

## STRUCTURAL FEATURES OF ORGANOACTINIDE COMPOUNDS

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Many organoactinide compounds have been synthesized, most within the past 15 years[1]. These compounds frequently have very high formal coordination numbers and cannot be characterized by electron counting procedures similar to the 18 electron rule of the transition element organometallics. For instance,  $U(\eta^5-Cp)_4$  would have a formal coordination number of 12 and a formal electron count of  $26 e^-$ . Raymond and Eigenbrot have recently proposed a formalism, based on structural data, that offers the first systematic explanation for the bonding of the organoactinides[2].

Although Uranium and Thorium are the only naturally occurring actinides and dominate organoactinide chemistry, representative compounds of all elements between Actinium ( $Z=89$ ) and Californium ( $Z=98$ ) are known[3]. Ionic radii are large ( $1.03\text{\AA}$  for 6-coordinate  $U^{+4}$  compared to  $0.85\text{\AA}$  for  $Hf^{+4}$  [4]) which allow for the high coordination numbers. In contrast with the lanthanides, which are mostly limited to the +3 oxidation state, the actinides display a variety of oxidation states. The organometallic chemistry of the early actinides is often compared to that of the group 4 transition elements rather than to that of the lanthanides [1a, 1b, 5].

Technologically encouraging catalytic activity has been observed by a SNAM PROGETTI group using Uranium  $\pi$ -allyl complexes as stereospecific butadiene catalysts[6]. Yields  $>98.5\%$  cis isomer are observed. Other catalytic activity can be envisioned involving the high oxygen affinity of the actinides, such as the activation of carbon monoxide or related compounds that Marks has been investigating[7].

### Classes of Organoactinide Compounds

Biscyclooctatetrane compounds of the actinides have been actively studied since Streitwieser reported synthesis of uranocene in 1968[8]. Initial reasoning for synthesis of this compound was based on the possible overlap of the LUMO of the cyclooctatetrane dianion with 5f-orbitals of the same symmetry. A subsequent SCF- $X\alpha$  MO study indicated that 5f-orbital overlap is indeed important, but also indicated important 6d-orbital overlap of equal or greater magnitude[9]. In a recent communication Streitwieser reports synthesis of bis(bicyclooctatetraenyl) diuranium or "biuranocene"[10]. Interestingly, the linked cyclooctatetrane rings are twisted with respect to each other, resulting in close contact between the  $\alpha$  hydrogens and both uranium atoms. This compound indicates mixed valence and mixed central metal compounds may be synthetically feasible.

The largest class of organoactinides is the cyclopentadienyls. Compounds of the general formulas  $M(Cp)_4$ ,  $M(Cp)_3$ ,  $M(Cp)_3X$ ,  $M(Cp)_2X_2$ ,  $M(Cp)_2X$  and  $M(Cp)X_3$  are known ( $M=U$  or  $Th$ ,  $X$ =halide, alkoxy, alkyl)[1]. These compounds appear to have more covalent chemical behavior than the corresponding lanthanides. Compounds analogous to the  $M(Cp)_2X_2$

actinides also exist for the group 4 transition elements (M=Ti, Zr or Hf). Comparison of these compounds by photoelectron spectroscopy reveals a striking degree of similarity, indicating that the mode of bonding is essentially similar[11].

### Structural Characteristics

Raymond and Eigenbrot have proposed a formalism based on the extensive structural data now available[2]. Within each class of f-element organometallics, two generalizations are maintained. First, the geometries of ionic compounds tend to be irregular and depend on the steric bulk, number, and charge of ligands. Coordination number observed will be the balance of ionic attractive forces and nonbonding repulsions. Secondly, bond lengths for a series of structurally similar compounds will systematically follow their "ion size" and coordination number; that is, ionic radii can be used to predict bond lengths. Predominantly covalent interactions should depart from these predictions.

Using Pauling's radius ratio approach[12] and Shannon's table of ionic radii[4], Raymond and Eigenbrot observed that the difference between the metal to carbon bond lengths and the ionic radius of the metal was essentially constant for f-element cyclopentadienyl and cyclooctatetranyl structures. In other words, the cyclopentadienyl and cyclooctatetranyl ligands have a constant ionic radius. When this system was applied to the d-block metallocenes they observed no single ionic radius for the cyclopentadienyl ligand. Thus, they conclude that the f-block organometallics have basically ionic metal-ligand interactions while the d-block metallocenes have basically covalent metal-ligand interactions.

Recently, Day et al. pointed out that  $\{U[\eta^5-(CH_3)_5C_5]u-Cl\}_3$  is not well described by this formalism[13]. Comparison of this species with other known bridged trimers does not give a consistent value for the ionic radius of the pentamethylcyclopentadienyl ligand. However, this may be due to steric interactions between the more restricted ligands in the trimer. In any case, the proposed formalism does give a systematic characterization for the mode of bonding in organoactinide compounds which has been lacking until now. Still to be explained are the observed chemical and spectroscopic properties which indicate a larger degree of covalency than the formalism would allow.

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