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, $(\eta^5\text{-}C_5H_5)_2Fe$, 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 organoactinide 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 organometallic chemistry would restrict consideration to compounds exclusively containing metal–carbon σ- or π-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 organoactinide complexes is that containing the cyclopentadienyl ligand $(C_5H_5^-)$, 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 $(\eta^5\text{-}C_5H_5)_3An$ (An = actinide). This ligand set support most members of the actinide series from thorium to californium (Table 25.1).
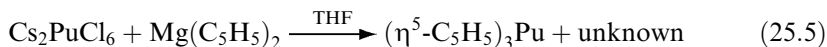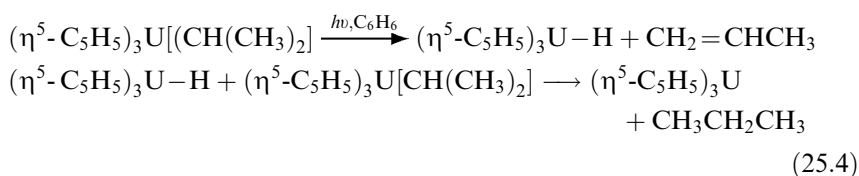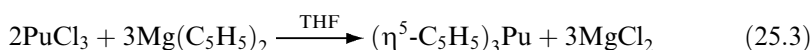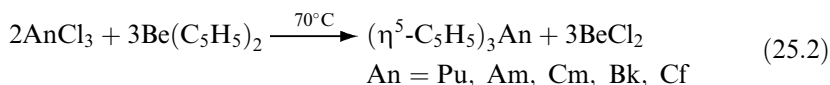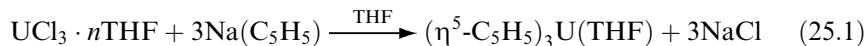
A number of synthetic routes have been reported to generate these species and their tetrahydrofuran (THF) adducts, including direct metathesis with alkali

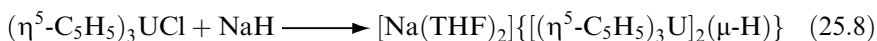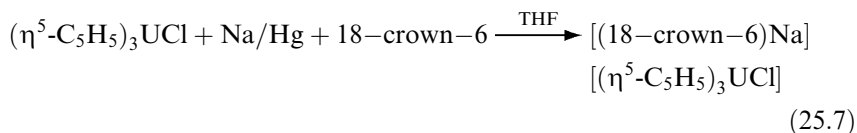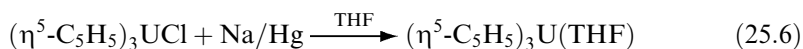**Table 25.1** *Tris(cyclopentadienyl)actinide complexes.*

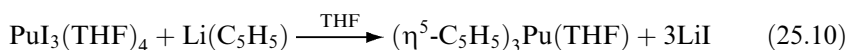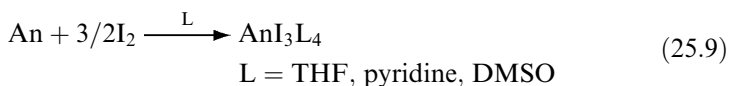| Compound	Color	Melting point (°C)	References
$(\eta^5\text{-}C_5H_5)_3Th$[a]	Green	–	Kanellakopolous *et al.* (1974a)
$(\eta^5\text{-}C_5H_5)_3U$	Brown	>200	Kanellakopolous *et al.* (1970)
$(\eta^5\text{-}C_5H_5)_3Np$	Brown	–	Karraker and Stone (1972)
$(\eta^5\text{-}C_5H_5)_3Pu$	Green	180 (dec.)	Baumgärtner *et al.* (1965)
$(\eta^5\text{-}C_5H_5)_3Am$	Flesh	330 (dec.)	Baumgärtner *et al.* (1966)
$(\eta^5\text{-}C_5H_5)_3Cm$	Colorless	–	Laubereau and Burns (1970a)
$(\eta^5\text{-}C_5H_5)_3Bk$	Amber	–	Laubereau and Burns (1970b)
$(\eta^5\text{-}C_5H_5)_3Cf$	Red	–	Laubereau and Burns (1970b)

[a] Compound not fully characterized.

metal salts (Crisler and Eggerman, 1974; Kanellakopolus *et al.*, 1974a, 1980; Moody and Odom, 1979; Wasserman *et al.*, 1983), or transmetallation with Be $(\eta^5\text{-}C_5H_5)_2$ or $Mg(\eta^5\text{-}C_5H_5)_2$ (Fischer and Fischer, 1963; Baumgärtner *et al.*, 1965, 1966, 1967, 1970; Laubereau and Burns, 1970a,b). In addition, the trivalent compounds may be obtained from chemical (Crisler and Eggerman, 1974) or photochemical (Kalina *et al.*, 1977; Bruno *et al.*, 1982) reduction of suitable tetravalent actinide precursors (Karraker and Stone, 1972; Chang *et al.*, 1979; Zanella *et al.*, 1980). Examples of these preparations are given in equations (25.1)–(25.5).

$$UCl_3 \cdot n\text{THF} + 3Na(C_5H_5) \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)_3U(\text{THF}) + 3NaCl \quad (25.1)$$

$$2AnCl_3 + 3Be(C_5H_5)_2 \xrightarrow{70°C} (\eta^5\text{-}C_5H_5)_3An + 3BeCl_2$$
$$An = Pu,\ Am,\ Cm,\ Bk,\ Cf \quad (25.2)$$

$$2PuCl_3 + 3Mg(C_5H_5)_2 \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)_3Pu + 3MgCl_2 \quad (25.3)$$

$$(\eta^5\text{-}C_5H_5)_3U[(CH(CH_3)_2] \xrightarrow{h\upsilon, C_6H_6} (\eta^5\text{-}C_5H_5)_3U-H + CH_2{=}CHCH_3$$
$$(\eta^5\text{-}C_5H_5)_3U-H + (\eta^5\text{-}C_5H_5)_3U[CH(CH_3)_2] \longrightarrow (\eta^5\text{-}C_5H_5)_3U$$
$$+ CH_3CH_2CH_3$$
$$(25.4)$$

$$Cs_2PuCl_6 + Mg(C_5H_5)_2 \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)_3Pu + \text{unknown} \quad (25.5)$$

More recently, a study was conducted on reduction products of $(\eta^5\text{-}C_5H_5)_3UCl$ with a variety of reducing agents (Le Marechal *et al.*, 1989). It was found that the composition of the product was a function of the reducing agent [equations (25.6)–(25.8)].

$$(\eta^5\text{-}C_5H_5)_3UCl + Na/Hg \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)_3U(THF) \qquad (25.6)$$

$$(\eta^5\text{-}C_5H_5)_3UCl + Na/Hg + 18-\text{crown}-6 \xrightarrow{\text{THF}} [(18-\text{crown}-6)Na]$$
$$[(\eta^5\text{-}C_5H_5)_3UCl]$$
$$(25.7)$$

$$(\eta^5\text{-}C_5H_5)_3UCl + NaH \longrightarrow [Na(THF)_2]\{[(\eta^5\text{-}C_5H_5)_3U]_2(\mu\text{-H})\} \quad (25.8)$$
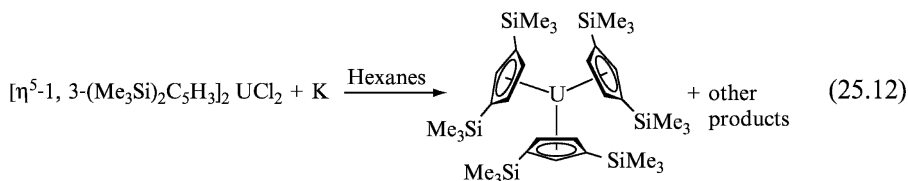
Perhaps the most useful development in the synthetic chemistry of trivalent actinide complexes in recent years has been the development of the more soluble iodide starting materials (Karraker, 1987; Clark *et al.*, 1989) AnI$_3$L$_4$ (An = U, Np, Pu; L = THF, pyridine, DMSO). These species, generated from actinide metals and halide sources in coordinating solvents, are readily soluble in organic solvents, and serve as convenient precursors to a variety of trivalent actinide species [equations (25.9)–(25.10)] (Zwick *et al.*, 1992).

$$An + 3/2I_2 \xrightarrow{\text{L}} AnI_3L_4$$
$$L = THF, \text{ pyridine, DMSO} \qquad (25.9)$$

$$PuI_3(THF)_4 + Li(C_5H_5) \xrightarrow{\text{THF}} (\eta^5\text{-}C_5H_5)_3Pu(THF) + 3LiI \qquad (25.10)$$

The solubility of the parent tris(cyclopentadienyl)actinide complexes is limited in non-polar media, presumably due to oligomerization through bridging cyclopentadienyl ligands. The molecular structures of these species have only been inferred by comparison of powder diffraction data with that obtained from known tris(cyclopentadienyl)lanthanide complexes. In response, a number of groups have explored the chemistry of substituted analogs of the cyclopentadienyl ligand for the light actinides (Th, U), including those with alkyl or silyl substituents, as well as the indenyl ligand. Tris(ligand) complexes have been reported and several examples have been structurally characterized. Tris(indenyl) complexes of thorium and uranium have been reported, and the complex $(\eta^5\text{-}C_9H_7)_3U$ was structurally characterized (Goffart, 1979; Meunier-Piret *et al.*, 1980). Several other trivalent substituted cyclopentadienyl complexes have been prepared by reduction of tetravalent precursors (Brennan *et al.*, 1986a; Zalkin *et al.*, 1988a; Stults *et al.*, 1990), as shown in equation (25.11).

$$(\eta^5\text{-}Me_3SiC_5H_4)_3UCl \;+\; {}^tBuLi \xrightarrow{\text{Toluene}}$$

$$(25.11)$$
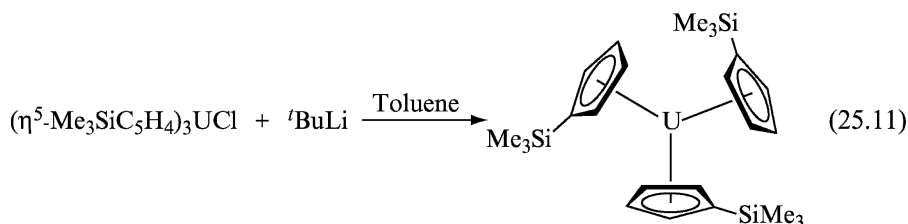
The complexes $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3U$ and $(\eta^5\text{-}C_5Me_4H)_3U$ have also been prepared by reduction of tetravalent precursors (del Mar Conejo *et al.*, 1999), although in the synthesis of $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3U$, ligand redistribution also takes place [equation (25.12)].

$$[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2\,UCl_2 + K \xrightarrow{\text{Hexanes}} \text{(structure)} + \text{other products} \qquad (25.12)$$

One of the more interesting members of the series of trivalent homoleptic cyclopentadienyl complexes is the well-characterized thorium example, $[\eta^5\text{-}(RMe_2Si)_2C_5H_3]_3Th$ (R = Me, ^tBu) (Blake *et al.*, 1986a, 2001). This complex was prepared in a manner similar to that shown in equation (25.12), by reduction of the metallocene dichloride or the tris(cyclopentadienyl) chloride in toluene by Na–K alloy. The compound is isolated in good yield as a dark blue crystalline material, which has been structurally characterized (Fig. 25.1).

As for most base-free tris(cyclopentadienyl)actinide complexes, the compound crystallizes in a pseudo-trigonal planar structure, with averaged ligand centroid–thorium–centroid angles near 120°, and averaged Th–C_{ring} distances of 2.80(2) Å. A particular element of interest for this complex has been its electronic structure. One of the most investigated aspects of actinide–cyclopentadienyl chemistry has been the nature of bonding between the metal and the ligand (Burns and Bursten, 1989). Most experimental studies of tris(cyclopentadienyl)actinide complexes, including ^{237}Np Mössbauer studies of $(\eta^5\text{-}C_5H_5)_3$ Np (Karraker and Stone, 1972) and infrared and absorption spectroscopic studies of plutonium, americium, and curium analogs (Baumgärtner *et al.*, 1965; Pappalardo *et al.*, 1969; Nugent *et al.*, 1971) suggest that while the bonding is somewhat more covalent than that in lanthanide analogs, the interaction between the metal and the cyclopentadienyl ring is still principally ionic. Theoretical treatments have suggested that the 6d orbitals are chiefly involved in interactions with ligand-based orbitals. While the 5f orbital energy drops across the series, creating an energy match with ligand-based orbitals, spatial overlap is poor, precluding strong metal–ligand bonding (Strittmatter and Bursten, 1991). Thorium lies early in the actinide series and the relatively high energy of the 5f orbitals (before the increasing effective nuclear charge across the series drops the energy of these orbitals) has lead to speculation that a Th(III) compound could in fact demonstrate a $6d^1$ ground state. In support of this, Kot *et al.* (1988) have reported the observation of an EPR spectrum with *g* values close to 2 at room temperature.

Despite the common use of the permethylated cyclopentadienyl ligand $(C_5Me_5^-)$ in actinide and lanthanide chemistry, it is only recently that a tris (cyclopentadienyl) actinide complex has been prepared with this ligand
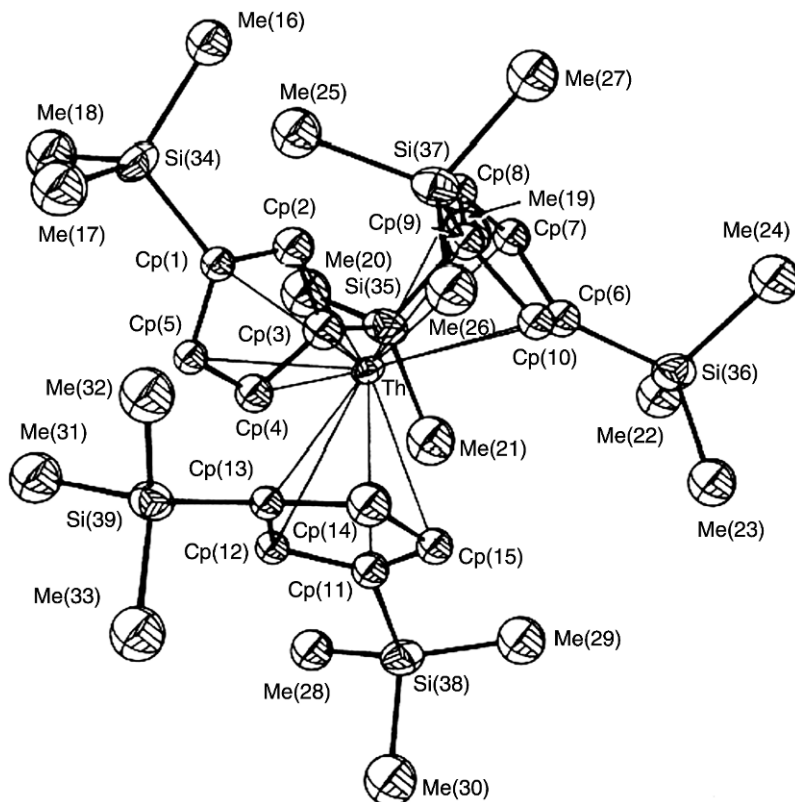
Fig. 25.1   *Crystal structure of* $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3Th$ *(Blake* et al., *1986a). (Reproduced by permission of The Royal Society of Chemistry.)*

(Evans *et al.*, 1997). It was previously anticipated that the large steric bulk associated with this ligand would preclude incorporation of three pentamethyl-cyclopentadienyl groups in the coordination sphere of an actinide, and in fact direct metathesis routes had not proven successful. The complex $(\eta^5\text{-}C_5Me_5)_3U$ was instead initially prepared by reaction of a trivalent hydride complex with tetramethylfulvene [equation (25.13)].
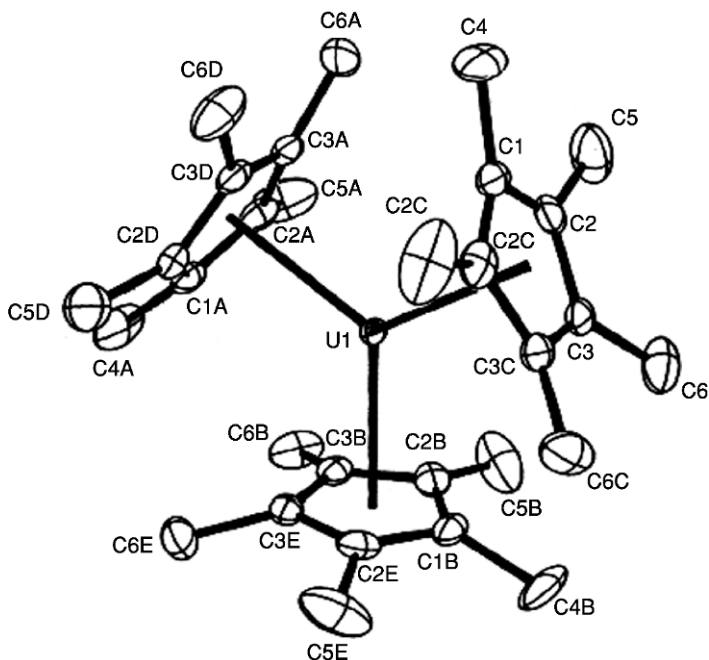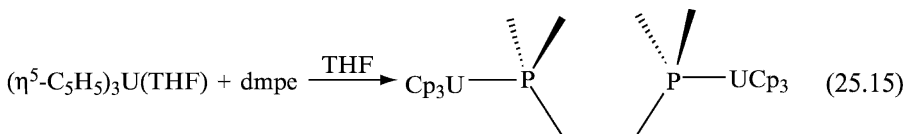
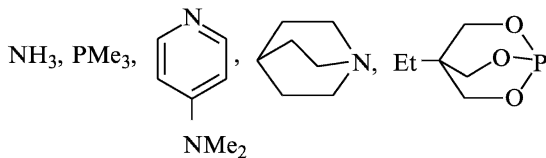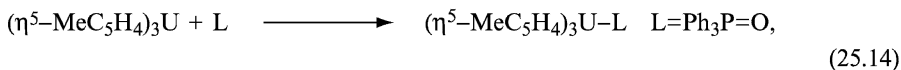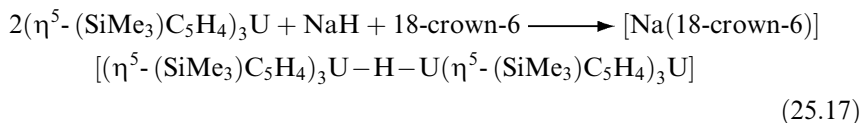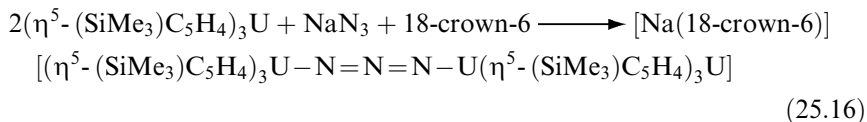$$(\eta^5\text{-}C_5Me_5)_2U(H)\,(dmpe) + \tag{25.13}$$
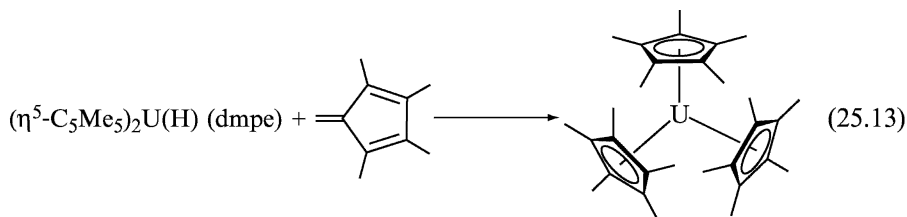
Fig. 25.2 *Crystal structure of* $(\eta^5\text{-}C_5Me_5)_3U$ *(Evans* et al*., 1997). (Reproduced with permission from John Wiley & Sons, Inc.)*

Since that time, however, several other routes have been reported to generate the compound (Evans *et al.*, 2002). The molecular structure is shown in Fig. 25.2. The average U–C$_{ring}$ bond distance in this compound [2.858(3) Å] is much larger than in other crystallographically characterized U(III) pentamethyl-cyclopentadienyl complexes (*ca.* 2.77 Å), suggesting a significant degree of steric crowding.

The tris(cyclopentadienyl)actinide complexes display a rich coordination chemistry, and one which sheds light on the nature of metal orbital participation in chemical bonding. Actinide metals generally are acidic and coordinate Lewis bases. As previously discussed, many of the tris(cyclopentadienyl)actinide complexes can be isolated as THF adducts directly from reactions carried out in that solvent. In addition, these complexes will coordinate other simple N-, O-, or P-donor bases. In most instances the complexes form simple 1:1 adducts [equation (25.14)] (Brennan and Zalkin, 1985; Brennan *et al.*, 1986b, 1988a; Zalkin and Brennan, 1987; Rosen and Zalkin, 1989; Adam *et al.*, 1993), while in select cases complexes have been isolated where two metal centers are bridged by a bidentate base [equation (25.15)] (Zalkin *et al.*, 1987b).

$$(\eta^5-\text{MeC}_5\text{H}_4)_3\text{U} + \text{L} \longrightarrow (\eta^5-\text{MeC}_5\text{H}_4)_3\text{U}-\text{L} \quad \text{L}=\text{Ph}_3\text{P}=\text{O},$$

$$(25.14)$$

$$\text{NH}_3,\ \text{PMe}_3, \quad [\text{pyridine with NMe}_2], \quad [\text{quinuclidine N}],\ \text{Et}-[\text{bicyclic } \text{P(O)}_3]$$

$$(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\text{THF}) + \text{dmpe} \xrightarrow{\text{THF}} \text{Cp}_3\text{U}-\text{P} \diagdown\!\!\diagup\diagdown\!\!\diagup\text{P}-\text{UCp}_3 \quad (25.15)$$

Similarly, reaction of tris(cyclopentadienyl) complexes with anionic reagents has been shown to produce either anionic [equation (25.16)] or anion-bridged bimetallic complexes [equation (25.17)] (Stults *et al.*, 1989; Berthet *et al.*, 1991a, 1992a):

$$2(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U} + \text{NaN}_3 + \text{18-crown-6} \longrightarrow [\text{Na(18-crown-6)}]$$
$$[(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U}-\text{N}{=}\text{N}{=}\text{N}-\text{U}(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U}]$$

$$(25.16)$$

$$2(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U} + \text{NaH} + \text{18-crown-6} \longrightarrow [\text{Na(18-crown-6)}]$$
$$[(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U}-\text{H}-\text{U}(\eta^5\text{-}(\text{SiMe}_3)\text{C}_5\text{H}_4)_3\text{U}]$$

$$(25.17)$$

Determination of the relative affinities of tris(cyclopentadienyl) complexes for various classes of ligands has been used to suggest the extent of metal-to-ligand π-back-donation. In order to compare the properties of actinides with lanthanides, ligand displacement series have been evaluated for the compounds $(\text{RC}_5\text{H}_4)_3\text{M}$ ($M = \text{U, Ce}$) (Brennan *et al.*, 1987). Both uranium and cerium complexes were found to have a preference for 'softer' phosphine donor ligands over 'harder' amine ligands, although in direct competition between the two metals, uranium always prefers the softer donors over cerium. Examination of the crystal structures of comparable uranium and cerium compounds reveals a slight shortening of the U–P bond (corrected for differences in metal radii); it has been suggested that this is a consequence of metal π-back-donation to phosphorus.

Another indication of the ability of low-valent early actinides to engage in π-back-donation may be found in the coordination of carbon monoxide to $(\text{R}_n\text{C}_5\text{H}_{5-n})_3\text{U}$ (Brennan *et al.*, 1986c; Parry *et al.*, 1995; del Mar Conejo *et al.*, 1999). Both structural and spectroscopic studies indicate that a strong degree of metal-to-ligand back donation occurs. The molecular structure of $(\eta^5\text{-C}_5\text{Me}_4\text{H})_3\text{U}(\text{CO})$ (Fig. 25.3) evidences a short U–C_{CO} bond distance of 2.383(6) Å.
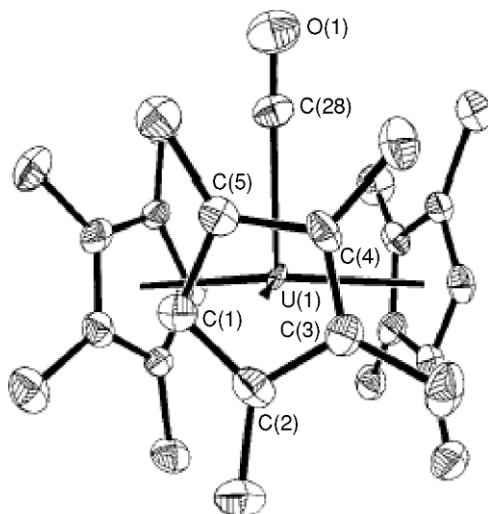
Fig. 25.3 *Crystal structure of* $[\eta^5\text{-}C_5Me_4H]_3U(CO)$ *(del Mar Conejo* et al.*, 1999).* (*Reprinted with permission from John Wiley & Sons, Inc.*)

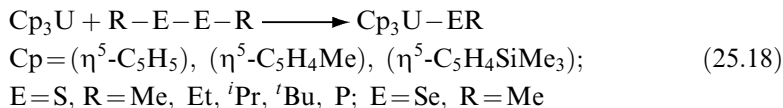**Table 25.2** *IR data of* $(\eta^5\text{-}R_nC_5H_{5-n})_3U(CO)$ *complexes.*

| Compound	ν_{CO} (cm^{-1})
$(\eta^5\text{-}C_5Me_4H)_3U(CO)$	1880
$(\eta^5\text{-}Me_3CC_5H_4)_3U(CO)$	1960
$(\eta^5\text{-}Me_3SiC_5H_4)_3U(CO)$	1976
$[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3U(CO)$	1988

Comparison of the ν_{CO} stretching frequencies for a series of compounds with varying ligand substituents (Table 25.2) demonstrates that electron-donating substituents on the ring contribute to increasing the electron density at the metal center, increasing metal-to-ligand back donation.

There is little comparable data for the heavier actinides, although the above bonding arguments would suggest that as the 6d orbital energy drops across the series, metal–ligand interactions would be weaker. Consistent with this picture, it has been reported that plutonium forms less robust adducts. While the complex $(\eta^5\text{-}C_5H_5)_3Pu(THF)$ can be isolated from solution, the THF is removed upon sublimation (Crisler and Eggerman, 1974); the analogous uranium compound remains intact upon sublimation (Wasserman *et al.*, 1983).

The early trivalent actinide cyclopentadienyl complexes are susceptible to one- and two-electron oxidation reactions. As an example, reaction of the tris (cyclopentadienyl) complexes have been reported to yield the corresponding U(IV) thiolate or selenolate complexes [equation (25.18)] (Leverd *et al.*, 1996).
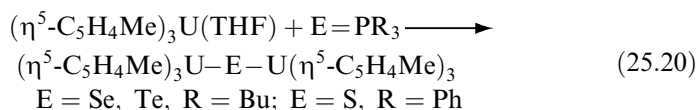
$$Cp_3U + R-E-E-R \longrightarrow Cp_3U-ER$$
$$Cp = (\eta^5\text{-}C_5H_5),\ (\eta^5\text{-}C_5H_4Me),\ (\eta^5\text{-}C_5H_4SiMe_3); \qquad (25.18)$$
$$E = S,\ R = Me,\ Et,\ {}^iPr,\ {}^tBu,\ P;\ E = Se,\ R = Me$$

Alkyl halides are similarly capable of oxidizing U(III) to generate equimolar mixtures of U(IV)–R and U(IV)–X as shown in equation (25.19) (Villiers and Ephritikhine, 1990).
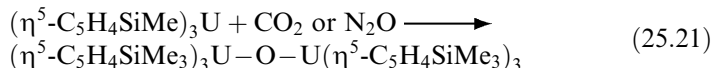
$$2(\eta^5\text{-}C_5H_5)_3U(THF) + R-X \longrightarrow (\eta^5\text{-}C_5H_5)_3U-R + (\eta^5\text{-}C_5H_5)_3U-X$$
$$(25.19)$$
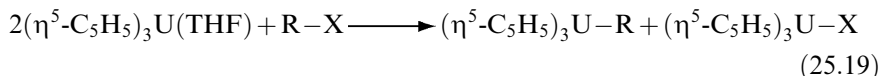
In the presence of sodium amalgam to reduce the uranium halide formed, the reaction can be made to be quantitative for formation of the alkyl species.

Reaction of $(\eta^5\text{-}C_5H_5)_3U(THF)$ with dioxygen produces the bridged bimetallic complex $[(\eta^5\text{-}C_5H_5)_3U]_2(\mu\text{-}O)$ (Spirlet *et al.*, 1996). The analogous μ-sulfido complex was produced by reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with freshly prepared K_2S. Chalcogen transfer reagents also oxidize tris(cyclopentadienyl) uranium complexes to yield bridged bimetallic species [equation (25.20)]; while most phosphine chalcogenides react readily, phosphine oxide does not oxidize U(III), but rather yields a base adduct (Brennan *et al.*, 1986b).

$$(\eta^5\text{-}C_5H_4Me)_3U(THF) + E{=}PR_3 \longrightarrow$$
$$(\eta^5\text{-}C_5H_4Me)_3U-E-U(\eta^5\text{-}C_5H_4Me)_3 \qquad (25.20)$$
$$E = Se,\ Te,\ R = Bu;\ E = S,\ R = Ph$$

An analogous bridging oxo complex has been generated by the reaction of $(\eta^5\text{-}C_5H_4SiMe_3)_3U$ with CO_2 or N_2O [equation (25.21)] (Berthet *et al.*, 1991b).
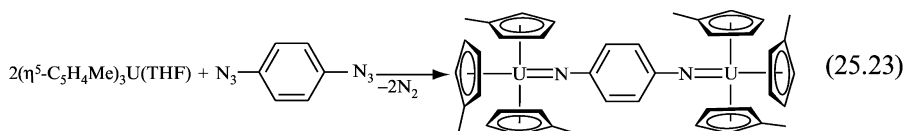
$$(\eta^5\text{-}C_5H_4SiMe)_3U + CO_2\ or\ N_2O \longrightarrow$$
$$(\eta^5\text{-}C_5H_4SiMe_3)_3U-O-U(\eta^5\text{-}C_5H_4SiMe_3)_3 \qquad (25.21)$$

This complex can also be prepared by the reaction of $(\eta^5\text{-}C_5H_4SiMe_3)_3U(OH)$ with $(\eta^5\text{-}C_5H_4SiMe_3)_3UH$ (Berthet *et al.*, 1993); pyrolysis of the hydroxide complex generates instead the trinuclear complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2U(\mu\text{-}O)]_3$.
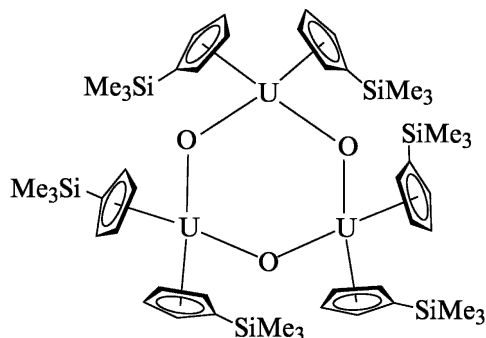
There are also a limited number of examples of two-electron oxidation reactions of tris(cyclopentadienyl)uranium compounds. Reaction of $(\eta^5\text{-}C_5H_4Me)_3U$ (THF) with organic azides (Brennan and Andersen, 1985) results in elimination of dinitrogen and formation of U(v) organoimido derivatives [equation (25.22)].

$$(\eta^5\text{-}C_5H_4Me)_3U + RN_3 \xrightarrow[-N_2]{} \quad U=N-R \qquad (25.22)$$

$$R = C_6H_6, SiMe_3$$
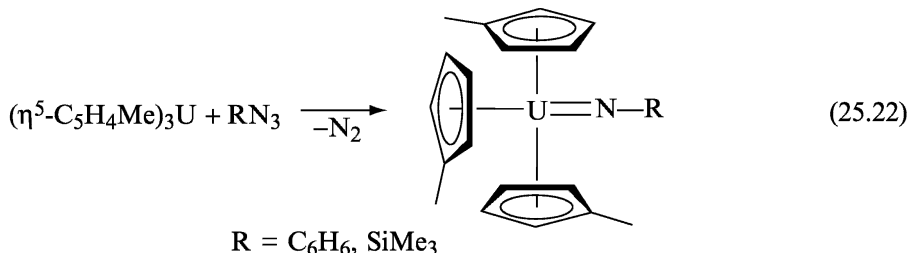
The related reaction with 1,3- or 1,4-diazidobenzene gives rise to bimetallic pentavalent products [equation (25.23)] (Rosen *et al.*, 1990).

$$2(\eta^5\text{-}C_5H_4Me)_3U(THF) + N_3\text{---}\langle\text{---}\rangle\text{---}N_3 \xrightarrow{-2N_2} \quad U=N\text{---}\langle\text{---}\rangle\text{---}N=U \qquad (25.23)$$

The product generated from 1,4-diazidobenzene supports electronic communication between the metal centers through an aromatic ligand conjugation-based superexchange pathway; antiferromagnetic coupling is observed between the unpaired spins on the two metal centers (Fig. 25.4). The compound derived from 1,3-diazidobenzene, however, cannot undergo similar conjugation, and the susceptibility data show no interaction between the metal centers.

