Zuschriften

Quantum Chemical Calculations Predict the Diphenyl Diuranium Compound [PhUUPh] To Have a Stable ^1A_g Ground State**

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Use of sterically hindered ligands to maintain the integrity of normally unstable chemical entities is a widespread technique in modern synthetic chemistry. Bulky aryl and alkyl substitu-

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ents have been designed to stabilize sensitive compounds, such as main-group-element dimers with multiple bonds,[1] including the alkyne analogues of heavier Group 14 elements.[2,3] This methodology was recently employed in the generation of a new stable low-valent chromium dimer that, according to experimental and theoretical evidence, exhibited a Cr—Cr quintuple bond.[4,5] The synthesis and characterization of this crystalline compound, [Ar′CrCrAr′] (Ar′ = C_6H_3-2,6(C_6H_3-2,6-iPr_2)_2$), has renewed interest in metal-metal multiple bonding. A subsequent computational study[5] on a simplified model for [Ar′CrCrAr′], [PhCrCrPh], predicted a fivefold bonding picture with filled bonding orbitals ($\sigma^2\pi^4\delta^4$) as the predominant electronic configuration in the singlet ground state.

In contrast to the multiple bonding between early transition metals, like, for example, the quadruple bond in $K_2[Re_2Cl_8]\cdot2\,H_2O$,[6] only rare examples of direct M—M interactions are known in actinide chemistry. The only known bonds of such type occur in the hydride $[H_2UUH_2]$[7] or in the U_2 species, experimentally trapped in argon matrices,[8] which we have previously described through high-level calculations.[9] In the U_2 dimer,[9] two uranium atoms bind to form a quintuple bond, thus suggesting that this U_2 unit could form the framework for the development of more diverse diuranium chemistry. The U_2^{2+} cation[10] was also found to be metastable, exhibiting a large number of low-lying electronic states with a short bond length of about 2.30 Å, compared to 2.43 Å in the neutral U_2 molecule.

The natural tendency of a uranium atom to be preferentially complexed by a ligand, rather than to explicitly form a direct U—U bond, has to date precluded the isolation of stable uranium species exhibiting direct metal–metal bonding. From the experimental point of view, the synthesis of multiply bonded uranium compounds poses many challenges. Although the uranium ionic radius is not exceedingly large, the presence of many electrons combined with the preference for certain coordination modes with common ligands make the task of stabilizing the hypothetical U—U bond difficult. With the relatively low first ionization energies of 584 (M→ M$^+$) and 1420 kJ mol^{-1} (M$^+$→M^{2+}) and the ground-state electron configuration corresponding to [Rn]$5f^3 6d^1 7s^2$, uranium seems nevertheless to be a promising candidate to form multiply bonded species in actinide chemistry. Despite the fact that this most common actinide exhibits a large range of oxidation states (the most common is U^{+6}, but less common oxidation states such as U^{+2}, U^{+3}, U^{+4}, and U^{+5} are also known), monovalent uranium ions have not yet been formally identified.[11]

Light atoms that are present in various organic ligands are known to bind tightly to uranium ions.[12–15] Furthermore, hexa- or tetrafluoro complexes with U^{6+} and U^{4+} are easily formed,[16] and tetravalent uranium is also stable in hydroxides, hydrated fluorides, and phosphates.[17] Hexavalent uranium is the most stable oxidation state, and the most commonly occurring uranium oxide is U_3O_8. Experimental studies taking advantage of the complex behavior of the f orbitals of uranium result in new variations of the already known moieties described above. For example, recent reports of uranium rings containing bimetallic nitride linkages[15] or of

an ammonium salt of uranium polyazide, $[U(N_3)_7]^{3-}$,[14] show that more can be done in this quickly expanding field.

