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Article

Quantum Chemical Characterization of the Bonding of *N*-Heterocyclic Carbenes to Cp_2MI Compounds [M = Ce(III), U(III)]

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The binding of *N*-heterocyclic carbenes to Ce(III) and U(III) compounds is characterized by quantum chemical methods. Density functional methods are in qualitative agreement with experiment that binding to U(III) is more favorable than to Ce(III); after correcting for basis-set superposition error, quantitative agreement with experiment is achieved with a multireference second-order perturbation theory approach accounting for relativistic effects. The small computed (and observed) preference derives from a combination of several small effects, including differences in electronic binding energies, rovibrational partition functions, and solvation free energies. Prospects for ligand modification to improve the differentiation between lanthanides and actinides are discussed on the basis of computational predictions.

Introduction

The identification of compounds capable of discriminating between lanthanide and actinide ions is a subject of considerable interest because of the potential utility of such ligands in the reprocessing of spent nuclear materials. A recent report by Mehdoui et al.[1] noted that the *N*-heterocyclic carbene (NHC) $C_3Me_4N_2$ binds more strongly to organometallic compounds of U(III) than to analogous compounds of Ce(III); in particular, they measured the equilibrium constant for eq 1 with L = $C_3Me_4N_2$ to be 16 at 296 K in tetrahydrofuran (THF) solvent.

$$\underset{\mathbf{1U}}{Cp^*_2UI} + \underset{\mathbf{2Ce}}{Cp^*_2CeI(L)} \rightleftharpoons \underset{\mathbf{2U}}{Cp^*_2UI(L)} + \underset{\mathbf{1Ce}}{Cp^*_2CeI} \quad (1)$$

This equilibrium constant corresponds to a standard-state free energy of reaction of -6.9 kJ mol^{-1}. In order to better understand the factors contributing to the stronger interaction between the NHC and the actinide, we have performed quantum chemical calculations for the various species in eq 1; in the interest of computational efficiency, we have replaced Cp* with Cp and L = $C_3Me_4N_2$ with L = $C_3Me_2N_2$, where methyl groups are only on the nitrogen atoms of the NHC. Henceforth we will use **1** and **2** to refer to these slightly simplified model systems.

We should note that a free energy difference of -6.9 kJ mol^{-1} is really quite small. It is noteworthy in this instance primarily because so many other ligands fail to differentiate equivalent actinide and lanthanide complexes to *any* extent. The prediction of so small a value poses significant challenges from a theoretical perspective because intrinsic errors in computational models for the participating heavy-element organometallic species might be expected to be larger than the free energy of reaction itself. Fortunately, eq 1 is an isodesmic equation to within metal identity, so that errors in computational models (e.g., in the substitution of Cp for Cp* in the computational model) may be relied upon to cancel to a large extent when the free energy of reaction is computed.[2] Computational chemistry has made considerable progress in the past 10 or 20 years in the understanding of systems containing heavy elements.[3−7] In the present case, even in the absence of a quantitative prediction, theory may prove particularly useful from a design perspective. That is,

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we describe calculations designed to determine how ligands may be modified in order to *increase* differentiation, and such predictions should be reliable independent of the absolute magnitude of any one predicted energy.

Computational Methods

Two levels of theory were employed, namely density functional theory (DFT) and multiconfigurational wave function based methods. We describe the technical details of each separately below.

DFT Calculations. Geometries for **1Ce** (doublet), **1U** (quartet), **2Ce** (doublet), and **2U** (quartet) were optimized at the hybrid B3LYP level[8−11] of density functional theory (DFT) using the split-valence basis set 6-31G(d)[12] for the H, C, and N atoms and relativistic pseudopotential basis sets for I,[13] Ce (28-electron core),[14] and U (60-electron core).[15] Analytic vibrational frequencies verified all stationary points as minima and permitted the computation of molecular partition functions, and thus free energies, using standard approximations.[2] Single-point energies were computed for the B3LYP geometries with two other functionals, namely *m*PWPW91[16−18] (a pure generalized gradient approximation (GGA) functional) and MPW1K[19] (a hybrid GGA functional containing a large fraction of exact Hartree−Fock exchange).