There exist relatively fewer examples of trivalent actinide complexes with two cyclopentadienyl rings. Compounds of the parent cyclopentadienyl ion are somewhat rare. Examples include the reported compounds $(\eta^5\text{-}C_5H_5)_2ThCl$ (Kanellakopulos *et al.*, 1974a) and $(\eta^5\text{-}C_5H_5)_2BkCl$ (Laubereau, 1970), thought to exist as dimers. The compounds $(\eta^5\text{-}C_5H_4Me)_2NpI(THF)_3$ and $(\eta^5\text{-}C_5H_4Me)NpI_2(THF)_3$ were prepared by reactions of $NpI_3(THF)_4$ with $Tl(C_5H_4Me)$ in tetrahydrofuran (Karraker, 1987). Given the propensity of sterically smaller ligands to redistribute and generate multiple species in solution, most complexes have been generated with more highly substituted cyclopentadienyl ligands, particularly $(\eta^5\text{-}C_5Me_5)$, $[\eta^5\text{-}(Me_3Si)_2C_5H_3]$, and $[\eta^5\text{-}(Me_3C)_2C_5H_3]$. One of the most investigated of these complexes is the chloride-bridged trimeric complex $[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3$ (Manriquez *et al.*, 1979; Fagan *et al.*, 1982). The complex can be prepared by a number of routes as shown in equations (25.24)–(25.26).
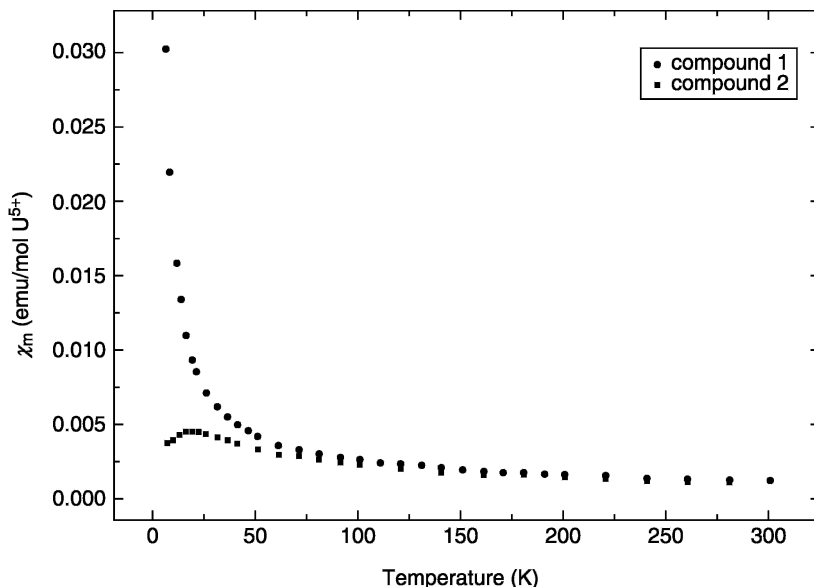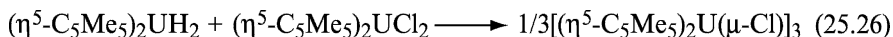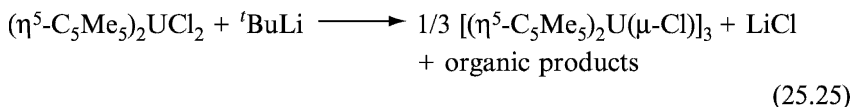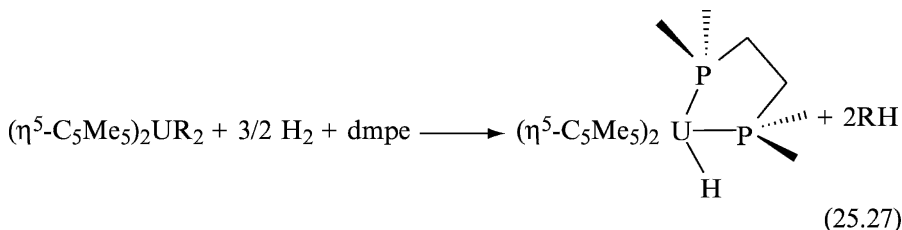
$$(\eta^5\text{-}C_5Me_5)_2U(Cl)(R) + 3/2\, H_2 \longrightarrow 1/3[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3 + 3RH$$

$$(25.24)$$
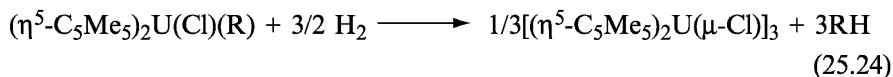
Fig. 25.4 *Magnetic susceptibility data for* $1,4\text{-}[(\eta^5\text{-}C_5H_4Me)_3U](=N\text{-}C_6H_4\text{-}N=)[U(\eta^5\text{-}C_5H_4Me)_3]$ *(compound 1) and* $1,3\text{-}[(\eta^5\text{-}C_5H_4Me)_3U](=N\text{-}C_6H_4\text{-}N=)[U(\eta^5\text{-}C_5H_4Me)_3]$ *(compound 2). (Reprinted with permission from Rosen* et al. *(1990). Copyright* 1990 *American Chemical Society.)*

$$(\eta^5\text{-}C_5Me_5)_2UCl_2 + {}^tBuLi \longrightarrow 1/3\ [(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3 + LiCl$$
$$+\ \text{organic products}$$

$$(25.25)$$

$$(\eta^5\text{-}C_5Me_5)_2UH_2 + (\eta^5\text{-}C_5Me_5)_2UCl_2 \longrightarrow 1/3[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3 \quad (25.26)$$

The reduction reaction shown in equation (25.24) has been extended to bis (alkyl) complexes to generate a stable mononuclear hydride complex stabilized by added ligand (Duttera *et al.*, 1982), as depicted in equation (25.27).

$$(\eta^5\text{-}C_5Me_5)_2UR_2 + 3/2\ H_2 + dmpe \longrightarrow (\eta^5\text{-}C_5Me_5)_2\ \ U\overset{P}{\underset{H}{-}}P + 2RH$$

$$(25.27)$$

The complex $[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3$ reacts with a variety of Lewis bases to generate monomeric adducts, and will undergo metathesis reactions (Fig. 25.5).
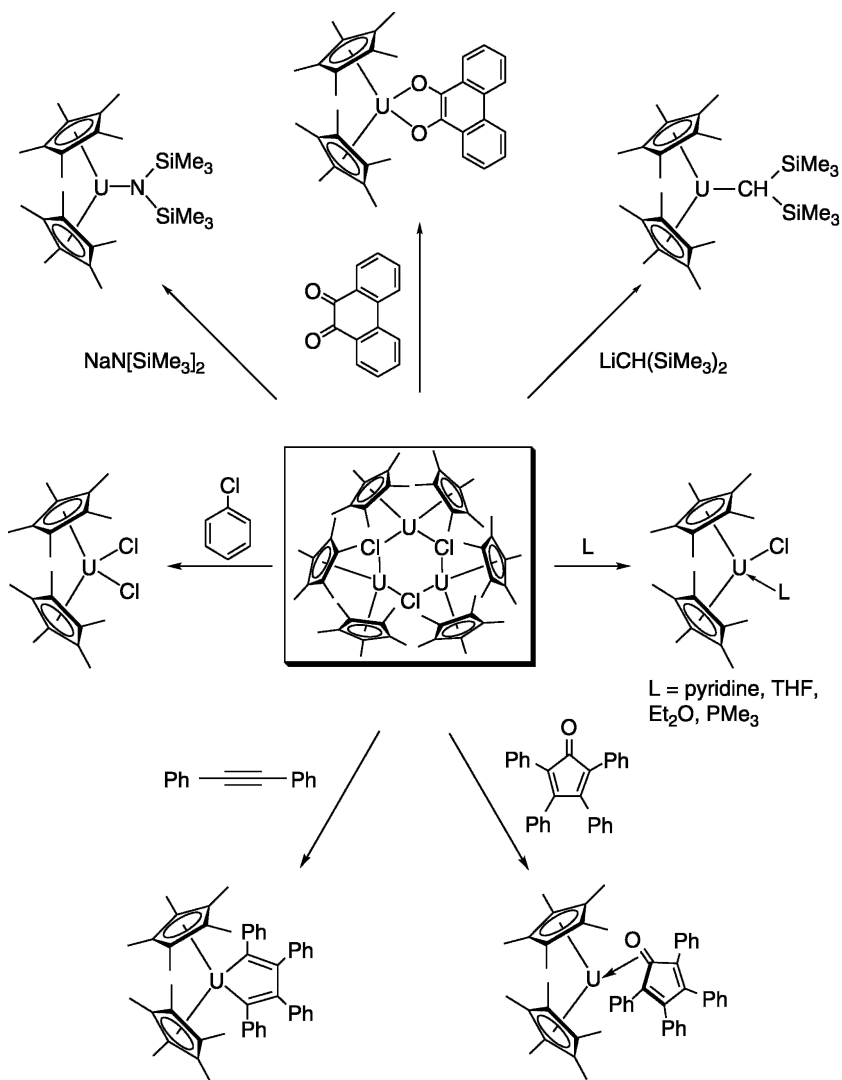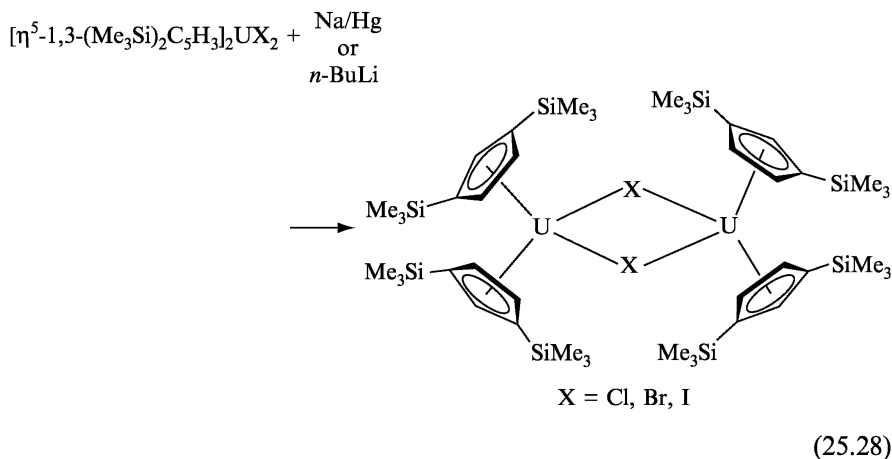
Fig. 25.5 *Reactions of* $[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3$ *(Fagan* et al.*, 1982).*

Alkyl complexes have been prepared by reaction with alkyllithium reagents, but are unstable at room temperature, except for R = CH(SiMe$_3$)$_2$. One of the most interesting reactions is that of $[(\eta^5\text{-}C_5Me_5)_2U(\mu\text{-}Cl)]_3$ with unsaturated substrates such as diphenylacetylene. In an apparent disproportionation, the reaction products include the metallacycle complex resulting from coupling of two alkyne ligands, as well as an equivalent amount of $(\eta^5\text{-}C_5Me_5)_2UCl_2$. Finke *et al.* (1981a,b) have examined the oxidation of the base adduct

(η^5-C$_5$Me$_5$)$_2$UCl(THF) with alkyl halides. Kinetic evidence supports an atom-abstraction oxidative addition mechanism to the coordinatively unsaturated (η^5-C$_5$Me$_5$)$_2$UCl. The rate of reaction is 10^4–10^7 faster than any known isolable transition metal system reacting by atom abstraction.

A cationic bis(pentamethylcyclopentadienyl)uranium(III) complex has been reported (Boisson *et al.*, 1997). The complex [(η^5-C$_5$Me$_5$)$_2$U(THF)$_2$][BPh$_4$] is generated by protonation of the complex (η^5-C$_5$Me$_5$)$_2$U[N(SiMe$_3$)$_2$] with [NH$_4$][BPh$_4$].

A number of U(III) complexes containing the [η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$] ligand have been prepared (Blake *et al.*, 1986b, 1987) by reduction of U(IV) precursors with Na–Hg or *n*-BuLi in toluene or hexanes [equation (25.28)].

[η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$]$_2$UX$_2$ + $\begin{matrix} \text{Na/Hg} \\ \text{or} \\ \text{\textit{n}-BuLi} \end{matrix}$

X = Cl, Br, I

(25.28)

In the presence of a coordinating ligand (e.g. TMEDA), a uranate salt ([η^5-(Me$_3$Si)$_2$C$_5$H$_3$](μ-Cl)$_2$U(L)) (L = ligand) is isolated (Blake *et al.*, 1988).

An expanded synthesis of these and related [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$] complexes has been reported involving reduction of tetravalent precursors by *t*-BuLi in hexanes (Lukens *et al.*, 1999b,c). A number of the dimeric complexes have been structurally characterized (Fig. 25.6) (Lukens *et al.*, 1999a). The solution behavior of a number of members of the class [{η^5-1,3-R$_2$C$_5$H$_3$}$_2$U(μ-X)]$_2$ (R = Me$_3$Si or Me$_3$C) have been examined by variable temperature NMR (Lukens *et al.*, 1999b). The complexes exist as dimers in solution at all temperatures examined. The dimers react with Lewis bases to yield monomeric mono- or bis-ligand adducts (Blake *et al.*, 1987; Beshouri and Zalkin, 1989; Zalkin and Beshouri, 1989); these serve as reagents in subsequent metathesis reactions (Blake *et al.*, 1987).

The complexes [{η^5-1,3-R$_2$C$_5$H$_3$}$_2$U(μ-OH)]$_2$ (R = Me$_3$Si or Me$_3$C) have been prepared by reaction of one equivalent of water with [η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$]$_3$U and [η^5-1,3-(Me$_3$C)$_2$C$_5$H$_3$]$_2$UH, respectively (Lukens *et al.*, 1996).

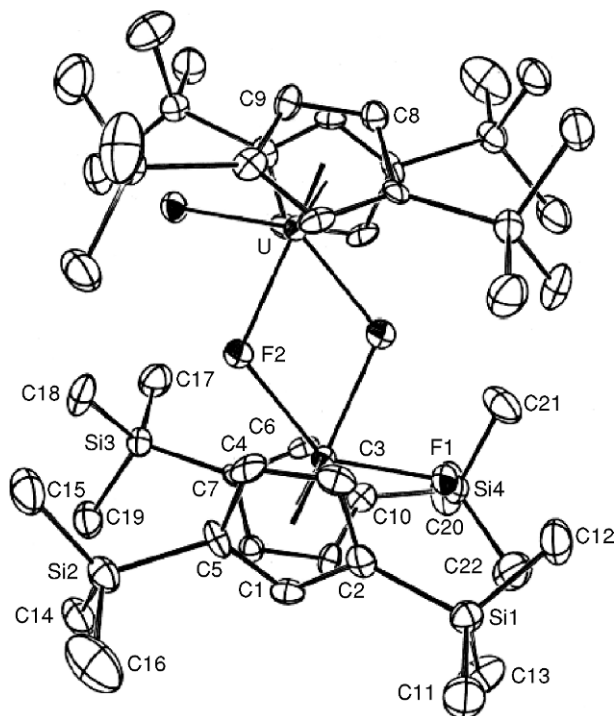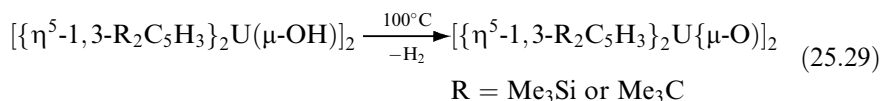**Fig. 25.6** *Crystal structure of* $[\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}_2U(\mu\text{-}F)]_2$. (*Reprinted with permission from Lukens* et al. (1999a). *Copyright* 1999 *American Chemical Society.*)

Upon heating, these complexes have been observed to undergo an unusual 'oxidative elimination' to yield the corresponding μ-oxo complexes [equation (25.29)].

$$[\{\eta^5\text{-}1,3\text{-}R_2C_5H_3\}_2U(\mu\text{-}OH)]_2 \xrightarrow[-H_2]{100^\circ C} [\{\eta^5\text{-}1,3\text{-}R_2C_5H_3\}_2U\{\mu\text{-}O)]_2 \quad (25.29)$$

$$R = Me_3Si \text{ or } Me_3C$$

The kinetics of this process have been examined, and the reaction is found to be intramolecular, probably involving a stepwise α-elimination process.

The reagent $UI_3(THF)_4$ has proven valuable in generating mono(cyclopentadienyl) uranium(III) complexes (Avens *et al.*, 2000). Reaction of one equivalent of $UI_3(THF)_4$ with $K(C_5Me_5)$ results in the formation of the complex $(\eta^5\text{-}C_5Me_5)UI_2(THF)_3$. In the solid state this complex exhibits a pseudo-octahedral *mer*, *trans* geometry, with the cyclopentadienyl group occupying the axial position.
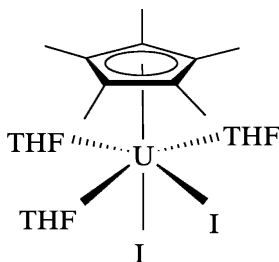
In the presence of excess pyridine, this complex can be converted to the analogous pyridine adduct, $(\eta^5\text{-}C_5Me_5)UI_2(py)_3$. $(\eta^5\text{-}C_5Me_5)UI_2(THF)_3$ will react further with $K(C_5Me_5)$ to generate the bis(ring) product, $(\eta^5\text{-}C_5Me_5)_2UI$ (THF), or will react with two equivalents of $K[N(SiMe_3)_2]$ to produce $(\eta^5\text{-}C_5Me_5)U[N(SiMe_3)_2]_2$. The solid state structure of the bis(trimethylsilyl)amide derivative reveals close contacts between the uranium center and two of the methyl carbons [2.80(2), 2.86(2) Å].

Oxidation of $(\eta^5\text{-}C_5Me_5)UI_2(THF)_3$ with CS_2 or ethylene sulfide produces a complex of the formula $[(\eta^5\text{-}C_5Me_5)UI_2(THF)_3]_2(S)$. This species undergoes slow decomposition in solution to yield a polynuclear complex (Clark *et al.*, 1995):
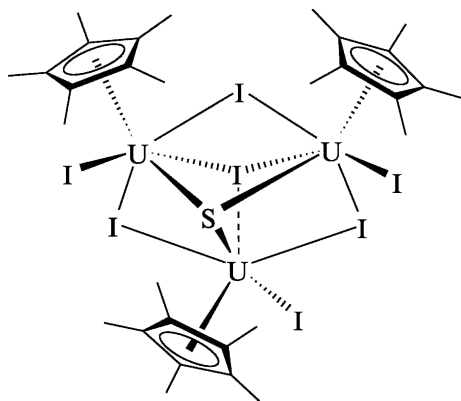
(b) Tetravalent chemistry

The tetravalent oxidation state dominates the cyclopentadienyl chemistry of the early actinide elements. Tetrakis(cyclopentadienyl) complexes were among the earliest actinide complexes prepared, and the complexes $(\eta^5\text{-}C_5H_5)_4An$ are known for Th (Fischer and Treiber, 1962), Pa (Baumgärtner *et al.*, 1969), U (Fischer and Hristidu, 1962), and Np (Baumgärtner *et al.*, 1968). Although only the uranium and thorium compounds have been structurally characterized (Burns, 1974; Maier *et al.*, 1993), IR spectral and X-ray powder data confirm

that all four complexes are isostructural. $(\eta^5\text{-}C_5H_5)_4U$ is found to be psuedo-tetrahedral, with a mean U–C_{ring} bond distance of 2.81(2) Å. This is somewhat longer than average U–C_{ring} distances for other U(IV) cyclopentadienyl complexes, reflecting the degree of steric crowding. The related tetrakis(indenyl) thorium compound has also been reported (Rebizant *et al.*, 1986). The thorium atom is bonded to the carbons of the five-membered ring portion of the indenyl ligand, although not in a η^5 fashion. The shortest Th–C bond distances [Th–C average = 2.83(3) Å vs 3.09(3) Å] are to the three non-bridging carbon atoms, leading to the overall designation of the rings as trihapto.
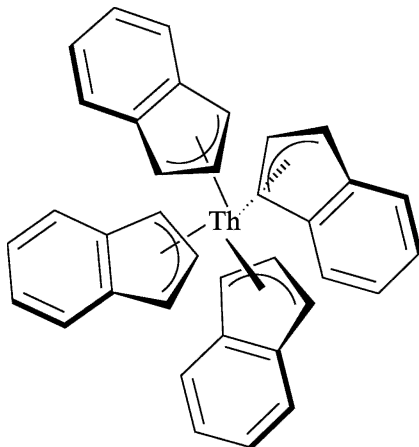
The first reported organoactinide complex was $(\eta^5\text{-}C_5H_5)_3UCl$ (Reynolds and Wilkinson, 1956), a member of the extensive class of complexes represented as Cp_3AnX. The complex was first prepared by the reaction of uranium tetrachloride with sodium cyclopentadienide in tetrahydrofuran. Comparable routes have been used to prepare $(\eta^5\text{-}C_5H_5)_3NpCl$ (Karraker and Stone, 1979), although this complex has also been prepared by reaction of $NpCl_4$ with $(C_5H_5)_2Be$ (Fischer *et al.*, 1966). Alternative routes have since been reported for the generation of $(\eta^5\text{-}C_5H_5)_3UCl$ (Marks *et al.*, 1976). Tris(indenyl)uranium and tris(indenyl)thorium complexes have been prepared by metathesis reactions with $K(C_9H_7)$ in THF (Burns and Laubereau, 1971; Laubereau *et al.*, 1971; Goffart *et al.*, 1975, 1981; Goffart and Duyckaerts, 1978).

Since the first report of cyclopentadienyl complexes, attempts have been made to assess the nature of the bonding in these complexes from their chemical reactivity. In contrast to complexes of lanthanides and Group 3 metals, $(\eta^5\text{-}C_5H_5)_3UCl$ does not react with $FeCl_2$ to produce ferrocene, and it decomposes relatively slowly in water. Although this is taken as some indication of increased covalency in chemical bonding, these complexes are still believed to be more ionic than the majority of d-transition metal cyclopentadienyl complexes (Burns and Bursten, 1989). The molecular structure of several Cp_3AnX complexes have

been determined, as well as several structures of closely related tris(indenyl) actinide halide complexes. Some comparative structural information is provided in Table 25.3, and a typical structure represented by $(\eta^5\text{-}C_5H_5)_3UBr$ is presented in Fig. 25.7.

Table 25.3   *Structural information for Cp₃AnX complexes.*

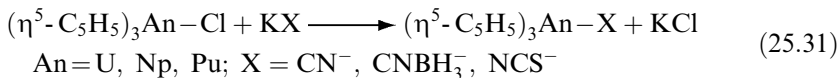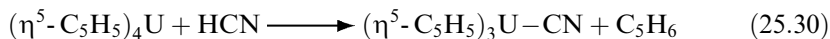| Compound	M–C (average) (Å)	M–X (Å)	References
$(\eta^5\text{-}C_5H_5)_3UCl$	2.74	2.559(16)	Wong *et al.* (1965)
$(\eta^5\text{-}C_5H_5)_3UBr$	2.72(1)	2.820(2)	Spirlet *et al.* (1989a)
$(\eta^5\text{-}C_5H_5)_3UI$	2.73(3)	3.059(2)	Rebizant *et al.* (1991)
$(\eta^5\text{-}C_5H_4CH_2Ph)_3UCl$	2.733(1)	2.627(2)	Leong *et al.* (1973)
$[\eta5\text{-}(Me_3Si)_2C_5H_3]_3UCl$	2.77(1)	2.614(2)	Blake *et al.* (1998)
$(\eta^5\text{-}C_5Me_4H)_3UCl$	2.79(1)	2.637	Cloke *et al.* (1994)
$(\eta^5\text{-}C_5Me_5)_3UF$	2.829(6)	2.43(2)	Evans *et al.* (2000)
$(\eta^5\text{-}C_5Me_5)_3UCl$	2.833(9)	2.90(1)	Evans *et al.* (2000)
$[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3ThCl$	2.84(1)	2.651(2)	Blake *et al.* (1998)
$[\eta^5\text{-}(Me_3Si)_2C_5H_3]_2(C_5Me_5)ThCl$	2.84(2)	2.657(5)	Blake *et al.* (1998)
$[\eta^5\text{-}(Me_2\text{-}^tBuSi)_2C_5H_3]_3ThCl$	2.85(1)	2.648(2)	Blake *et al.* (1998)
$\{\eta^5\text{-}[(Me_3Si)_2CH]C_5H_4\}_3ThCl$	2.83(1)	2.664(2)	Blake *et al.* (1998)
$(\eta^5\text{-}C_9H_7)_3UBr$	2.71(2), 2.85(2)	2.747(2)	Spirlet *et al.* (1987)
$(\eta^5\text{-}C_9H_7)_3UI$	2.68(2), 2.88(2)	3.041(1)	Rebizant *et al.* (1988)
$(\eta^5\text{-}C_9HMe_6)_3UCl$	–	2.621(1)	Spirlet *et al.* (1992a)
$(\eta^5\text{-}C_9H_6Et)_3ThCl$	2.78(1), 2.93(1)	2.673(3)	Spirlet *et al.* (1990)
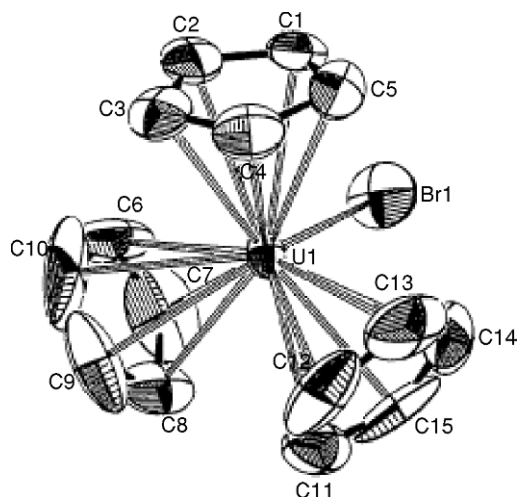
Fig. 25.7   *Crystal structure of $(\eta^5\text{-}C_5H_5)_3UBr$ (Spirlet* et al.*, 1989a). (Reprinted with permission of the International Union of Crystallography.)*

All complexes possess pseudo-tetrahedral geometry, with the halide ligand on an approximate three-fold axis of symmetry. The An–C and An–X bond lengths are consistent for most of the complexes; Th–C and Th–X values are slightly larger, as would be expected for the larger ionic radius. The average U–C_{ring} and U–X bond lengths are longer than would be expected in complexes (η^5-$C_5Me_5)_3UX$ (X = Cl, F); the U–Cl bond length in (η^5-$C_5Me_5)_3UCl$ is >0.15 Å longer than that for related complexes. The origin of this difference appears to be significant steric crowding in the molecule. Interligand repulsions between the bulky pentamethylcyclopentadienyl ligands results in the most signficant distortion from tetrahedral geometry; the cyclopentadienyl rings lie within a crystallographic plane of symmetry, requiring the angle X–U–$C_{centroid}$ to be rigorously 90°. This in turn results in repulsion between the rings and the halide, lengthening the bond.

As observed in the An(indenyl)$_4$ complexes, the tris(indenyl) complexes all evidence a 'slip' of the rings towards a trihapto bonding, resulting in two separate sets of U–C distances. The compound ($C_9HMe_6)_3UCl$ possesses a highly substituted hexamethylindenyl ligand (Spirlet *et al.*, 1992a). The steric encumbrance associated with this ligand induces a further slippage of the ring; the resulting complex has indenyl rings that are essentially monohapto towards the metal center, with mean U–C bonds of 2.622(6) Å (Fig. 25.8).

A number of approaches have been employed to generate derivatives of Cp$_3$AnX (von Ammon *et al.*, 1969; Kanellakopulos *et al.*, 1974b; Marks and Kolb, 1975; Fischer and Sienel, 1976, 1978; Bagnall *et al.*, 1982a,b; Spirlet *et al.*, 1996). Prototype reactions include protonation of (η^5-$C_5H_5)_4U$ [equation (25.30)] and metathesis [equation (25.31)].

$$(\eta^5\text{-}C_5H_5)_4U + HCN \longrightarrow (\eta^5\text{-}C_5H_5)_3U-CN + C_5H_6 \qquad (25.30)$$

$$(\eta^5\text{-}C_5H_5)_3An-Cl + KX \longrightarrow (\eta^5\text{-}C_5H_5)_3An-X + KCl$$
$$An = U, \ Np, \ Pu; \ X = CN^-, \ CNBH_3^-, \ NCS^- \qquad (25.31)$$

Reactions such as that between (η^5-$C_5H_5)_3UCl$ and KCN may be carried out in water (Bagnall *et al.*, 1982b), indicating the stability of the metal–ligand bonding in these complexes. In fact, it has been suggested that (η^5-$C_5H_5)_3UCl$ ionizes in water to yield the five-coordinate adduct $[(\eta^5\text{-}C_5H_5)_3U(H_2O)_2]^+$ (Fischer *et al.*, 1982). This spurred further interest in investigating other five coordinate species, e.g. $[(\eta^5\text{-}C_5H_5)_3UXY]^-$. The anionic complexes $[(\eta^5\text{-}C_5H_5)_3An(NCS)_2]^-$ (An = U, Np, Pu) can be isolated, provided that the cation is sufficently large (Bagnall *et al.*, 1982b). Spectrophotometric and other evidence indicates a trigonal–bipyramidal geometry for these species. The assignment of the geometry of these species is further supported by structural characterization of neutral base adducts (η^5-$C_5H_5)_3AnXL$, such as (η^5-$C_5H_5)_3U(NCS)(NCMe)$ (Fischer *et al.*, 1978; Aslan *et al.*, 1988) or (η^5-$C_5H_5)_3U(NCBH_3)(NCMe)$ (Adam *et al.*, 1990);
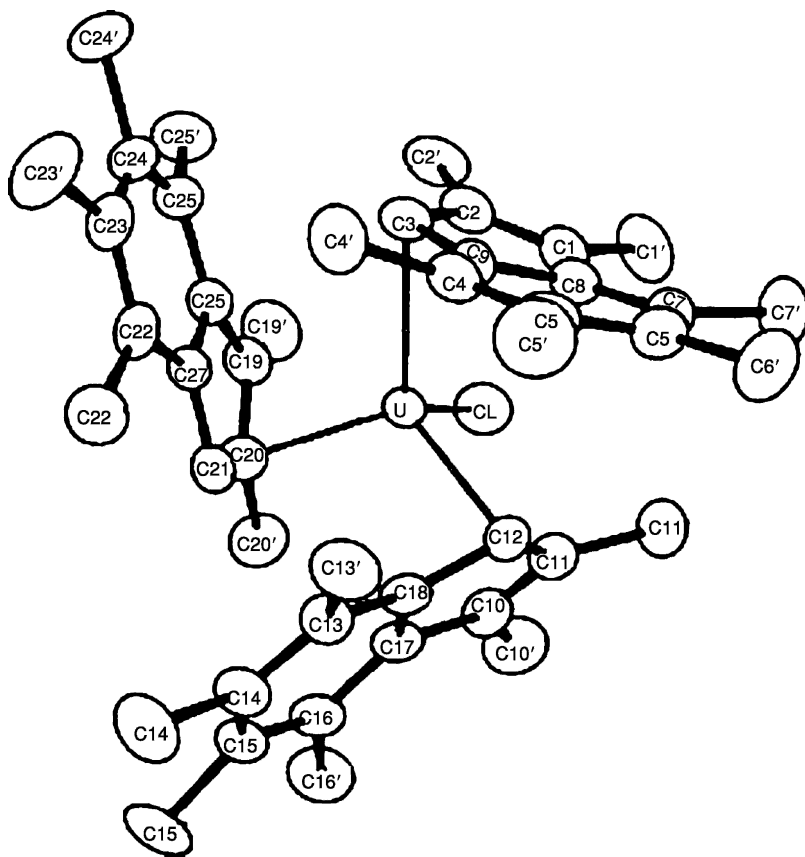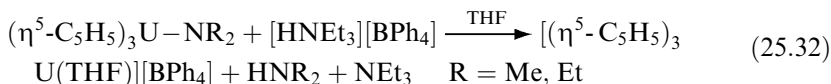
Fig. 25.8 *Crystal structure of* $(C_9HMe_6)_3UCl$ (*Spirlet* et al., *1992a*). (*Reprinted with permission of the International Union of Crystallography.*)

these complexes exibit a trigonal-bipyramidal geometry, with the smaller ligands adopting the axial positions.

Cationic species can also be produced. The compound $[(\eta^5\text{-}C_5H_5)_3U(NCMe)_2]^+$ has been isolated as a $[BPh_4]^-$ salt by the reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ and $NaBPh_4$ in water/acetonitrile mixtures (Aslan *et al.*, 1988). The cationic complex $[(\eta^5\text{-}C_5H_5)_3U(THF)]BPh_4$ was generated by protonation of the neutral amide precursor with $[NHEt_3]^+$ as illustrated in equation (25.32) (Berthet *et al.*, 1995).
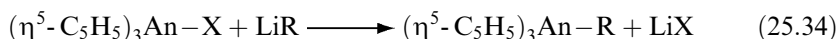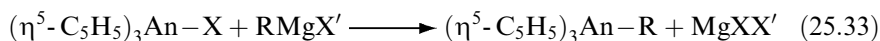
$$(\eta^5\text{-}C_5H_5)_3U-NR_2 + [HNEt_3][BPh_4] \xrightarrow{\text{THF}} [(\eta^5\text{-}C_5H_5)_3 \atop U(THF)][BPh_4] + HNR_2 + NEt_3 \quad R = Me, Et \qquad (25.32)$$

Similarly, treatment of precursor alkyl or amide complexes with pyridinium triflate gives rise to the triflate complex $(\eta^5\text{-}C_5H_5)_3U(O_3SCF_3)$ (Berthet *et al.*, 2002).

The crystal structure of the ^tBuCN adduct has also been determined (Berthet *et al.*, 1998).

Metathesis and protonation routes have been used to generate $L_3An(IV)$ (L = cyclopentadienyl, indenyl) complexes containing alkoxide (OR), amide (NR_2), phosphide (PR_2), and thiolate (SR) ligands (Jamerson *et al.*, 1974; Goffart *et al.*, 1977; Karraker and Stone, 1979; Arduini *et al.*, 1981; Paolucci *et al.*, 1985; Leverd *et al.*, 1996; De Ridder *et al.*, 1996). Both magnetic susceptibility measurements and ^{237}Np Mössbauer spectroscopy have been employed to assess the qualitative order of ligand field strengths for a variety of ligands in the complexes $(\eta^5\text{-}C_5H_5)_3NpX$ (Karraker and Stone, 1979). The identified order of donor strength from this study is $X = Cl^- \sim BH_4^- > OR^- > R^- > C_5H_5^-$.

One of the best studied classes of $(\eta^5\text{-}C_5H_5)_3AnR$ (Th, U, Np) complexes is that containing alkyl or aryl ligands. The literature on alkyl complexes is extensive (e.g. Brandi *et al.*, 1973; Calderazzo, 1973; Gabala and Tsutsui, 1973; Marks *et al.*, 1973; Tsutsui *et al.*, 1975; Marks, 1979). The complexes are most often prepared by reaction of $(\eta^5\text{-}C_5H_5)_3AnX$ (X = halide) with Grignard [equation (25.33)] or alkyllithium [equation (25.34)] reagents.

$$(\eta^5\text{-}C_5H_5)_3An-X + RMgX' \longrightarrow (\eta^5\text{-}C_5H_5)_3An-R + MgXX' \quad (25.33)$$

$$(\eta^5\text{-}C_5H_5)_3An-X + LiR \longrightarrow (\eta^5\text{-}C_5H_5)_3An-R + LiX \quad (25.34)$$

Comparable indenylactinide derivatives have also been prepared (e.g. Goffart *et al.*, 1977). While there is a dearth of thermally stable U(IV) hydride complexes, the complexes $[\eta^5\text{-}(Me_3Si)C_5H_4]_3UH$ and $[\eta^5\text{-}(Me_3C)C_5H_4]_3UH$ can be obtained by reaction of the corresponding chlorides with $KBEt_3H$ (Berthet *et al.*, 1992b).

The molecular structures of several $(\eta^5\text{-}C_5H_5)_3AnR$ complexes have been determined; compounds display pseudo-tetrahedral geometries. Typical metal–carbon bond lengths for the alkyl ligand are 2.40 Å. All three cyclopentadienyl ligands are pentahapto, which nearly saturates the coordination environment of the metal center, as evidenced by the observation that allyl ligands can only be accomodated in a simple σ-bonded fashion (Halstead *et al.*, 1975) as shown in Fig. 25.9.

This monohapto geometry is also the low-temperature limiting structure for $(\eta^5\text{-}C_5H_5)_3U(\text{allyl})$ in solution (Marks *et al.*, 1973) although at room temperature the allyl ligand is fluxional, presumably interconverting sites by means of a π-bound intermediate. The relative coordinative saturation is reflected in the thermal stabilities of alkyl derivatives: primary > secondary > tertiary. Primary alkyl ligands are resistant to β-hydride elimination; thermal decomposition is presumed to take place through U–C bond homolysis and abstraction of a ring proton by the caged alkyl radical (although metal-containing products have not been definitively identified).
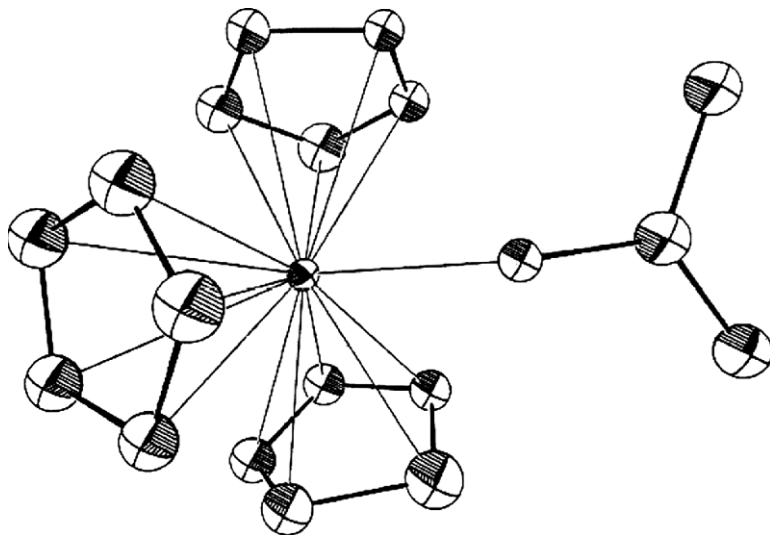
Fig. 25.9 *Crystal structure of $(\eta^5\text{-}C_5H_5)_3U[CH_2C(CH_3)_2]$. (Reprinted with permission from Halstead* et al. *(1975). Copyright 1975 American Chemical Society.)*

Further indication of the steric saturation of the complex may be found in the observation that reaction of $(\eta^5\text{-}C_5H_5)_3UR$ with excess alkyllithium does not result ultimately in the formation of anionic bis(alkyl) complexes. Rather, reaction products either result from alkyl exchange (Tsutsui *et al.*, 1975) or reduction of the metal center (Arnaudet *et al.*, 1983, 1986) as shown in equation (25.35).

$$(\eta^5\text{-}C_5H_5)_3U\text{–}R + LiR \longrightarrow Li[(\eta^5\text{-}C_5H_5)_3U\text{–}R] + \text{organic products}$$
$$(25.35)$$
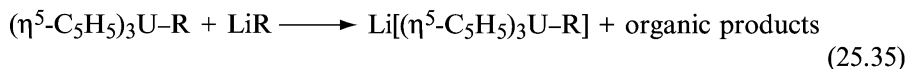
It has been reported that the complex $[(\eta^5\text{-}C_5H_5)_3UMe_2]^-$ can be observed as an intermediate in solution by NMR spectroscopy (Villiers and Ephritikhine, 1991).