To obtain direct metal–metal bonds, at least two conditions must be fulfilled. A proper supporting ligand has to be prepared, and one has to control the oxidation state of the dimeric metal moiety. To maximize the bonding interactions between metal centers, the number of orbitals engaged in metal–ligand bonding should be reduced, and each metal center should have a maximum number of valence electrons to fill the remaining bonding orbitals. These criteria can be achieved if the metal is in a low oxidation state and bound to a monodentate ligand. The ligand, in turn, must be sufficiently bulky as to stabilize the metal center and prevent further reaction. In the case of uranium, however, the tendency for the higher oxidation states would suggest that if a multiple bond is to be formed between uranium atoms, such a species would rather bear several ligands on each multivalent U center. We have recently studied computationally such multiply bonded molecules (U_2Cl_6, $[U_2Cl_8]^{2-}$).[18] On the other hand, there is no evidence against formation of a lower oxidation state for uranium, and experimental evidence exists for the formation of several uranium hydrides (UH, UH_2, UH_3, U_2H_2, UH_4, U_2H_4), thus implying that a continuous range of oxidation states is available.[7]

Although U−O, U−N, and U−C bonds with σ character form easily,[19] several studies indicate that such bonds might already possess a multiple character.[15, 20–24] This property is mainly a result of the presence of the 5f and 6d orbitals that can directly participate in the bonding. It is therefore difficult to predict to what extent the bonding between two uranium atoms will be characterized by a higher bond order.

Based on several experimental reports of compounds in which the uranium center is bound to a carbon atom, we have considered the possibility that a {CUUC} core containing two U^{1+} ions could be incorporated between two sterically hindered ligands. Herein, we present the results of a theoretical study of a simplified model for such a hypothetical molecule, namely [PhUUPh]. We have chosen to mimic the bulky terphenyl ligands, which could be potentially promising candidates for the stabilization of multiply bonded uranium compounds, by using the simplest phenyl moiety. We demonstrate that [PhUUPh] could be a stable chemical entity with a singlet ground state.

The complete active space (CAS) self-consistent field (SCF) method[25] was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation theory calculations of the dynamic correlation energy (CASPT2). Additional density functional theory (DFT) calculations were also performed.

The structures of two isomers were initially optimized using DFT, namely the bent-planar [PhUUPh] isomer **A** and the linear isomer **B** (Figure 1). Starting from a *trans*-bent-planar structure, the geometry optimization for isomer **A** predicted a rhombic structure (a bis(μ-phenyl) structure) belonging to the D_{2h} point group and analogous to the experimentally known species U_2H_2.[7] Linear structure **B** also belongs to the D_{2h} point group.

CASPT2 geometry optimizations for several electronic states of various spin multiplicities were performed on
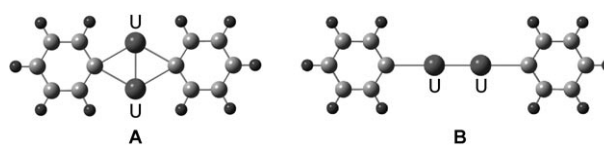
Figure 1. The bent-planar [PhUUPh] isomer (**A**) and the linear [PhUUPh] isomer (**B**).

selected structural parameters, namely the U−U and U−C bond lengths, while the geometry of the phenyl fragment was kept fixed. The most relevant CASPT2 structural parameters for the lowest electronic states of the isomers **A** and **B**, together with the relative CASPT2 energies, are reported in Table 1. The ground state of [PhUUPh] is a ^1A_g singlet with a

