''_3U]^-$,[3,5] $[Cp^{tet}_3U]^-$,[4] and $[U(NR_2)_3]^-$,[4] and the arene-tethered complex $(NHAr^{iPr_6})_2U$[6] (Scheme 1).

The first three tris(ligand) complexes have been assigned a $5f^36d^1$ electron configuration based on the UV−visible spectroscopy, magnetic data, and structural data and their analogy to the lanthanide compounds.[24,25,47] The arene-tethered complex $(NHAr^{iPr_6})_2U$ was described as a $5f^4$ configuration based on the X-ray distances and spectroscopic evidence.

$[Cp''_3U]^-$. Geometry optimizations of $[Cp''_3U]^-$ resulted in a ground state where the highest occupied molecular orbital (HOMO) had significant $6d_{z^2}$-like character with 7s admixture (Figure 1). This orbital is essentially nonbonding with respect to the cyclopentadienyl ligands. The next three HOMOs were
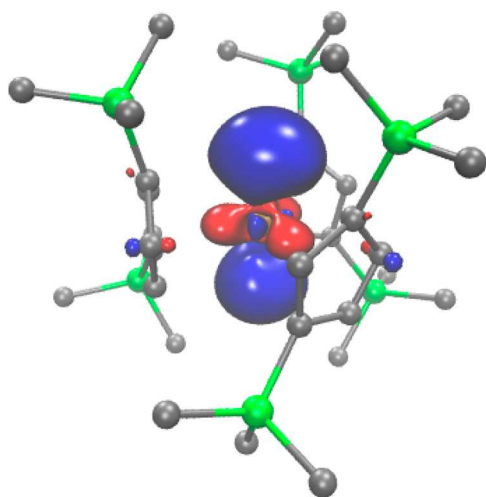
Figure 1. Calculated HOMO of $[Cp''_3U]^-$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energy $\varepsilon = -1.453$ eV.

Figure 3. Calculated HOMO of $[Cp^{tet}_3U]^-$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energy $\varepsilon = -1.069$ eV.

5f orbitals, yielding an overall electron configuration best described as $5f^3 6d^1$. This electronic configuration is in agreement with the spectroscopic assignment in the literature[3] as well as previous studies on $[Cp''_3Ln]^-$[23,47] and other tris(cyclopentadienyl) f-block complexes.[10,20,21,23,24,47−50]

The simulated UV−visible spectrum of $[Cp''_3U]^-$ is shown along with the experimental spectrum in Figure 2. The transitions between 1000 and 550 nm are metal-based with 6d-to-5f character. In addition, three transitions are calculated to occur from occupied 5f into 7p orbitals at 577 nm, one transition occurs from the occupied 6d orbital into the 7s orbital at 514 nm, and three transitions are from occupied 5f to the 7s orbital at 422 nm. Below 500 nm, the transitions are mostly metal-to-ligand in character, from occupied 5f and 6d orbitals to unoccupied π orbitals on the Cp'' rings.

$[Cp^{tet}_3U]^-$. Calculations on $[Cp^{tet}_3U]^-$ also resulted in a $5f^3 6d^1$ ground-state electronic configuration. The HOMO was found to have $6d_{z^2}$-like character (Figure 3), like that of $[Cp''_3U]^-$ above.

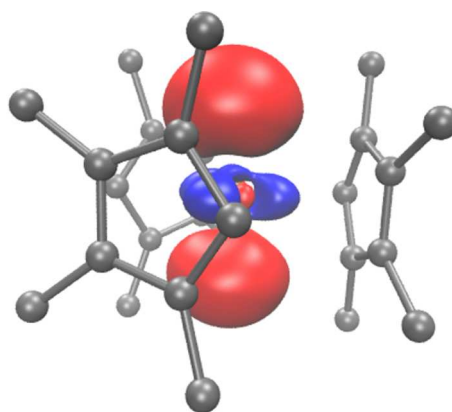The simulated UV−visible spectrum along with the experimental spectrum is shown in Figure 4. The broad absorption around 800 nm is assigned as a 6d-to-7p transition. Additional transitions with 6d-to-5f character are also observed in this region. The experimental spectrum is similar to those of $[(C_5Me_5)_2U(NR_2)]^-$ and $[(C_5Me_5)U(NR_2)_2]^-$, which featured broad absorptions centered at 750 and 684 nm, respectively, which were assigned as 6d-to-7p transitions.[15] These features are different from those observed for $[Cp'_3U]^-$ and $[Cp''_3U]^-$ (Figure 2), which feature mostly 6d-to-π/5f and π-to-6d/5f transitions at higher energy.[1] The calculated spectrum for $[Cp^{tet}_3U]^-$ is also similar to those of the $[Cp^{tet}_3Ln]^-$ lanthanide analogues in which a 5d-to-6p absorption dominates within the visible region.[24]