Other derivatives of the Group 14 elements have been prepared. Reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with $Li(EPh_3)$ affords the silyl- and germyluranium derivatives $(\eta^5\text{-}C_5H_5)_3U(EPh_3)$ [E = Si (Porchia *et al.*, 1986, 1989), E = Ge (Porchia *et al.*, 1987)], whereas the stannyl analog $(\eta^5\text{-}C_5H_5)_3U(SnPh_3)$ was best made from a the reaction of $(\eta^5\text{-}C_5H_5)_3U(NEt_2)$ with $HSnPh_3$. It can also be made from the transmetallation reaction of $HSnPh_3$ with $(\eta^5\text{-}C_5H_5)_3U(EPh_3)$ (E = Si, Ge) (Porchia *et al.*, 1989). The silyl compound is very reactive; under a number of conditions it can be transformed into $(\eta^5\text{-}C_5H_5)_3U(OSiPh_3)$. Insertion of xylylisocyanide into U–E bonds generates the corresponding η^2-iminoacyl complexes $[(\eta^5\text{-}C_5H_5)_3U\{C(EPh_3) = N(xylyl)\}]$ (E = Si, Ge).

$$E = Si, Ge$$
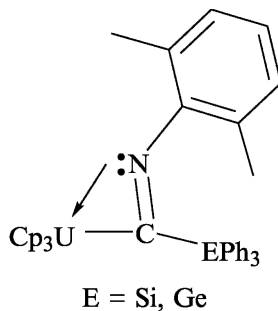
Several groups have conducted investigations of the thermochemistry of organoactinide complexes in order to determine the enthalpies of metal–ligand bonds, and thereby shed light on the nature of bonding and the anticipated reaction patterns. An excellent overview of available data on organouranium complexes has appeared recently (Leal *et al.*, 2001). Data compiled for tris (cyclopentadienyl)uranium(IV) complexes are presented in Table 25.4. Values tabulated in Leal *et al.* (2001) are based upon several types of measurements: solution titration experiments involving reaction with iodine or alcohols, static bomb combustion calorimetry, or gas-phase or solution equilibrium experiments. A few general trends may be noted. The enthalpy values for all U–C (sp^3) bonds are relatively consistent; U–C(sp^2) and U–C(sp) bonds increase in strength, as might be expected for a bond involving a higher degree of s-orbital involvement. While the bonds involving all Group 14 element bonds are reasonably close in energy, uranium bonds to Group 16 or Group 17 elements are somewhat stronger. The reason for the disparity between D(U–S) for the EtS$^-$ and ^{t}BuS$^-$ may be due to the greater steric bulk associated with the latter.

Comparable experiments have been carried out for the complexes (η^5-C$_5$H$_5$)$_3$ThR (Sonnenberger *et al.*, 1985); results of these measurements are found in Table 25.5. The thorium–carbon bond strengths are found to be overall higher than for comparable uranium species. This has been rationalized in terms of the greater stability of the U(III) complexes, resulting from homolytic loss of an alkyl radical.

The reaction of carbon monoxide with (η^5-C$_5$H$_5$)$_3$AnR (An = Th, U; R = alkyl, hydride) yields an acyl complex as shown in equation (25.36).
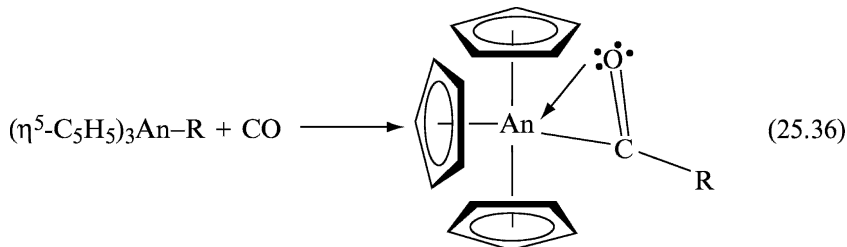

$$(\eta^5\text{-}C_5H_5)_3An\text{–}R + CO \longrightarrow \qquad\qquad (25.36)$$

Table 25.4 *Bond dissociation enthalpies for Cp₃UX and (indenyl)₃UX complexes.*[a]

Compound	R	$D(U–R)$ (kJ mol⁻¹)	Reference
$(\eta^5\text{-}C_5H_5)_3UR$	SiPh₃	156 ± 18	Nolan *et al.* (1991)
	GePh₃	163 ± 19	Nolan *et al.* (1991)
	SnPh₃	156 ± 17	Nolan *et al.* (1991)
	Fe(CO)₂Cp	129 ± 13	Nolan *et al.* (1991)
	Ru(CO)₂Cp	169 ± 17	Nolan *et al.* (1991)
	Cp	299 ± 10[b,c]	Telnoy *et al.* (1979)
	i-Bu	$D[Cp_3U–Cp] –$ (70 ± 35)[c,d]	Telnoy *et al.* (1989)
	OBu	$D[Cp_3U–Cp] +$ (247 ± 28)[c,d]	Telnoy *et al.* (1989)
	Cl	$D[Cp_3U–Cp] +$ (73 ± 31)[c,d]	Telnoy *et al.* (1989)
$[\eta^5\text{-}(Me_3Si)C_5H_4]_3UR$	Me	185 ± 2	Schock *et al.* (1988)
	Bu	152 ± 8	Schock *et al.* (1988)
	CH₂SiMe₃	168 ± 8	Schock *et al.* (1988)
	CH₂Ph	149 ± 8	Schock *et al.* (1988)
	CH=CH₂	223 ± 10	Schock *et al.* (1988)
	CCPh	363	Schock *et al.* (1988)
	I	262 ± 1	Schock *et al.* (1988)
		265.6 ± 4.3	Jemine *et al.* (1992)
	SEt	266 ± 9	Jemine *et al.* (1994)
	S-*t*-Bu	158 ± 8	Jemine *et al.* (1994)
	H	253.7 ± 5.1	Jemine *et al.* (1992)
$[\eta^5\text{-}(Me_3C)C_5H_4]_3UR$	H	251.6 ± 5.7	Jemine *et al.* (1992)
	I	246.3 ± 5.3	Jemine *et al.* (1992)
	SEt	252 ± 8	Jemine *et al.* (1994)
$(\eta^5\text{-}C_9H_7)_3UR$	Me	195 ± 5	Bettonville *et al.* (1990)
	OCH₂CF₃	301 ± 9	Bettonville *et al.* (1989, 1990)
	I	267 ± 3	Bettonville *et al.* (1990)
$(\eta^5\text{-}C_9H_6Et)_3UR$	Me	187 ± 6	Bettonville *et al.* (1989, 1990)
$(\eta^5\text{-}C_9H_6SiMe_3)_3UR$	SEt	158 ± 8	Jemine *et al.* (1994)

[a] Determined using reaction–solution calorimetry unless otherwise indicated.
[b] Mean bond dissociation enthalpy.
[c] Static bomb combustion calorimetry.
[d] This notation means that the bond is the stated amount stronger or weaker than the first bond dissociation enthalpy in $U(\eta^5\text{-}C_5H_5)_4$.

These reactions have been studied mechanistically (Sonnenberger *et al.*, 1984) for a series of thorium deriatives (R = *i*-Pr, *s*-Bu, *neo*-C₅H₁₁, *n*-Bu, CH₂Si(CH₃)₃, Me, and CH₂C₆H₅). Under the conditions employed, insertion is first order in thorium complex and first order in CO. The relative rates of insertion for
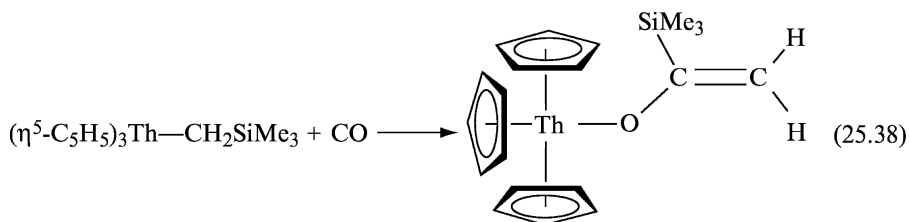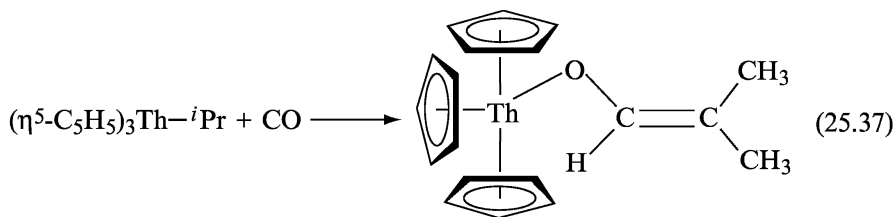
Table 25.5 *Bond dissociation enthalpies for Cp$_3$ThR complexes.*

Compound	R	$D(Th–R)$ (kJ mol^{-1})
(η^5-C$_5$H$_5$)$_3$ThR	CH$_3$	374.9 (4.6)
	CH(CH$_3$)$_2$	342.2 (10.9)
	CH$_2$C(CH$_3$)$_3$	333.0 (11.7)
	CH$_2$Si(CH$_3$)$_3$	367.8 (15.1)
	CH$_2$C$_6$H$_5$	315.1 (9.2)

the ligands was found to be *i*-Pr > *s*-Bu > *neo*-C$_5$H$_{11}$ > *n*-Bu > CH$_2$Si(CH$_3$)$_3$ > Me > CH$_2$C$_6$H$_5$. The relative rates of insertion correlate reasonably well with the bond enthalpies reported in Table 25.5, and as expected, were accelerated by photolysis. Where R = *s*-Bu, *neo*-C$_5$H$_{11}$, *n*-Bu, Me, and CH$_2$C$_6$H$_5$, the chief isolated product was the insertion (η^2-acyl) product shown in equation (25.36). This complex has been discussed as having a 'carbene-like' resonance form:
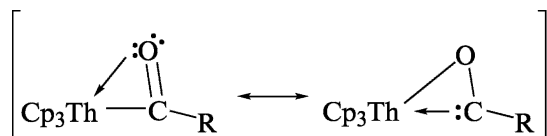

In the case of *i*-Pr and CH$_2$Si(CH$_3$)$_3$, however, the only products that could be isolated were those arising from 1,2-rearrangement [equations (25.37)–(25.38)].

$$(\eta^5\text{-C}_5\text{H}_5)_3\text{Th}-^i\text{Pr} + \text{CO} \longrightarrow \qquad (25.37)$$

$$(\eta^5\text{-C}_5\text{H}_5)_3\text{Th}-\text{CH}_2\text{SiMe}_3 + \text{CO} \longrightarrow \qquad (25.38)$$
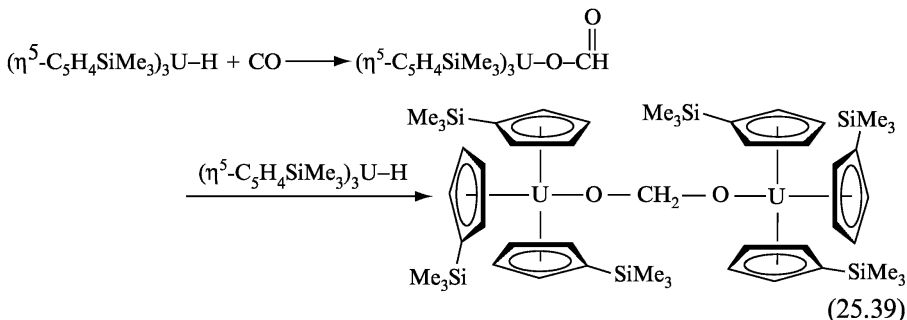
A comparative study of CO_2 insertion to generate carbonate complexes showed that carboxylation is significantly slower than carbonylation, and exhibits different trends in the dependence of rate on the alkyl ligand (Sonnenberger *et al.*, 1984).

Similar insertion reactions of carbon monoxide have been investigated for complexes of the type $(\eta^5\text{-}C_5H_4R)_3UR'$ (Paolucci *et al.*, 1984; Villiers and Ephritikhine, 1994). Villiers and Ephritikhine performed mechanistic studies, which showed that the insertion reaction appears first order under conditions of excess CO. The rate of insertion varies as a function of the cyclopentadienyl ring, with the rate decreasing in the order R = H > Me > ^{i}Pr > ^{t}Bu, as might be expected from steric considerations. The rate also depends on the identity of the alkyl ligand in the unusual order R' = n-Bu > ^{t}Bu > Me > ^{i}Pr. The resulting η^2-acyl product was not stable and rearranged to yield alkylbenzenes C_6H_4RR', suggested to arise from ring enlargement of the cyclopentadienyl ligand by incorporation of the CR' fragment. The reaction was observed to follow first-order kinetics, with the rate varying with the alkyl ligand in the order R' = Me > n-Bu > ^{i}Pr > ^{t}Bu. In benzene solvent, the rates varied with R in the order ^{t}Bu > ^{i}Pr > Me > H, while the opposite order was observed in THF solvent. For a given solvent, the relative proportions of *meta*- and *para*-isomers were invariant with R and R'. The proposed mechanism involved a cyclopropyl intermediate, resulting from addition of the oxycarbene group to the cyclopentadienyl ligand.

$[U] = (\eta^5\text{-}C_5H_4R)_2U$
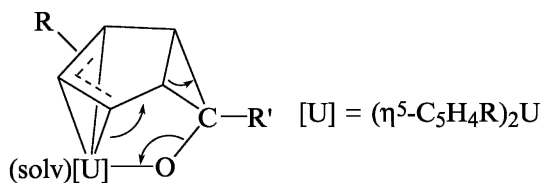
Carbon monoxide will also insert into the U–H bond of $(\eta^5\text{-}C_5H_4SiMe_3)_3UH$ (Berthet and Ephritikhine, 1992). As shown in equation (25.39), the initial product is believed to be a formate complex, which reacts further with the hydride to yield a dioxymethylene species.
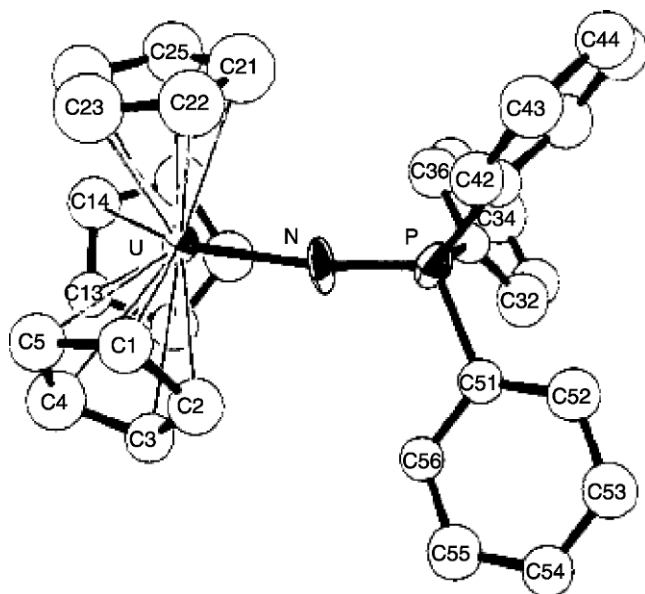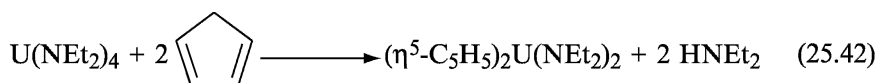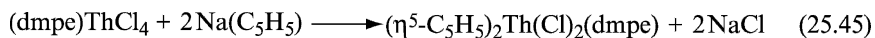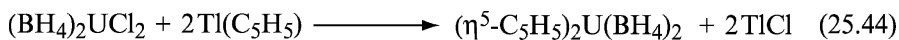

(25.39)

Isoelectronic isocyanide ligands will also undergo insertion into uranium–carbon or uranium–nitrogen bonds (Dormond *et al.*, 1984; Zanella *et al.*, 1987) to yield η^2-iminoalkyl and η^2-iminocarbamoyl adducts.

$$\left[\begin{array}{c} \overset{R'}{\underset{Cp_3U-C-R}{N}} \longleftrightarrow \overset{R'}{\underset{Cp_3U\leftarrow:C-R}{N}} \end{array} \right] \quad \left[\begin{array}{c} \overset{R'}{\underset{Cp_3U-C-NR_2}{N}} \longleftrightarrow \overset{R'}{\underset{Cp_3U\leftarrow:C-NR_2}{N}} \end{array} \right]$$

$$\eta^2\text{-Iminoalkyl} \qquad\qquad\qquad \eta^2\text{-Iminocarbamoyl}$$

A unique class of $(\eta^5\text{-}C_5H_5)_3AnR$ complexes has been generated by Cramer *et al.* (1981, 1983, 1988). Reaction of $(\eta^5\text{-}C_5H_5)_3AnCl$ with lithium ylide or phosphine imide salts yields the following species [equations (25.40) and (25.41)]:

$$(\eta^5\text{-}C_5H_5)_3U\text{–}Cl + Li[(CH_2)_2P(CH_3)(C_6H_5)] \longrightarrow$$

$$(\eta^5\text{-}C_5H_5)_3U[(CH)P(CH_3)_2(C_6H_5)] \tag{25.40}$$

$$(\eta^5\text{-}C_5H_5)_3An\text{–}Cl + Li[NP(C_6H_5)_3] \longrightarrow (\eta^5\text{-}C_5H_5)_3An[NP(C_6H_5)_3] \tag{25.41}$$

An = Th, U

The molecular structure of the uranium phosphine imide complex is shown in Fig. 25.10.

While the overall geometry of these complexes is similar to most $(\eta^5\text{-}C_5H_5)_3AnX$ compounds, these species are characterized by unusually short U–C(N) bonds. The U–C(1) bond distance in the ylide complex is 2.29(3) Å [significantly shorter than the average uranium–alkyl bond in $(\eta^5\text{-}C_5H_5)_3UR$ complexes, *ca.* 2.43 Å], and the U–N bond distance in the phosphine imide complex is 2.07(2) Å. Two useful descriptions have been presented for the bonding in these complexes, consistent with the resonance forms depicted for the phosphoylide complex:

$$\left[\begin{array}{ccc} Cp_3U=C\overset{H}{\underset{\underset{\oplus}{PPh_3}}{}} & \longleftrightarrow & Cp_3U-\overset{..}{C}\overset{H}{\underset{\underset{\oplus}{PPh_3}}{\ominus}} & \longleftrightarrow & Cp_3U\leftarrow C\overset{H}{\underset{PPh_3}{}} \end{array} \right]$$

One model would suggest that a multiple bond is formed between the metal and the carbon. This is supported by theoretical calculations at the extended Hückel level (Tatsumi and Nakamura, 1984; Cramer *et al.*, 1988) that reveal an important overlap population in the U–C bond of the phosphoylide complex and U–N bond of the phosphine imine complex. A second description would

Fig. 25.10 *Crystal structure of* $(\eta^5\text{-}C_5H_5)_3U[NP(C_6H_5)_3]$. (*Reprinted with permission from Cramer* et al. *(1988). Copyright* 1988 *American Chemical Society.*)

suggest that the compounds are principally ionic, with the short U–C bond attributed to the Coulombic attraction between the electropositive metal and the residual charge on the ligand, as well as the smaller radial extent of the sp^2-hybridized ligand-based orbital. In reality, these models are probably merely extreme descriptions of the true bonding situation, and both are valid.

Unlike other complexes with metal–ligand multiple bonds (*vide infra*), the phosphoylide complex reacts as a U(IV) alkyl, however, undergoing a variety of insertion reactions (Cramer *et al.*, 1982, 1984a,b, 1986, 1987a,b) as shown in Fig. 25.11.

Complexes of the general formula $(\eta^5\text{-}C_5H_5)_2AnX_2$ have proven very difficult to synthesize, given the instability of the metallocene complex with respect to ligand redistribution to yield mono- and tris(ring) species (Kanellakopulos *et al.*, 1974c). Alternative approaches to generate complexes of this formula have generally involved introduction of the cyclopentadienyl ligands in the presence of other ligands that inhibit redistribution, as in equations (25.42)–(25.45) (Jamerson and Takats, 1974; Zanella *et al.*, 1977, 1987).

$$U(NEt_2)_4 + 2 \; \text{(cyclopentadiene)} \longrightarrow (\eta^5\text{-}C_5H_5)_2U(NEt_2)_2 + 2 \; HNEt_2 \quad (25.42)$$

$$UCl_4 + NaBH_4 \longrightarrow (BH_4)_2UCl_2 + 2NaCl \qquad (25.43)$$

$$(BH_4)_2UCl_2 + 2Tl(C_5H_5) \longrightarrow (\eta^5\text{-}C_5H_5)_2U(BH_4)_2 + 2TlCl \quad (25.44)$$

$$(dmpe)ThCl_4 + 2Na(C_5H_5) \longrightarrow (\eta^5\text{-}C_5H_5)_2Th(Cl)_2(dmpe) + 2NaCl \quad (25.45)$$
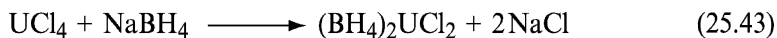
The bis(indenyl) complex $(\eta^5\text{-}C_9H_7)_2U(BH_4)_2$ has been generated by the reaction of $Na(C_9H_7)$ with $U(BH_4)_2$, and the structure reported (Spirlet *et al.*, 1989b). Peralkylated indenyl ligands have also been used to produce metallocene derivatives. Reaction of $ThCl_4$ with $Li(C_9Me_7)$ yields the dichloride complex $(\eta^5\text{-}C_9Me_7)_2ThCl_2$ (Trnka *et al.*, 2001). This species serves as a reagent for the synthesis of a number of derivatives, including $(\eta^5\text{-}C_9Me_7)_2ThMe_2$, $(\eta^5\text{-}C_9Me_7)_2Th(NMe_2)_2$, $(\eta^5\text{-}C_9Me_7)_2Th(NC_4H_4)_2$, and $(\eta^5\text{-}C_9Me_7)_2Th(\eta^3\text{-}H_3BH)_2$. The permethylindenyl ligand in all of these derivatives binds with nearly an idealized η^5-coordination mode, with the Th–C bonds for the five-membered ring of the indenyl ligands varying by no more than 0.05 Å. The indenyl rings are not entirely planar, indicating that there are steric repulsions between the proximal methyl groups of the two $(\eta^5\text{-}C_9Me_7)$ ligands, although these distortions are smaller than in related zirconium compounds, consistent with the larger radius of the thorium ion.

The principal synthetic means employed to stabilize bis(cyclopentadienyl) actinide complexes against ligand redistribution has been to use substituted cyclopentadienyl ligands. The first reports of successfully stabilizing bis(cyclopentadienyl) complexes involved the use of peralkylated derivatives (C_5Me_5: Manriquez *et al.*, 1978; Fagan *et al.*, 1981a; C_5Me_4Et: Green and Watts, 1978). The pentamethylcyclopentadienyl ligand has come to be one of the most widely used ligands in organoactinide chemistry due to the thermal stability, solubility, and crystallinity of its compounds. Initial synthetic routes involved alkylation of the metal tetrahalides by Grignard [equation (25.46)] or tin [equation (25.47)] reagents:

$$AnCl_4 + 2(C_5Me_5)MgCl \cdot THF \longrightarrow (\eta^5\text{-}C_5Me_5)_2AnCl_2 + 2MgCl_2$$
$$An = Th, U \qquad (25.46)$$

$$UCl_4 + 2(C_5Me_4Et)SnBu_3 \longrightarrow (\eta^5\text{-}C_5Me_4Et)_2UCl_2 + 2Bu_3SnCl \quad (25.47)$$
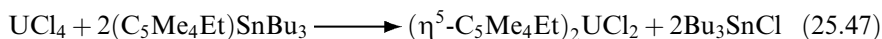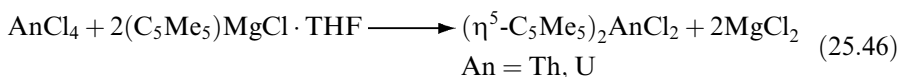
The molecular structure of $(\eta^5\text{-}C_5Me_5)_2UCl_2$ has been determined (Spirlet *et al.*, 1992b; Fig. 25.12), as have those of $(\eta^5\text{-}C_5Me_5)_2ThX_2$ (X = Cl, Br, I) (Spirlet *et al.*, 1992b; Rabinovich *et al.*, 1997, 1998).

All exist as monomeric complexes with a pseudo-tetrahedral, 'bent metallocene' geometry. The complex $(\eta^5\text{-}C_5Me_5)_2NpCl_2$ was generated in a manner similar to that in equation (25.46) (Sonnenberger and Gaudiello, 1986); reaction of the tetrahalide with $Tl(C_5Me_5)$ had previously been reported to yield a THF

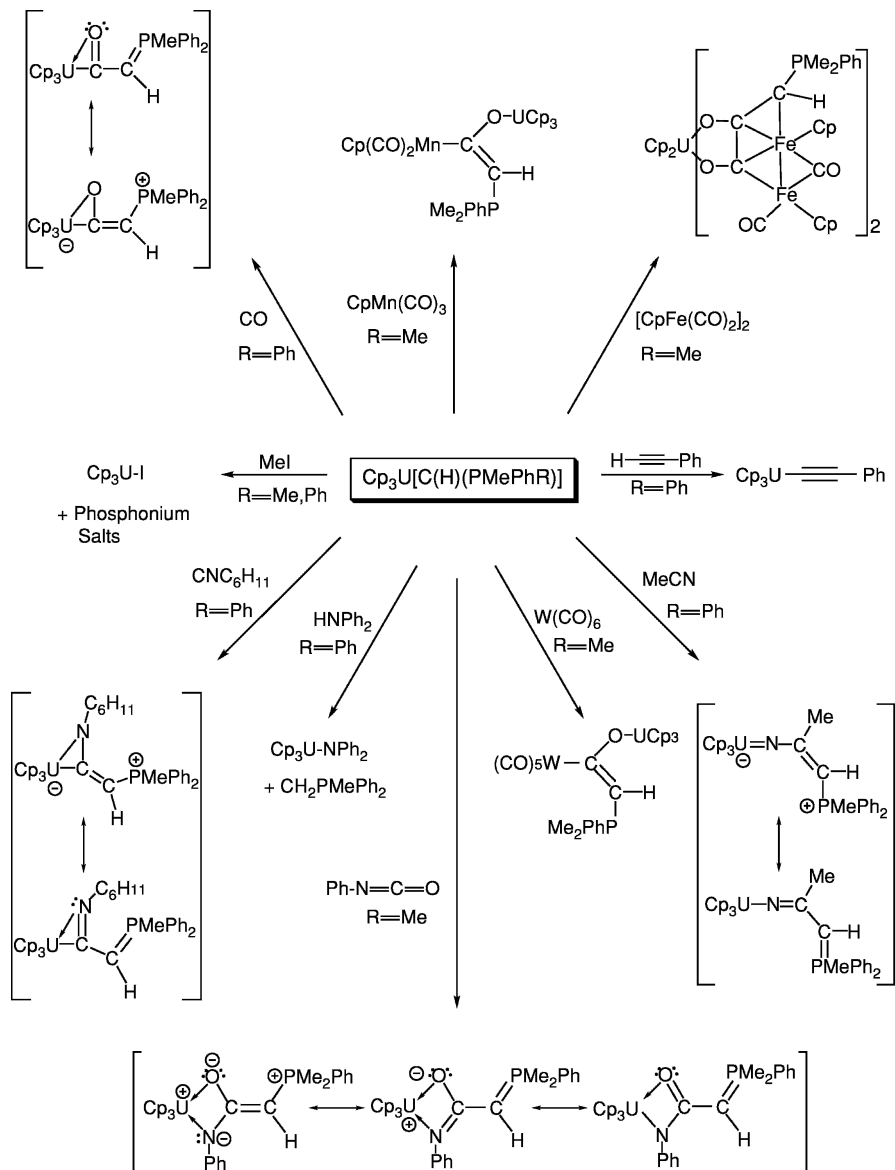**Fig. 25.11** *Reactions of $(\eta^5\text{-}C_5H_5)_3U[(CH)P(CH_3)(C_6H_5)(R)]$, where $R = CH_3, C_6H_5$.*

adduct (Karraker, 1983). The electrochemistry of $(\eta^5\text{-}C_5Me_5)_2NpCl_2$ reveals a reversible one-electron reduction wave at -0.68 V versus a ferrocene internal standard. A one-electron reversible reduction is also reported for $(\eta^5\text{-}C_5Me_5)_2UCl_2$ at -1.30 V (Finke *et al.*, 1982). Interestingly, the difference in
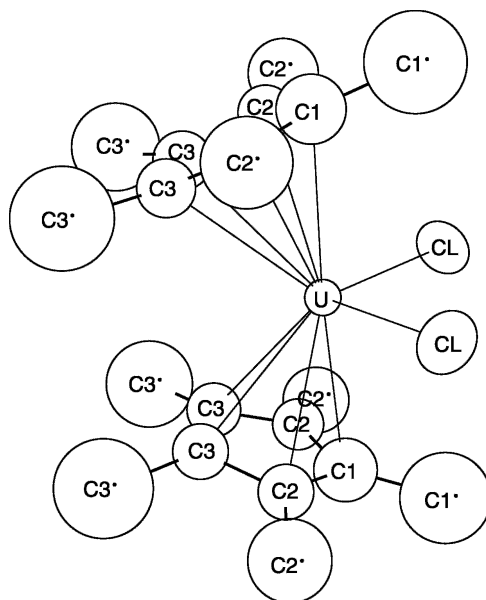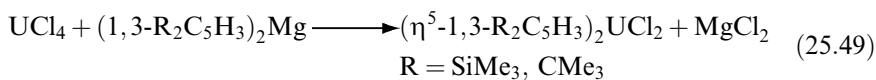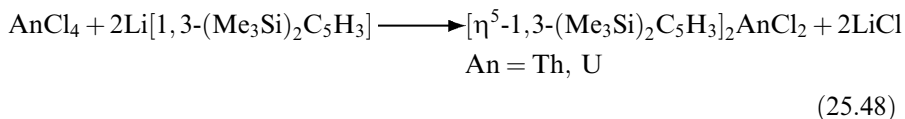
Fig. 25.12 *Crystal structure of $(\eta^5\text{-}C_5Me_5)_2UCl_2$ (Spirlet et al., 1992b). (Reprinted with permission of the International Union of Crystallography.)*

the U and Np non-aqueous reduction potentials is very close to the difference in their aqueous reduction potentials.

Other substituted cyclopentadienyl ligand sets have been generated and used to stabilize tetravalent metallocenes, particularly $[1,3\text{-}(Me_3Si)_2C_5H_3]$ and $[1,3\text{-}(Me_3C)_2C_5H_3]$. The metal complexes have been prepared by reaction of the metal tetrahalides with either cyclopentadienyllithium reagents [equation (25.48)] (Blake *et al.*, 1995) or the substituted magnesocenes [equation (25.49)] (Lukens *et al.*, 1999a).

$$AnCl_4 + 2Li[1,3\text{-}(Me_3Si)_2C_5H_3] \longrightarrow [\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2AnCl_2 + 2LiCl$$
$$An = Th, U$$

(25.48)

$$UCl_4 + (1,3\text{-}R_2C_5H_3)_2Mg \longrightarrow (\eta^5\text{-}1,3\text{-}R_2C_5H_3)_2UCl_2 + MgCl_2$$
$$R = SiMe_3, CMe_3$$

(25.49)

In the latter case, all metatheses were performed with the chloride salt, and the chloride product was subsequently converted to other halides by reaction with $XSiMe_3$ ($X = Br, I$) or $BF_3 \cdot Et_2O$. The molecular structures of the complexes $[\eta^5\text{-}1,3\text{-}R_2C_5H_3]_2UX_2$ ($R = SiMe_3$, $X = F, Cl, Br$; $R = {}^tBu$, $X = F, Cl$) have

been reported, as has the structure of $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2ThCl_2$. All exist as monomers in the solid state, except for $[\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}_2UF(\mu\text{-}F)]_2$, which is a dimer (see Fig. 25.6). A detailed study of the solution behavior of the complexes has been conducted (Lukens *et al.*, 1999a). Both fluoride complexes are found to display a monomer–dimer equilibrium in solution. The ^1H NMR chemical shifts and magnetic susceptibility data for the complexes further suggest that the ligands $[1,3\text{-}(Me_3Si)_2C_5H_3]$ and $[1,3\text{-}(Me_3C)_2C_5H_3]$ produce significantly different electronic environments at the metal center.

Despite the kinetic stability that the sterically larger cyclopentadienyl ligands provide, in a limited number of cases base adducts have been generated. The complex $(\eta^5\text{-}C_5Me_5)_2UCl_2(pz)$ (pz = pyrazole) has been reported (Eigenbrot and Raymond, 1982), as has the chelating phophshine adduct $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2ThCl_2(dmpe)$ (Edelman *et al.*, 1995). The complex $(\eta^5\text{-}C_5Me_5)_2U(OTf)_2(H_2O)$ (OTf = trifluoromethylsulfonate) was isolated in low yield from the reaction of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ with triflic acid (Berthet *et al.*, 1998). In compounds of the formula $(\eta^5\text{-}C_5Me_5)_2UX_2(L)$ (L = neutral ligand), the coordinated base generally occupies the central position in the equatorial wedge.

A second strategy for kinetically stabilizing actinide metallocenes against redistribution reactions is to employ the chelate effect by linking the two cyclopentadienyl rings (*ansa* metallocenes). The most common of these ligands are the *ansa* ligand sets.
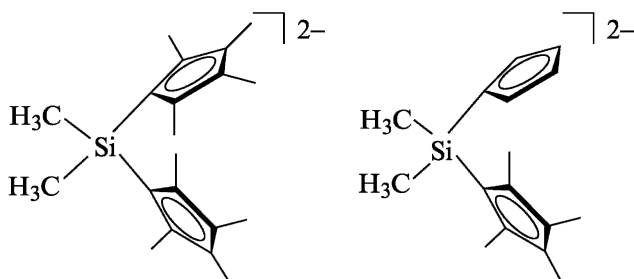
The molecular structure of $[(\eta^5\text{-}C_5Me_4)_2(\mu\text{-}SiMe_2)]U(\mu\text{-}Cl)_4[Li(TMEDA)]_2$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) is shown in Fig. 25.13.