The optimized B3LYP geometries for **1Ce** and **1U** are found to have C_{2v} symmetry. In the case of **1U**, the ground state is $^4A_2$; in the case of **1Ce**, the KS SCF solution is of broken symmetry, but the most proper assignment of the ground state would be $^2A_1$. The optimized B3LYP geometries for **2Ce** and **2U** are nearly C_s symmetric: the only significant deviations from symmetry are associated with rotation of the methyl groups on the nitrogen atoms of the carbene. Enforcement of C_s symmetry and reoptimization led to negligible changes in electronic energy (less than 10^{-5} E_h), but one small positive frequency did change into an imaginary frequency. Given the tiny change in energy, the methyl groups may be considered effectively to be free rotors. Because the presence of a plane of symmetry facilitated multireference calculations, the C_s B3LYP geometries were used in such calculations.

Multireference Calculations. The complete active space (CAS) SCF method[20] was used to generate molecular orbitals (MOs) and reference functions for subsequent multiconfigurational second-order perturbation calculations of the dynamic correlation energy (CASPT2).[21] Relativistic effects were accounted for using a Douglas−Kroll−Hess (DKH) Hamiltonian.[22,23] We employed all electron basis sets of atomic natural orbital type, developed for relativistic calculations with the DKH Hamiltonian. For uranium, a primitive set 26s23p17d13f5g3h was contracted to 8s7p5d3f1g, for cerium, a primitive set 25s22p15d11f4g2h was contracted to 7s6p4d2f, and for iodine, a primitive set 22s19p13d5f3g was contracted to 6s5p3d1f. For the NHC carbon and nitrogen atoms, the primitive set 14s9p4d3f2g was contracted to 3s2p1d, while for the Cp carbons the same primitive was contracted to 3s2p. For hydrogen, the primitive set 8s4p3d1f was contracted to 1s. Overall, then, the basis set is of double-ζ plus polarization quality for U, Ce, I, and the NHC atoms, while it is of double-ζ quality for the Cp carbons. These basis sets are available in the MOLCAS-6.2 library.[24]

For the cerium(III) compounds, which have a valence electronic configuration $4f^1$, a minimal active space would be composed of one electron in the seven 4f orbitals. This active space was extended to five electrons in 11 orbitals (5/11). The four extra active orbitals, two occupied and two virtual, consisted of linear combinations of Ce 5d and I 5p orbitals. These orbitals were included in the active space on the basis of their occupation numbers and influence on the electronic energies in trial calculations. No additional orbitals were identified as important. In CASPT2 calculations using these CAS reference wave functions, core orbitals up to and including 4d for Ce and 3d for I were kept frozen. Compounds **1Ce** and **2Ce** were found to have single-configurational $^2A_1$ and $^2A'$ electronic ground states within the C_{2v} and C_s point groups, respectively.

In the uranium(III) compounds, which have a valence electronic configuration $5f^5$, a minimal active space would be composed of three electrons in the seven 5f orbitals. This active space was extended to nine electrons in 12 orbitals (9/12). The five extra active orbitals, three occupied and two virtual, consisted of linear combinations of U 7s, U 6d, and I 5p orbitals. These orbitals were included in the active space on the basis of their occupation numbers and influence on the electronic energies in trial calculations. No additional orbitals were identified as important. In CASPT2 calculations using these CAS reference wave functions, core orbitals up to and including 5d for U and 3d for I were kept frozen. Compounds **1U** and **2U** were found to have single-configurational $^4A_2$ and $^4A''$ electronic ground states within the C_{2v} and C_s point groups, respectively. These ground states and those of **1Ce** and **2Ce** noted above agree with the B3LYP predictions.