$[U(NR_2)_3]^-$. The optimized structure of $[U(NR_2)_3]^-$ resulted in a C_1-symmetric ground state. C_3- and D_3-symmetric structures were found to be 1.6 and 4.2 kcal/mol higher in energy. However, the D_3-symmetric structure was a transition state with a single imaginary frequency of 10.62 cm^{-1}. It is possible that the D_3-symmetric structure is, in fact, a ground state and the single imaginary mode is an artifact of the calculation, but this fact does not affect the remaining analysis. For the C_1- and C_3-symmetric structures, Mulliken population
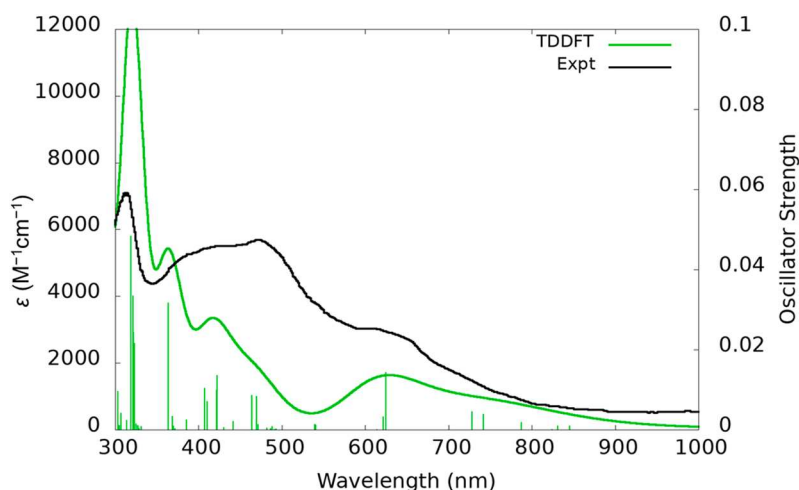

Figure 2. Experimental[3] (black) and simulated (green) UV−visible spectra of $[Cp''_3U]^-$. A Gaussian line broadening of 0.15 eV was applied, and the computed excitation spectrum was empirically blue-shifted by 0.40 eV.

Figure 4. Experimental[4] (black) and simulated (green) UV−visible spectra of $[Cp^{tet}_3U]^-$. A Gaussian line broadening of 0.15 eV was applied, and the computed excitation spectrum was empirically blue-shifted by 0.40 eV and scaled by a factor of 0.5 to ease comparison with the experimental spectrum.
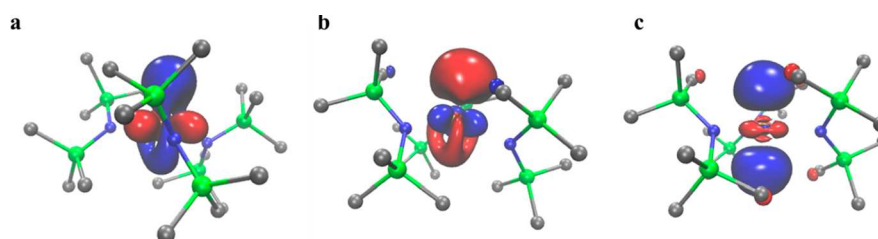
Figure 5. (a) HOMO, (b) HOMO−1, and (c) HOMO−3 of the C_1-, C_3-, and D_3-symmetric structures of $[U(NR_2)_3]^-$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energies ε = −1.689, −1.594, and −1.449 eV, respectively.
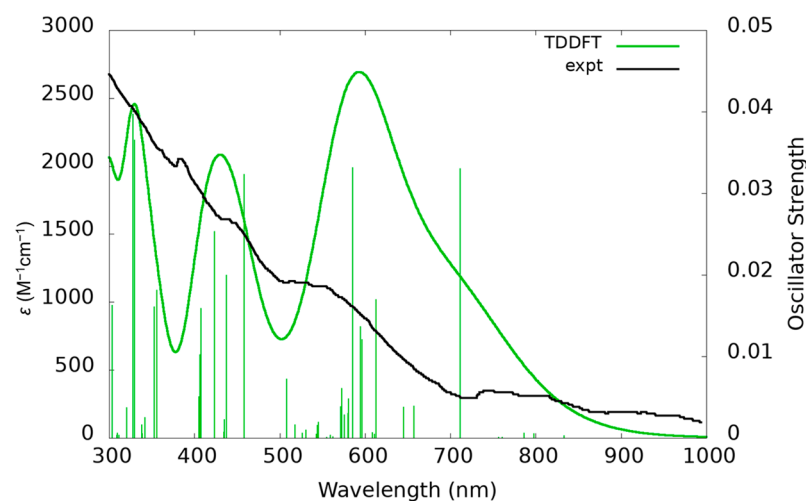
Figure 6. Experimental[4] (black) and simulated (green) UV−visible spectra of $[U(NR_2)_3]^-$ computed in C_1 symmetry. A Gaussian line broadening of 0.15 eV was applied, and the computed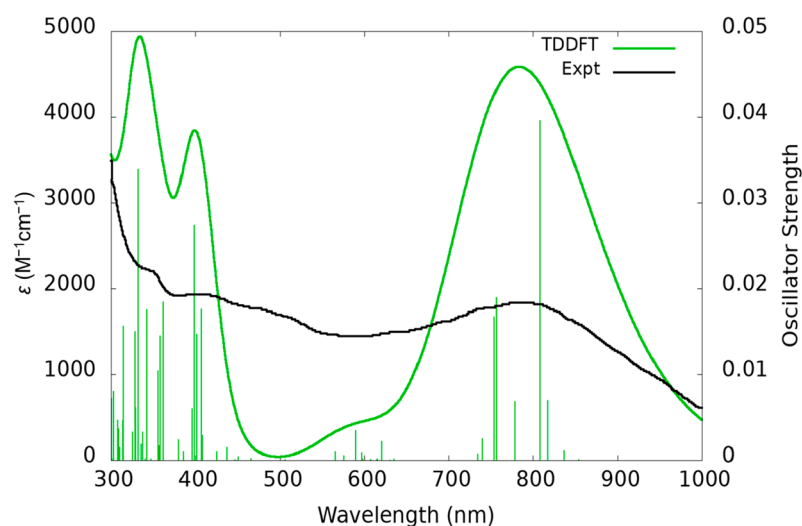 excitation spectrum was empirically blue-shifted by 0.40 eV and scaled by a factor of 0.15 to ease comparison with the experimental spectrum.

