CHAPTER TWENTY FIVE

ORGANOACTINIDE CHEMISTRY: SYNTHESIS AND CHARACTERIZATION

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25.1 INTRODUCTION

The advent of modern organometallic chemistry has often been cited as the report of the preparation of ferrocene, \((\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}\), the first metallic complex containing a π-complexed ligand (Pauson, 1951). It was not long after the report of this compound that comparable analogs of the lanthanides and actinides were reported (Reynolds and Wilkinson, 1956). Since that time, the organometallic chemistry of the actinides has lagged in comparable developments to the chemistry of the transition metals. Recent years, however, have witnessed a resurgence of interest in the non-aqueous chemistry of the actinides, in part due to the availability of a much wider array of ancillary ligands capable of stabilizing new compounds and introducing new types of reactivity. Equally important in stimulating new interest has been the realization by numerous researchers that the organometallic chemistry of these elements provides types of chemical environments that effectively probe the metals’ ability to employ valence 6d and 5f orbitals in chemical bonding. Modern organoactinide chemistry is now characterized by the existence not only of actinide analogs to many classes of d-transition metal complexes (particularly those of Groups 3 and 4), but increasingly common reports of compounds (and types of reactions) unique to the actinide series. Most developments in the non-aqueous chemistry of the
actinides have involved the use of thorium and uranium, both due to their lower specific activity, and to the apparent chemical similarity these elements bear to Group 4 metals in organometallic transformations. Uranium has further demonstrated the ability to access a wide range of oxidation states (3$^+$ to 6$^+$) in organic solvents, providing for greater flexibility in effecting chemical transformations.

The earliest technological interest in organometallic actinide chemistry focused on its potential for application in isotope separation processes (Gilman, 1968). More recent reports continue to discuss the volatility of organoaactinide compounds as a possible benefit in separation processes (gas chromatography, fractional sublimation) or in chemical vapor deposition processes (Mishin et al., 1986). At the same time, interest has emerged in the behavior of the actinide elements in stoichiometric and catalytic transformations, particularly in comparison to d-transition metal analogs. The relatively large size and abundance of valence orbitals associated with the actinide metals can facilitate transformations of substrates at the metal center, or enable new types of reactions. These reactions will be discussed further in Chapter 26.

This chapter will provide an overview of the preparation and properties of the major classes of actinide complexes; the material will be organized by major ancillary ligand type. Within a class of ligands, compounds will be discussed based upon assigned formal oxidation states. While earlier definitions of organo-metallic chemistry would restrict consideration to compounds exclusively containing metal–carbon $\sigma$- or $\pi$-bonds, for the purposes of this treatise we will briefly consider select classes of ancillary ligands based principally coordination of the metal center by elements of Group 15 or Group 16, particularly where these ligand sets serve to support novel molecular transformations at the metal center.

25.2 CARBON-BASED ANCILLARY LIGANDS

25.2.1 Cyclopentadienyl ligands

(a) Trivalent chemistry

The most common class of organoaactinide complexes is that containing the cyclopentadienyl ligand ($\text{C}_5\text{H}_5^-$), or one of its substituted derivatives. The use of variants of the cyclopentadienyl ligand has dominated the field of organometallic chemistry over the past 50 years, given their ability to stabilize a wide variety of oxidation states and coordination environments (Cotton et al., 1999). The cyclopentadienyl ligand itself dominated the early development of organoactinide chemistry. The coordination environment that likely has been reported for the largest number of the actinide elements is the homoleptic compound ($\eta^5\text{C}_5\text{H}_5$)$_3\text{An}$ (An = actinide). This ligand set support most members of the actinide series from thorium to californium (Table 25.1).

A number of synthetic routes have been reported to generate these species and their tetrahydrofuran (THF) adducts, including direct metathesis with alkali