Observation of single-configurational wave functions for **1U** and **2U** is mildly unusual given the tendency of uranium(III) compounds to have many low energy states varying in f orbital occupations. In the case of **1U** the simplicity of the wave function is associated primarily with high symmetry. State-average CASPT2 calculations with two roots place the first $^4A_2$ excited state 11.6 kJ mol^{-1} above the ground state, which is a sufficiently large separation to maintain single-configurational character in the lower state. However, low-energy quartet states belonging to different irreducible representations do exist: the lowest $^4A_1$ states are at 3.9 and 5.9 kJ mol^{-1} above the ground state, the lowest $^4B_1$ states are at 5.1 and 6.3 kJ mol^{-1} above the ground state, and the lowest $^4B_2$ states are at 6.9 and 13.2 kJ mol^{-1} above the ground state. The situation with **2U** is more complicated. State-average CASPT2 calculations with four roots find four states having A′ symmetry within 6.4 kJ mol^{-1} of the ground state, and three states of A″ symmetry within 7.4 kJ

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mol^{-1} of the ground state (which is the fourth root). Root switching takes place when state-average orbitals are used, so that the single configurational state identified as lowest in energy at the CAS level for the single root calculation becomes the third root at 4.6 kJ mol^{-1} above the ground state, which is two configurational. The nature of state-average calculations, and of second-order multireference perturbation theory, is such that there is some ambiguity as to the nature of the ground state. For the sake of simplicity, we have chosen to use the single-root, single-configurational wave function for **2U** in our analysis (in part because of its formal correspondence to the single-determinantal Kohn−Sham wave function from our DFT calculations). In essence, the variation in this root's energy depending on the nature of the CASPT2 calculation must be regarded as a measure of potential error in the calculation, of which we remain mindful.

Spin−orbit coupling, which would be expected to further couple the states from *all* irreducible representations, was not included in the multireference Hamiltonian because it is expected to affect the energies of the cerium and uranium compounds before and after carbene complexation equivalently, and thus to cancel in the free energy change associated with eq 1. CASPT2 energies were corrected for basis-set superposition error using the standard procedure of Boys and Bernardi.[25]

Solvation Effects. Free energies of solvation in tetrahydrofuran (THF), the experimental solvent for eq 1, were computed using the SM5.43R solvation model.[26] Coulomb radii of 2.0 Å and atomic surface tensions of 0.0 cal mol^{-1} Å^{-2} were employed for the metal atoms (i.e., no surface tensions).

Software. DFT calculations were performed with the Gaussian 03 program suite.[27] CAS and CASPT2 calculations were accomplished using MOLCAS 6.2.[24] SM5.43R calculations were done with MN-GSM.[28]

Results and Discussion

DFT Calculations. Geometry optimizations were begun from X-ray crystal structures with excised methyl groups replaced by hydrogen atoms. However, it was not a trivial matter to converge the Kohn−Sham (KS) self-consistent field (SCF) equations. Various automated and manual procedures for guessing the starting KS orbitals could not be converged by any of the standard schemes available in the Gaussian 03 package. Attempts to converge Hartree−Fock (HF) SCF solutions met with no greater success. Ultimately, it did prove possible to converge the restricted KS SCF equations for species from which all f electrons had been removed (i.e., monocationic singlets for **1Ce** and **2Ce** and tricationic singlets for **1U** and **2U**). When the orbitals of the cationic singlet systems were used as the initial guesses for their open-shell neutral analogues, convergence of the now unrestricted KS SCF equations proved possible, but often the converged solutions proved to be unstable to occupied/virtual orbital swaps, so that every solution had to be evaluated for stability. Finally, after such stability had been established, geometry optimization could be accomplished.

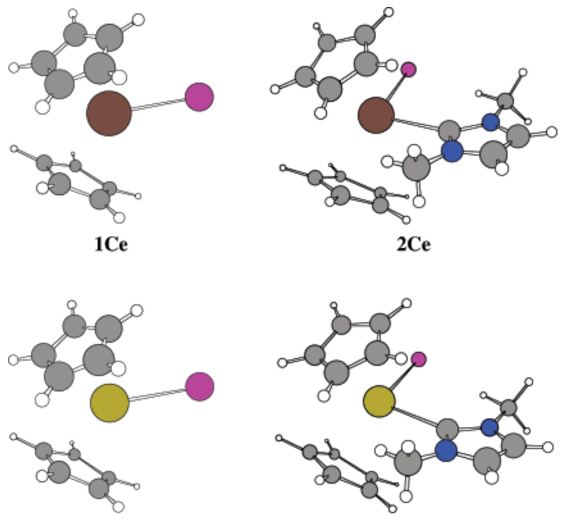
1Ce **2Ce**
1U **2U**

Figure 1. B3LYP optimized geometries for **1Ce** and **1U** (C_{2v} symmetry) and **2Ce** and **2U** (C_s symmetry).