analyses revealed that the HOMO was roughly half-6d and half-5f character (Figures 5 and S3), while the HOMO−3 of the D_3-symmetric structure was purely $6d_{z^2}$ with 7s admixture (Figure 5 and Table S3).

All three geometries (C_1, C_3, and D_3) are likely to be accessible in solution because of the small energy difference. In fact, $[K(crypt)][U(NR_2)_3]$ crystallizes in the $R32$ space group

with D_3 molecular symmetry.[4] The lanthanide analogue $[Gd(NR_2)_3]^-$ was previously analyzed by DFT and assigned as a $4f^75d^1$ configuration in a D_3-symmetric ground state.[25] On the basis of the present theoretical results and the structural and spectroscopic data,[4] a $5f^36d^1$ configuration is assigned to $[U(NR_2)_3]^-$, although this assignment is based on a single-electron approximation. The present calculations suggest that

the overall configuration and the amount of orbital mixing can possibly be controlled by small geometrical changes.

The simulated electronic absorption spectrum for the C_1-symmetric state of $[U(NR_2)_3]^-$ is shown in Figure 6 along with the experimental spectrum. The lack of defining features in the experimental spectrum is consistent with the fact that electronic transitions were found to occur over the entire UV−visible region. Transitions at wavelengths greater than 400 nm were metal-based, while transitions at wavelengths shorter than 400 nm were found to be metal-to-ligand charge transfers. Strong transitions attributed to 6d-to-7p transitions were found at 670 nm, and 5f-to-7p transitions were found between 650 and 600 nm. Transitions from 6d-to-7s were found at 480 nm. Other transitions between 1000 and 400 nm were 6d-to-5f, 5f-to-6d, and 5f-to-5f in character. Further details can be found in the SI.

$(NHAr^{iPr_6})_2U$. The arene-tethered complex was found to have a $5f^4$ electron configuration by our DFT analysis, in agreement with the reported assignment.[6] The optimized ground-state structure was found to have C_2 symmetry, consistent with the solid-state structure. The HOMO of $(NHAr^{iPr_6})_2U$ is shown in Figure 7. The 5f orbitals on uranium

Figure 7. HOMO of $(NHAr^{iPr_6})_2U$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energy $\varepsilon = -3.132$ eV.
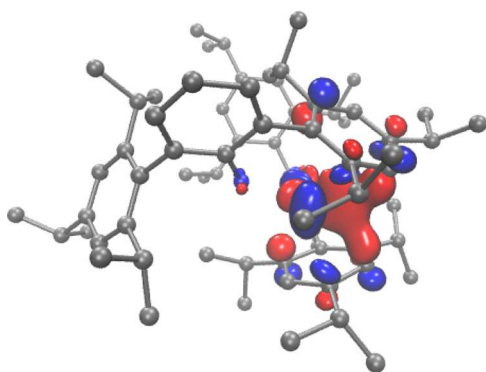
have an interaction with the arene π system, much like what was observed by Meyer and co-workers for $5f^4$ $[K(crypt)]$-$\{[(^{Ad,Me}ArO)_3mes]U\}$.[2] Thus, the 5f arene interaction may be important in stabilizing the $5f^4$ electronic configuration.