As for most *ansa* metallocenes, the complex is characterized by a more acute centroid–metal–centroid angle (114.1°) than non-linked metallocenes (133–138°). This leaves more room in the equatorial wedge, accounting for the ability to accommodate four bridging chloride ligands. The more open coordination environment generated by 'tying' back the cyclopentadienyl ligands also enhances the reactivity of the resulting metal complex. The complex $[(\eta^5\text{-}C_5Me_4)_2 (\mu\text{-}SiMe_2)]Th(n\text{-}Bu)_2$, generated by reaction of the structurally characterized precursor $[(\eta^5\text{-}C_5Me_4)_2(\mu\text{-}SiMe_2)]Th(\mu\text{-}Cl)_4[Li(DME)]_2$ with *n*-BuLi, was found to be a very active catalyst for the dimerization of terminal alkynes and the hydrosilylation of terminal alkynes or alkenes with $PhSiH_3$ (Dash *et al.*, 2001).
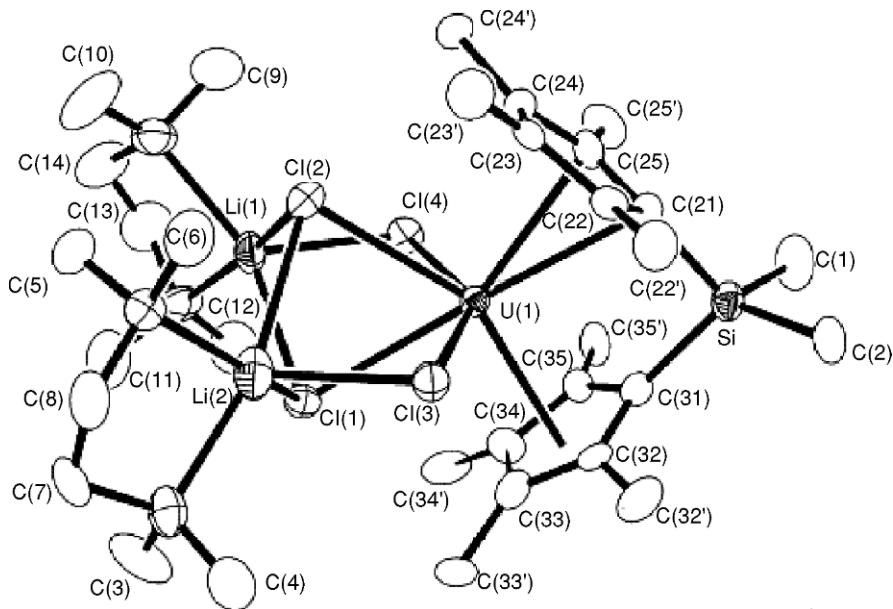
Fig. 25.13 *Crystal structure of* $[(\eta^5\text{-}C_5Me_4)_2(\mu\text{-}SiMe_2)]U(\mu\text{-}Cl)_4[Li(TMEDA)]_2$ (*Schnabel* et al., 1999). (*Reprinted with permission from Elsevier.*)

Other ligand sets have been explored that append Lewis base groups to the ring that will coordinate to the metal center to help prevent ring redistribution. A bis(cyclopentadienyl) substituted pyridine ligand has been used to generate the complex $[\eta^5\text{-}C_5H_4(CH_2)]_2(C_6H_5N)UCl_2$ (Paolucci *et al.*, 1991), and the pendant ether complex $[\eta^5\text{-}C_5H_4(CH_2CH_2OCH_3)]_2UCl_2$ has also been reported (Deng *et al.*, 1996):
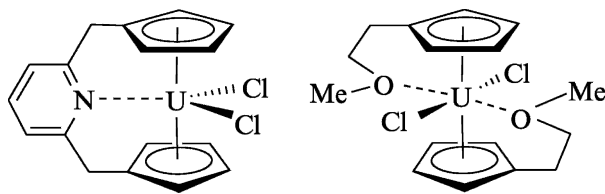
Metathesis and protonation reactions have been employed to produce a wide array of derivatives of the metallocene unit. A limited number of complexes exist with bonds to Group 14 elements other than carbon. Reaction of $(\eta^5\text{-}C_5Me_5)_2ThCl_2$ with the bulkyl silyl salt $(THF)_3Li[Si(SiMe_3)_3]$ yields an unstable complex $(\eta^5\text{-}C_5Me_5)_2Th(Cl)[Si(SiMe_3)_3]$ that could be trapped by reaction with two equivalents of carbon monoxide to produce a ketene complex $(\eta^5\text{-}C_5Me_5)_2Th(Cl)[O\text{-}C(=C=O)Si(SiMe_3)_3]$.
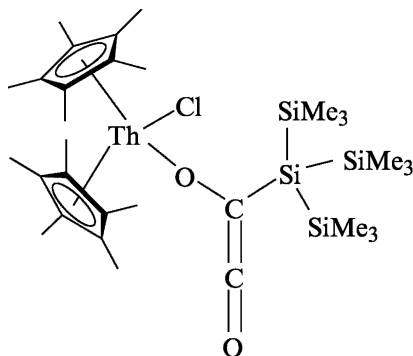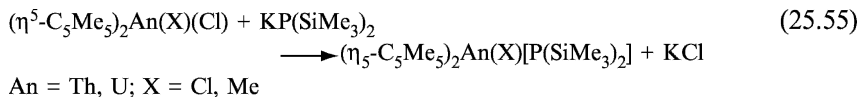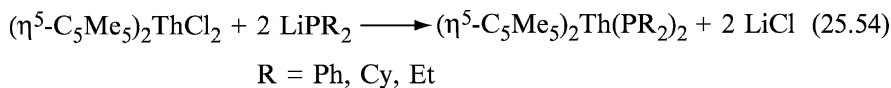
The analogous silyl compound $(\eta^5\text{-}C_5Me_5)_2ThCl(Si^tBuPh_2)$ could be isolated and its reaction with CO gave a similar silylthoroxyketene compound, and in this case the transient η^2-acyl complex $(\eta^5\text{-}C_5Me_5)_2ThCl[\eta^5\text{-}CO(Si^tBuPh_2)]$ could be detected (Radu *et al.*, 1995).

Metathesis [equations (25.50), (25.52), and (25.53)] and protonation [equations (25.42) and (25.51)] reactions are the most widely used routes to generate metallocene amide complexes (Fagan *et al.*, 1981a,b; Eigenbrot and Raymond; 1982).
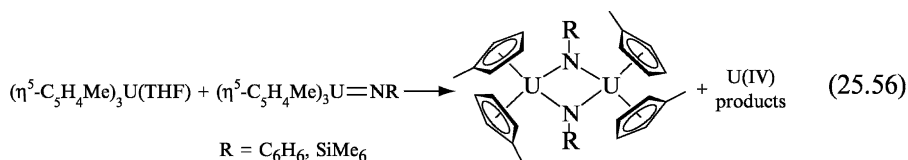
$$(\eta^5\text{-}C_5Me_5)_2AnCl_2 + 2\,LiNMe_2 \xrightarrow[-2\,LiCl]{} (\eta^5\text{-}C_5Me_5)_2U(NMe_2)_2$$
$$An = Th,\ U \tag{25.50}$$

$$(\eta^5\text{-}C_5Me_5)_2AnR_2 + 2\,HNEt_2 \xrightarrow[-2\,RH]{} (\eta^5\text{-}C_5Me_5)_2U(NEt_2)_2$$
$$An = Th,\ U \tag{25.51}$$

$$(\eta^5\text{-}C_5Me_5)_2UCl_2 + Na(pz) \longrightarrow (\eta^5\text{-}C_5Me_5)_2U(Cl)(pz) + NaCl \tag{25.52}$$
$$pz = \text{pyrazolate}$$

$$(\eta^5\text{-}C_5Me_5)_2UCl_2 + 2\,Na(pz) \longrightarrow (\eta^5\text{-}C_5Me_5)_2U(pz)_2 + 2\,NaCl \tag{25.53}$$
$$pz = \text{pyrazolate}$$
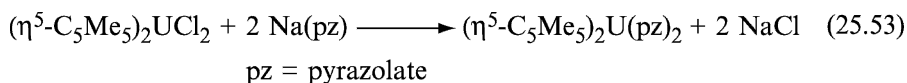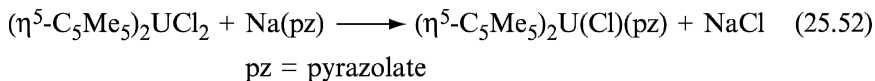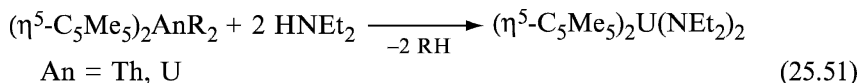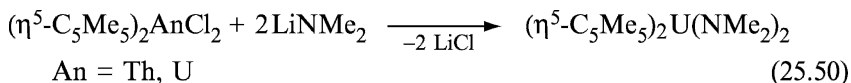
Metallocene phosphide complexes have been generated by metathesis routes [equations (25.54) and (25.55)] (Wrobleski *et al.*, 1986a; Hall *et al.*, 1993).

$$(\eta^5\text{-}C_5Me_5)_2ThCl_2 + 2\,LiPR_2 \longrightarrow (\eta^5\text{-}C_5Me_5)_2Th(PR_2)_2 + 2\,LiCl \tag{25.54}$$
$$R = Ph,\ Cy,\ Et$$

$$(\eta^5\text{-}C_5Me_5)_2An(X)(Cl) + KP(SiMe_3)_2 \tag{25.55}$$
$$\longrightarrow (\eta_5\text{-}C_5Me_5)_2An(X)[P(SiMe_3)_2] + KCl$$
$$An = Th,\ U;\ X = Cl,\ Me$$

For the bis(trimethylsilyl)phosphide substituent, a bis(phosphido) complex cannot be produced. Solution ^{1}H NMR spectra indicate that there is restricted rotation about the An–P bond at room temperature. The complexes (η^5-C$_5$Me$_5$)$_2$AnMe[P(SiMe$_3$)$_2$] decompose thermally by elimination of methane to generate a metallacyclic complex:

An = Th, U
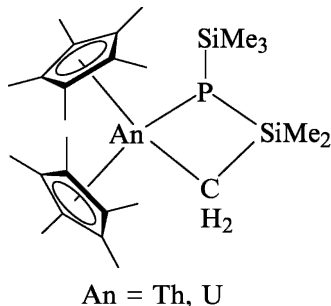
The metallocene framework has also been integral to the isolation of organoimido and phosphinidene complexes. Comproportionation of U(III) and U(V) metallocenes results in the formation of uranium(IV) organoimido complexes [equation (25.56)] (Brennan *et al.*, 1988b).

$$(\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{U(THF)} + (\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{U}{=}\text{NR} \longrightarrow \qquad + \begin{array}{c}\text{U(IV)}\\\text{products}\end{array} \qquad (25.56)$$

R = C$_6$H$_6$, SiMe$_6$

The molecular structure of [(η^5-MeC$_5$H$_4$)$_2$U(μ-NPh)]$_2$ is shown in Fig. 25.14.

The complexes exist as centrosymmetric dimers with asymmetric bridging organoimido ligands; the degree of asymmetry in the U–N bonds depends on the identity of the imido substituent.

It is only recently that terminal organoimido complexes of U(IV) have been isolated (Arney and Burns, 1995). α-Elimination reactions have been employed to generate the monoimido complex (η^5-C$_5$Me$_5$)$_2$U(=N-2,4,6-^{t}Bu$_3$C$_6$H$_2$) [equation (25.57)].

$$(\eta^5\text{-C}_5\text{Me}_5)_2\text{UMe}_2 + \text{H}_2\text{N}\!\!-\!\!\text{...} \xrightarrow[-2\text{CH}_4]{\Delta} \qquad (25.57)$$
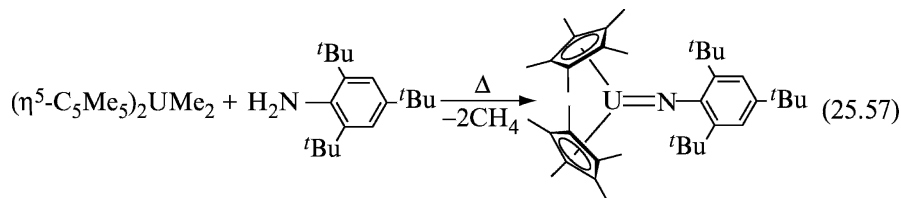
The complex is isolated even from ethereal solvents as a base-free species. The complex displays a very short U–N bond distance [1.95(1) Å], and a large
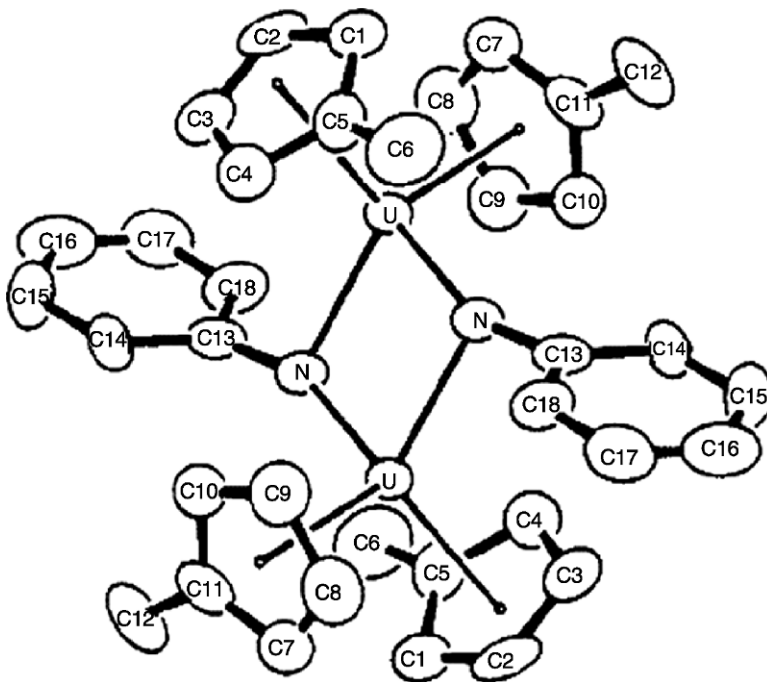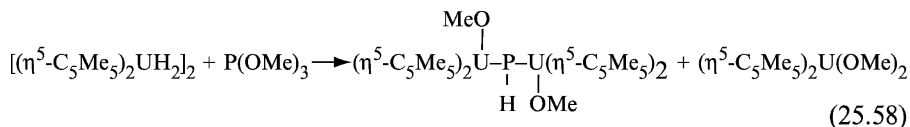
Fig. 25.14   *Crystal structure of* $[(\eta^5\text{-}MeC_5H_4)_2U(\mu\text{-}NPh)]_2$. (*Reprinted with permission from Brennan* et al. (1988b). *Copyright* 1988 *American Chemical Society.*)

U–N–C angle [162.3(10)°]. Unlike the phosphoylide and phosphine imide complexes described previously, the organoimido complex is relatively inert; it does not undergo insertion reactions, suggestive of a bond order greater than 1. The steric bulk of the aryl group is important in stabilizing a base-free organoimido complex; the smaller $(\eta^5\text{-}C_5Me_5)_2U(=\text{N-2,6-}^iPr_2C_6H_3)$ is best isolated as the THF adduct, and the parent phenylimido has only been isolated as a uranate salt, $[\text{Li(TMEDA)}][(\eta^5\text{-}C_5Me_5)_2U(=NC_6H_5)Cl]$. Organoimido complexes of U(IV) and Th(IV) have been implicated as intermediates in the catalytic intermolecular hydroamination of terminal alkynes (Straub *et al.*, 1996, 2001). It has been proposed that monoimido derivatives of the formula $(\eta^5\text{-}C_5Me_5)_2An$ $(=NR')$ are formed in the reaction of $(\eta^5\text{-}C_5Me_5)_2AnMe_2$ with primary amines $R'NH_2$. These undergo metathesis reaction with alkynes to yield four-membered azametallacyclic intermediates, which can undergo subsequent amine protonation (with isomerization) to yield the product imines. The mechanism of this reaction is discussed further in Chapter 26. Although the organoimido intermediates involving aliphatic amines have not been isolated, analogs such as $(\eta^5\text{-}C_5Me_5)_2Th(=\text{N-2,6-}Me_2C_6H_3)(\text{THF})$ have been structurally

characterized (Haskel *et al.*, 1996; Straub *et al.*, 2001). As in the case of the uranium organoimido complex, the thorium complex displays a short Th–N bond [2.045(8) Å] and a near-linear Th–N–C_{ipso} angle (171.5(7)°).

Similarly, bridging actinide phosphinidene complexes predated their terminal counterparts. The hydride complex [(η^5-C_5Me_5)$_2UH_2$]$_2$ reacts with P(OMe)$_3$ to generate a bridging phosphinide complex [(η^5-C_5Me_5)$_2$U(OMe)]$_2$(μ-PH) by P–O cleavage with sacrificial formation of (η^5-C_5Me_5)$_2$U(OMe)$_2$ [equation (25.58)] (Duttera *et al.*, 1984).

$$[(\eta^5\text{-}C_5Me_5)_2UH_2]_2 + P(OMe)_3 \longrightarrow (\eta^5\text{-}C_5Me_5)_2U\overset{\overset{\displaystyle MeO}{|}}{\underset{\underset{\displaystyle H}{|}}{P}}\overset{}{\underset{\underset{\displaystyle OMe}{|}}{}}U(\eta^5\text{-}C_5Me_5)_2 + (\eta^5\text{-}C_5Me_5)_2U(OMe)_2$$

$$(25.58)$$

A terminal phosphinidene complex has also been reported (Arney *et al.*, 1996). Reaction of (η^5-C_5Me_5)$_2$U(Me)Cl with KPH(2,4,6-$^tBu_3C_6H_2$) in the presence of trimethylphosphine oxide yields the base adduct of the phosphinidene complex (η^5-C_5Me_5)$_2$U(=P-2,4,6-$^tBu_3C_6H_2$)(OPMe$_3$) (Fig. 25.15).

The complex displays a short U–P distance [2.562(3) Å]. The U–P–C angle 143.7(3)°; the nonlinear angle is not unusual in comparison to d-transition metal terminal phosphinidene complexes. No product is isolated in the absence of coordinating base, except for when the ancillary ligand set is [(η^5-C_5Me_4)$_2$(μ-SiMe$_2$)]. In the case of the less congested *ansa*-metallocene; a phosphinidene-bridged dimer [{(η^5-C_5Me_4)$_2$(μ-SiMe$_2$)}U(μ-PR)]$_2$ (R = 2,4,6-$^tBu_3C_6H_2$) is generated.
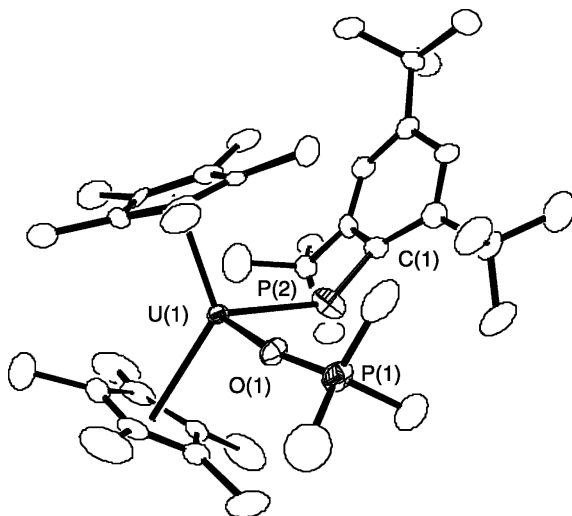
Fig. 25.15 *Crystal structure of (η^5-C_5Me_5)$_2$U(=P-2,4,6-t-$Bu_3C_6H_2$)(OPMe$_3$). (Reprinted with permission from Arney* et al. *(1996). Copyright 1996 American Chemical Society.)*
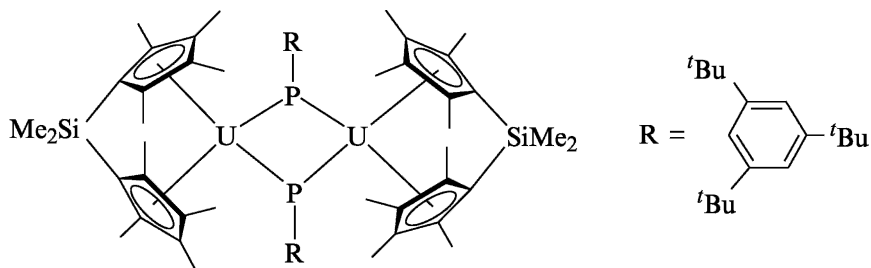
An interesting series of polypnictide complexes have been generated by the reaction of $(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)_2Th(\eta^4\text{-}C_4H_6)$ with P_4 or As_4. The main group elements react to generate a hexapnictide complex: $[(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)_2 Th]_2(\mu,\eta^3,\eta^3\text{-}E_6)$ (E = P, As) (Scherer *et al.*, 1991, 1994).

E = P, As
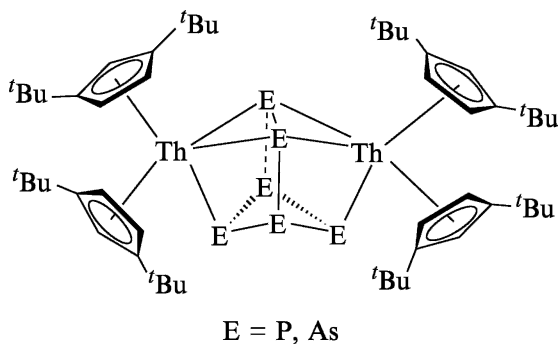
In the presence of magnesium chloride, however, only the complex: $[(\eta^5\text{-} 1,3\text{-}{}^tBu_2C_5H_3)_2Th](\mu,\eta^3\text{-}P_3)[Th(Cl)(\eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3)_2]$ is formed in the reaction with phosphorus.
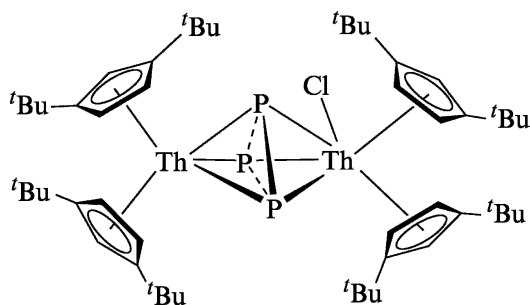
One of the earliest descriptions of metallocene thiolate complexes involved reactions of $(\eta^5\text{-}C_5H_5)_2U(NEt_2)_2$ with monothiols and dithiols (Jamerson and Takats, 1974). While compounds with the chelating thiols are stable (generally dimers), compounds of monodentate thiols $(\eta^5\text{-}C_5H_5)_2U(SR)_2$ were reported to

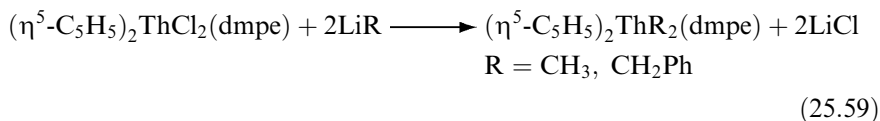be unstable and decomposed to form $(\eta^5\text{-}C_5H_5)_2U(SR)$. Two other reports of bis (pentamethylcyclopentadienyl) metallocene dithiolates have been appeared: $(\eta^5\text{-}C_5Me_5)_2Th(SPr)_2$ (Lin *et al.*, 1988) and $(\eta^5\text{-}C_5Me_5)_2U(SR)_2$ (R = Me, ^{i}Pr, ^{t}Bu, Ph) (Lescop *et al.*, 1999).

Two reports have appeared featuring cyclopentadienyl-supported actinide chalcogenide complexes. Reaction of $(\eta^5\text{-}C_5Me_5)_2ThCl_2$ with Li_2S_5 generates the compound $(\eta^5\text{-}C_5Me_5)_2Th(S_5)$ (Wrobleski *et al.*, 1986b); the molecular structure of this complex shows that the six-membered ring formed by the S_5 ligand and the Th has a twist-boat conformation. Bonding of the ligand was characterized as η^4 on the basis of close contacts between the β-sulfides and the metal center. Variable temperature NMR data show that the ligand is fluxional at room temperature.
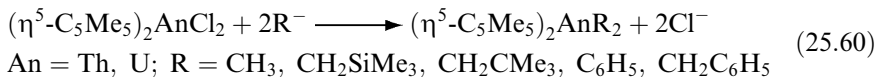
The complex $(\eta^5\text{-}C_5Me_5)_2U(S^tBu)_2$ is reported to undergo reduction by Na–Hg with cleavage of a C–S bond (Ventelon *et al.*, 1999). The product was isolated with 18-crown-6 and proved to be a complex with a terminal sulfido ligand bound to the sodium counter-ion. The complex $[Na(18\text{-crown-}6)][(\eta^5\text{-}C_5Me_5)_2U(S^tBu)(S)]$ possesses a short U–S bond distance [2.462(2) Å], which is significantly shorter than typical U–SR bond distances (*ca.* 2.64 Å).
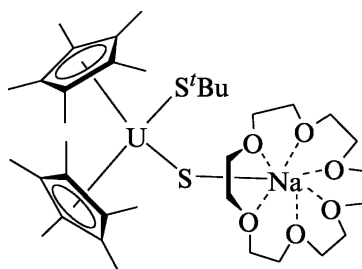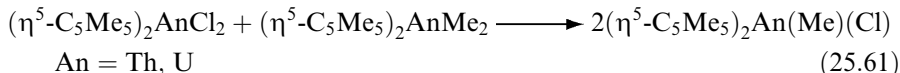

Given the relative importance of d-transition metal metallocene alkyl chemistry in Group 4 organometallic chemistry, it is to be expected that the alkyl chemistry of the actinide metallocene complexes would also be extensively studied. The majority of this chemistry has employed the more highly substituted ligand sets, although less sterically hindered metallocene frameworks can be alkylated in the presence of a stabilizing base as shown in equation (25.59) (Zalkin *et al.*, 1987a):

$$(\eta^5\text{-}C_5H_5)_2ThCl_2(dmpe) + 2LiR \longrightarrow (\eta^5\text{-}C_5H_5)_2ThR_2(dmpe) + 2LiCl$$
$$R = CH_3,\ CH_2Ph$$

$$(25.59)$$

Complexes employing the pentamethylcyclopentadienyl ligand can be prepared for a wide range of alkyl and aryl groups (Fagan *et al.*, 1981a; Erker *et al.*, 1986; Smith *et al.*, 1986), where the alkylating agents can be either alkyllithium, Grignard, or dialkylmagnesium reagents [equation (25.60)].

$$(\eta^5\text{-}C_5Me_5)_2AnCl_2 + 2R^- \longrightarrow (\eta^5\text{-}C_5Me_5)_2AnR_2 + 2Cl^-$$
$$An = Th, \ U; \ R = CH_3, \ CH_2SiMe_3, \ CH_2CMe_3, \ C_6H_5, \ CH_2C_6H_5 \tag{25.60}$$

The corresponding mixed alkyl halide complexes can be prepared in most cases by reaction of $(\eta^5\text{-}C_5Me_5)_2AnCl_2$ with one equivalent of alkylating agent, although the methyl chloride complex is best prepared by redistribution from the dichloride and dimethyl complexes [equation (25.61)].

$$(\eta^5\text{-}C_5Me_5)_2AnCl_2 + (\eta^5\text{-}C_5Me_5)_2AnMe_2 \longrightarrow 2(\eta^5\text{-}C_5Me_5)_2An(Me)(Cl)$$
$$An = Th, \ U \tag{25.61}$$

The complexes are generally thermally stable, although some undergo elimination reactions at elevated temperatures (*vide infra*). The dimethyl complexes react with acetone, alcohols, and iodine to produce the corresponding *t*-butoxide, alkoxides (with generation of methane), and iodides (with generation of methyl iodide) (Fagan *et al.*, 1981a). Competition experiments at $-78°C$ indicate that the thorium complexes are more reactive than those of uranium, consistent with its larger ionic radius.

Two alternate descriptions have appeared for the complex $(\eta^5\text{-}C_5Me_5)_2Th$ $(\eta^4\text{-}C_4H_6)$. The complex and its derivatives have been termed both butadiene and 2-buten-1,4-diyl complexes, although the latter description is generally favored. The molecular structure of $(\eta^5\text{-}C_5Me_5)_2Th(\eta^4\text{-}C_4H_6)$ is shown in Fig. 25.16.

The crystal structure supports the η^4-hapticity of the organic ligand, given that the average Th–C distance to the terminal carbon atoms of the ligand [2.57 (3) Å] is only slightly smaller than that to the internal carbon atoms [2.74(2) Å], and are comparable to those found in other thorium alkyl complexes. The C(1)–C(2) and C(3)–C(4) average distances (average of four independent molecules in the unit cell) is 1.46(5) Å, and the average C(2)–C(3) distance is 1.44(3) Å. The complex displays fluxional behavior in solution, with equilibration of the cyclopentadienyl and α-methylene protons occurring via the intermediacy of a planar metallacyclopentene structure.
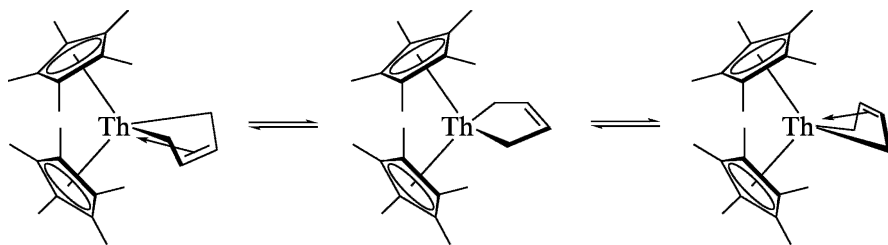
The actinide–carbon bonds in these complexes appear to be reasonably polar; they undergo hydrogenolysis under one atmosphere of dihydrogen to yield the dihydride complexes [equation (25.62)]:
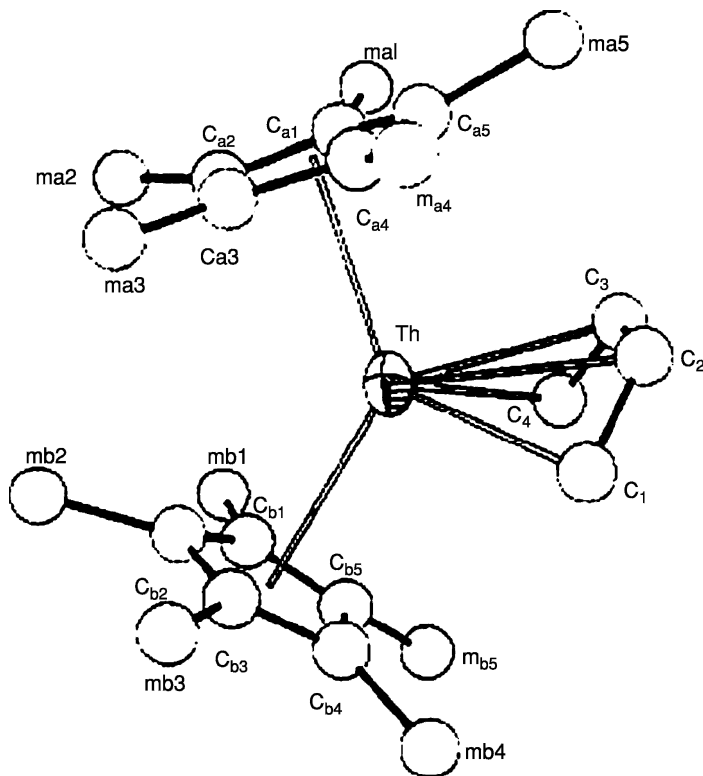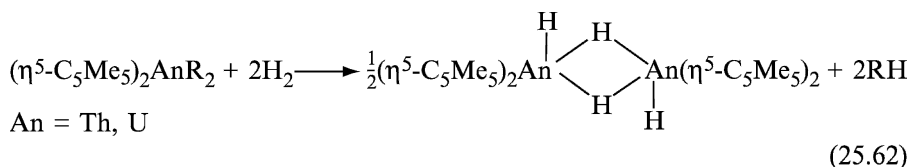
Fig. 25.16 *Crystal structure of* $(\eta^5\text{-}C_5Me_5)_2Th(\eta^4\text{-}C_4H_6)$. (*Reprinted with permission from Smith* et al. *(1986). Copyright* 1986 *American Chemical Society.*)

$$(\eta^5\text{-}C_5Me_5)_2AnR_2 + 2H_2 \longrightarrow \tfrac{1}{2}(\eta^5\text{-}C_5Me_5)_2An \begin{matrix} H & H \\ & \diagdown \diagup \\ & \diagup \diagdown \\ H & H \end{matrix} An(\eta^5\text{-}C_5Me_5)_2 + 2RH$$

An = Th, U

$$(25.62)$$

The dimeric formulation of the dihydride complexes is supported both by cryoscopic molecular weight determinations and a single-crystal neutron diffraction structure of the thorium compound (Broach *et al.*, 1979); ^{1}H NMR experiments indicate that the bridge and terminal hydrides exchange rapidly in solution to – 85°C. Under an atmosphere of D_2, H/D exchange in the hydride positions is very rapid. In the case of uranium, the ring methyl protons appear to interchange rapidly with the hydrides, resulting in isotopic scrambling. The thorium complex is thermally stable; in contrast, the uranium complex loses dihydrogen at room temperature *in vacuo* over a period of 3 h to generate a U(III) hydride.

Dialkyl complexes of an *ansa*-metallocene $[(\eta^5\text{-}C_5Me_4)_2(\mu\text{-}SiMe_2)]ThR_2$ (R = CH_2SiMe_3, CH_2CMe_3, C_6H_5, $n\text{-}C_4H_9$, and $CH_2C_6H_5$) have also been reported (Fendrick *et al.*, 1988). The ring centroid-metal-centroid angle (118.4°) is again much reduced from that typically found in non-linked metallocene complexes (135–138°). The dialkyl complexes undergo rapid hydrogenolysis under H_2 to yield a light-sensitive dihydride complex $[\{(\eta^5\text{-}C_5Me_4)_2(\mu\text{-}SiMe_2)\}ThH_2]_2$. IR spectroscopy and structural data [a short Th···Th distance of 3.632(2) Å] are evidence cited in support of a formulation of the compound as one with four bridging hydride ligands.

Thermochemical investigations have tabulated the bond disruption enthalpies for a number of metallocene alkyl halide and dialkyl complexes; these values are given in Table 25.6 (Bruno *et al.*, 1983, 1986b). As noted previously, the Th–R bond enthalpies are uniformly larger than those for U–R. It has also been noted (Leal *et al.*, 2001) that there appears to be significantly different values for certain bond enthalpy values (e.g. U–Me in Tables 25.4 and 25.6). The authors note that these values are based upon different reactions (alcholysis vs reaction with iodine), and therefore are based upon different assumed enthalpy values for product species. A potential correction was proposed, leading to a more self-consistent description of uranium bond enthalpies.

A further observation from the thermochemistry of thorium complexes is that the bond dissociation enthalpy for Th–H in $[(\eta^5\text{-}C_5Me_5)_2Th(\mu\text{-}H)H]_2$ (407.9 ± 2.9 kJ/mol), while somewhat larger than typical Th–C values (300–380 kJ mol^{-1}), is not larger enough to produce as strong a driving force for the

Table 25.6 *Mean bond dissociation enthalpies for* $(\eta^5\text{-}C_5Me_5)_2AnR_2$ *and* $(\eta^5\text{-}C_5Me_5)_2AnRX$ *complexes (Bruno et al., 1983, 1986b).*

| Compound	R	$D(An\text{–}R)$ (kJ mol^{-1})
$(\eta^5\text{-}C_5Me_5)_2UR_2$	Me	300 ± 11
	CH_2Ph	244 ± 8
	CH_2SiMe_3	307 ± 8
$(\eta^5\text{-}C_5Me_5)_2URCl$	Me	312 ± 8
	CH_2Ph	263 ± 12
	Ph	358 ± 11
$(\eta^5\text{-}C_5Me_5)_2ThR_2$	Me	345.2 ± 3.5
	Et	313.4 ± 6.7
	n-Bu	303.8 ± 9.2
	Ph	379.3 ± 10.3
	CH_2CMe_3	312.1 ± 15.7
	CH_2SiMe_3	339.3 ± 13.0
$(\eta^5\text{-}C_5Me_5)_2ThRCl$	Et	302.1 ± 7.5
	CH_2Ph	285.3 ± 5.9
	Ph	380.8 ± 16

formation of hydrides. Therefore, unlike mid- to late-transition metal compounds, reactions such as β-hydride elimination will not be strongly favored. This energetic situation, similar to that found for early transition metals, makes actinide metallocenes suitable species to effect C–C bond forming reactions, such as olefin polymerization (see Chapter 26).

One of the predominant reaction patterns of bis(cyclopentadienyl)actinide complexes is insertion chemistry. Insertion of unsaturated substrates such as CO, CNR, CO_2, and CS_2 into U–C, U–Si, U–N, and U–S bonds has been observed (Fagan *et al.*, 1981a,b; Erker *et al.*, 1986; Porchia *et al.*, 1989; Lescop *et al.*, 1999). The products of insertion generally display η^2-C(R) =E bonding. As an example, insertion of CO into An–R bonds yields η^2-acyl derivatives. Theoretical studies (Tatsumi *et al.*, 1985) have been conducted, both to explain the geometry of the η^2-complexes, as well as to understand the origin of the 'carbene-like' reactivity (Fig. 25.17).

