
Preface

This volume reviews recent developments in the fields of organometallic and coordination chemistry of the actinides, and in particular uranium. Actinide chemistry in general has recently been rejuvenated with demonstrations of unprecedented structures, reactivity, and physical properties. While organouranium chemistry can be traced back to the Manhattan Project, most of these efforts were unsuccessful. However, by the mid-1950s the first uranium cyclopentadienyl (Cp) complexes were being reported, e.g. tricyclopentadienyl uranium(IV) chloride, $(C_5H_5)_3UCl$. The late 1960s heralded the synthesis and structural elucidation of “uranocene,” bis(cyclooctatetraenyl)uranium(IV), $U(C_8H_8)_2$, an expanded-ring sandwich compound that provided tantalizing evidence that 5f orbitals might be involved in bonding. One of the chapters in this volume details the expansion of this kind of work to include mixed sandwich U(III) cyclooctatetraene and pentalene complexes. As discussed by several of the authors, the availability of easily prepared mid-valent starting materials has been one of the primary factors involved in reinvigorating this field. Of particular interest to many readers will be the binding of small molecules by both organometallic and coordination compounds of uranium. Some of the holy grails of this chemistry include the activation of dinitrogen, carbon monoxide, and carbon dioxide. Various aspects of this work can be found in all three chapters, but are detailed in particular by O.T. Summerscales and F.G.N. Cloke.

The origins of coordination compounds of uranium are difficult to define precisely because the definition of what constitutes a coordination compound versus a purely inorganic compound can be difficult to differentiate. However, the coordination chemistry of uranium is very old, dating back to at least the early 1800s. There is tremendous diversity in the type of ligands that have been found to form stable complexes with uranium. Recent work has focused on highly tailored ligand sets to yield specific physico-chemical responses. This work has included the development of uranium complexes that specifically bind small molecules such as carbon dioxide. In addition, heterometallic 3d-5f systems are now being developed to explore magnetic interactions. It is important not to overlook early pioneering efforts by T.J. Marks and co-workers, who among other key discoveries found that uranyl cations can template the formation of superphthalocyanines. S.C. Bart and K. Meyer’s chapter details

more recent advances in the coordination chemistry of uranium in mid- to high oxidation states.

One of the most exciting and active areas of actinide research involves the development of novel catalysts. Thorium and uranium metallocene complexes have been shown to react in highly specific manners that in some cases parallel those of early transition metals, and in others the reactions are unique to the actinides. M. Sharma and M.S. Eisen's chapter details metallocene organoactinide chemistry with a special focus on novel reaction pathways that have in some cases been deduced from thermochemical studies.

In summary, the publication of this volume is a strong indicator of the substantial activity currently taking place in the organometallic and coordination chemistries of the actinides. The future promises to hold many more surprises.

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