Model U(II) systems. The above results, in addition to the study on heteroleptic uranium systems,[15] provide further evidence that the ligand geometry around the uranium center has a direct impact on the electron configuration. It appears that planar geometries yield $5f^36d^1$ electron configurations for U(II) complexes, while less planar or complexes with arene interactions, like those found in $[K(crypt)]\{[(^{Ad,Me}ArO)_3mes]-U\}$[2] and $(NHAr^{iPr_6})_2U$,[6] yield $5f^4$ electron configurations. Described below are DFT studies on seven model U(II)

compounds in trigonal-planar, square-planar, linear, tetrahedral, and octahedral ligand environments. Each complex is derived from known U(III) or U(IV) compounds.
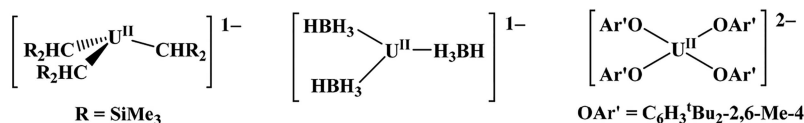
$[U(CHR_2)_3]^-$, $[U(H_3BH)_3]^-$, and $[U(OAr')_4]^{2-}$. Initially, three hypothetical homoleptic complexes were investigated (Scheme 2). $[U(CHR_2)_3]^-$ (R = $SiMe_3$) was examined because the $[CHR_2]^-$ ligand is the alkyl analogue of the $[NR_2]^-$ ligand used to form the known $[K(crypt)][U-(NR_2)_3]$.[4] Geometry optimizations of $[U(CHR_2)_3]^-$ afforded a pyramidalized C_1-symmetric ground state that is similar to the structure of $[U(NR_2)_3]^-$ discussed above. The electronic configuration was found to be $5f^36d^1$, with a $6d_{z^2}$-like HOMO (Figure 8). Electron density was observed on the $SiMe_3$ moieties, which was previously observed for $[(C_5Me_5)_2U-(NR_2)]^-$ and $[(C_5Me_5)U(NR_2)_2]^-$.[15] This suggests that the reduction of $U(CHR_2)_3$ may ultimately form a cyclometalated product such as $[U(CHR_2)_2(CH_2SiMe_2CHR-\kappa C,\kappa C)]^-$.[15]

Geometry optimizations of $[U(H_3BH)_3]^-$ yielded a $5f^36d^1$ electronic ground state, with population of a $6d_{z^2}$-like orbital (Figure 8). Each tetrahedral $(BH_4)^-$ ligand had three hydrides coordinated to the uranium center. To a first approximation, the $(BH_4)^-$ ligand is similar to a cyclopentadienide $(C_5R_5)^-$ ligand in that both are monoanions with three electron pairs available for coordination. It is therefore not too surprising that the electron configuration of $[U(H_3BH)_3]^-$ is identical with that of the tris(cyclopentadienyl)uranium(II) complexes $(Cp'_3U)^-$, $(Cp''_3U)^-$, and $(Cp^{tet}_3U)^-$. From these results, along with those of $[(C_5Me_5)_2U(NR_2)]^-$ and $[(C_5Me_5)U-(NR_2)_2]^-$,[15] it appears that the identity of the donor atom in trigonal complexes does not affect the electron configuration.

In addition to the homoleptic tris(alkyl) and tris-(borohydride) complexes, the tetrakis(aryloxide) environment was investigated. The Th(III) compound $[Th(OAr')_4]^-$ (OAr' = $C_6H_2^tBu_2$-2,6-Me-4) was recently synthesized and found to be square-planar with a $6d^1$ ground state.[36] The U(II) analogue, $[U(OAr')_4]^{2-}$, was analyzed in C_1, C_2, and C_4 symmetry. The optimized ground-state geometry was square-planar and had C_2 symmetry. The C_1- and C_4-symmetric square-planar structures were local minima only 0.16 and 0.14 kcal/mol higher in energy than the C_2-symmetric structure, respectively, which are within the expected error margins of the electronic structure methods used here. The ground state of $[U(OAr')_4]^{2-}$ was found to have a $5f^36d^1$ electron config-uration, again populating a $6d_{z^2}$-like orbital (Figure 8). This suggests that the planarity about the metal center can lead to f^nd^1 configurations even as the number of ligands is varied from three to four. The $5f^3$ U(III) compound $\{K[U(OAr)_4]\}_n$ (OAr = $OC_6H_3^tBu_2$-2,6) has been previously reported and adopts a tetrahedral geometry around the uranium center.[51]

$[(C_8H_8)_2U]^{2-}$. The U(II) complex formed by the two-electron reduction of bis(cyclooctatetraenyl)uranium, urano-cene (Figure 9), was also studied. The ground-state configuration of the dianionic U(II) species $[(C_8H_8)_2U]^{2-}$ was found to be $5f^36d^1$ in D_{8h} symmetry. Various lower-symmetry structures were analyzed, and all converged to the