A second common reaction pattern observed in metallocene complexes is thermally induced intramolecular elimination reactions. The dominant classes of elimination reactions are those involving formation of four-membered metallacyle complexes [equation (25.63)] (Bruno *et al.*, 1986a).

$$(\eta^5\text{-}C_5Me_5)_2Th(CH_2EMe_3)_2 \xrightarrow{\Delta} \quad + EMe_4 \quad (25.63)$$

$$E = C, Si$$
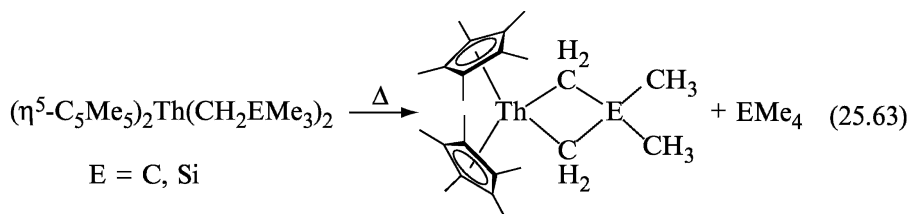
Kinetic and labeling studies in the cyclometallation reactions indicate that intramolecular γ-C–H activation is the rate-limiting step. It is believed that the reaction is chiefly entropically driven, with some driving force coming from relief of steric strain associated with the thorium dialkyl complex. The cyclometallated products have extensive reaction chemistry that is characterized by insertion of unsaturated substrates into Th–C bonds, as well as intermolecular activation of C–H bonds of other substrates, even saturated hydrocarbons such as methane [equation (25.64)] (Fendrick and Marks, 1986).
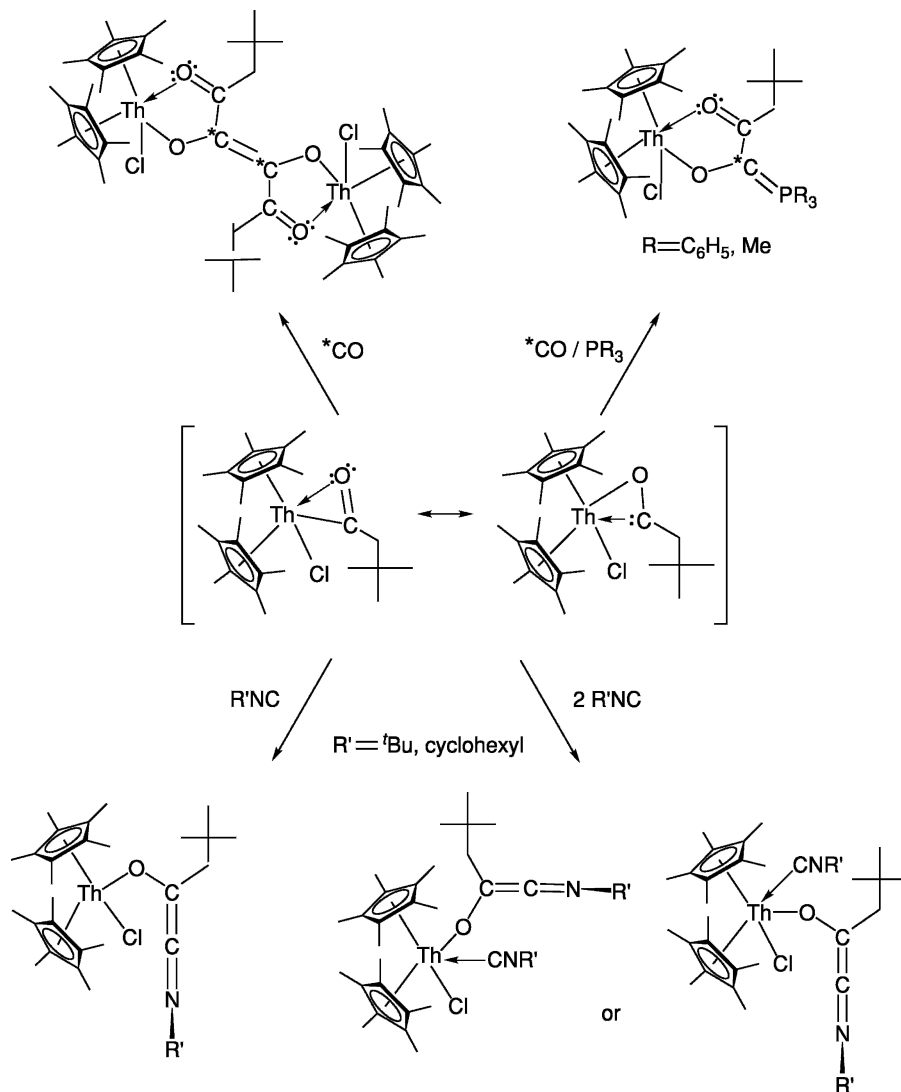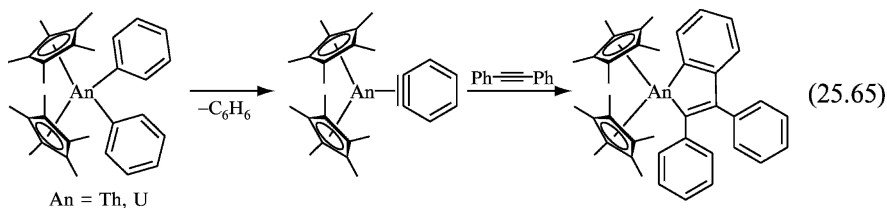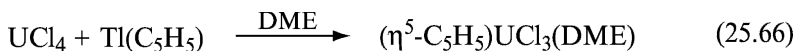
$$+ \ CH_4 \longrightarrow \qquad (25.64)$$

$$E = C, Si$$
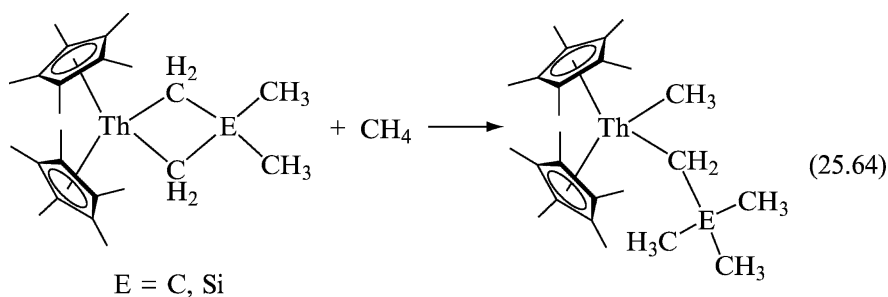
Fig. 25.17   *Reactivity of actinide η^2-Acyl complexes (Moloy et al., 1983).*

A second class of reactions is the elimination of benzene from diaryl complexes to form *o*-diphenylene, or benzyne-type complexes [equation (25.65)] (Fagan *et al.*, 1981a).

$$An = Th, U$$

$$(25.65)$$

The uranium complexes undergo this *ortho*-activation process ($k_U \gg k_{Th}$); although the intermediate benzyne complex is not stable, it can be trapped with diphenylacetylene to yield a metallacyclopentadiene product.

Despite the early report of mono-ring complexes of the formula (η^5-C$_5$H$_5$)UCl$_3$(DME) (DME = 1,2-dimethoxyethane) (Doretti *et al.*, 1972), there are far fewer reports of compounds containing a single cyclopentadienyl ring. The complex was initially prepared by reaction of UCl$_4$ with Tl(C$_5$H$_5$) in DME [equation (25.66)].

$$\text{UCl}_4 + \text{Tl(C}_5\text{H}_5) \xrightarrow{\text{DME}} (\eta^5\text{-C}_5\text{H}_5)\text{UCl}_3(\text{DME}) \qquad (25.66)$$
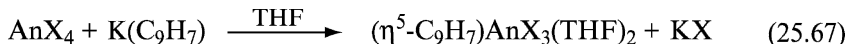
Since that time, a number of other base adducts of the uranium mono-ring compound have been prepared using both monodentate (Bagnall and Edwards, 1974; Bagnall *et al.*, 1978a; Bombieri *et al.*, 1978) and bidentate bases (Ernst *et al.*, 1979). The complex U(BH$_4$)$_4$ similarly reacts with Tl(C$_5$H$_5$) to yield (η^5-C$_5$H$_5$)U(BH$_4$)$_3$ (Baudry and Ephritikhine, 1988), although base adducts of this compound are reported to redistribute to generate (η^5-C$_5$H$_5$)$_2$U(BH$_4$)$_2$ (Baudry *et al.*, 1988). The structure of the (η^5-C$_5$H$_5$)U(BH$_4$)$_3$(THF)$_2$ complex has been proposed to be *mer*-octahedral with *cis* THF ligands on the basis of solution NMR investigations with a pentahapto cyclopentadienyl ring; this structure was confirmed for the complex (η^5-MeC$_5$H$_4$)UCl$_3$(THF)$_2$.
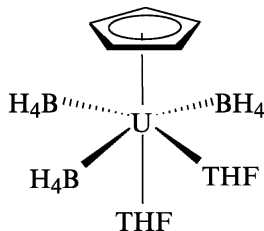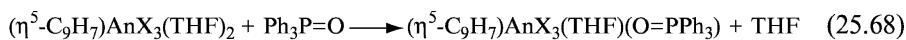

A later NMR study (Le Marechal *et al.*, 1986) reported an equilibrium between two isomers in solution for a variety of base adducts of (η^5-C$_5$H$_5$) UCl$_3$. Analogous compounds of the formula (η^5-C$_5$H$_5$)AnX$_3$L$_2$ (X = halide, NCS$^-$) have been produced for thorium (Bagnall and Edwards, 1974), neptunium (Karraker and Stone, 1972; Bagnall *et al.*, 1986), and plutonium (Bagnall *et al.*, 1985).

A variety of substituted cyclopentadienyl ligands have been introduced to generate cyclopentadienylthorium and cyclopentadienyluranium compounds by reaction with Grignard or alkali metal reagents. Indenyl complexes of the formula $(\eta^5\text{-}C_9H_7)AnX_3L$ (X = halide, L = base) can be prepared as shown in equations (25.67) and (25.68) (Goffart *et al.*, 1980; Meunier-Piret *et al.*, 1980).

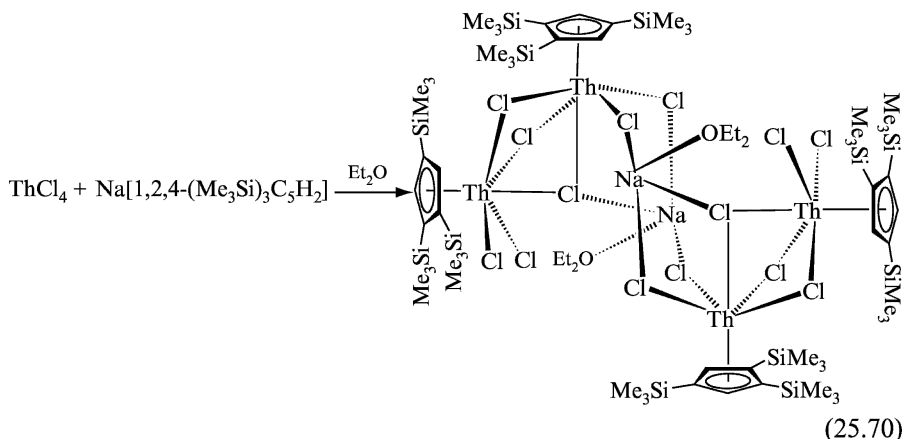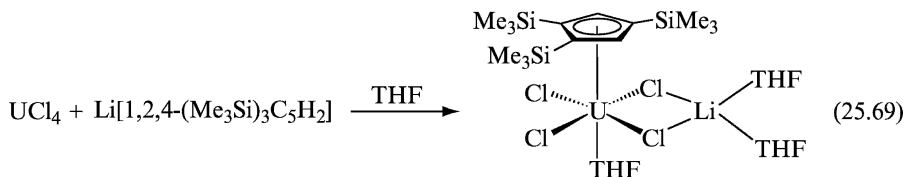$$AnX_4 + K(C_9H_7) \xrightarrow{\text{THF}} (\eta^5\text{-}C_9H_7)AnX_3(THF)_2 + KX \qquad (25.67)$$
An = Th, U, Np; X = Cl, Br

$$(\eta^5\text{-}C_9H_7)AnX_3(THF)_2 + Ph_3P{=}O \longrightarrow (\eta^5\text{-}C_9H_7)AnX_3(THF)(O{=}PPh_3) + THF \quad (25.68)$$
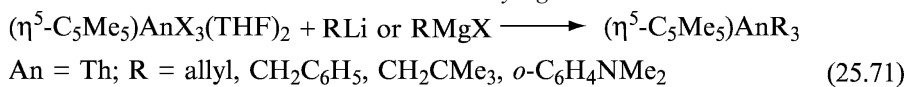An = Th, U, Np; X = Cl, Br

The use of alkali metal cyclopentadienyl reagents can lead to the formation of uranate-type complexes [equations (25.69) and (25.70)] (Edelman *et al.*, 1987, 1995):


$$UCl_4 + Li[1,2,4\text{-}(Me_3Si)_3C_5H_2] \xrightarrow{\text{THF}} \qquad (25.69)$$

$$ThCl_4 + Na[1,2,4\text{-}(Me_3Si)_3C_5H_2] \xrightarrow{Et_2O} \qquad (25.70)$$

Mono-ring pentamethylcyclopentadienyl thorium and pentamethylcyclopenta-dienyl uranium complexes can also be synthesized from reaction of the tetra-halides with $(C_5Me_5)MgCl$ (Mintz *et al.*, 1982; Butcher *et al.*, 1996), and their base adducts prepared. Spectroscopic data would again indicate a meridional disposition of the chloride ligands in a pseudo-octahedral geometry. As described in equation (25.71), these complexes can be alkylated with either organolithium or Grignard reagents to yield a limited number of stable alkyl derivatives (Mintz *et al.*, 1982; Cymbaluk *et al.*, 1983a; Marks and Day, 1985; Marks, 1986).

$(\eta^5\text{-}C_5Me_5)AnX_3(THF)_2 + RLi$ or $RMgX \longrightarrow (\eta^5\text{-}C_5Me_5)AnR_3$

An = Th; R = allyl, $CH_2C_6H_5$, CH_2CMe_3, $o\text{-}C_6H_4NMe_2$ (25.71)

An = U; R = allyl, 2-methylallyl, $CH_2C_6H_5$

One study has been conducted of the metathesis chemistry of $(\eta^5\text{-}C_5Me_5)$ $ThBr_3(THF)_3$ with aryloxide salts (Butcher *et al.*, 1996). Both the mono(aryl-oxide) and bis(aryloxide) complexes $(\eta^5\text{-}C_5Me_5)ThBr_2(OAr)(THF)$ and $(\eta^5\text{-}C_5Me_5)ThBr(OAr)_2$ (OAr = $O\text{-}2,6\text{-}^tBu_2C_6H_3$) may be produced by reaction with one or two equivalents of KOAr. The dibromide complex may be further alkylated to generate $(\eta^5\text{-}C_5Me_5)Th(CH_2SiMe_3)_2(OAr)$. Thermolysis of this compound in the presence of triphenylphosphine oxide permits the isolation of a rare example of an f-element compound with a cyclometallated aryloxide ligand.
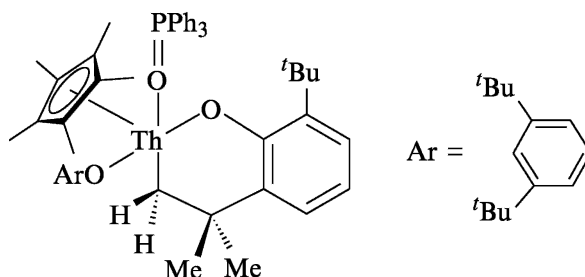
(c) Pentavalent chemistry

Pentavalent complexes of the actinides containing organic ligands are rare. They are anticipated to be limited to uranium, given the increasing stability of lower oxidation states for the later actinides. Most pentavalent organouranium complexes are supported by multiply bonded functional groups, such as those present in the complexes $(\eta^5\text{-}C_5H_4Me)_3U{=}NR$ previously described [see equation (25.22)]. The complex $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2UCl(THF)$ has been reported to react with Me_3SiN_3 to liberate N_2 and generate the U(v) organoimido complex $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2U({=}NSiMe_3)(Cl)$ (Blake *et al.*, 1987). Oxo transfer has also been effected to a U(III) precursor; the complex $(\eta^5\text{-}C_5Me_5)U$ $(OAr)(THF)$ (Ar = $2,6\text{-}^iPr_2C_6H_3$) reacts with pyridine *N*-oxide to yield the oxo derivative $(\eta\text{-}C_5Me_5)U({=}O)(OAr)$ (Arney and Burns, 1993). The molecular structure of this complex has been determined. The complex exists as a typical pseudo-tetrahedral metallocene complex, with a U–O (oxo) bond length of 1.859(6) Å, slightly longer than that common for a mutliply-bonded oxo group in the uranyl ion (UO_2^{2+}).

   Attempts to prepare U(VI) dioxo complexes supported by cyclopentadienyl groups has recently generated another rare example of a pentavalent oxo complex. Reaction of $(\eta^5\text{-}^tBu_3C_5H_2)_2UCl_2$ with KC_8, followed by oxidation with pyridine N-oxide, results in the formation of the complex $(\eta^5\text{-}^tBu_3C_5H_2)_4U_6O_{13}(bipy)_2$ (Duval *et al.*, 2001) (Fig. 25.18).
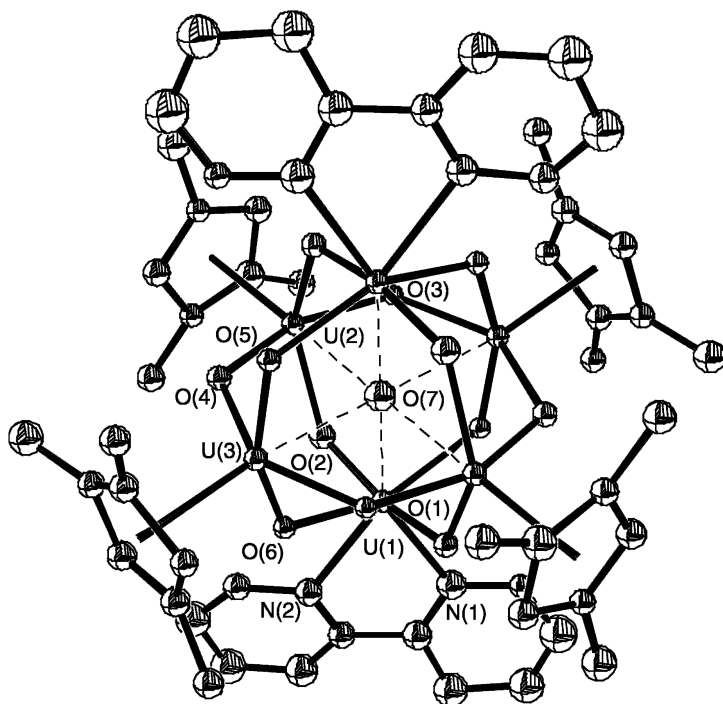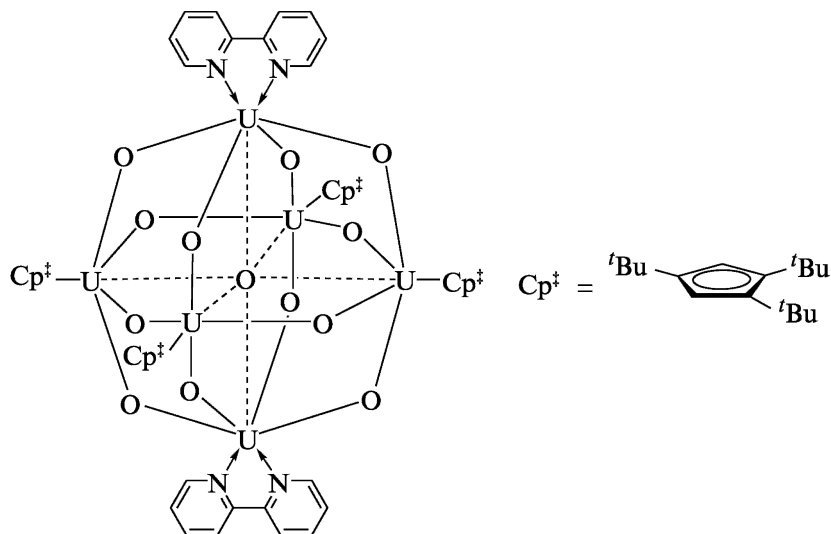
Fig. 25.18   *Crystal structure of* $(\eta^5\text{-}^tBu_3C_5H_2)_4U_6O_{13}(bipy)_2$ *(methyl carbons of* tert-*butyl groups are omitted for clarity)* (*Duval* et al., 2001). (*Reprinted with permission from John Wiley & Sons, Inc.*)

The core of the complex is a U_6O_{13} aggregate. Four uranium atoms in an equatorial plane are capped with a tri-*tert*-butylcyclopentadienyl ligand, while the two apical uranium atoms are ligated by 2,2'-bipyridine ligands, apparently derived from the by-product pyridine. The proposed mechanism for the formation of the aggregate is the generation and assembly of 'UO_2' and '$(\eta^5\text{-}^tBu_3C_5H_2)_2UO_2$' fragments from homolytic ring loss. Although the central metal oxo unit is structurally similar to the Lindqvist class of polyoxometallate anions, there is no indication of electronic delocalization in the complex. Magnetic susceptibility measurements suggest that the uranium centers behave as independent U(v) f^1 paramagnets.

Another approach to U(v) organometallic complexes has recently been reported. Oxidation of neutral precursors $(\eta^5\text{-}C_5Me_5)U(NMe_2)_3(THF)$ and $(\eta^5\text{-}C_5Me_5)_2U(NEt_2)_2$ with $AgBPh_4$ gives rise to the corresponding cationic derivatives $[(\eta^5\text{-}C_5Me_5)U(NMe_2)_3(THF)][BPh_4]$ and $[(\eta^5\text{-}C_5Me_5)_2U(NEt_2)_2]$ $[BPh_4]$ (Boisson *et al.*, 1995). The electronic structure of these complexes was subsequently examined by EPR in frozen solution (Gourier *et al.*, 1997). It was shown that the interaction of the metal 5f orbitals with the cyclopentadienyl and amido ligands are sufficiently small and that the $J = 5/2$ ground state quantum number for U(v) remains a good quantum number for the complexes; the 5f orbitals are essentially nonbonding, and any covalent bonding interaction must therefore involve metal 6d orbitals.

(d) Hexavalent chemistry

Historically, there have been extremely few examples of non-aqueous compounds of hexavalent actinides, despite the prevalence of the actinyl ion (AnO_2^{2+}) for the elements U to Am. Attempts to prepare alkyl- or cyclopentadienyl compounds of the actinyl ions were met with reduction of the metal center (Seyam, 1982). In the last 10 years, a class of formally hexavalent cyclopentadienyluranium complexes has been prepared that is alternatively stabilized by the presence of organoimido substituents. The complex $(\eta^5\text{-}C_5Me_5)_2U(=NC_6H_5)_2$ was first prepared by the oxidation of $[Li(TMEDA)]$ $[(\eta^5\text{-}C_5Me_5)_2U(=NC_6H_5)Cl]$ with phenyl azide (Arney *et al.*, 1992; Arney and Burns, 1995), although other routes have since been devised (Fig. 25.19). The structure of the complex is shown in Fig. 25.20.

The complex has a pseudo-tetrahedral bent metallocene geometry, with a N–U–N angle of 98.7(4)°. This bent E=U=E moiety is quite different from the linear O=U=O angle found in the uranyl ion, and may be attributed to the strong donor character of the pentamethylcyclopentadienyl groups. The short uranium–nitrogen distances [1.952(7) Å], and the near-linear U–N–C bond angle [177.8(6)°] are consistent with the formulation of the ligands as organoimido groups. The organoimido ligands are remarkably unreactive in comparison with their Group 4 d-transition metal counterparts (Walsh *et al.*, 1988, 1992, 1993; Baranger *et al.*, 1993), showing no reaction with unsaturated
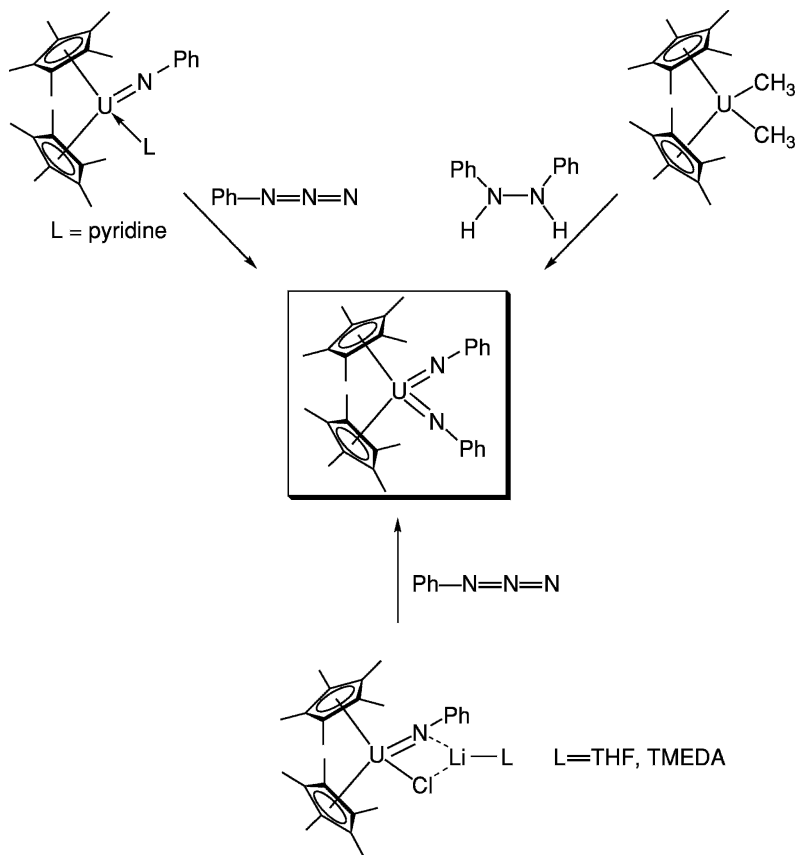
Fig. 25.19 *Synthetic pathways to (η^5-C_5Me_5)$_2$U(=NC$_6$H$_5$)$_2$ (Arney et al., 1995).*

substrates, MeI, or ammonia. This, coupled with the observation that the U–C$_{ring}$ bond distances [2.72(1)–2.75(1) Å] are comparable with those found in typical U(IV) metallocenes, argues for some degree of covalency in the U–N bonding. In order to invoke a higher bond order, it is necessary to suggest the involvement of 5f orbitals in stabilizing the nitrogen 2p lone pair electrons, as there is no 6d orbital of the appropriate symmetry. The U(VI) character of the complex is demonstrated in the lack of observable metal-based electronic transitions (f–f, f–d) in the near-IR spectrum, as well as the observation in the ^{1}H NMR spectrum that the complex appears to act as a temperature-independent paramagnet (Arney et al., 1992).

Since the initial report, other U(VI) bis(imido) compounds have been prepared with substituted arylimido and trimethylsilylimido ligands. In addition, U(VI) imido-oxo complexes (η^5-C$_5$Me$_5$)$_2$U(=NAr)(=O) (Ar = 2,4,6-Me$_3$C$_6$H$_2$, 2,4,6-^{t}Bu$_3$C$_6$H$_2$, 2,6-^{i}Pr$_2$C$_6$H$_3$) have been synthesized (Arney and Burns, 1995). These complexes have similar geometries to the bis(imido)
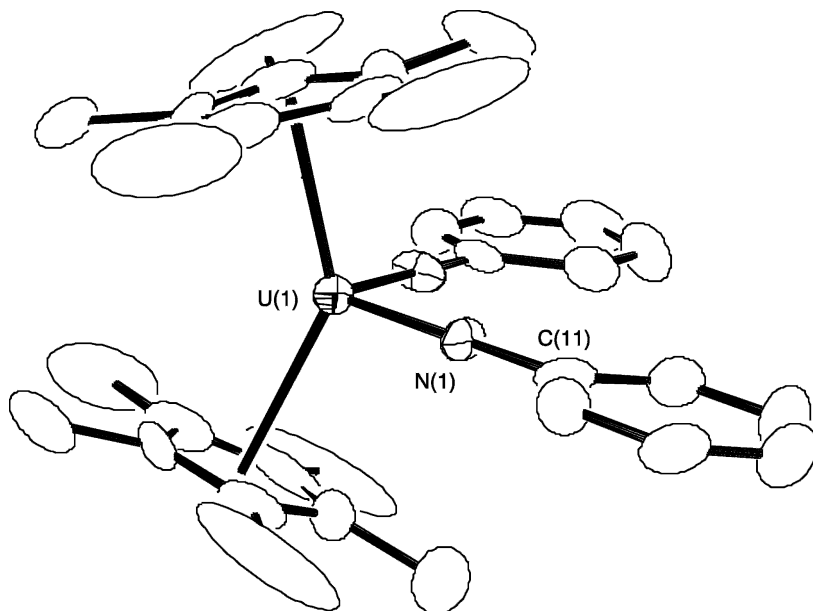
Fig. 25.20 *Crystal structure of* (η^5-C_5Me_5)$_2$U(=NC$_6$H$_5$)$_2$. (*Reprinted with permission from Arney* et al. (1992). *Copyright* 1992 *American Chemical Society.*)

derivatives, with a U–O bond length of 1.844(4) Å for the complex (η^5-C$_5$Me$_5$)$_2$U(=N-2,6-^{i}Pr$_2$C$_6$H$_3$)(=O). This bond length is significantly longer than that observed for uranyl ions, which may reflect a reduced bond order.

The ancillary ligand appears to make a difference in the accessibility of the U (VI) oxidation state. Complexes of uranium with the chelating ligand sets [Me$_2$Si (η^5-C$_5$Me$_4$)$_2$]$^{2-}$ and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]$^{2-}$ have been prepared and employed in analogous reactions to prepare organoimido complexes (Schnabel et al., 1999). While the bis(tetramethylcyclopentadienyl) *ansa*-metallocene successfully produces a bis(imido) compound, reaction of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]U(CH$_2$C$_6$H$_5$)$_2$ with N,N′-diphenylhydrazine yields only the tetravalent bridging imido complex and [{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}U(μ-NPh)]$_2$. Electrochemical investigations of the chloride compounds [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$] UCl$_2$ · 2LiCl · 4(Et$_2$O) and [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]UCl$_2$ · 2LiCl · 4(THF) suggest that the ancillary ligands have the capacity to significantly alter the redox activity of the metal center; [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)]UCl$_2$ · 2LiCl · 4 (THF) is more difficult to oxidize than [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$]UCl$_2$ · 2LiCl · 4 (Et$_2$O) by ∼ 0.24 V (vs [Cp$_2$Fe]$^{0/+}$). It has also been proposed that *ansa* bis (cyclopentadienyl) ligands sets generate more electrophilic metal centers (Lee et al., 1998; Shin et al., 1999).

As mentioned previously, the uranium imido complexes are generally unreactive, although a limited number of bond activation reactions have been

reported. The complex $(\eta^5\text{-}C_5Me_5)_2U(=NC_6H_5)_2$ will effect the homolytic cleavage of dihydrogen to yield a bis(amide) compound [equation (25.72)].

$$(25.72)$$
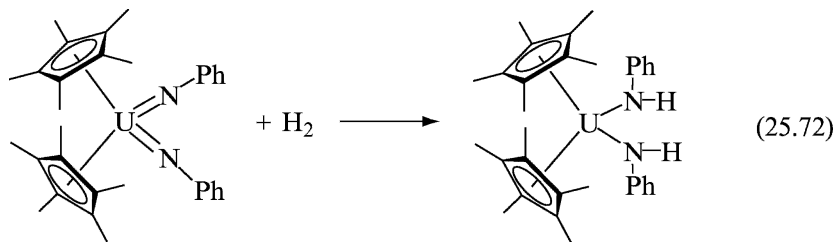
In an attempt to prepare more reactive organoimido functional groups, the more electron-rich adamantylimido complex $(\eta^5\text{-}C_5Me_5)_2U(=NAd)_2$ (Ad = Adamantyl) was prepared (Warner *et al.*, 1998). This complex undergoes decomposition under thermolysis to generate a complex derived from C–H activation of a pentamethylcyclopentadienyl methyl group (Peters *et al.*, 1999).
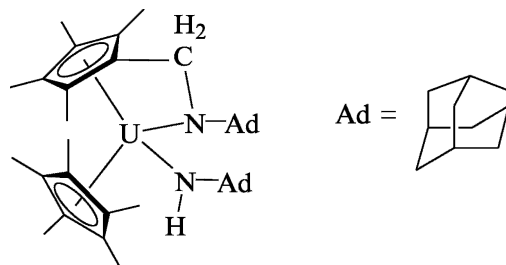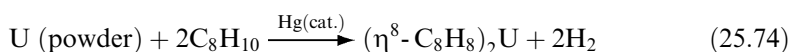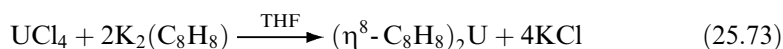

More reactive uranium–nitrogen multiple bonds may be generated by heteroatom substitution. The reaction of tetravalent $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$ with diphenyldiazomethane generates the mixed bis(imido) complex $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)(=N\text{-}N=CPh_2)$, which undergoes a cyclometallation reaction upon mild thermolysis to generate a uranium(IV) bis(amide) complex that results from net addition of a C–H bond of an ortho *tert*-butyl group across the N=U=N core (Kiplinger *et al.*, 2002).
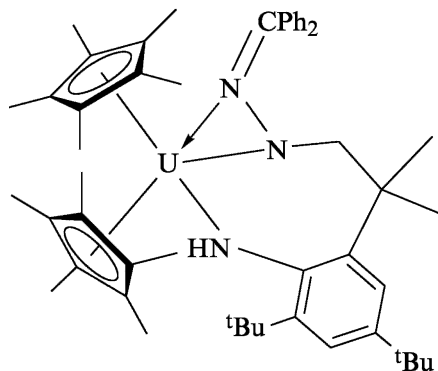
In select cases, U(VI) will catalyze chemical transformations; these will be discussed further in Chapter 26.

25.2.2 Cyclooctatetraenyl ligands

The chemistry of the cyclooctatetraenyl ligand and its substituted variants is significant in the development of actinide organometallic chemistry, and highlights differences between the f-elements and transition metals. The recognition that the lanthanides and actinides possess f-orbitals of the appropriate symmetry to interact with this carbocyclic ligand led to the theoretical prediction that a 'sandwich' compound could be prepared (Fischer, 1963). This prediction was subsequently validated by the preparation of $(\eta^8\text{-}C_8H_8)_2U$ (or 'uranocene') by the reaction of UCl_4 and the potassium salt of the dianion of cyclooctatetraene, $K_2(C_8H_8)$ [equation (25.73)] (Streitwieser and Müller-Westerhoff, 1968). Since that time, other synthetic routes to bis(cyclooctatetraenyl) complexes of the actinides have appeared [equations (25.74) and (25.75)] (Starks and Streitwieser, 1973; Starks *et al.*, 1974; Chang *et al.*, 1979; Rieke and Rhyne, 1979):

$$UCl_4 + 2K_2(C_8H_8) \xrightarrow{\text{THF}} (\eta^8\text{-}C_8H_8)_2U + 4KCl \qquad (25.73)$$

$$U \text{ (powder)} + 2C_8H_{10} \xrightarrow{\text{Hg(cat.)}} (\eta^8\text{-}C_8H_8)_2U + 2H_2 \qquad (25.74)$$

$$UF_4 + 2Mg(C_8H_8) \longrightarrow (\eta^8\text{-}C_8H_8)_2U + 2MgF_2 \qquad (25.75)$$

Bis(cyclooctatetraenyl) complexes of a number of other actinide elements have also been prepared, including Th (Streitwieser and Yoshida, 1969; Goffart *et al.*, 1972; Starks and Streitwieser, 1973), Pa (Goffart *et al.*, 1974; Starks *et al.*, 1974), Np (Karraker *et al.*, 1970), and Pu (Karraker *et al.*, 1970). Most are prepared by the methods of equations (25.73) and (25.74), although the plutonium compound was prepared from Cs_2PuCl_6.