Table 1: Most significant CASPT2 structural parameters and relative energies for the lowest electronic states of isomer **A** and **B** of [PhUUPh].
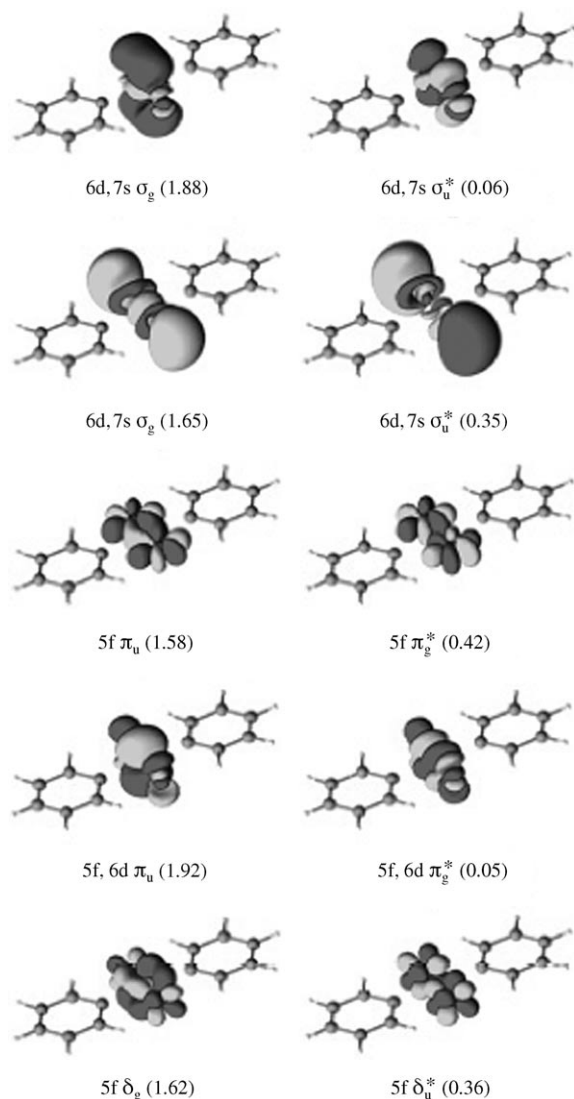
Isomer	State	d(U−U) [Å]	d(U−C) [Å]	U-C-U [°]	C-U-C [°]	ΔE [kcal mol^{-1}]
A	^1A_g	2.286	2.315	59.2	120.8	0 (-2.46378)[a]
A	^3A_g	2.263	2.325	58.3	121.8	$+0.76$
A	$^5B_{3g}$	2.537	2.371	64.7	115.3	$+4.97$
A	$^5B_{3u}$	2.390	2.341	61.4	118.6	$+7.00$
A	$^3B_{3g}$	2.324	2.368	58.8	121.2	$+7.00$
A	$^1B_{3g}$	2.349	2.373	59.3	120.7	$+7.14$
B	$^5B_{2u}$	2.304	2.395		180	$+19.67$
B	$^3B_{3g}$	2.223	2.430		180	$+22.16$
B	^3A_g	2.221	2.430		180	$+22.69$
B	$^1B_{3g}$	2.255	2.416		180	$+27.62$

[a] For the ^1A_g ground state the total CASPT2 energy is reported in parentheses (Hartree). The other total energies and the full structure of ^1A_g are reported in the Supporting Information.

bis(μ-phenyl) structure (**A**, Figure 1) and an electronic configuration $\sigma^2\sigma^2\pi^4\delta^2$, thus corresponding to a formal U−U quintuple bond. This configuration has a total weight of 49% in the CASSCF wave function. The following occupation numbers are obtained from the CASSCF calculation: σ_g (1.88), σ_u^* (0.06), σ_g (1.65), σ_u^* (0.35), π_u (3.50), π_g^* (0.47), δ_g (1.62), δ_u^* (0.36), thus yielding an effective bond order of 3.7 between the two uranium atoms.

It is interesting to compare the electronic configurations of the formal U_2^{2+} moiety in [PhUUPh] and the bare metastable U_2^{2+} cation.[10] The U_2^{2+} cation has a singlet ground state with a total orbital angular momentum quantum number (Λ) equal to 10, corresponding to a ^1N_g state. The $^1\Sigma_g^+$ state lies 279 cm^{-1} above the ground state and is degenerate with a triplet state. The ground state of U_2^{2+} has an electronic configuration $\sigma^2\pi^4\delta_g^1\delta_u^1\varphi_u^1\varphi_g^1$, thus corresponding to a triple bond between the two U atoms and four fully localized electrons. In [PhUUPh], the electronic configuration is different, mainly because the molecular environment decreases the coulomb repulsion between the two U^{1+} centers, thus making the U−U bond stronger than in U_2^{2+}. The corresponding U−U bond length (2.29 Å) is also slightly shorter than in U_2^{2+} (2.30 Å). A single bond is present between the U and C atoms. The molecular orbitals that form

the chemical bonds between the U−U and U−C atoms are represented in Figure 2.