Scheme 2. Molecular Structures of $[U(CHR_2)_3]^-$, $[U(H_3BH)_3]^-$, and $[U(OAr')_4]^{2-}$

$$\left[\begin{array}{c} R_2HC_{\text{\tiny\textbackslash\textbackslash\textbackslash}}U^{II}\text{---}CHR_2 \\ R_2HC \end{array} \right]^{1-} \left[\begin{array}{c} HBH_3 \\ U^{II}\text{---}H_3BH \\ HBH_3 \end{array} \right]^{1-} \left[\begin{array}{cc} Ar'O & OAr' \\ U^{II} \\ Ar'O & OAr' \end{array} \right]^{2-}$$

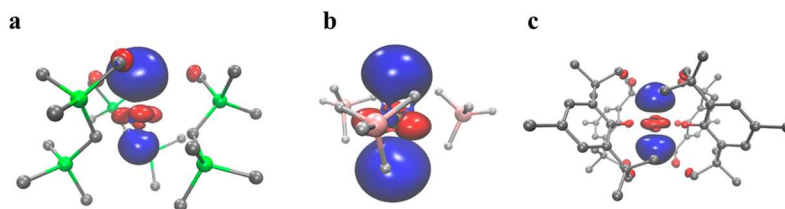R = $SiMe_3$ OAr' = $C_6H_3^tBu_2$-2,6-Me-4

Figure 8. HOMOs of (a) $[U(CHR_2)_3]^-$, (b) $[U(H_3BH)_3]^-$, and (c) $[U(OAr')_4]^{2-}$, plotted with a contour value of 0.05. Hydrogen atoms, except those attached to boron, are omitted for clarity. Calculated orbital energies $\varepsilon = -1.596$, -2.352, and -0.394 eV, respectively.
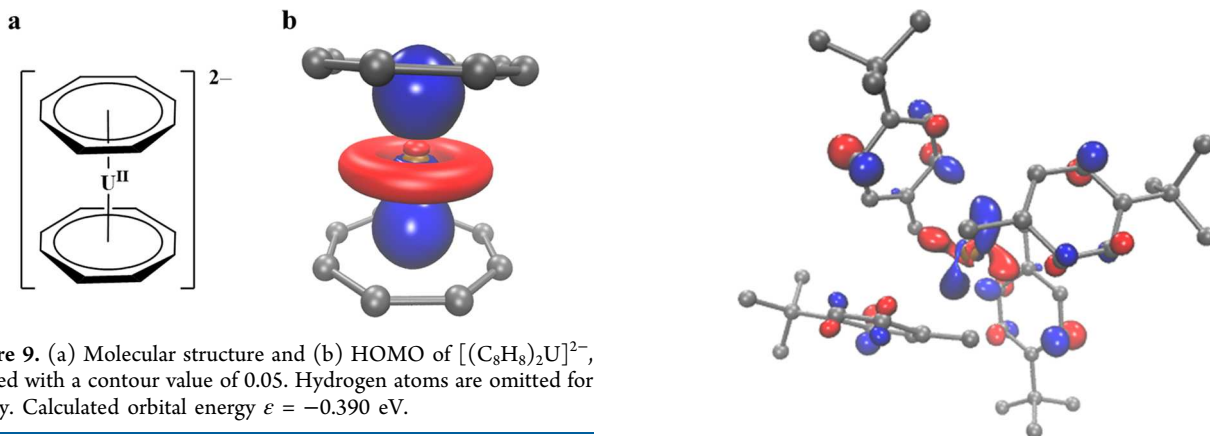

Figure 9. (a) Molecular structure and (b) HOMO of $[(C_8H_8)_2U]^{2-}$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energy $\varepsilon = -0.390$ eV.

Figure 10. HOMO of $[U(bnz')_4]^{2-}$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energy $\varepsilon = -0.128$ eV.

D_{8h}-symmetric local minimum. The HOMO appears to be a nonbonding $6d_{z^2}$ orbital (Figure 9). Previously, similar theoretical analysis on the linear U(II) species $(C_5^{i}Pr_5)_2U^{52}$ found a $5f^36d^1$ electron configuration without π interactions in the $6d_{z^2}$-like orbital.[7,52] The U(III) complex $[(C_8H_8)_2U]^-$ has a $5f^3$ configuration (Figure S4) with a $6d_{z^2}$-like LUMO that is evidently populated upon the addition of another electron to form $[(C_8H_8)_2U]^{2-}$.