A large number of substituted (cyclooctatetraenyl) complexes have also been reported. The addition of substituents has been employed to improve solubility, alter electronic properties, or investigate the dynamics of ring rotation reactions. The largest class of these are the 1,1′-disubstituted derivatives (Harmon *et al.*, 1977; Spiegl, 1978; Miller and DeKock, 1979; Spiegl and Fischer, 1979) prepared by the method of equation (25.76):

$$UCl_4 + 2K_2(C_8H_7R) \longrightarrow (\eta^8\text{-}C_8H_7R)_2U + 4KCl \qquad (25.76)$$
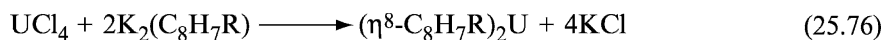
R = Me, Et, *n*-Bu, cyclo-C_3H_5, CH=CH_2, C_6H_5, OMe, OEt, O^{t}Bu, CO_2Et, *p*-C_6H_4R, NR_2, *p*-$C_6H_4NMe_2$, PR_2, $SiMe_3$, $SnMe_3$

1,1′-Disubstituted derivatives (R = Et, *n*-Bu) of neptunium and plutonium have also been prepared (Karraker, 1973). A number of uranocene derivatives with higher degrees of substitution have been reported (Streitwieser *et al.*, 1971;

Streitwieser and Harmon 1973; Streitwieser and Walker, 1975; Solar *et al.*, 1980; LeVanda and Streitwieser, 1981; Miller *et al.*, 1981; Lyttle *et al.*, 1989), including several with exocyclic ligands (Luke *et al.*, 1981; Zalkin *et al.*, 1982; Streitwieser *et al.*, 1983). The silylated derivatives $[\eta^5\text{-}1,3,5\text{-}(SiMe_3)_3C_8H_5]_2An$ have been prepared for An = Th, U, and Np (Apostolidis *et al.*, 1999). There is also one example of a bridged, or linked uranocene, $[\eta^8\text{:}\eta^8\text{-}1,2\text{-bis(cyclooctatetrae-nyldimethylsilyl)ethane]uranium}$ (Streitwieser *et al.*, 1993).
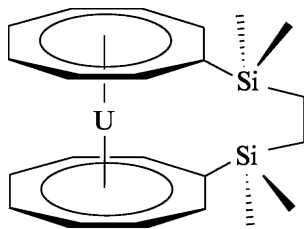
The molecular structure of many uranocene derivatives have been determined; the molecular structure of $(\eta^8\text{-}C_8H_8)_2U$ is shown in Fig. 25.21 (Zalkin and Raymond, 1969, Avdeef *et al.*, 1972).

The molecule possesses rigorous D_{8h} symmetry, with the eight-membered rings arranged in an eclipsed conformation. The averaged U–C_{ring} bond distance is 2.647(4) Å; all atoms of the cyclooctatetraene ligand lie within the plane

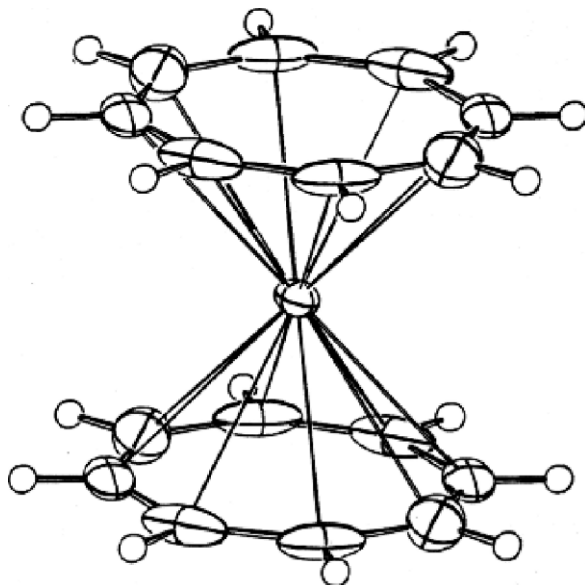**Fig. 25.21** *Crystal structure of* $(\eta^8\text{-}C_8H_8)_2U.$ *(Reprinted with permission from Zalkin and Raymond (1969). Copyright 1969 American Chemical Society.)*

to 0.02 Å. A comparison of the average C–C bond lengths for alternate sets of four bonds within the rings [1.396(5) and 1.388(27) Å] confirms the aromatic nature of the ligand. Substituted uranocene derivatives can show staggered ring geometries in the solid state; the rings in the complex bis(η^8-1,3,5,7-tetraphenylcyclooctatetraene)uranium are eclipsed (Templeton *et al.*, 1976), while the structure of bis(η^8-1,3,5,7-tetramethylcycloctatetraene)uranium reveals two symmetry-independent molecules in the asymmetric unit: one with staggered rings and one in which the rings are nearly eclipsed (Hodgson and Raymond, 1973).

The bonding in these highly symmetric compounds has been studied extensively by theoretical and experimental methods. The first theoretical treatments assumed that the principal metal–ligand interactions occurred through 5f orbitals, and that 6d orbitals would be too high in energy to interact with ligand-based orbitals. Improvement in computation methods (such as the inclusion of spin–orbit coupling) and inclusion of relativistic corrections have amended this bonding description. An *ab initio* calculation on uranocene incorporating relativistic core potentials and spin–orbit CI calculations suggests a significant degree of covalency in metal–ligand bonding; the 6d orbitals play a primary role in these interactions, and the 5f orbital involvement is secondary (Chang and Pitzer, 1989). A qualitative molecular orbital diagram is shown in Fig. 25.22.

The principal bonding interaction involves the metal $6d\delta$ and ligand $3e_{2g}$ orbitals, as well as the metal $5f\delta$ and ligand $3e_{2u}$ combination. Minimal interaction also exists between the metal $5f\phi$ orbitals and the ligand-based e_{3u} orbitals. The dashed line in the figure shows the impact of including relativistic effects in the calculations, further stabilizing a d_{z^2} orbital, making it the lowest unoccupied molecular orbital, housing any unpaired metal electrons (the orbital is essentially metal–ligand nonbonding).

Experimental probes of bonding in actinocenes have included chemical reactivity, magnetism, NMR spectroscopy, optical spectroscopy, Np-237 Mössbauer spectroscopy, and photoelectron spectroscopy (PES) (Burns and Bursten, 1989, and references therein). The initial observation of the stability of (η^8-C_8H_8)$_2$U to hydrolysis (relative to (η^8-C_8H_8)$_2$Th) suggested a higher degree of covalency in bonding in the uranium complex. Attempts have been made to derive the magnetic moment for bis(cyclooctatetraene) complexes of U, Np, and Pu. For example, (η^8-^{t}BuC$_8$H$_7$)$_2$Pu is reported to have a $J = 0$ ground state and exhibits temperature-independent paramagnetism (Karraker, 1973). The first predictions of the magnetism were based on the assumption of ionic bonding (weak crystal-field perturbations) and simple *L*–*S* coupling models (Karraker *et al.*, 1970). Deviations of the calculated moments from the observed were corrected by application of an empirical 'orbital reduction factor' described as a measure of covalency in bonding. Later non-relativistic calculations provided a better fit to experimentally observed magnetic moments between 10 and 80 K (Hayes and Edelstein, 1972). These calculations suggested a significant degree of covalency, but it was pointed out that the high value assumed for the
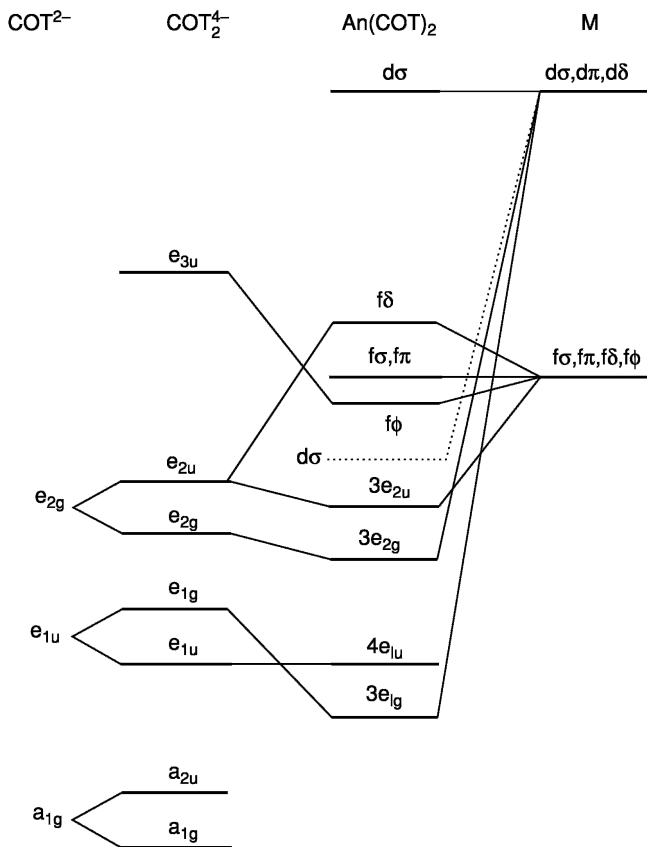
Fig. 25.22 *Molecular orbital diagram of* $(\eta^8\text{-}C_8H_8)_2U$. *(Reprinted with permission from Parry* et al. *(1999). Copyright 1999 American Chemical Society.)*

5f valence state ionization potential could cause an overestimation of the covalence in bonding.

Some of the most compelling evidence for the degree of covalency in uranocene (and particularly for a 5f orbital role) comes from variable energy photoelectron spectroscopy (Brennan *et al.*, 1989). In general, metal-based electrons are known to have an energy-dependent cross section. In $(\eta^8\text{-}C_8H_8)_2U$ (over the energy range 24–125 eV), the f-band shows cross-section features attributable to 5f resonant photoemission in the vicinity of the 5d–5f giant resonant absorption ($h\nu = 101$ and 110 eV). The e_{2g} and e_{2u} bands also show small cross-section maxima at these energies; that for the e_{2u} ionization being the more intense. The mapping of the intensity changes of the f-band by the e_{2u} band provides strong evidence for f-orbital contribution to valence orbitals in this molecule (Fig. 25.23).

Ring dynamics (rotation and exchange) have been studied by means of variable-temperature NMR spectroscopy for substituted derivatives. It is
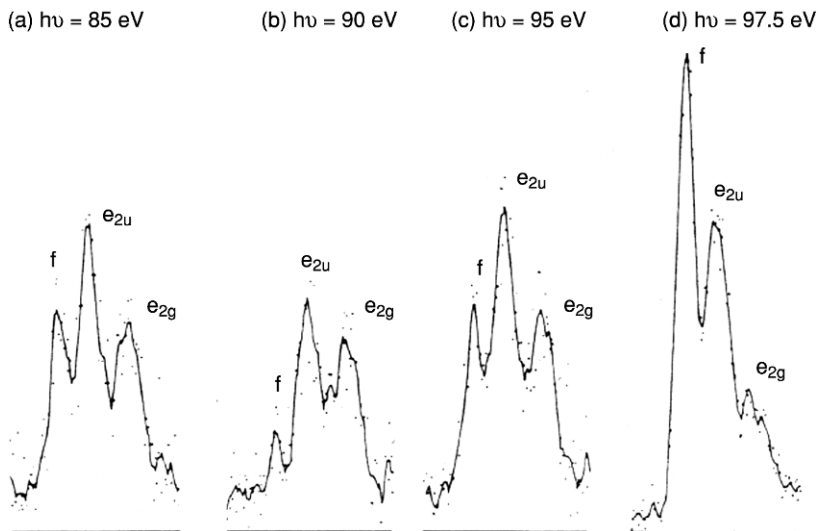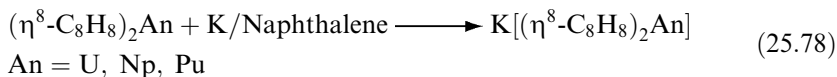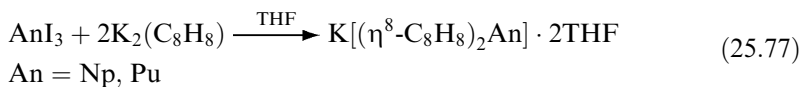
Fig. 25.23 *Variable energy photoelectron spectrum of (η^5-C$_8$H$_8$)$_2$U. (Reprinted with permission from Brennan et al. (1989). Copyright 1989 American Chemical Society).*

found that uranocenes undergo rapid ligand exchange with cyclooctatetraene dianions (LeVanda and Streitwieser, 1981). The barrier to ring rotation has been estimated at 8.3 kcal mol^{-1} for (η^8-1,4-^{t}Bu$_2$C$_8$H$_6$)$_2$U; this compares with a value of 13.1 kcal mol^{-1} for a d-transition metal metallocene analog (η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Fe (Luke and Streitwieser, 1981).

In addition to the neutral tetravalent actinocenes, synthetic routes have been devised to anionic trivalent derivatives, [(η^8-C$_8$H$_8$)$_2$An]$^-$, either by treatment of trivalent precursors with K$_2$(C$_8$H$_8$) [equation (25.77)], or by reduction of the actinocene [equation (25.78)] (Karraker and Stone, 1974; Billiau *et al.*, 1981; Eisenberg *et al.*, 1990).
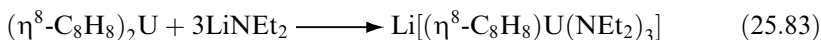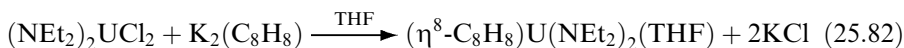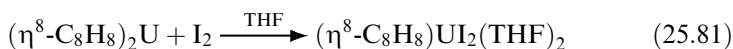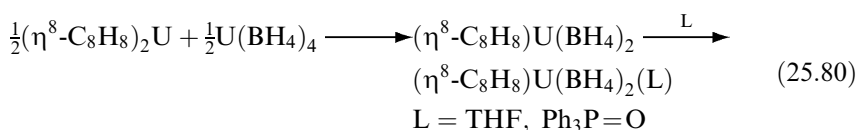
$$\text{AnI}_3 + 2\text{K}_2(\text{C}_8\text{H}_8) \xrightarrow{\text{THF}} \text{K}[(\eta^8\text{-C}_8\text{H}_8)_2\text{An}] \cdot 2\text{THF}$$
$$\text{An} = \text{Np, Pu}$$
(25.77)

$$(\eta^8\text{-C}_8\text{H}_8)_2\text{An} + \text{K/Naphthalene} \longrightarrow \text{K}[(\eta^8\text{-C}_8\text{H}_8)_2\text{An}]$$
$$\text{An} = \text{U, Np, Pu}$$
(25.78)

The Mössbauer spectrum of the neptunium compound [(η^8-C$_8$H$_8$)$_2$Np]$^-$ confirms that the metal is in the trivalent oxidation state, and suggests a lower overall degree of covalency in metal–ligand bonding than in tetravalent derivatives. Most recently, the reduction route has been extended to generate trivalent actinocenes K(DME)$_2$[{η^8-1,4-(^{t}BuMe$_2$Si)$_2$C$_8$H$_6$}$_2$An] (An = Th, U), wherein the bulky silyl substituents are proposed to provide both kinetic and

thermodynamic stabilization of the Th(III) compound (Parry *et al.*, 1999). The complexes display asymmetric An–C_{ring} distances, owing to the 'capping' of one ring by close association with the potassium counter-ion. The observed magnetic moment for the thorium compound is $1.20\mu_B$ at 293 K, which is low when compared to the spin-only value for one unpaired electron ($1.73\mu_B$). It has been proposed that the low moment is due to mixing of the ground state magnetic component with low-lying excited states.

   Intermolecular electron-transfer rates have been studied for uranocene and substituted derivatives of uranium, neptunium, and plutonium (Eisenberg *et al.*, 1990) by examining the variable-temperature NMR spectra of mixtures of $(\eta^8\text{-}C_8H_8)_2An$ and $[(\eta^8\text{-}C_8H_8)_2An]^-$. In all cases, electron transfer rates are rapid. Specific rates could not be derived for uranium and plutonium derivatives due to the small chemical shift differences between analogous An(IV) and An(III) compounds, but in the case of $(\eta^8\text{-}^tBuC_8H_7)_2Np$, the rate has been estimated to be of the same order of magnitude as comparable lanthanide cyclooctatetraene compounds ($\sim 10^7\ \text{M}^{-1}\text{s}^{-1}$).

   The chemistry of actinide complexes containing a single cyclooctatetraenyl ring began with a report of $(\eta^8\text{-}C_8H_8)NpI\cdot x$THF, prepared by reaction of $NpI_3(THF)_4$ and $K_2(C_8H_8)$ in THF (Karraker and Stone, 1977). The first structurally characterized examples of this class of compounds included both derivatives of uranium $[(\eta^8\text{-}C_8H_8)UCl_2(\text{pyridine})_2$ and $(\eta^8\text{-}C_8H_8)U(\text{MeCOCH-COMe})_2$; Boussie *et al.*, 1990] and thorium $[(\eta^8\text{-}C_8H_8)ThCl_2(THF)_2$; Zalkin *et al.*, 1980]. Since these initial reports, other entries into mono-ring chemistry have been established, principally those involving redistribution [equations (25.79) and (25.80)] (LeVanda *et al.*, 1980; Gilbert *et al.*, 1988; Baudry *et al.*, 1990a), halogenation [equation (25.81)] (Berthet *et al.*, 1990), and metathesis [equations (25.82) and (25.83)] (Boisson *et al.*, 1996a).

$$\tfrac{1}{2}(\eta^8\text{-}C_8H_8)_2Th + ThCl_4 \longrightarrow (\eta^8\text{-}C_8H_8)ThCl_2 \qquad (25.79)$$

$$\tfrac{1}{2}(\eta^8\text{-}C_8H_8)_2U + \tfrac{1}{2}U(BH_4)_4 \longrightarrow (\eta^8\text{-}C_8H_8)U(BH_4)_2 \xrightarrow{\ L\ }$$
$$(\eta^8\text{-}C_8H_8)U(BH_4)_2(L) \qquad (25.80)$$
$$L = THF,\ Ph_3P{=}O$$

$$(\eta^8\text{-}C_8H_8)_2U + I_2 \xrightarrow{\ THF\ } (\eta^8\text{-}C_8H_8)UI_2(THF)_2 \qquad (25.81)$$

$$(NEt_2)_2UCl_2 + K_2(C_8H_8) \xrightarrow{\ THF\ } (\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF) + 2KCl \quad (25.82)$$

$$(\eta^8\text{-}C_8H_8)_2U + 3LiNEt_2 \longrightarrow Li[(\eta^8\text{-}C_8H_8)U(NEt_2)_3] \qquad (25.83)$$
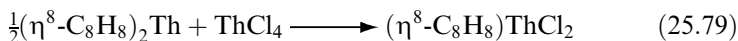
Collectively, these complexes further serve as precursors to a variety of mono (cyclooctatetraenyl) derivatives, including alkyl (Berthet *et al.*, 1994), alkoxide (Arliguie *et al.*, 1992), amide (Gilbert *et al.*, 1988; Le Borgne *et al.*, 2000), and

thiolate (Leverd *et al.*, 1994; Arliguie *et al.*, 2000) complexes. Mixed-ring derivatives containing both cyclooctatetraenyl and cyclopentadienyl ligands have similarly been prepared by metathesis reactions (Gilbert *et al.*, 1989; Berthet *et al.*, 1994, Boisson *et al.*, 1996b). The complex $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)$ Th$[CH(SiMe_3)_2]$ undergoes hydrogenolysis to yield the hydride compound $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)$ThH (Gilbert *et al.*, 1989).

An interesting example of the introduction of a bridging cyclooctatetraenyl ligand is found in the reaction of $(\eta^5\text{-}C_5Me_5)_3$U with cyclooctatetraene (Evans *et al.*, 2000). As previously discussed, the bulky tris(pentamethylcyclopentadienyl) complex can act as a multi-electron reductant. Reaction with C_8H_8 produces the complex $[(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)U]_2(\mu\text{-}C_8H_8)$, along with $(C_5Me_5)_2$. The complex consists of two mixed-ring U(IV) units coordinated to a bridging $C_8H_8^{2-}$ ligand (Fig. 25.24). The bridging ring is non-planar and appears bound to the two metal centers in an unusual η^3:η^3 manner, with one carbon in common.

Cationic derivatives of the formula $[(\eta^8\text{-}C_8H_8)U(NEt_2)(THF)_2][BPh_4]$ and $[(\eta^8\text{-}C_8H_8)U(BH_4)(THF)_2][BPh_4]$ may be produced by protonation of the respective tetravalent precursors $(\eta^8\text{-}C_8H_8)UX_2(THF)$ with $[NEt_3H][BPh_4]$ (Boisson *et al.*, 1996b; Cendrowski-Guillaume *et al.*, 2000). Reaction of the latter with additional ammonium salt in the presence of hexamethylphosphoramide (HMPA) yields the unique dicationic species $[(\eta^8\text{-}C_8H_8)U(HMPA)_3]$ $[BPh_4]_2$. The U–N bond in the complex $[(\eta^8\text{-}C_8H_8)U(NEt_2)(THF)_2][BPh_4]$ is susceptible to protonation by alcohols and thiols, and will insert CO_2, CS_2, or MeCN to generate the complexes $[(\eta^8\text{-}C_8H_8)U(E_2CNEt_2)(THF)_2][BPh_4]$ (E = O, S) and $[(\eta^8\text{-}C_8H_8)U(NC(Me)NEt_2)(THF)_2][BPh_4]$.

Few trivalent derivatives of mono(cyclooctatetraenyl)uranium have been isolated, likely due to the facile ligand redistribution and disproportionation
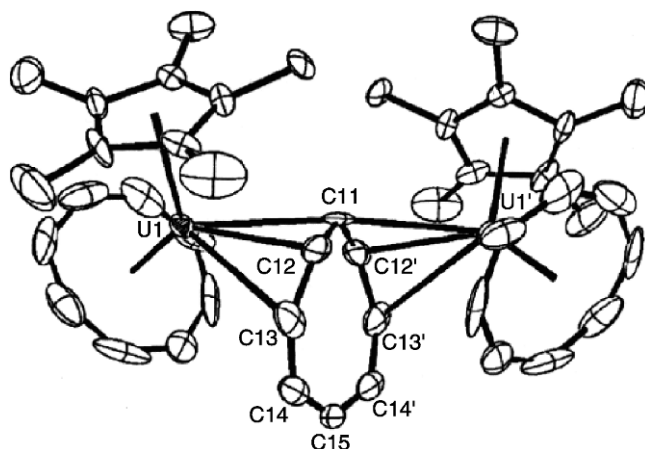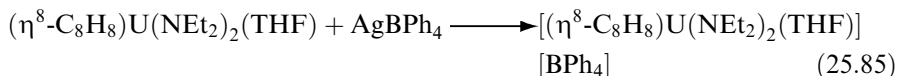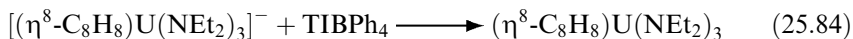

Fig. 25.24 *Crystal structure of* $[(\eta\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)U]_2(\mu\text{-}C_8H_8)$ *(Evans* et al.*, 2000).* *(Reprinted with permission from John Wiley & Sons, Inc.)*

reactions that give rise to uranocene. The complex $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)U$ (THF) is produced by reaction of $(\eta^5\text{-}C_5Me_5)UI_2(THF)$ with $K_2(C_8H_8)$ (Schake *et al.*, 1993); the 4,4′-dimethyl-2,2′-bipyridine adduct has been structurally characterized. The complex exists as a bent metallocene with a ring centroid–uranium–ring centroid angle of 138.2°. The average M–C_{ring} distances are consistent with the larger ionic radius of U(III). The aforementioned dication $[(\eta^8\text{-}C_8H_8)U(HMPA)_3][BPh_4]_2$ can be reduced by sodium amalgam to generate a monocation $[(\eta^8\text{-}C_8H_8)U(HMPA)_3][BPh_4]$ (Cendrowski-Guillaume *et al.*, 2001).

An interesting new class of pentavalent complexes supported by the cyclooctatetraenyl ligand has recently been developed. Oxidation of anionic U(IV) mono-ring amide complexes with TlBPh$_4$ or AgBPh$_4$ generates the corresponding pentavalent amide complexes as shown in equations (25.84) and (25.85) (Berthet and Ephritikhine, 1993; Boisson *et al.*, 1995).

$$[(\eta^8\text{-}C_8H_8)U(NEt_2)_3]^- + TIBPh_4 \longrightarrow (\eta^8\text{-}C_8H_8)U(NEt_2)_3 \qquad (25.84)$$

$$(\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF) + AgBPh_4 \longrightarrow [(\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF)] \\ [BPh_4] \qquad (25.85)$$

The molecular structure of $[(\eta^8\text{-}C_8H_8)U(NEt_2)_2(THF)][BPh_4]$ has been determined (Boisson *et al.*, 1996a). The amide ligands are susceptible to protonation by alcohols to yield alkoxide complexes. Pentavalent cyclooctatetraenyluranium compounds have been studied by EPR (Gourier *et al.*, 1997) and X-ray absorption spectroscopy (Den Auwer *et al.*, 1997). Analysis of EPR spectra suggested that (as for cyclopentadienyl ligands) chemical bonding with the cyclooctatetraenyl ligand occurs principally with the uranium 6d orbitals, except in the case of the tris(*iso*-propoxide) complex $(\eta^8\text{-}C_8H_8)U(O^iPr)_3$. In this complex, it was proposed that the 5f–O interaction is strong, so that *J* is no longer a good quantum number, and the weak-field approximation can no longer be considered valid.

25.2.3   Other carbocyclic ligands

(a)   Arene ligands

Although arene compounds of the d-transition metals were prepared early in the 20th century, their identity as η^6-ligands was not recognized until many years later. All previous carbocyclic ligands discussed in this article may be regarded to have a formal charge (e.g. $C_5H_5^-$, $C_8H_8^{2-}$), and so therefore may bind more strongly to actinide centers via Coulombic forces. In contrast, arenes are often regarded as neutral ligands, and so any interaction with a metal center might best be regarded as one involving significant electrostatic polarization of the ligand π-electrons, or alternatively, covalent bonding. Given the propensity of the later actinides to engage principally in ionic bonding, it is therefore not

surprising that arene complexes are restricted to the early actinides. Only uranium has been found to generate arene complexes. This suggests a greater propensity for uranium to engage in covalent bonding, consistent with the observation that U–C bonding in uranocene appears to be more covalent than in its thorium analog.

The initial method employed to prepare π-arene complexes of d-transition metals was the reducing Friedel–Crafts route developed by Fischer and Hafner (1955), involving reduction of a metal salt with aluminum powder, followed by reaction with an arene ligand. Extension of this method to reaction with UCl_4 produced the first π-arene complex, the trivalent species $(\eta^6\text{-}C_6H_6)U(AlCl_4)_3$ (Cesari *et al.*, 1971). The molecular structure of the complex consists of a pseudotetrahedral arrangement of the four ligands about uranium, with two bridging chlorides between each aluminum and uranium. The benzene ring was refined as an idealized model, with uranium–carbon distances of 2.91–2.92 Å. Toluene and hexamethylbenzene analogs have also been described (Cotton and Schwotzer, 1987; Garbar *et al.*, 1996). Subsequently, two polymetallic tetravalent complexes were prepared by a variant of this procedure as depicted in equation (25.86) (Cotton and Schwotzer, 1985; Campbell *et al.*, 1986):

$$UCl_4 + AlCl_3 + C_6Me_6 \xrightarrow{\text{hexanes}}$$ $$(25.86)$$
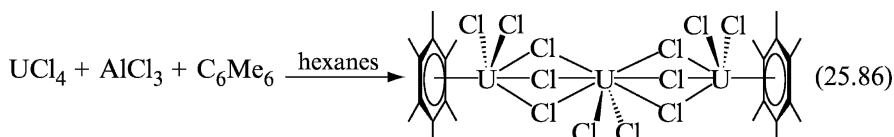
The complex $[(\eta^6\text{-}C_6Me_6)Cl_2U(\mu\text{-}Cl)_3UCl_2(\eta^6\text{-}C_6Me_6)][AlCl_4]$ was isolated by further reduction with zinc powder. Once isolated, the compounds are insoluble in non-coordinating solvents. The cation of the molecule $[(\eta^6\text{-}C_6Me_6)Cl_2U(\mu\text{-}Cl)_3UCl_2(\eta^6\text{-}C_6Me_6)][AlCl_4]$ is shown in Fig. 25.25.

The arene ligands in these complexes are all found to be weakly bound, and are readily displaced by other bases such as THF or acetonitrile. Detailed structural studies have been conducted on these arene complexes. In no case does the arene ring appear to significantly deviate from planarity. The U–C_{arene} bond distances in these complexes are long for actinide–carbocyclic ligands; they fall in the range 2.89(2)–2.96(2) Å.

η^6-Arene complexes of trivalent uranium have also been isolated from the thermolysis of $U(BH_4)_4$ in aromatic solvents (Baudry *et al.*, 1989a). The mesitylene complex $(\eta^6\text{-mesitylene})U(BH_4)_3$ was initially isolated from that solvent. The weakly coordinated arene is readily displaced by other aromatic substrates, however, and the hexamethylbenzene complex is reported to be more stable to displacement in toluene solution.

More recently, reduction of tetravalent actinide amide complexes has been found to give rise to an interesting series of 'inverted sandwich', or bridging arene complexes (Diaconescu *et al.*, 2000; Diaconescu and Cummins, 2002). Reduction of $[N(^tBu)Ar]_3UI$ (Ar = 3,5-$Me_2C_6H_3$) by KC_8 in toluene generates the complex $[N(^tBu)Ar]_2U(\mu\text{-}\eta^6,\eta^6\text{-}C_7H_8)U[N(^tBu)Ar]_2$. The related compound
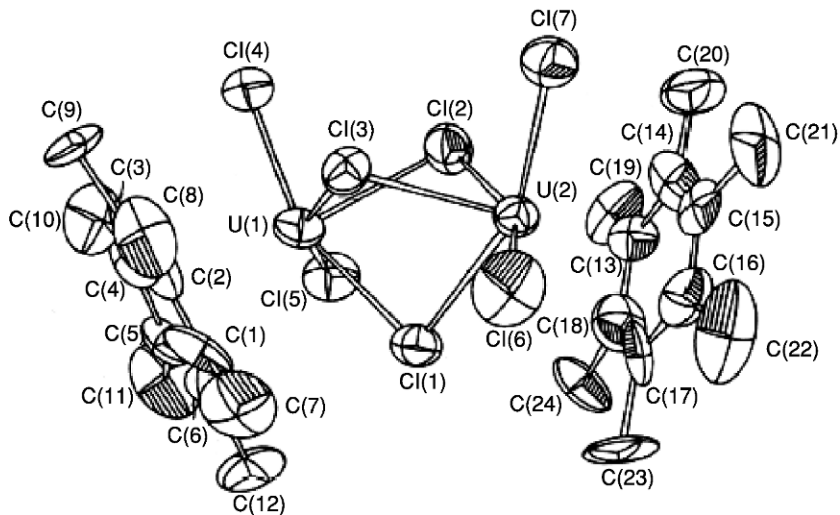
Fig. 25.25   *Molecular structure of* $[(\eta^6\text{-}C_6Me_6)Cl_2U(\mu\text{-}Cl)_3UCl_2(\eta^6\text{-}C_6Me_6)]^+$. (*Reprinted with permission from Campbell* et al. (1986). *Copyright* 1986 *American Chemical Society.*)

$[N(R)Ar]_2U(\mu\text{-}\eta^6,\eta^6\text{-}C_7H_8)U[N(R)Ar]_2$ (R = adamantyl; Ar = 3,5-$Me_2C_6H_3$), could also be generated in low yield by reaction of $UI_3(THF)_4$ with $(Et_2O)LiN$ (R)Ar in toluene. Structural characterization reveals that the complex contains a bridging toluene molecule bound symmetrically to the two metal centers (Fig. 25.26).

The U–C_{ring} distances are short relative to other η^6-arene complexes, ranging from 2.503(9) to 2.660(8) Å. In addition, there is a slight distortion in the bound toluene ligand; the average C–C distances increase by approximately 0.04 Å from that in free toluene. Density functional calculations carried out on the molecule suggest that four electrons are engaged in the formation of two δ-symmetry back-bonds involving U 6d and 5f orbitals and the LUMO of the bridging arene molecule. The complex acts as a 'uranium(II)' reagents in subsequent reactions, and can effect four-electron reduction of substrates.

(b)   Other carbocyclic ligands (cycloheptatrienyl, pentalene, endohedral metallofullerenes)

Complexes of actinides with five-, six-, and eight-membered rings have already been described. It is only recently that this series has been completed with the preparation of complexes employing the cycloheptatrienyl ligand. Unlike the other members of this series, the first complex to be prepared was not the sandwich complex, but rather the 'inverse sandwich' compound $[X_3U(\mu\text{-}\eta^7, \eta^7\text{-}C_7H_7)UX_3]^-$ (X = NEt_2, BH_4), formed in the reaction of $U(NEt_2)_4$ or
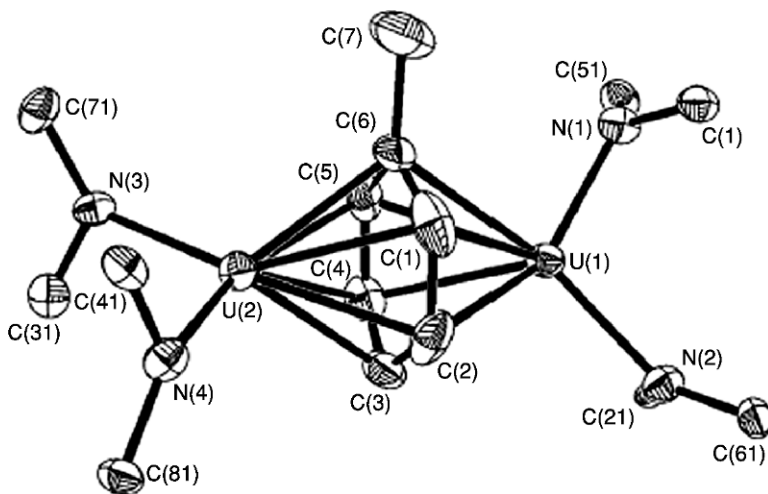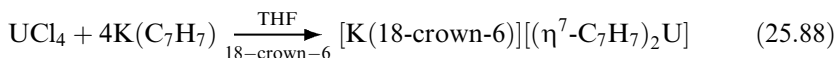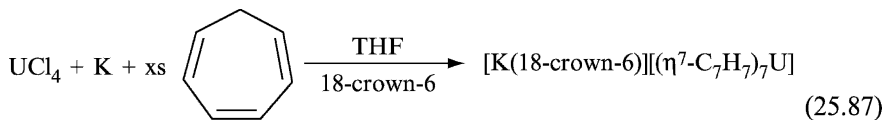
Fig. 25.26 *Molecular structure of* $[N(R)Ar]_2U(\mu\text{-}\eta^6,\eta^6\text{-}C_7H_8)U[N(R)Ar]_2$ *(R = adamantyl, Ar = 3,5-Me$_2$C$_6$H$_3$). Bulky peripheral substituents omitted for clarity.* (*Reprinted with permission from Diaconescu* et al. (2000). *Copyright* 2000 *American Chemical Society.*)

$U(BH_4)_4$ with $K(C_7H_9)$ (Arliguie *et al.*, 1994). The sandwich complex [K(18-crown-6)][$(\eta^7\text{-}C_7H_7)_2U$] has subsequently been prepared [equations (25.87) and (25.88)] (Arliguie *et al.*, 1995).

$$UCl_4 + K + xs \quad \overset{\text{THF}}{\underset{\text{18-crown-6}}{\longrightarrow}} \quad [K(18\text{-crown-6})][(\eta^7\text{-}C_7H_7)_7U] \tag{25.87}$$

$$UCl_4 + 4K(C_7H_7) \xrightarrow[\text{18-crown-6}]{\text{THF}} [K(18\text{-crown-6})][(\eta^7\text{-}C_7H_7)_2U] \tag{25.88}$$

The molecular structure of the anion $[(\eta^7\text{-}C_7H_7)_2U]^-$ is shown in Fig. 25.27.

The complex consists of a sandwich of crystallographic C_{2h} symmetry. The cycloheptatrienyl ligands are planar to within 0.02 Å, and display a regular heptagonal geometry. The two rings are staggered. The uranium–carbon bond distances average 2.53(2) Å, significantly shorter than those found for typical tetravalent uranium cyclopentadienyl and cyclooctatetraenyl complexes. Similar bond shortening has been observed in M–C bonds in early transition metal cycloheptatrienyl complexes, and has been explained as reflecting electron transfer from the metal to the ligand, with an increase in metal valency. Some attention has therefore been given to the assignment of oxidation state in this complex. A density functional study examined the question of bonding in the complexes $(\eta^7\text{-}C_7H_7)_2An$ (Li and Bursten, 1997). It was found that the 5f δ-symmetry orbitals not only participate in the bonding with e_2'' pπ orbitals of the C_7H_7 rings, but are as important as the
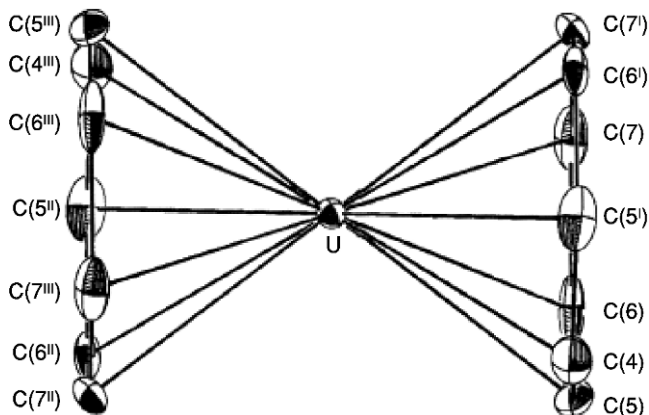
Fig. 25.27   *Molecular structure of* $[(\eta^7\text{-}C_7H_7)_2U]^-$ *(Arliguie et al., 1995). (Reproduced by permission of The Royal Society of Chemistry.)*

symmetry-appropriate 6d orbitals in stabilizing the ligand-based fragment orbitals. The 5f percentage in frontier e_2 molecular orbitals increases across the series, although not the energetic stabilization. The most important bonding interactions are shown in Fig. 25.28.