The optimized B3LYP geometries are shown in Figure 1, and full geometric details are available in the Supporting Information. Agreement with reported X-ray crystal structural data[1] for the fully methylated metallocarbenes is quite good, with the largest deviations being associated with the metal−iodide and metal−carbene carbon distances, e.g., in Å, for **2U** r(U−I) = 3.127 (expt); 3.119 (theory), r(U−Ccarbene) = 2.687 (expt); 2.728 (theory), and for **2Ce** r(Ce−I) = 3.160 (expt); 3.137 (theory), r(Ce−Ccarbene) = 2.724 (expt); 2.776 (theory). While deviations of up to 0.05 Å in bond lengths to the metal center may be considered large, it must be noted that the bonding potentials associated with these coordinates are extremely flat. For instance, we compared energies for the fully optimized B3LYP structures to alternative structures in which the metal−iodide and metal−carbene carbon bond lengths were reset to the X-ray crystal structure distances while holding all other degrees of freedom constant. At the CASPT2 level, the alternative structures for **2Ce** and **2U** differed in electronic energy from their optimized originals by less than 0.8 kJ mol^{-1}. Such a flat coordinate would be expected to permit substantial distortion in response to crystal packing forces, for example, so that the gas-phase B3LYP optimized geometries may be considered to be reasonable models for further analysis.

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Table 1. Energy Components for the Equilibrium of Equation 1 at Various Theoretical Levels[a]

eq 1 quantity	B3LYP	*m*PWPW91	MPW1K	CASPT2[b]	expt
ΔE_{elec}, kJ mol^{-1}	−15.9	−21.7	−15.4	−0.5 (−13.3)	
$\Delta\Delta G^{\circ}_{\mathrm{trv}}$, kJ mol^{-1}	−2.1				
$\Delta\Delta G^{\circ}_{\mathrm{solv}}$, kJ mol^{-1}	−3.8				
ΔG°, kJ mol^{-1}	−21.8	−27.6[c]	−21.2[c]	−6.4[c] (−19.2)[c]	−6.9
K_{eq}	6600	68000	5200	13 (2300)	16

[a] All structures optimized at the B3LYP level (see Figure 1 and Supporting Information). [b] Values in parentheses are prior to correction for BSSE. [c] Computed using the thermal and solvation contributions from the B3LYP level.

In the gas phase, the electronic energy changes for the binding of the NHC to **1U** and **1Ce** are predicted at the B3LYP level to be −134.5 and −118.5 kJ mol^{-1}, respectively. Including thermal contributions, the B3LYP free energies of binding are −79.4 and −61.4 kJ mol^{-1}, respectively. Although **2U** and **2Ce** are characterized by several very low-frequency modes, which may in principle cause the harmonic-oscillator approximation to be inappropriate for the computation of vibrational entropies,[2] the difference between the differential thermal *enthalpy* vibrational contribution and the differential thermal *free energy* vibrational contribution is only 0.5 kJ mol^{-1}. Thus, although there may be some uncertainty in the absolute binding energies of the NHC to the organometallic compounds, any such error appears to cancel in the computation of the free energy change associated with eq 1.

The THF solvation free energies computed at the SM5.43R level for **1U**, **1Ce**, **2U**, and **2Ce** are predicted to be −43.3, −51.0, −79.3, and −83.3 kJ mol^{-1}, respectively. We note that **1Ce** and **2Ce** are both marginally better solvated than their uranium-containing analogues. This is associated with a somewhat larger ionic character in the cerium compounds. Thus, natural population analysis[29] predicts partial atomic charges on cerium of 2.315 and 2.284 for **1Ce** and **2Ce**, respectively, while the analogous uranium charges in **1U** and **2U** are 2.261 and 2.221, respectively. Most of the charge difference in each case is displaced onto the iodine atom, which thus bears a more negative partial atomic charge in the cerium compounds.