$[U(bnz')_4]^{2-}$, $[U(H_3BH)_3(THF)_3]^-$, and the U-in-crypt System. The tetrahedral geometry for U(II) was examined starting with the previously reported U(IV) complex $U(\eta^4$-bnz')$_4$.[38] DFT analysis of the monoanionic complex $[U(bnz')_4]^-$ revealed a tetrahedral structure with a $5f^3$ configuration for the U(III) center (Figure S5). However, the ground state for the dianionic species, $[U(bnz')_4]^{2-}$, was found to have three electrons localized on the uranium atom (Figure S6) and one electron delocalized in the π system of the benzyl ligands (Figure 10). This is formally a U(III) complex with a ligand radical. The energy of the π system of the benzyl ligands is clearly close to the energy of the $5f$ orbitals because the LUMO was predominantly localized in the π system of the benzyl ligands while the LUMO+1, LUMO+2, and LUMO+3 had significantly more $5f$ character (Figure S7). The calculations were also performed with an infinite dielectric constant within the COSMO model, but the only change was the overall lowering of all orbital energies. The resulting electronic configuration was still $5f^3$ with a ligand radical.

The benzyl π system in $[U(bnz')_4]^{2-}$ is not in the correct spatial orientation to interact with the $5f$ orbitals, in contrast to $(NHAr^{i}Pr_6)_2U$ and $[K(crypt)]\{[(^{Ad,Me}ArO)_3mes]U\}$,[2] where the π system of the arene anchor was found to interact with the $5f$ orbitals on uranium (Figure 7). It can be concluded that the $5f$ manifold is lower in energy than the $6d$ orbitals because there was not an orbital with significant $6d$ character close to the HOMO−LUMO gap. In the present calculations, the ligands are best described as η^3-bnz' based on their Δ and Δ'

values[38,53] in each of the three geometry-optimized structures $U(bnz')_4$, $[U(bnz')_4]^-$, and $[U(bnz')_4]^{2-}$.

An octahedral complex was also investigated. Initially, the crystal structure of $U(H_3BH)_3(THF)_3$ was used as a starting point and the electronic configuration was found to be $5f^3$, as expected for a U(III) ion. The structure maintained an octahedral geometry. The four lowest unoccupied molecular orbitals (LUMO through LUMO+3) were all $5f$ in character (Figures 11 and S8). The addition of one electron and subsequent reoptimization of $[U(H_3BH)_3(THF)_3]^-$ resulted in a structure that had three BH_4 units in a much more planar arrangement around the uranium atom than in the neutral complex and three THF molecules further from the uranium center at distances of 2.667−2.681 Å (Figure 11). For comparison, the crystal structure of $U(H_3BH)_3(THF)_3$ has U−O distances of 2.54(1)−2.579(8) Å.[39] Excluding the THF molecules, the geometry around the uranium atom in $[U(H_3BH)_3(THF)_3]^-$ was practically identical with $[U(H_3BH)_3]^-$ discussed above. The resulting $5f^36d^1$ electron configuration with a $6d_{z^2}$-like HOMO (Figure 11) was the same as $[U(H_3BH)_3]^-$. The calculations predict that the reduction of $U(H_3BH)_3(THF)_3$ would likely result in the dissociation of THF and the formation of $[U(H_3BH)_3]^-$. This suggests that an octahedral environment around the uranium center does not effectively lower any $6d$ orbitals enough to be comparable in energy to the $5f$ orbitals.

The crypt ligand system was also investigated because it surrounds the metal center in a somewhat symmetrical way such that all $6d$ orbitals should have similar energy. Recently, the compounds $Ln(crypt)(OTf)_2$ (Ln = Nd, Sm; OTf = O_3SCF_3) were reported and assigned $4f^4$ and $4f^6$ configurations for Nd and Sm, respectively.[54] The spherical ligand environment of the crypt does not appear to split the $5d$ orbitals
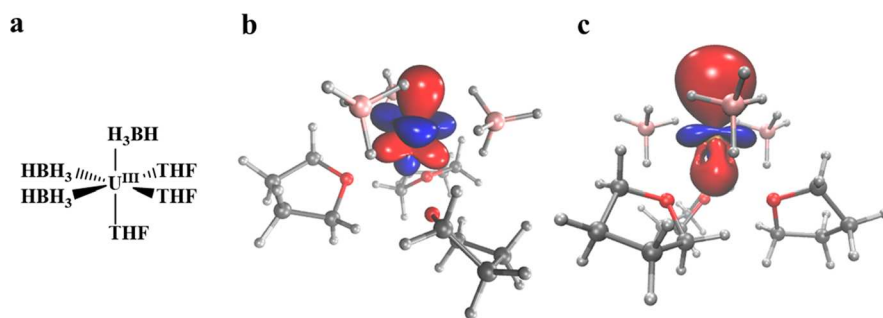
Figure 11. (a) Molecular structure of U(H$_3$BH)$_3$(THF)$_3$, (b) calculated 5f LUMO of U(H$_3$BH)$_3$(THF)$_3$, and (c) 6d$_{z^2}$-like HOMO of [U(H$_3$BH)$_3$(THF)$_3$]$^-$. Calculated orbital energies ε = −0.600 and −0.928 eV, respectively.

strongly enough to allow population of a 5d$_{z^2}$ orbital in the lanthanide complexes. To determine if the crypt system would impart similar chemistry for uranium, the structures of [U(crypt)]$^{2+}$ and U(crypt)(OMe)$_2$ were optimized. The triflate anions were replaced with methoxides because geometry optimizations on U(crypt)(OTf)$_2$ led to triflate dissociation.