Although only one valence electron resides in a principally 5f localized orbital in the known uranium complex, a formal oxidation state of +3 ($5f^3$) was assigned to uranium, based on the fact that the $3e_2''$ molecular orbitals (occupied by four electrons) are nearly 50% 5f in character, and so two of these electrons were assigned to the metal. EPR and ENDOR studies of $[(\eta^7\text{-}C_7H_7)_2U]^-$ suggest that the complex could be treated as $5f^1$, with a ground state molecular orbital comprised of both $5f_\pi$ and $5f_\sigma$ orbitals (Gourier et al., 1998).

Although the cyclooctatetraenyl dianion has been extensively employed in actinide organometallic chemistry, another C8 ligand, the pentalene dianion $(C_8H_6^{2-})$ has been far less studied, due to the difficulty inherent in its preparation. The ligand may be considered to be derived from $C_8H_8^{2-}$ by removal of two hydrogen atoms with generation of a C–C bond to yield two fused five-membered rings.
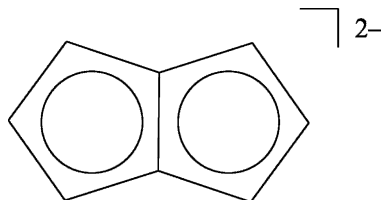
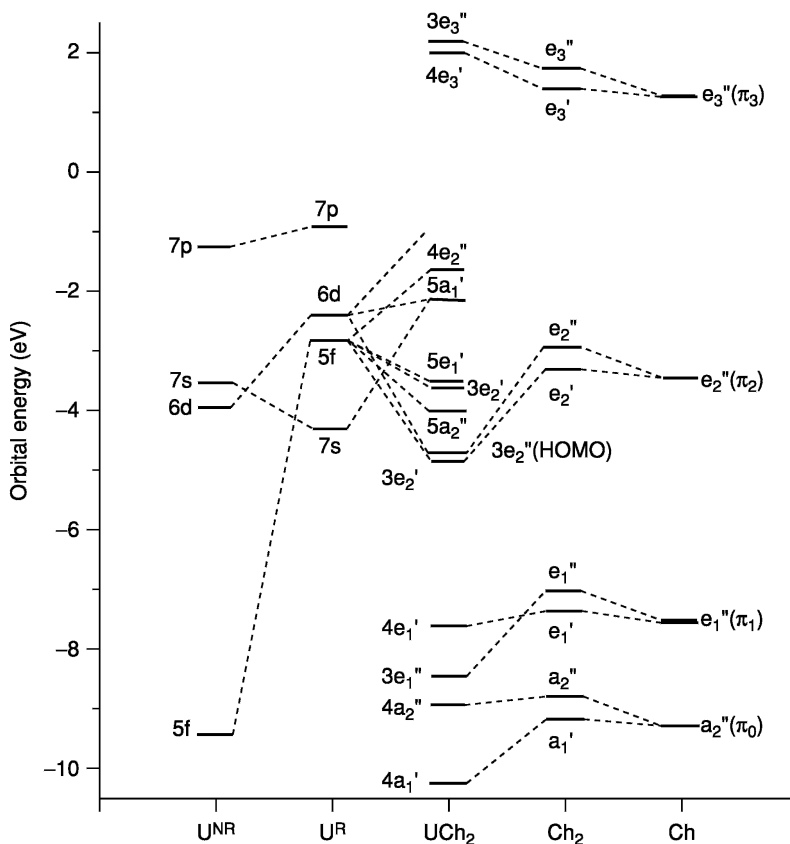**Fig. 25.28** *Bonding interactions in $[(\eta^7\text{-}C_7H_7)_2U]^-$ under D_{7h} symmetry. U^{NR} and U^R indicate atomic orbital energies at the nonrelativistic and relativistic levels, respectively. $Ch = \eta^7\text{-}C_7H_7$. (Reprinted with permission from Li and Bursten (1997). Copyright 1997 American Chemical Society.)*

A substituted derivative of the pentalene ligand, $[1,5\text{-}(Si^iPr_3)_2C_8H_4]^{2-}$, has been employed to generate the neutral bis(ligand) uranium and thorium compounds $[\eta^8\text{-}1,5\text{-}(Si^iPr_3)_2C_8H_4]_2Th$ and $[\eta^8\text{-}1,5\text{-}(Si^iPr_3)_2C_8H_4]_2U$, which are rare examples of η^8-coordinated pentalene ligands (Cloke and Hitchcock, 1997; Cloke *et al.*, 1999). The molecular structure of the thorium compound revealed it to be a near-equal mixture of staggered and eclipsed sandwich isomers in a disordered structure. The two isomers are generated by thorium binding to two different prochiral faces of the ligand; as such the isomers are not found in NMR studies to interconvert on any timescale in solution.
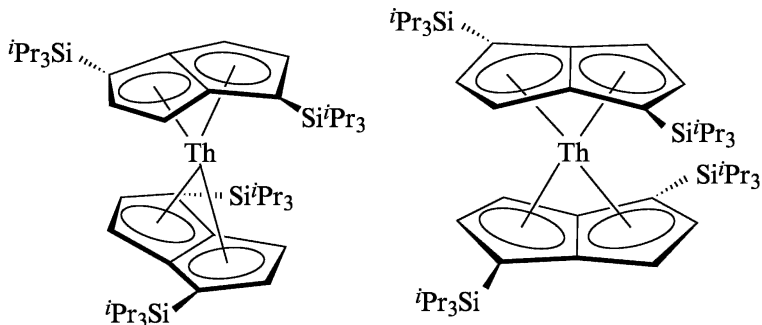
The larger actinide ion accommodates a smaller bending, or 'folding' angle about the bridgehead C–C bond (24°, compared to 33° in a related tantalum compound). The Th–C_{ring} bond lengths vary from 2.543(10) to 2.908(11) Å. Photoelectron spectroscopy studies and density functional calculations present a consistent picture of the bonding in these complexes. Metal–ligand bonding takes place chiefly through four molecular orbitals with both 6d and 5f orbital involvement (although 6d orbitals again make a larger contribution); the uranium compound further houses two unpaired electrons in 5f-based orbitals. Both the f-ionization and the highest lying ligand orbitals have lower ionization energies than uranocene or $(\eta^5\text{-}C_5H_5)_4U$, suggesting that the pentalene dianion is a stronger donor ligand than other carbocyclic groups.

Among the largest discrete organometallic ligands that could be identified would be fullerenes, and many metal-encapsulated derivatives, or endometallo-fullerene complexes have been identified. The first reports of possible uranium encapsulation (Haufler *et al.*, 1990; Guo *et al.*, 1992) suggested that the principal products from laser vaporization experiments with graphite and UO_2 in a supersonic cluster beam apparatus included $U@C_{60}$ and the product of the unusually small cage $U@C_{28}$. XPS studies of the bulk product suggested a uranium valence of 4+ in the complex. A subsequent report identified $U@C_{60}$ and $U@C_{82}$ in the sublimed soot (Diener *et al.*, 1997). Most recently, metallo-fullerenes of uranium, neptunium, and americium have been produced via arc-discharge using a carbon rod containing lanthanum as a carrier with [237]U, [239]Np, and [240]Am as radiotracers (Akiyama *et al.*, 2001). The metallofullerenes were purified by CS_2 extraction and toluene HPLC elution. The dominant products identified for neptunium and americium were $An@C_{82}$. Two uranium-containing metallofullerenes were identified, $U@C_{82}$ and $U_2@C_{80}$. Based upon comparison with the optical spectra of lanthanide analogs, it was suggested that the oxidation state in these complexes might best be regarded as +3.

Electronic structure calculations have been carried out on $U@C_{60}$, $U@C_{28}$, and $Pa@C_{28}$ (Chang *et al.*, 1994; Zhao and Pitzer, 1996). The ground state of $Pa@C_{28}$ was found to have one electron in a cage π^* orbital, suggested a higher overall oxidation state for the metal. Similarly, $U@C_{28}$ had a $(\pi^*)^1(5f)^1$

diamagnetic ground state. In all cases, the complexes show extensive mixing of π-orbitals with both 6d and 5f orbitals, suggesting strong bonding.

25.2.4 Allyl, pentadienyl and related π-ligands

Allyl complexes with associated cyclopentadienyl ligands have been discussed previously. There are, however, several classes of complexes reported for thorium and uranium that contain allyl or other 'open' π-system ligands. Tetrakis (allyl) and substituted allyl complexes of thorium and uranium can be prepared by the reaction of the tetrachloride complexes with the appropriate Grignard reagent (Wilke *et al.*, 1966; Lugli *et al.*, 1969; Brunelli *et al.*, 1973), although they are thermally unstable and decompose at temperatures greater than –20°C [equation (25.89)].

$$\text{AnCl}_4 + 4\text{C}_3\text{H}_5\text{MgX} \longrightarrow \text{[An]} + 4\text{MgXCl} \qquad (25.89)$$

An = Th, U

Mixed-ligand complexes are known to be somewhat more stable. As an example, the reaction of $(\eta^5\text{-C}_3\text{H}_5)_4\text{U}$ with aliphatic alcohols has been reported to generate the mixed-ligand complexes $[(\eta^5\text{-C}_3\text{H}_5)_2\text{An(OR)}_2]_2$ (Brunelli *et al.*, 1979); the structure of the isopropoxide derivative has been determined. The complex exists as a dimer in the solid state, with two bridging alkoxide ligands, although they are proposed to be monomeric in THF solution. The allyl ligands are bound trihapto, which is consistent with the proposed mode of coordination for allyl ligands in the homoleptic compounds, as determined by solution NMR studies. A further example is provided by the reaction of $(\eta^5\text{-C}_3\text{H}_5)_4\text{U}$ with 2,2′-bipyridine. The product generated is more thermally stable, likely due to the incorporation of three Lewis bases into the coordination sphere of the metal. It is proposed that this is made possible by the transfer of two of the allyl groups to one or more of the bipyridine ligands (Vanderhooft and Ernst, 1982).

A more stable 'open' π-system is provided by the pentadienyl ligand. Since pentadienyl complexes are generally considered to be more reactive than cyclopentadienyl ligands, it has often proven necessary to employ substituted derivatives. The 2,4-dimethylpentadienyl ligand was first used in the generation of a homoleptic compound of U(III) [equation (25.90)] (Cymbaluk *et al.*, 1983b).

$$\text{UCl}_3 \cdot n\text{THF} + 3\text{K(2,4-Me}_2\text{C}_5\text{H}_5) \longrightarrow \text{[U]} + 3\text{KCl} \quad (25.90)$$
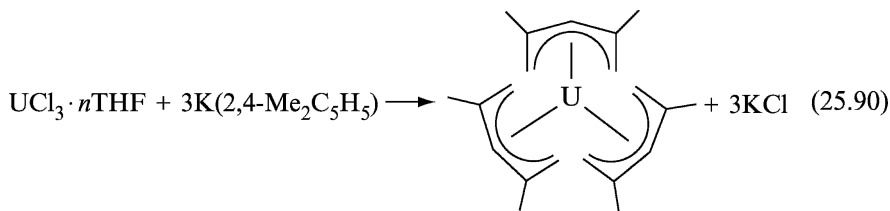
The mixed-ligand complex [K(18-crown-6)][$(\eta^5$-2,4-Me$_2$C$_5$H$_5)_2$U(BH$_4)_2$] has been prepared either by reaction of $(\eta^5$-mesitylene)U(BH$_4)_3$ with K(2,4-Me$_2$C$_5$H$_5$), or by reaction of $(\eta^5$-2,4-Me$_2$C$_5$H$_5)_3$U with KBH$_4$ (Baudry *et al.*, 1989b). The reaction of $(\eta^5$-2,4-Me$_2$C$_5$H$_5)_3$U with [Et$_3$NH][BPh$_4$] has been reported to generate a cationic complex [$(\eta^5$-2,4-Me$_2$C$_5$H$_5)_2$U][BPh$_4$]. The tetravalent derivatives $(\eta^5$-2,4-Me$_2$C$_5$H$_5)_2$U(BH$_4)_2$ and $(\eta^5$-2,4-Me$_2$C$_5$H$_5$)U(BH$_4)_3$ have been generated by the reactions of $(\eta^5$-2,4-Me$_2$C$_5$H$_5)_3$U with TlBH$_4$ or U(BH$_4)_4$ with K(2,4-Me$_2$C$_5$H$_5$), respectively (Baudry *et al.*, 1989c).

Comparable reactions have also been carried out with the related 6,6-dimethylcyclohexadienyl ligand. Reaction of U(BH$_4)_4$ with K(6,6-Me$_2$C$_6$H$_5$) generates the bis(ligand) compound, $(\eta^5$-6,6-Me$_2$C$_6$H$_5)_2$U(BH$_4)_2$ as shown in equation (25.91) (Baudry *et al.*, 1990b).

$$\text{U(BH}_4)_4 + 2\text{ K(6,6-Me}_2\text{C}_6\text{H}_5) \longrightarrow \qquad\qquad (25.91)$$
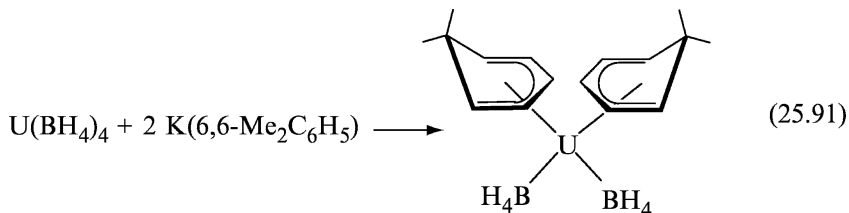
In order to generate the mono(ligand) compound, $(\eta^5$-6,6-Me$_2$C$_6$H$_5$)U(BH$_4)_3$, it is necessary to react U(BH$_4)_4$ with $(\eta^5$-6,6-Me$_2$C$_6$H$_5)_2$U(BH$_4)_2$ in a ligand redistribution reaction (Baudry *et al.*, 1990b). The anionic compounds [K(18-crown-6)][$(\eta^5$-6,6-Me$_2$C$_6$H$_5)_2$UX$_2$] (X = Cl, BH$_4$) were synthesized by treatment of UCl$_4$ or $(\eta^6$-mesitylene)U(BH$_4)_3$ with K(6,6-Me$_2$C$_6$H$_5$).

Although no alkyne coordination complex of an actinide has been isolated, alkyne complexes have been proposed as intermediates in the catalytic dimerization of terminal alkynes by cationic amide complexes, based upon spectroscopic evidence (Wang *et al.*, 1999; Dash *et al.*, 2000).

25.2.5   Alkyl ligands

Early attempts to prepare homoleptic alkyl complexes of the actinides resulted only in the formation of organic decomposition products and uranium metal, suggesting thermal instability (Gilman, 1968). Various methods of steric stabilization have been employed to enhance the stability of alkyl complexes, including reactions designed to generate uranate complexes, and the introduction of ancillary bases to block the elimination reactions believed to occur during decomposition.

The reactions of uranium and thorium tetrachlorides with excess alkyllithium reagents yield isolable products [equations (25.92) and (25.93)] (Andersen *et al.*, 1975; Sigurdson and Wilkinson, 1977; Lauke *et al.*, 1984).

$$UCl_4 + XS\,RLi \xrightarrow{\text{xs}\,L} [Li(L)_n]_2[UR_6]$$
$$R = CH_3,\ C_6H_5,\ CH_2(SiMe_3)_2 \tag{25.92}$$
$$L = Et_2O,\ THF,\ n = 4;\ L = TMEDA,\ n = 3.5$$

$$ThCl_4 + xs\,CH_3Li + xs\,TMEDA \longrightarrow$$
$$[Li(TMEDA)]_3[TH(CH_3)_7] \cdot TMEDA + 4LiCl \tag{25.93}$$
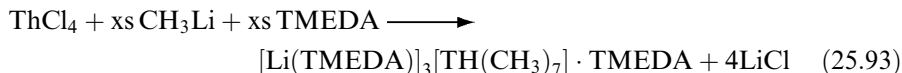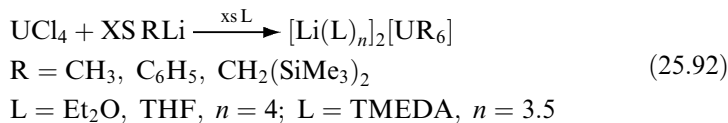
While the uranium compounds are reported to decompose above room temperature, the thorium compound is stable for hours at room temperature, and the crystal structure has been determined. The thorium is hepta-coordinate, with a monocapped trigonal prismatic geometry. Six of the methyl groups also bridge to the three lithium counter-ions [Th–C = 2.667(8)–2.765(9) Å], while the seventh methyl group is terminal [Th–C = 2.571(9) Å].

The other proven route to stabilization of alkyl complexes involves the use of coordinating phosphines to sterically saturate the coordination sphere. The bis (1,2-dimethylphosphino)ethane (dmpe) complexes of uranium and thorium tetrachloride have been prepared; metathesis reactions with these precursors yield thermally stable alkyl complexes [equations (25.94) and (25.95)] (Edwards *et al.*, 1981, 1984):

$$(dmpe)_2AnCl_4 + 4RLi \longrightarrow (dmpe)_2AnR_4$$
$$An = Th,\ U \tag{25.94}$$
$$R = CH_3,\ CH_2C_6H_5$$

$$(dmpe)_2AnCl_4 + 3Li(CH_2C_6H_5) + LiCH_3 \longrightarrow (dmpe)_2An(CH_3)(CH_2C_6H_5)_3$$
$$An = Th,\ U$$
$$\tag{25.95}$$
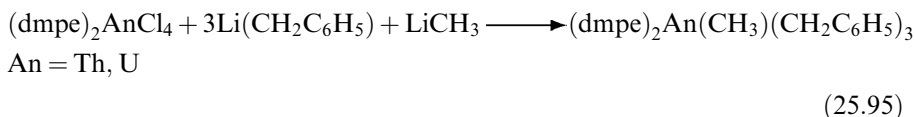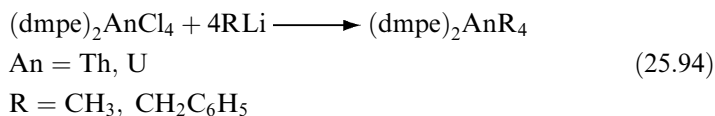
The only neutral homoleptic actinide complex characterized to date is $U[CH(SiMe_3)_2]_3$, produced by the reaction of $U(O\text{-}2,6\text{-}^tBu_2C_6H_3)_3$ with $Li[CH(SiMe_3)_2]$ in hexane (Van Der Sluys *et al.*, 1989). The molecular structure is shown in Fig. 25.29.

Unlike comparable first-row transition metal tris(alkyl) complexes, the compound has a pyramidal geometry, with a C–U–C angle of 107.7(4)°, and a U–C bond distance of 2.48(2) Å. The complex is thermally stable in the solid state at room temperature, but decomposes with loss of alkane at temperatures greater than 60°C. Reaction of $UCl_3(THF)_x$ with three equivalents of $Li[CH(SiMe_3)_2]$ does not generate the neutral complex, but rather an ionic complex formulated as $[Li(THF)_3][(Cl)U\{CH(SiMe_3)_2\}_3]$. The neptunium and plutonium analogs $An[CH(SiMe_3)_2]_3$ have been reported (Zwick *et al.*, 1992), although not fully characterized.

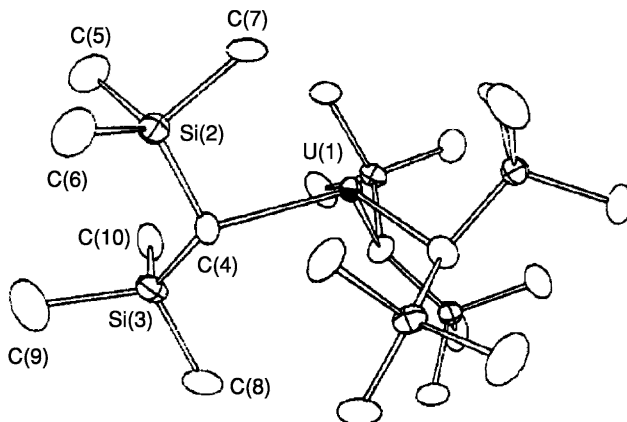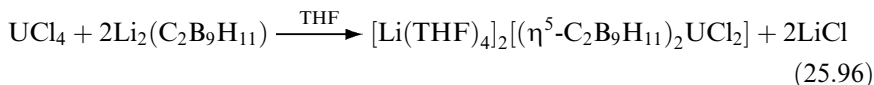**Fig. 25.29**   *Molecular structure of* [CH(SiMe₃)₂]₃U. (*Reprinted with permission from Van Der Sluys* et al. (1989). *Copyright* 1989 *American Chemical Society*.)

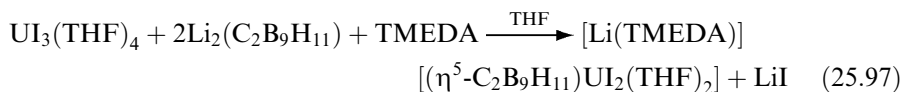### 25.3   HETEROATOM-CONTAINING π-ANCILLARY LIGANDS

25.3.1   Dicarbollide ligands

Although not strictly carbocyclic ligands, 1,2-dicarbollide groups $(C_2B_9H_{11}^{2-})$ have been employed as ancillary ligands in organoactinide chemistry, and deserve inclusion owing to their structural analogy to cyclopentadienyl groups. This ligand has been used in the synthesis of a number of mono- and bis-ligand analogs of cyclopentadienyl complexes. The first report of a dicarbollide complex was the generation of an anionic 'bent metallocene analog' [equation (25.96)] (Fronczek *et al.*, 1977).

$$UCl_4 + 2Li_2(C_2B_9H_{11}) \xrightarrow{\text{THF}} [Li(THF)_4]_2[(\eta^5\text{-}C_2B_9H_{11})_2UCl_2] + 2LiCl$$
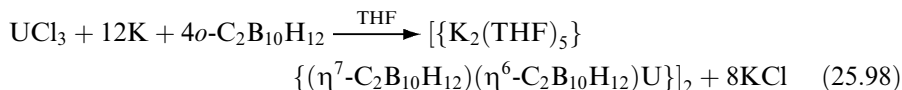
$$(25.96)$$

The complex has a geometry analogous to a typical metallocene complex, with pentahapto dicarbollide ligands. The two carbons of the capping face could not be definitively distinguished, although a model was suggested that placed the carbon atoms closest to the coordinated chloride ligands. The U–B(C) bond distances range from 2.64(3) to 2.86(3) Å. The average value of 2.73(2) Å is similar to that found in typical U(IV) cyclopentadienyl complexes. A uranium(IV) dibromide analog has since been reported (Rabinovich *et al.*, 1996), as have thorium complexes $[Li(THF)_4]_2[(\eta^5\text{-}C_2B_9H_{11})_2ThX_2]$ (X = Cl, Br, I) (Rabinovich *et al.*, 1997). The uranium(IV) dibromide complex can be chemically reduced to generate a uranium(III) complex, $[Li(THF)_x]_2[(\eta^5\text{-}C_2B_9H_{11})_2UBr (THF)]$ (de Rege *et al.*, 1998). Trivalent mono-ligand complexes can also be generated by metathesis reactions with $UI_3(THF)_4$ [equation (25.97)]
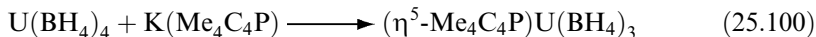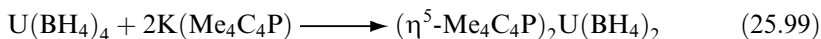
(Rabinovich *et al.*, 1996):

$$UI_3(THF)_4 + 2Li_2(C_2B_9H_{11}) + TMEDA \xrightarrow{THF} [Li(TMEDA)]$$
$$[(\eta^5\text{-}C_2B_9H_{11})UI_2(THF)_2] + LiI \quad (25.97)$$

A single report has appeared on the complexation of uranium by another carborane anion [equation (25.98)] (Xie *et al.*, 1999).

$$UCl_3 + 12K + 4o\text{-}C_2B_{10}H_{12} \xrightarrow{THF} [\{K_2(THF)_5\}$$
$$\{(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U\}]_2 + 8KCl \quad (25.98)$$

25.3.2 Phospholyl ligands

The closest π-ligand analogs to cyclopentadienyl groups in this class are phosphole compounds and their derivatives. Of these potential ligands, the tetramethylphospholyl group has been employed to generate actinide complexes. The initial report involved introduction of the phospholyl ligand to the metal center by metathesis [equations (25.99) and (25.100)] (Gradoz *et al.*, 1992a):

$$U(BH_4)_4 + 2K(Me_4C_4P) \longrightarrow (\eta^5\text{-}Me_4C_4P)_2U(BH_4)_2 \quad (25.99)$$

$$U(BH_4)_4 + K(Me_4C_4P) \longrightarrow (\eta^5\text{-}Me_4C_4P)U(BH_4)_3 \quad (25.100)$$

Reduction of these complexes in THF by sodium amalgam affords trivalent uranate anions. Reaction of trivalent uranium precursors with the phospholyl salt also yields the uranate species. The molecular structure of the U(IV) product $(\eta^5\text{-}Me_4C_4P)_2U(BH_4)_2$ has been described and is presented in Fig. 25.30 (Baudry *et al.*, 1990c).

The complex is structurally very similar to a bis(cyclopentadienyl) metallocene. The phospholyl ring remains planar upon coordination to the uranium center, and coordinates in a pentahapto manner. The average metal–carbon bond distance is 2.81(4) Å, comparable to that found in U(IV) metallocene complexes, and the U–P distance is 2.905(8) Å. The complex $(\eta^5\text{-}Me_4C_4P)_2UCl_2$ was subsequently generated from the reaction of UCl$_4$ with the potassium salt of the phospholyl (Gradoz *et al.*, 1994a).

The tris(phospholyl) complexes have been produced from uranium tetrachloride [equation (25.101)] (Gradoz *et al.*, 1992b):

$$UCl_4 + 3K(Me_4C_4P) \longrightarrow (\eta^5\text{-}Me_4C_4P)_3UCl + 3KCl \quad (25.101)$$

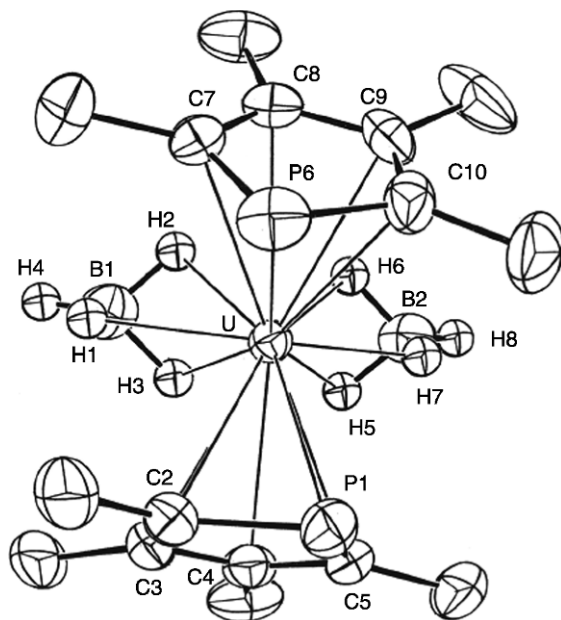The chloride may be further substituted to generate alkyl, hydrido, and alkoxide species.

Fig. 25.30 *Molecular structure of* $(\eta^5\text{-}Me_4C_4P)_2U(BH_4)_2$ (*Baudry* et al., 1990c). (*Reprinted with permission from John Wiley & Sons, Inc.*)

Mono-ring complexes of the formula $(\eta^5\text{-}Me_4C_4P)UCl_3(DME)$ and $(\eta^5\text{-}Me_4C_4P)UCl_3(THF)_2$ are prepared by the reaction of UCl_4 and $K(Me_4C_4P)$ in the appropriate solvent (Gradoz *et al.*, 1994a). It is the borohydride derivative $(\eta^5\text{-}Me_4C_4P)U(BH_4)_3$ and its pentamethylcyclopentadienyl analog $(\eta^5\text{-}C_5Me_5)U(BH_4)_3$ that serve as reagents in most reported subsequent metathesis reactions as illustrated in equation (25.102) for the preparation of the mixed-ring complex $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}Me_4C_4P)U(BH_4)_2$:

$$(\eta^5\text{-}C_5Me_5)U(BH_5)_3 + K(Me_4C_4P) \longrightarrow \qquad (25.102)$$
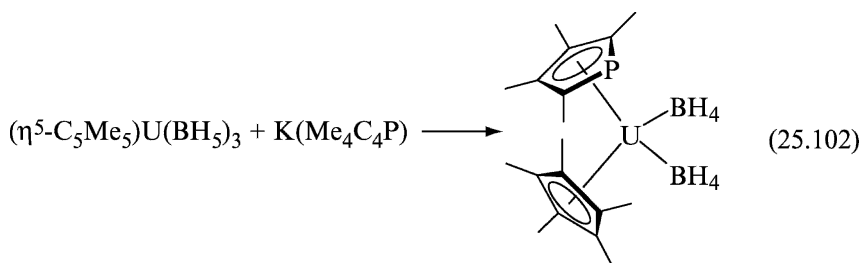
The complexes $(\eta^5\text{-}Me_4C_4P)_2U(BH_4)_2$, $(\eta^5\text{-}Me_4C_4P)U(BH_4)_3$, and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}Me_4C_4P)U(BH_4)_2$ serve as precursors for a number of alkyl and alkoxide derivatives ($R = Me$, CH_2SiMe_3, OEt, O^iPr, and O^tBu).

The mixed-ring compounds $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}Me_4C_4P)U(BH_4)(THF)$ and $K[(\eta^8\text{-}C_8H_8)(\eta\text{-}Me_4C_4P)_2U(BH_4)(THF)_x]$ can be generated by the reaction of

$(\eta^8\text{-}C_8H_8)U(BH_4)_2(THF)$ or $[(\eta^8\text{-}C_8H_8)U(BH_4)(THF)_2][BPh_4]$, respectively, with $K(Me_4C_4P)$. The cationic complex $[(\eta^8\text{-}C_8H_8)U(\eta^5\text{-}Me_4C_4P)(HMPA)_2]$ $[BPh_4]$ is isolated from the reaction of $[(\eta^8\text{-}C_8H_8)U(HMPA)_3][BPh_4]$ with the potassium phospholyl salt (Cendrowski-Guillaume *et al.*, 2002).

The dimeric trivalent compound $[(\eta^5\text{-}Me_4C_4P)(\mu,\eta^5,\eta^1\text{-}Me_4C_4P)U(BH_4)]_2$ constitutes a rare example of a dimeric phospholyl complex, in which each phospholyl ligand phosphorus atom serves as a donor to the other uranium atom (Gradoz *et al.*, 1994b). The molecular structure of the complex reveals pseudo-tetrahedral uranium coordination, with the borohydride ligands on the same side of the U_2P_2 plane (Fig. 25.31).

The metrical data indicate no apparent strain introduced by the dimer formation; U-ring atom bond distances and centroid-metal-centroid angles are not significantly distorted from the values found for $(\eta^5\text{-}Me_4C_4P)_2U$ $(BH_4)_2$ [U–C_{ave} = 2.84(3) Å, U–P_{ave} = 2.970(3) Å] (Fig. 25.30). The bridging P→U distance is 2.996(3) Å. Although it has been suggested that the phosphorus lone pair of the phospholyl group should lie in the ring plane, the P→U-ring centroid angle in this complex is 159.0(3)°, suggesting that U_2P_2 'ring closure' imposes a steric requirement for bending about the donor phosphorus atom.

25.3.3 Pyrrole-based ligands

The nitrogen-based analog, the pyrrole ligand, has not been found by itself to support pentahapto coordination to actinide centers, presumably due to the relative 'hard' basic character of the nitrogen in the heterocycle. Examples of $(\eta^5\text{-}C_4N)$ coordination may instead be found in the reaction products of uranium halides with the tetraanion of the macrocycle $[\{(-CH_2-)_5\}_4\text{-calix}[4]\text{tetrapyr-}$ role] (Korobkov *et al.*, 2001a). As described in equation (25.103), the reaction of $UI_3(THF)_4$ with the potassium salt of the tetrapyrrolide in THF generates a dinuclear U(IV) complex, $[\{[\{(-CH_2-)_5\}_4\text{-calix}[4]\text{tetrapyrrole}]UK(THF)_3\}_2$ $(\mu\text{-O})]\cdot 2THF$; the oxo group is proposed to come from deoxygenation of a THF molecule.

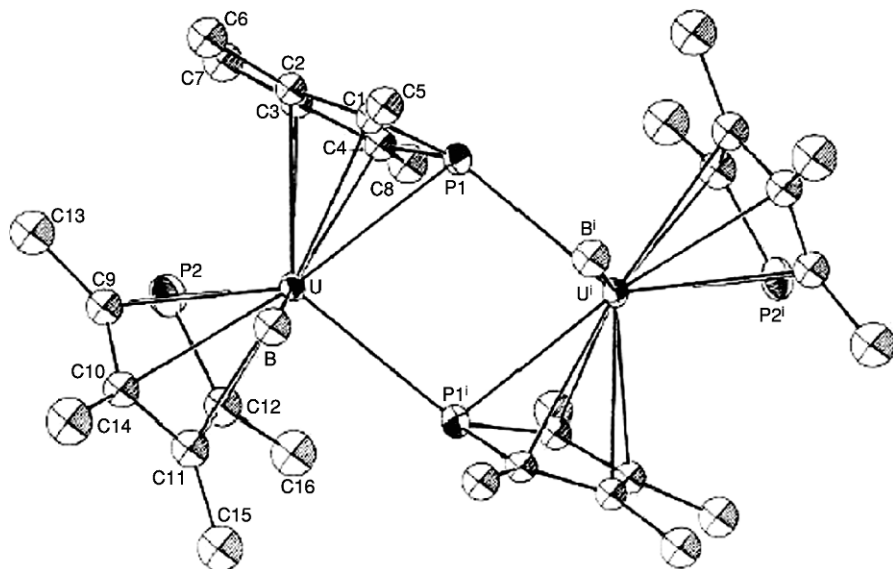$UI_3(THF)_4$ + $[K(THF)_4]$ [calix-[4]-tetrapyrrole] $\longrightarrow$

(25.103)
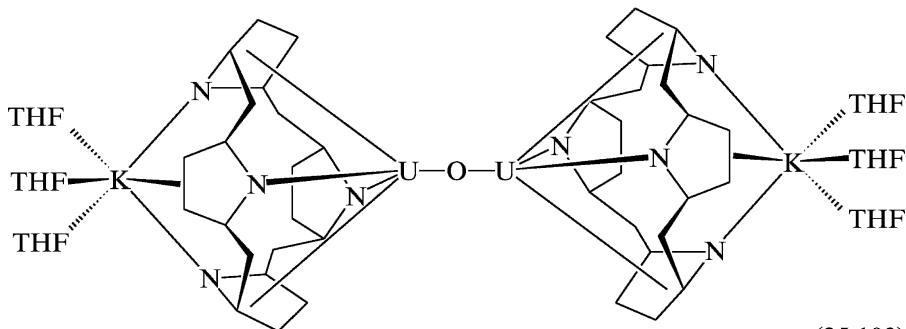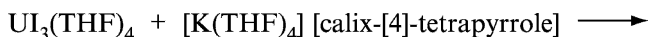
Fig. 25.31 *Molecular structure of* $[(\eta^5\text{-}Me_4C_4P)(\mu\eta^5\eta^1\text{-}Me_4C_4P)U(BH_4)]_2$. *The H atoms of the BH$_4$ ligand have been omitted for clarity* (*Gradoz* et al., *1994b). (Reprinted with permission from Elsevier.*)

Reaction of UI$_3$(THF)$_4$ with the corresponding lithium tetrapyrrolide salt in a 1:2 ratio generates instead $[\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}ULi(THF)_2]_2 \cdot$ hexane, in which the β-carbon of one of the pyrrole rings has undergone a metallation reaction (Fig. 25.32).