Combining the B3LYP gas-phase free energies with the SM5.43R solvation free energies we predict the free energy change for the reaction in eq 1 to be −21.8 kJ mol^{-1} (see Table 1). To assess the sensitivity of this prediction to different DFT functionals, we performed single-point electronic energy calculations on our B3LYP structures using the *m*PWPW91 and MPW1K functionals. These functionals were chosen because the first is a pure functional (i.e., containing no HF exchange) while the other contains roughly 42.8% HF exchange; B3LYP contains 20% HF exchange. Assuming thermal contributions and solvation effects to be unchanged, ΔG° for eq 1 is predicted to be −27.6 and −21.2 kJ mol^{-1} at the *m*PWPW91 and MPW1K levels, respectively. Thus, sensitivity of the equilibrium constant to the choice of functional is overall low, although the pure *m*PWPW91 functional predicts greater differentiation than either of the two hybrid functionals.

The free energy changes predicted at the various DFT levels of theory have the correct sign, but they are all too large in magnitude. We return to the molecular energetics below, but first we examine other results from the DFT calculations that shed light on the nature of the interaction between the metal complexes and the HNC ligand.

Both prior to and after NHC complexation, the U and Ce compounds have similar polarities, although we have already noted above the slightly more ionic character of the cerium compounds. At the B3LYP level, **1U** and **1Ce** have dipole moments of 4.8 and 5.2 D, and **2U** and **2Ce** have dipole moments of 9.9 and 10.2 D, respectively. Solvation in THF causes these four dipole moments to increase to 7.1, 7.8, 13.3, and 13.7 D, respectively, indicating the molecules also to be similarly polarizable. These results are consistent with the small differential solvation effect of −3.8 kJ mol^{-1} predicted for eq 1.

Natural bond orbital (NBO) analysis[30,31] was also performed for **2U** and **2Ce** at the B3LYP level. As already noted above, there is little change in the ionic character of the metals after NHC complexation. Analysis of the interactions between the metal and its fragments with the NBO model indicates, not surprisingly, that the carbene acts as a strong σ donor to the metal center. Although NHCs can also function as π acceptors, no such interaction is predicted for **2Ce**. In **2U** the interaction exists, but the $f \rightarrow \pi^*$ delocalization energy computed from second-order perturbation theory in the natural bond orbital basis[30,31] is a mere 1% of the interaction energy computed for the σ donor interaction, which limits the strength of this interaction to only 1 kJ mol^{-1} or so.

The occupied f orbitals are consistent with this analysis: each is essentially pure (Figure 2). If a reduced isodensity contour is used for the second of the uranium f orbitals in Figure 2, a contribution from the appropriate π^* acceptor orbital on the NHC can be identified, but clearly only a small amount of back-bonding is manifest. The occupied f orbital in **2Ce** has no detectable interaction with the NHC π^*.

The situation with **2U** is similar to that described by Lee and Hu for a series of organochromium(0) species coordinated to saturated and unsaturated NHCs.[32] On the basis of the insensitivity of NHC binding energies to saturation of the heterocycle, Lee and Hu concluded that π back-bonding did not contribute significantly to metal−NHC binding. Coming to a similar conclusion, Boehme and Frenking analyzed the binding interactions of imidazol-2-ylidene with CuCl, AgCl, and AuCl and found π back-bonding to be minimal.[33] A contrasting case, however, has been reported for the NHC complex of a different uranium(III) species, namely $[((Me_3Si)_2N)_3U^{III}]$(tetramethylimidazol-2-ylidene), where DFT calculations showed a much more substantial

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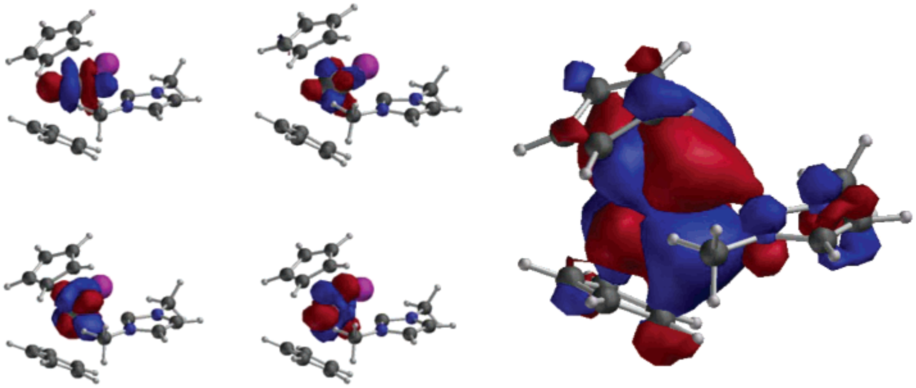