Contrary to the Nd and Sm systems, calculations on [U(crypt)]$^{2+}$ are consistent with a 5f^{3}6d^1 ground state with a 6d$_{z^2}$-like HOMO (Figure 12). The optimized structure had

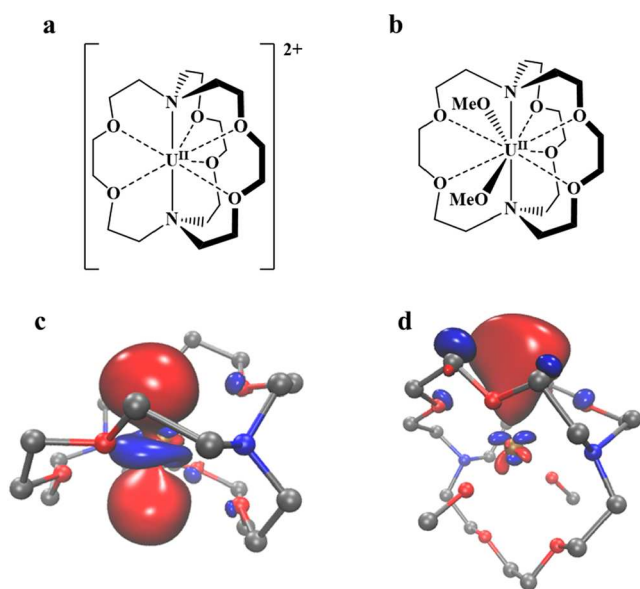**Figure 12.** Molecular structures of (a) [U(crypt)]$^{2+}$ and (b) U(crypt)(OMe)$_2$. HOMO of (c) [U(crypt)]$^{2+}$ and (d) U(crypt)-(OMe)$_2$, plotted with a contour value of 0.05. Hydrogen atoms are omitted for clarity. Calculated orbital energies ε = −7.811 and −0.596 eV, respectively.

space between the arms of the crypt ligand in which no donor atoms are located. It is in this space that the 6d$_{z^2}$-like orbital is located. However, the ground state of U(crypt)(OMe)$_2$ had a HOMO with significantly less 6d character (Figure 12). The HOMO of U(crypt)(OMe)$_2$ is still metal-centered, but it is predominantly 7p in character by Mulliken population analysis (44% 7p, 36% 7s, and 10% 6d). The OMe ligands bind to the uranium center in the space between crypt arms. Thus, the 6d orbital that is populated in [U(crypt)]$^{2+}$ is clearly higher in energy in U(crypt)(OMe)$_2$.

■ DISCUSSION

5f^{3}6d^1 U(II). The calculated electronic structures of [Cp″$_3$U]$^-$,[3,5] [Cp$^{tet}_3$U]$^-$,[4] [U(H$_3$BH)$_3$]$^-$, and [U(OAr′)$_4$]$^{2-}$ were all found to have 5f^{3}6d^1 ground-state electron configurations with population of a 6d$_{z^2}$-like orbital. These results are consistent with other previously characterized U(II) species [Cp′$_3$U]$^-$,[1] [(C$_5$Me$_5$)$_2$U(NR$_2$)]$^-$,[15] and [(C$_5$Me$_5$)U-(NR$_2$)$_2$]$^-$.[15] In each of these cases, the planar ligand environment leads to one low-lying 6d$_{z^2}$-like orbital, which is similar in energy to the 5f orbitals. The identity of the ligands and donor atoms seems less important than the geometry of the coordination environment. Clearly, planar complexes favor 5f^{3}6d^1. In addition, the trigonal-pyramidal complexes [U-(NR$_2$)$_3$]$^-$[4] and [U(CHR$_2$)$_3$]$^-$ also have 5f^{3}6d^1 ground-state electron configurations with population of a 6d$_{z^2}$-like orbital. Hence, even in these pyramidal structures, the 5f^{3}6d^1 configuration is lowest in energy.

The 5f^{3}6d^1 electronic configuration in [Cp′$_3$U]$^-$ (eq 1) could be rationalized[1] based on the d-orbital splitting of the tris(cyclopentadienyl) ligand framework.[11] Simple crystal-field splitting would not put the 6d$_{z^2}$ orbital lowest for all of the above complexes, but inclusion of 7s orbital mixing with 6d$_{z^2}$ could explain how the 6d$_{z^2}$-like orbital is comparable in energy to the 5f orbitals. Indeed, 7s character was observed in most of the 6d$_{z^2}$-like orbitals (see the SI). Another possible explanation involves π donation from the lone pairs of the donor atom, which could destabilize the d orbitals with the appropriate symmetry.[55−57]

The uranocene dianion [(C$_8$H$_8$)$_2$U]$^{2-}$ was also found to have a 5f^{3}6d^1 ground-state electron configuration with population of a 6d$_{z^2}$-like orbital. This result is similar to that of another parallel-plane metallocene, (C$_5$^{i}Pr$_5$)$_2$U.[7,52] These compounds differ in the ground state from the arene complexes discussed in the next section.