6d, 7s σ$_g$ (1.88)   6d, 7s σ$_u^*$ (0.06)

6d, 7s σ$_g$ (1.65)   6d, 7s σ$_u^*$ (0.35)

5f π$_u$ (1.58)   5f π$_g^*$ (0.42)

5f, 6d π$_u$ (1.92)   5f, 6d π$_g^*$ (0.05)

5f δ$_g$ (1.62)   5f δ$_u^*$ (0.36)

Figure 2. Active molecular orbitals of the bent-planar isomer ^1A_g.

Inspection of Table 1 shows that the lowest triplet state, ^3A_g, is almost degenerate with the ground state (0.76 kcal mol^{-1} higher). Several triplet and quintet states lie 5–7 kcal mol^{-1} above the ground state. The lowest electronic states of the linear structure lie about 20 kcal mol^{-1} above the ground state of the bis(μ-phenyl) structure.

Since the ^1A_g and the ^3A_g states are close in energy, they may interact through the spin–orbit coupling operator. To evaluate the impact of such an interaction, the spin–orbit coupling between several singlet and triplet states was computed at the ground-state (^1A_g) geometry. First, the ordering of the electronic states is not affected by the inclusion of spin–orbit coupling. Analogous computation with the geometry of the ^3A_g state yields the singlet as the lowest state. The only difference concerns the energy difference ΔE_{S1-S2} between the two lowest spin states (^1A_g and ^3A_g), which is reduced to 0.3 kcal mol^{-1}.

To assess the strength of the U−U bond in [PhUUPh], its bonding energy was computed as the difference between the energy of [PhUUPh] and those of the two unbound [PhU] fragments. The ground state of [PhU] (with the U, C1, and C2 atoms collinear) was found to be a quartet ($^4B_2$) in C_{2v} symmetry. The CASPT2 Ph−U bond length is 2.38 Å. [PhUUPh] is lower in energy than two [PhU] fragments by about 60 kcal mol^{-1}, with the inclusion of a basis-set superposition error correction.

The question that one would like to answer is how to make [PhUUPh] and similar species experimentally. [PhUUPh] could in principle be formed in a matrix—analogous to the already detected diuranium polyhydride species[7]—by laser ablation of uranium and co-deposition with biphenyl in an inert matrix. The phenyl ligand might however be too large to be made in a matrix, and species such as [CH$_3$UUCH$_3$] may be more feasible.

Experimental Section

The calculations were performed using the software MOLCAS 6.2.[26] All electron basis sets of atomic natural-orbital type, developed for relativistic calculations with the Douglas–Kroll–Hess Hamiltonian,[27] were employed for all atoms. For uranium, a primitive set 26s23p17d13f5g3h was contracted to 8s7p5d3f1g. For carbon, the primitive set 14s9p4d3f2g was contracted to 3s2p1d. For hydrogen, the primitive set 8s4p3d1f was contracted to 2s1p.

The starting geometries were obtained from DFT geometry optimizations by using the B3LYP exchange correlation functional with the same basis set as described above. The C_{2h} symmetry constraint was imposed during the geometry optimization.

Subsequent multiconfigurational wave function calculations, followed by second-order perturbation theory, were performed using the CASSCF/CASPT2[28] method available in MOLCAS 6.2.

The active space was formed by 14 molecular orbitals (MOs), which are linear combinations of uranium 7s, 6d, 5f, and carbon (bonded to the U atoms) 2p orbitals. Ten active electrons were distributed in the 14 MOs.

In the subsequent CASPT2 calculations the orbitals up to and including the U 5d orbital were kept frozen. Selected bond lengths (U−U, U−C) were reoptimized at the CASPT2 level of theory.

Spin–orbit effects were taken into account by using the RASSCF state interaction method (RASSI),[29] which allows CASSCF wave functions for different electronic states to interact under the influence of a spin–orbit Hamiltonian.

The CASSCF/CASPT2/RASSI methods and the basis sets used here have been successful in a number of studies on dimetal compounds.[30,31]

The effective bond order between the two U atoms in [PhUUPh] was calculated as the sum of the occupation numbers of the bonding orbitals minus the sum of the occupation numbers of the antibonding orbitals, divided by two.

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