Figure 2. Singly occupied f orbitals from B3LYP for **2Ce** (upper right in group of 4) and **2U** (remaining 3 in group of 4) at the 0.04 au contour level. At far right the second of the f orbitals for **2U** (lower left in group of 4) is shown at the 0.01 au contour level to illustrate the small amount of π back-bonding that is associated with this orbital.

contribution of the NHC π^* orbital to a singly occupied f orbital analogous to that shown in Figure 2.[34] It seems likely that this difference must be associated with the nature of the bis(trimethylsilyl)amido ligands, which are very strong electron donors compared to, say, the pentamethylcyclopentadienide and iodide ligands in **2U**.

CASPT2 Calculations. In order possibly to assess more accurately the energetics associated with eq 1, we performed electronic energy calculations for the B3LYP geometries using multireference second-order perturbation theory (CASPT2).[21] This approach has demonstrated good agreement with experiment for the prediction of structural and energetic properties of molecules containing actinides or lanthanides.[35−38] CAS reference wave functions[20] were computed using nine electrons in 12 orbitals for **1**/**2U** and five electrons in 11 orbitals for **1**/**2Ce**. Atomic natural orbital, relativistic all-electron basis sets were used, and relativistic effects were accounted for using the second-order Douglas−Kroll−Hess Hamiltonian,[22,23] as described in more detail in the Computational Methods section.

At the CASPT2 level, the electronic energy change associated with eq 1 is −13.3 kJ mol^{-1}. If we add to this value the thermal and solvation contributions computed at the B3LYP level (since such calculations are impractical at the CASPT2 level and are not expected to be very sensitive to level of theory in any case), then the CASPT2 predicted equilibrium constant for eq 1 is in marginally better agreement with experiment compared to the DFT models. However, the binding potential energies computed for the NHC to the metals in **2U** and **2Ce** are −557.1 and −543.8 kJ mol^{-1}, respectively; these values are vastly larger than those computed at the B3LYP level and suggest that there is a large amount of basis set superposition error (BSSE) in the CASPT2 calculations. To correct for BSSE, we employed the standard counterpoise technique of Boys and Bernardi.[25] After correction, the CASPT2 binding potential energies are reduced to −156.8 and −153.9 kJ mol^{-1}, respectively, and these values are in much better agreement with those from B3LYP (which is expected to be substantially less sensitive to BSSE;[2] attempts to compute BSSE at the B3LYP level were not successful as it proved impossible to converge KS SCF solutions when ghost-atom basis functions were added to **1Ce** or **1U**). After accounting for thermal contributions to the free energy of binding, which are unfavorable owing to loss of entropy, the BSSE-corrected CASPT2 binding free energies of the NHC to **2U** and **2Ce** are predicted to be −101.7 and −96.7 kJ mol^{-1}, respectively. Such relatively strong binding is consistent with the observation of Mehdoui et al.[1] that the NHC ligand is not displaced by solvents containing oxygen or nitrogen donor atoms (e.g., THF).

Using the BSSE-corrected CASPT2 energies for **2U** and **2Ce**, we predict the free energy change for eq 1 to be −0.5 kJ mol^{-1} (note that there is a difference between the energy change for eq 1 and the differential NHC binding energies for **1U** and **1Ce** because the NHC itself is subject to different BSSE corrections in **2U** and **2Ce** that are relevant only to the calculation of the binding energy, but not the equilibrium). After addition of thermal and solvation contributions, the free energy change for eq 1 is predicted to be −6.4 kJ mol^{-1}, which agrees with experiment to within 0.5 kJ mol^{-1}. Such good agreement clearly entails some cancellation of errors but nevertheless allows analysis to proceed with increased confidence.