5f^4 U(II). The arene-tethered U(II) complex (NHAr^{iPr_6})$_2$U was found to have a 5f^4 electron configuration. In this case, the 5f orbitals have an interaction with the π system of the arene ring, as was found in the 5f^4 U(II) complex [K(crypt)]-{[(^{Ad,Me}ArO)$_3$mes]U}. In these two complexes, the arene rings have the correct spatial orientation to interact with the 5f orbitals, whereas the arene rings in the benzyl complex [U(bnz′)$_4$]$^{2-}$ do not interact with the 5f orbitals, despite the calculated energy similarity. For [U(bnz′)$_4$]$^{2-}$, this leads to reduction of the arene rings instead of the formation of U(II).

It is unclear whether the arene interaction is a requirement to stabilize the 5f^4 electron configuration. In the case of U(H$_3$BH)$_3$(THF)$_3$, which has no π system available to interact with the 5f manifold, the four LUMOs are still 5f orbitals,

which suggests that reduction within a pseudooctahedral environment would also favor a $5f^4$ electron configuration. The synthesis of a U(II) complex within a spherical ligand environment that does not have π systems is a reasonable target that will help further determine how the deviation from planarity affects the electron configuration.

U(II)-in-crypt System. The calculations on $[U(crypt)]^{2+}$ differ from those above in that they do not match calculations on the lanthanide analogues.[53] Additionally, the predicted ground-state changes when additional ligands are present. For $[U(crypt)]^{2+}$, a $5f^36d^1$ ground state with $6d_{z^2}$-like HOMO is predicted. However, the inclusion of two OMe groups binding to the uranium center directly affects the $6d_{z^2}$ orbital energy, and the resulting HOMO of $U(crypt)(OMe)_2$ was found to be predominantly 7p in character. The orbital shape and location are suggestive of a Rydberg state, and indeed the inclusion of a diffuse p primitive to the uranium basis functions helps to more accurately describe 6d-to-7p electronic transitions.[15,24,25] The present calculations suggest that binding additional ligands to the U(II) center within the crypt ligand framework could directly change the electron configuration. In contrast, calculations on both $[Nd(crypt)]^{2+}$ and $Nd(crypt)(OTf)_2$ indicate $4f^4$ ground-state configurations.[53] The ramifications of this difference are under investigation.

Overall Charge of the U(II) Complexes. A reviewer has noted that most of the U(II) complexes that have been synthesized are anions. This raises the question of the importance of the overall charge of the complex. On a simplistic basis, it makes sense for electropositive metals like uranium, that are typically surrounded with anionic ligands, that reduction of the oxidation state of the metal will require the overall complex to be an anion. In addition, for large metals like uranium, more than two ligands are typically needed to sterically saturate the coordination sphere. However, because the formation of anion complexes provides the benefit of lattice energy in the formation of a salt, it is possible that this factor is important in isolating these complexes. Anionic U(II) compounds do not clearly favor one configuration over the other, as $[K(crypt)][Cp''_3U]$ has a $5f^36d^1$ configuration while $[K(crypt)]\{[(^{Ad,Me}ArO)_3mes]U\}$ has a $5f^4$ configuration.

CONCLUSION

Electronic structure calculations on four known and seven hypothetical U(II) complexes predict that, with planar symmetry, $5f^36d^1$ electron configurations are the expected ground states regardless of the nature of the ligand, donor atoms, or number of ligands. If the symmetry of the complex does not place a 6d orbital comparable in energy to the 5f manifold, the $5f^4$ configuration could become the ground state. In some complexes like those of crypt and borohydride, additional ligation effects the orbital energies and may change the overall electronic configuration. This study provides information to guide synthetic efforts and suggests how to change the electronic configuration of low-valent uranium complexes. These results may be transferrable to other low-valent f-block compounds.

ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02161.

TDDFT of $[U(NR_2)_3]^-$ and $[Cp^{tet}_3U]^-$ without additional diffuse p primitive function, spin-state energies for $[Cp''_3U]^-$ and $[Cp^{tet}_3U]^-$, and $\langle S^2 \rangle$ values, orbital energies, orbital plots, electronic excitation summaries, and geometry-optimized coordinates for compounds in this study (PDF)

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Notes

The authors declare the following competing financial interest(s): Principal investigator F.F. has an equity interest in Turbomole GmbH. The terms of this arrangement have been reviewed and approved by the University of California, Irvine, in accordance with its conflict of interest policies.

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