It is noteworthy that theory suggests that the preference of the NHC ligand for U compared to Ce is actually a rather subtle combination of effects. The total differentiation of −6.4 kJ mol^{-1} is predicted to be composed of −0.5 kJ mol^{-1} differential metal−ligand electronic interaction energy, −2.1 kJ mol^{-1} differential thermal contributions (deriving from a large number of very slightly larger frequencies in **2Ce** compared to corresponding modes in **2U**), and −3.8 kJ mol^{-1} differential solvation free energies. Because of the nature of eq 1, which is very nearly isodesmic,[2] one may expect some favorable cancellation of errors in our calculations such that the critical differential energies are more trustworthy than their individual components. For example, we do not expect spin−orbit effects on the individual molecular energies to be small, but we expect them to be the same for each metal

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before and after carbene complexation so that they have no significant effect on the equilibrium. Even with such isodesmic leveling, the magnitudes of our predicted differential energies are sufficiently small in an absolute sense that it would likely be ill advised to ascribe too much significance to the relative importance of the three components: electronic, thermal, and solvation. Instead, a more cautious interpretation would be simply to consider each of the three to have the potential to be equally important.

It is perhaps worth noting that any interpretation, whether based on experiment or theory, of a phenomenon whose energetic manifestation has a magnitude of only 6.9 kJ mol^{-1} is inevitably fraught with a certain degree of peril. Small energetic differences are rarely associated with dramatic changes in other molecular properties, so that one expects to find significant similarities in this case between the cerium and uranium systems, and indeed we do find this.

However, while theory does not identify any one feature of metal−NHC binding that is decisive in differentiating U from Ce, it does offer the opportunity for some computational alchemy to further the design of ligands having increased selectivity for U. To explore this question, we have considered NHC ligands modified so as to influence their donor or acceptor characters. While such modifications in synthetic systems would involve substitution with chemical functional groups, in the computational model a more simple approach is to adjust the nuclear charge of the heterocyclic N atoms (this is particularly true given the difficulty we would expect to have obtaining converged KS SCF solutions in substituted systems). When the N nuclear charge is increased, the NHC is a less good σ donor and a better π acceptor, and the opposite situation obtains when the N nuclear charge is decreased. Without changing the molecular geometries, we have considered the effect of charge modifications of ±0.4 and ±0.8 a.u. per N nucleus on the ΔE_{elec} associated with eq 1 (Table 2).

Table 2. Changes in ΔE_{elec} for Equation 1 and ΔE_{bind} for NHC to **1U** and **1Ce** (kJ mol^{-1}) as a Function of Nuclear Charge on N^a

Δq, a.u.	$\Delta\Delta E_{\text{elec}}$, eq 1	$\Delta\Delta E_{\text{bind}}$, **1U**	$\Delta\Delta E_{\text{bind}}$, **1Ce**
0.8	−6.3	99.5	105.8
0.4	−4.7	58.3	62.5
0.0	0.0	0.0	0.0
−0.4	−4.3	−74.5	−70.7
−0.8	−7.0	−164.3	−157.8

We find that either increasing *or* decreasing the N nuclear charge is predicted to improve the discrimination for U over Ce; for changes of ±0.8 a.u. the 298 K equilibrium constant for eq 1 would be predicted to increase by about 1 order of magnitude. As the NHC becomes a stronger σ donor (decreasing N nuclear charge), its binding to both metals becomes increasingly strong and the proportionately larger increase for U compared to Ce is consistent with the larger nephelauxetic effect observed for actinides compared to lanthanides.[39] Interestingly, a quantitatively similar improvement in discrimination for U over Ce is predicted with *increasing* N nuclear charge. As expected for this weaker σ donor, the overall binding energy of the NHC is substantially decreased, but the effect is somewhat smaller for U than for Ce. This presumably reflects the increasing influence of metal-to-ligand π back-bonding as the NHC becomes increasingly electron poor; this interaction, consistent with the NBO analysis described above, is available only to U because of its more chemically active 5f orbitals. However, while this result is intriguing, the absolute binding energy does tend toward zero as the NHC becomes increasingly electron poor (reflecting the much greater impact of the σ bonding interaction compared to the π). So, from a practical standpoint it seems more fruitful to examine NHCs with enhanced electron-donating characteristics in future experimental design.

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Supporting Information Available: Molecular geometries and electronic energies for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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