Reaction of the potassium salt with UI$_3$(DME)$_4$ avoids the complication of THF activation, and the simple trivalent uranate complex, $[\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}U(DME)][K(DME)]$, is generated. The geometry about the metal center in these compounds is qualitatively similar to a metallocene complex. The ligand adopts a σ/π-bonding mode, in which two of the four pyrrole rings in the macrocycle are η^5-bonded to the uranium, and the other two rings are σ-coordinated only through the pyrrole nitrogen. The U–N (σ) bond lengths for the tetravalent derivatives range from 2.39 to 2.47 Å; these distances are slightly longer in the trivalent derivative (*ca.* 2.53 Å). The π-coordination of the pyrrole ring yields somewhat longer U–N bond distances (*ca.* 2.65 Å in tetravalent compounds, 2.74 Å in the trivalent compound), and U–C$_{\text{pyrrole}}$ bond distances that range from 2.68 to 2.88 Å.

Reaction of UI$_3$(THF)$_4$ with [Li(THF)]$_4\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}$ in a substoichiometric (2:1) ratio generates the dinuclear complex [Li(THF)$_4$]$_2$ [U$_2$I$_4\{[(-CH_2-)_5]_4\text{-calix}[4]\text{-tetrapyrrole}\}]$ (Fig. 25.33) in moderate yield (Korobkov *et al.*, 2001b).
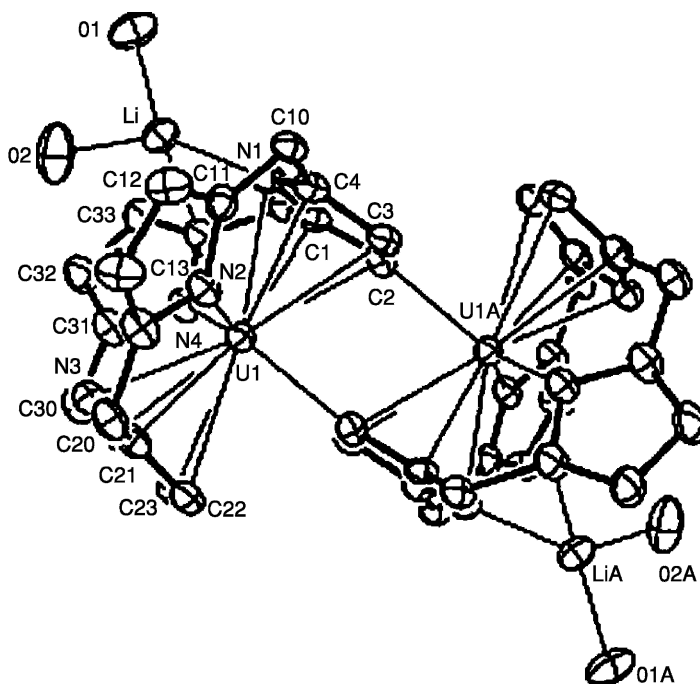
Fig. 25.32 *Molecular structure of* [{(–CH₂–)₄-*calix*[4]-*pyrrole*}*ULi*(*THF*)₂]₂. (*Reprinted with permission from Korobkov* et al. (2001a). *Copyright* 2001 *American Chemical Society*.)

Partial reduction of UCl₄, followed by reaction with one half of an equivalent of the lithium salt is reported to generate the mixed-valence compound [Li(THF)₂](μ-Cl)₂{U₂[(–CH₂–)₅]₄-calix[4]tetrapyrrole}Cl₂·THF. Both of these complexes display alternate σ/η⁵, π-coordination to opposite pairs of pyrrole ligands in a single tetrapyrrole group. The bridging nature of the macrocyclic ligand brings the uranium centers into relatively close proximity (3.4560(8) and 3.365(6) Å, respectively); magnetic susceptibility measurements on the U(III)/U(III) dimer suggests weak antiferromagnetic coupling occurs between metal centers.

25.3.4 Other nitrogen-containing π-ligands

Amidinate ligands have been employed as ancillary ligands in the generation of organometallic compounds of tetravalent uranium and thorium, as well as complexes with the uranyl ion. Reaction of Li[N(SiMe₃)₂] and Na[N(SiMe₃)₂] with *para*-substituted benzonitriles yields the benzamidinate ligands M[4-RC₆H₄C(NSiMe₃)₂] (M = Li, Na; R = H, Me, OMe, CF₃).
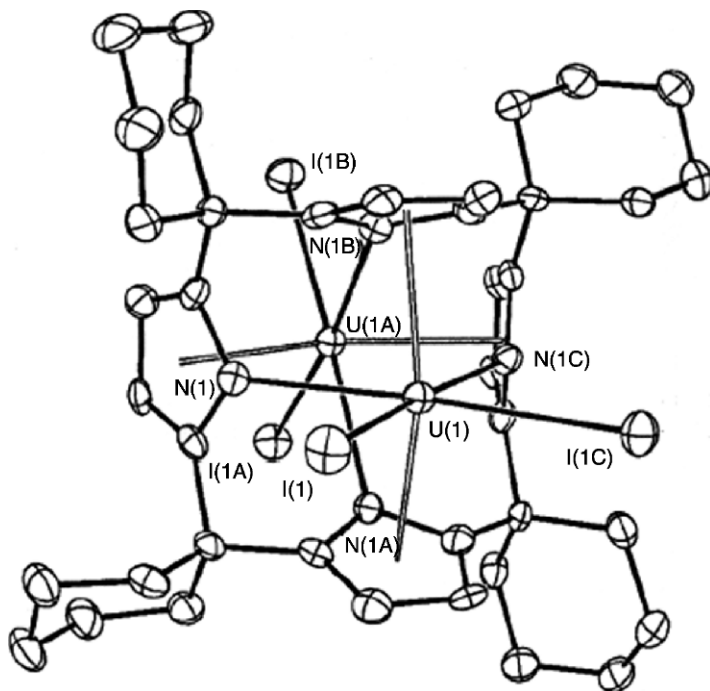
Fig. 25.33 *Molecular structure of* $[Li(THF)_4]_2[U_2I_4\{[(-CH_2-)_5]_4\text{-}calix[4]\text{-}tetrapyrrole\}]$. (*Reprinted with permission from Korobkov* et al. (2001b). *Copyright* 2001 *American Chemical Society*.)
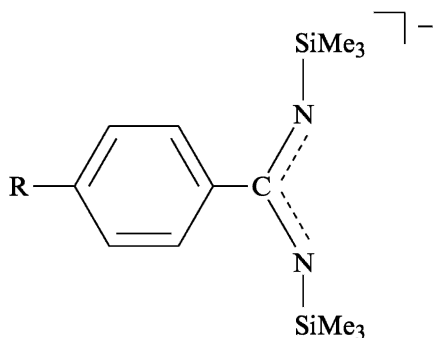
Alternatively, more substituted ligands $Li[2,4,6\text{-}R_3C_6H_2C(NSiMe_3)_2]$ (R = CF_3, Me) are generated by the addition of aryllithium reagents to $Me_3SiN=C=NSiMe_3$. The amidinate ligands (L) have been used to generate complexes of the formula L_2AnCl_2 (An = Th, U) and L_3AnCl (for less

sterically demanding substituents) by metathesis reactions (Wedler *et al.*, 1990). Substitution of the halide precursors has been reported to generate methyl and borohydride derivatives (Wedler *et al.*, 1992a). The molecular structure of the complex $[C_6H_5C(NSiMe_3)_2]_3UMe$ has been determined. The benzamidinate ligands coordinate to the metal center in a η^3-manner; the relatively long U–C σ bond of 2.498(5) Å is taken as an indication of steric crowding in the complex.

The benzamidinate ligands have been found to support a range of oxidation states in uranium chemistry. The uranyl complex $[C_6H_5C(NSiMe_3)_2]_2UO_2$ complex was prepared by a metathesis reaction with UO_2Cl_2 (Wedler *et al.*, 1988), and the interesting pentavalent derivative $[4\text{-}MeC_6H_4C(NSiMe_3)_2]_2UCl_3$ was produced by adventitious aerobic oxidation during reaction of UCl_4 with the corresponding silylated benzimidine [equation (25.104)] (Wedler *et al.*, 1992b).

$$(25.104)$$
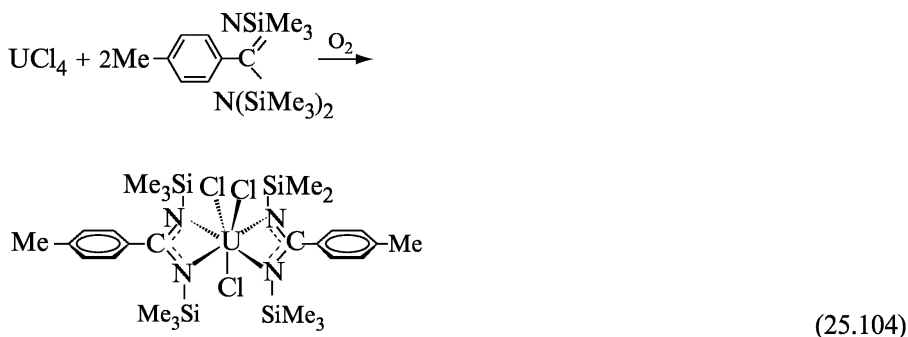
Related amidinate and 1-aza-allyl ligands also have been shown to generate bis(ligand)thorium dichloride complexes (Hitchcock *et al.*, 1997), as well as an interesting mixed-valence U(III)/U(VI) complex (Hitchcock *et al.*, 1995).

$$R = SiMe_3; \; Ph = C_6H_5$$
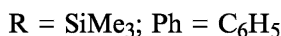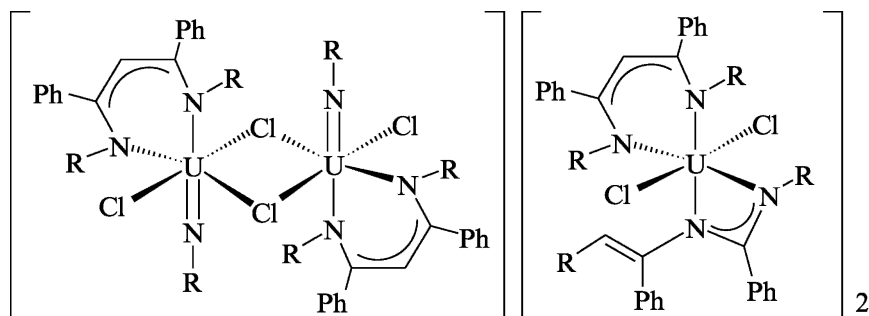
A rare example of a U–C interaction in hexavalent actinide chemistry is found in the isolation of a bis(iminophosphorano)methanide uranyl complex (Sarsfield *et al.*, 2002). Reaction of $[UO_2Cl_2(THF)_2]_2$ with $Na[CH(Ph_2P=NSiMe_3)_2]$ generates the dimer $[UO_2(\mu\text{-}Cl)\{CH(Ph_2P=NSiMe_3)_2\}]_2$.

R = SiMe$_3$
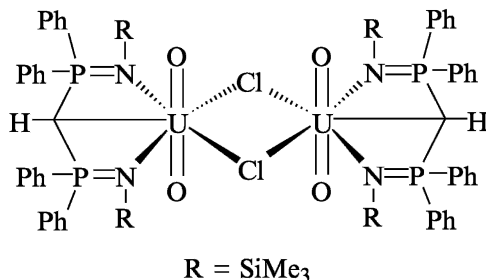
The U–C distance is 2.691(8) Å; the length indicates a very weak inter-action, although it falls within the sum of the van der Waals radii of the two atoms.

25.4 HETEROATOM-BASED ANCILLARY LIGANDS

Although complexes containing primarily heteroatom-donor ligands are less likely to be regarded as organometallic species, these ligands are playing an increasing important role in the development of non-aqueous f-element chemistry. The flexible steric and electronic characteristics of these ligands can stabilize unusual oxidation states and promote novel substrate activation reactions at actinide centers, making their study more attractive. Although not all 'inorga-nometallic' chemistry will be comprehensively reviewed here, discussion is warranted for certain classes of ligands that have played a significant role in the development of non-aqueous actinide chemistry.

25.4.1 Bis(trimethylsilyl)amide

As an ancilliary ligand, the bis(trimethylsilyl)amide ligand $[N(SiMe_3)_2]^-$ has been shown to support a wide array of oxidation states of uranium. It has further been used in tetravalent actinide chemistry (An = U, Th) to support metal centers that can effect a number of organic transformations.

Trivalent homoleptic complexes $[(SiMe_3)_2N]_3An$ have been prepared for uranium, neptunium, and plutonium (Andersen, 1979; Clark *et al.*, 1989; Zwick *et al.*, 1992) by metathesis reactions [equations (25.105) and (25.106)].

$$UCl_3 \cdot (THF)_x + 3Na[N(SiMe_3)_2] \xrightarrow{\text{THF}} [(SiMe_3)_2N]_3U \qquad (25.105)$$

$$AnI_3(THF)_4 + 3Na[N(SiMe_3)_2] \xrightarrow{\text{THF}} [(SiMe_3)_2N]_3An$$
$$An = U, Np, Pu \qquad\qquad\qquad\qquad\qquad\qquad\qquad (25.106)$$
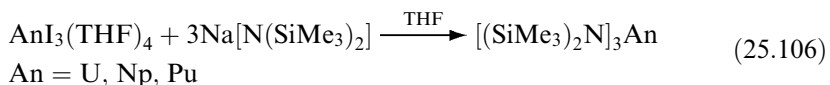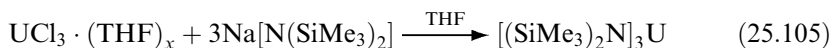
The molecular structure of $[(SiMe_3)_2N]_3U$ has been determined (Stewart and Andersen, 1998). The geometry about the uranium center is trigonal pyramidal, with a U–N distance of 2.320(4) Å, and a N–U–N angle of 116.24(7)°. The

magnetic susceptibility shows that the complex has effective moments comparable to those determined for trivalent metallocenes and halides ($\mu_{eff} = 3.354(4)$, $\theta = -13$ K at 5 kG), consistent with a $5f^3$ electronic configuration. This is confirmed by the photoelectron spectroscopy, which demonstrates a low-energy 5f ionization band (Green *et al.*, 1982). The steric congestion about the metal center prohibits isolation of stable base coordination compounds.

Tetravalent complexes of the formula $[(SiMe_3)_2N]_3AnCl$ (An = Th, U) have been prepared (Turner *et al.*, 1979a) from the 3:1 reaction of $NaN(SiMe_3)_2$ with $AnCl_4$ [(equation (25.107)], and the complex $[(SiMe_3)_2N]_2UCl_2(DME)$ can be generated from a 2:1 reaction of ligand:halide salt (McCullough *et al.*, 1981).

$$AnCl_4 + 3Na[N(SiMe_3)_2] \xrightarrow{\text{THF}} [(SiMe_3)_2N]_3An{-}Cl$$
$$An = Th, U \tag{25.107}$$
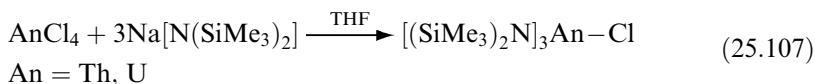
Substituted complexes of the formula $[(SiMe_3)_2N]_3AnR$ (An = Th, U; R = Me, Et, ^iPr, Bu, BH_4) are formed by the reaction of $[(SiMe_3)_2N]_3AnCl$ with the appropriate lithium or magnesium reagent (Turner *et al.*, 1979a; Dormond *et al.*, 1988). Unlike comparable cyclopentadienyl analogs, the methyl compound does not undergo ready insertion of CO, although a number of other insertion and protonation reactions have been reported, including insertion of ketones, aldehydes, isocyanides, and aliphatic nitriles (Dormond *et al.*, 1987b, 1988). The methyl ligand is further susceptible to removal by protic reagents such as secondary amines.

The hydride compounds $[(SiMe_3)_2N]_3AnH$ (An = Th, U) are the sole products of attempts to introduce an additional equivalent of the bis(trimethylsilyl) amide ligand to $[(SiMe_3)_2N]_3AnCl$ (Turner *et al.*, 1979b). Pyrolysis of the hydride results in the loss of dihydrogen and the formation of an unusual metallacycle (Simpson and Andersen, 1981a).
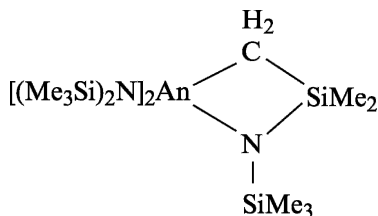
The metallacycles of uranium and thorium have been shown to undergo a large number of insertion and protonation reactions (Simpson and Andersen, 1981b; Dormond *et al.*, 1985, 1986a,b, 1987a,b, 1989a,b; Baudry *et al.*, 1995), as shown in Fig. 25.34.

In some cases these reactions (such as reduction of carbonyl-containing organic compounds) have been found to be stereoselective.

As in the case of substituted cyclopentadienyl complexes, the bis(trimethylsilyl)amide ligand is capable of supporting the formation of organoimido
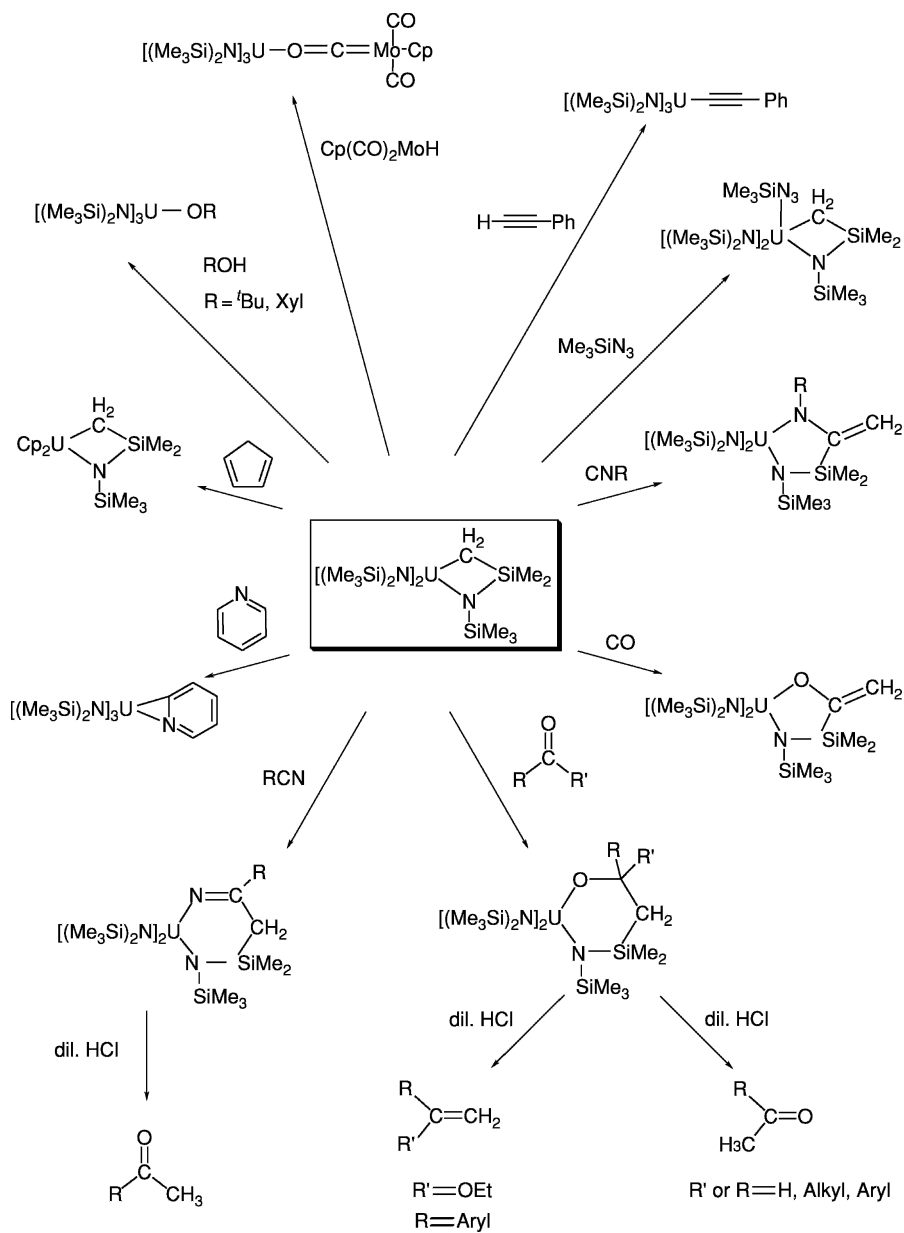
Fig. 25.34 *Reactions of uranium metallacycle.*

complexes. The tetravalent uranium dimer $[\{(SiMe_3)_2N\}_2U(\mu\text{-}N\text{-}p\text{-}C_6H_4Me)]_2$ was prepared by reaction of $[(SiMe_3)_2N]_3UCl$ with $Li[N(H)(p\text{-}C_6H_4Me)]$ [equation (25.108)] (Stewart and Andersen, 1995), presumably by α-elimination of $HN(SiMe_3)_2$ from an intermediate amide complex:

$$[(SiMe_3)_2N]_3U—Cl + Li[N(H)(p\text{-}C_6H_4M_e)]$$

$$\longrightarrow [(SiMe_3)_2N]_2U \diagdown \diagup U[N(SiMe_3)_2]_2$$

(25.108)
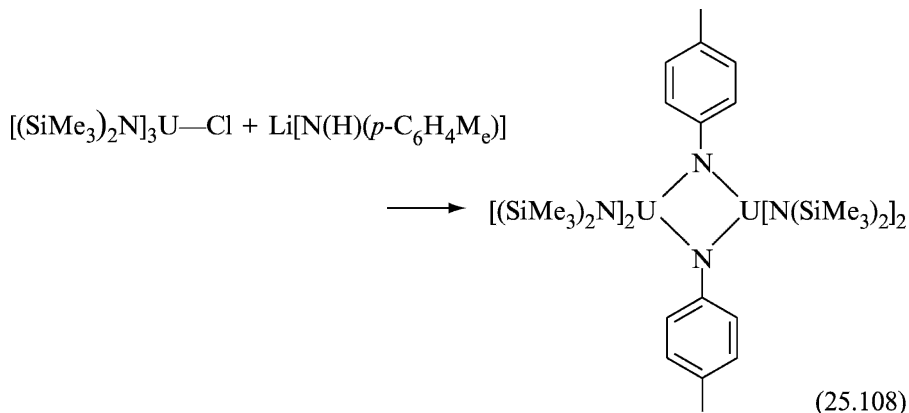
As in the case of the related cyclopentadienyl compound, the arylimido ligand bridges the two metal centers in an asymmetric fashion, with U–N bond distances of 2.378(3) and 2.172(2) Å.

Reaction of $[(SiMe_3)_2N]_3U$ with Me_3SiN_3 generates the uranium(v) organoimido complex $[(Me_3Si)_2N]_3U(=NSiMe_3)$ (Zalkin *et al.*, 1988b). Both this and the related phenylimido complex are oxidized by mild oxidants such as $AgPF_6$ or $[Cp_2Fe][PF_6]$ to generate the U(vi) imido fluoride complexes $[(Me_3Si)_2N]_3U$ $(=NR)F$ (R = $SiMe_3$, Ph) as shown in equation (25.109) (Burns *et al.*, 1990).

(25.109)

R = SiMe$_3$, Ph
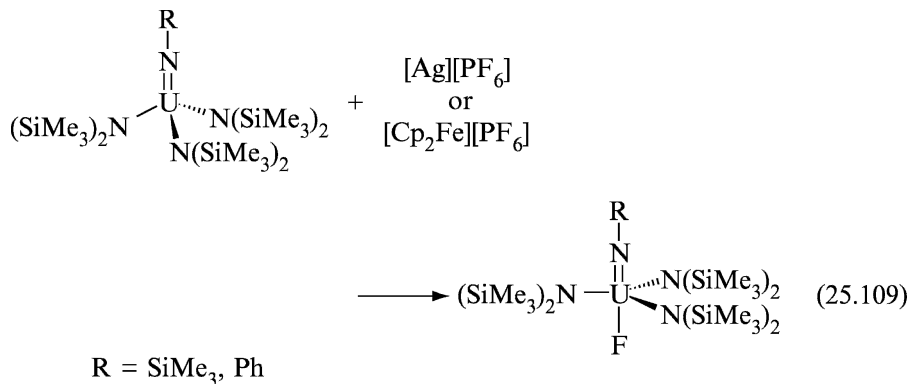
Both U(vi) complexes are trigonal bipyramidal with the bis(trimethylsilyl) amido groups occupying the equatorial positions. The F–U–N$_{imido}$ angles are near linear, as are the U–N–Si(C) angles. The U=N$_{imido}$ bond lengths are 1.85 (2) and 1.979(8) Å, respectively, for the silylimido and phenylimido complexes.

25.4.2　Pyrazolylborate

Monoanionic poly(pyrazolyl)borate ligands ($B(pz)_4^-$, $HB(pz)_3^-$, $H_2B(pz)_2^-$, and substituted derivatives, pz = pyrazol-1-yl) have found broad application as ancillary ligands in d-transition metal chemistry as substitutes for cyclopentadienyl ligands (Trofimenko, 1993). Their σ-donor strength is comparable to that of a cyclopentadienyl ligand, although the precise ordering depends on the metal (Tellers *et al.*, 2000). These ligands most commonly bind to f-elements in either a trihapto or dihapto geometry through nitrogen atoms in the pyrazolyl substituents.

The first report of an actinide complex employing a poly(pyrazolyl)borate ligand was the preparation of complexes of the formula $[H_2B(pz)_2]_4U$, $[HB(pz)_3]_4U$, and $[HB(pz)_3]_2UCl_2$ by reaction of UCl_4 with the potassium salt of the appropriate ligand (Bagnall *et al.*, 1975). On the basis of ^{13}C NMR spectroscopy, the $HB(pz)_3$ ligands were assigned as bidentate in the complex $[HB(pz)_3]_2UCl_2$, while the complex $[HB(pz)_3]_4U$ was speculated to have two bidentate and two tridentate ligands (Bagnall *et al.*, 1976).

Since the initial identification of these compounds, the chemistry of poly-(pyrazolyl)borate ligands has expanded to include representatives involving trivalent actinides, most encompassing the substituted ligand $HB(3,5\text{-}Me_2pz)_3$. The complex $[HB(3,5\text{-}Me_2pz)_3]UCl_2$ has been generated either by metathesis reaction of UCl_3 with $K[HB(3,5\text{-}Me_2pz)_3]$ (Santos *et al.*, 1985, 1986) or reduction of the U(IV) precursor $[HB(3,5\text{-}Me_2pz)_3]UCl_3$ with sodium naphthalenide (Santos *et al.*, 1987). The complex is somewhat unstable, and upon recrystallization can be oxidized to generate the tetravalent oxo complex $[\{HB(3,5\text{-}Me_2pz)_3\}UCl(\mu\text{-}O)]_4$ (Domingos *et al.*, 1992a).
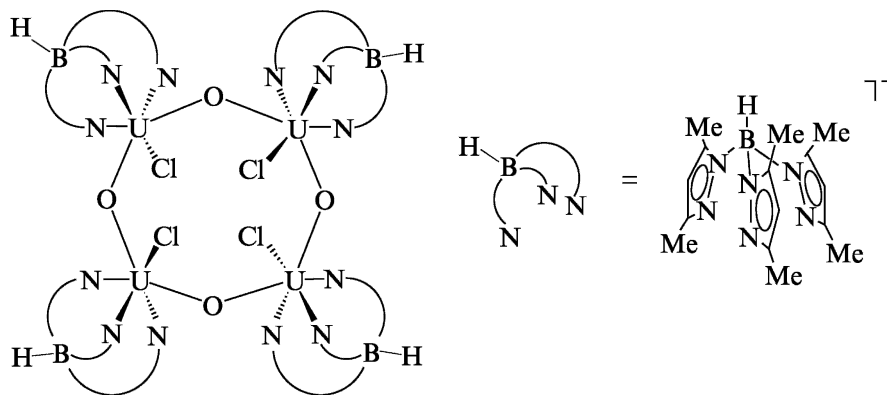
Recently, the use of uranium triiodide has become more common in the synthesis of trivalent complexes. Reaction of $UI_3(THF)_4$ with $M[HB(3,5\text{-}Me_2pz)_3]$ (M = Na, K) in a 1:1 or 1:2 ratio results in the formation of the compounds $[HB(3,5\text{-}Me_2pz)_3]UI_2(THF)_2$ and $[HB(3,5\text{-}Me_2pz)_3]_2UI$, respectively (McDonald *et al.*, 1994; Sun *et al.*, 1994). In the monoligand compound,

the pyrazolylborate ligand is tridentate, while the bis(ligand) compound demonstrates two different coordination modes for the two [HB(3,5-Me$_2$pz)$_3$] groups.
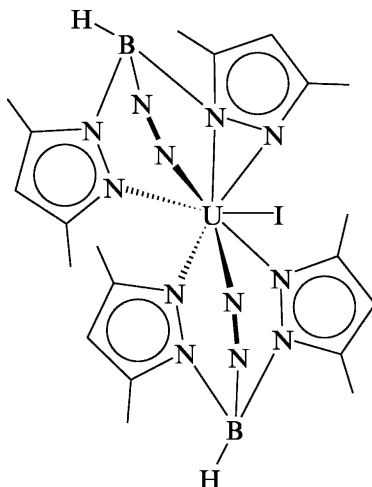
One of the ligands is η^3-coordinated to the metal center, while in the second ligand, one of the pyrazolyl rings appears to coordinate in a 'side-on' type of arrangement with the N–N bond of the ring within a bonding distance to the uranium atom. Upon abstraction of the iodide ligand with TlBPh$_4$, however, this ligand reverts to a conventional tridentate geometry; the uranium center is seven-coordinate in [{HB(3,5-Me$_2$pz)$_3$}$_2$U(THF)]$^+$, with the tetrahydrofuran ligand occupying the seventh site (McDonald *et al.*, 1994).

A limited number of U(III) complexes have been reported with other pyrazolylborate ligands. Uranium trichloride or triiodide reacts with the bis(pyrazolyl)borate ligands H$_2$B(3,5-Me$_2$pz)$_2$ and H$_2$B(pz)$_2$ to generate the species [H(μ-H)B(3,5-Me$_2$pz)$_2$]$_3$U and [H(μ-H)B(pz)$_2$]$_3$U(THF) (Carvalho *et al.*, 1992; Sun *et al.*, 1995). The coordinated tetrahydrofuran may be removed from the latter to yield the base-free complex [H(μ-H)B(pz)$_2$]$_3$U. The solid state structure of [H(μ-H)B(3,5-Me$_2$pz)$_2$]$_3$U reveals that the metal lies in a trigonal prismatic arrangement of six pyrazole nitrogen atoms, with the three rectangular faces of the trigonal prism capped by three B–H bonds (Fig. 25.35).

When a related ligand devoid of B–H bonds is employed (Ph$_2$B(pz)$_2$), the resulting tris(ligand) complex [Ph$_2$B(pz)$_2$]$_3$U contains a six-coordinate uranium center (Maria *et al.*, 1999). The lower coordination number is considered to be the origin of slightly shorter U–N bond distances (2.53(3) Å versus 2.59(3) or 2.58(3) Å in the ten- and nine-coordinate complexes, respectively). A mixed-alkyl substituted bis(pyrazolyl)borate complex has been produced by the reaction of UI$_3$(THF)$_4$ with K[H$_2$B(3-^{t}Bu,5-Mepz)$_2$]. The complex [H$_2$B(3-^{t}Bu,5-Mepz)$_2$]UI$_2$(THF)$_2$ reacts with Ph$_3$P=O to yield the base adduct [H$_2$B(3-^{t}Bu,5-Mepz)$_2$]UI$_2$(O=PPh$_3$)$_2$ (Maria *et al.*, 1999).
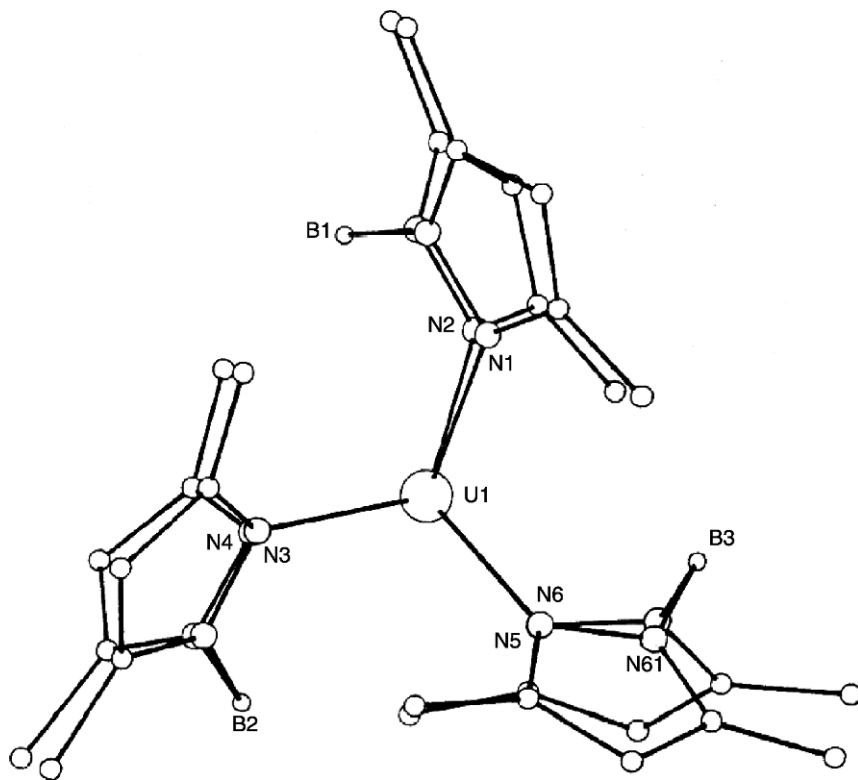
Fig. 25.35 *Molecular structure of* $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3U$. *The PLUTO view is in the plane of one of the triangular faces of the trigonal prism* (*Carvalho* et al., *1992*). (*Reprinted with permission from Elsevier.*)

Only one complex of a trivalent transuranic metal has been reported; reaction of $PuCl_3$ with $K[HB(3,5\text{-}Me_2pz)_3]$ in refluxing THF generates the dimeric complex $[PuCl(\mu\text{-}Cl)\{HB(3,5\text{-}Me_2pz)_3\}(3,5\text{-}Me_2pzH)]_2$ (Apostolidis et al., 1991, 1998).
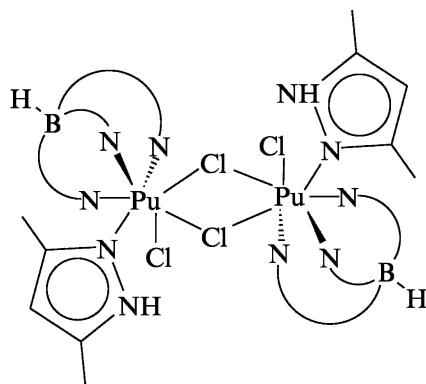
The chemistry of tetravalent actinides with poly(pyrazolyl)borates has been explored more extensively. The first report of metathesis reactions with thorium involved the preparation of the compounds $[HB(pz)_3]_{4-n}ThX_n$ ($n = 2$, $X = Cl$, Br; $n = 1$, $X = Cl$), $[HB(3,5-Me_2pz)_3]_2ThCl_2$, $[B(pz)_4]_2ThBr_2$, and base adducts of the complexes $[HB(pz)_3]ThCl_3$ and $[HB(pz)_3]_4Th$ (Bagnall *et al.*, 1978b), although subsequent reports have appeared describing other derivatives, including $[HB(3,5-Me_2pz)_3]ThCl_3$ (Ball *et al.*, 1987). The larger ionic radius of thorium enables higher coordination numbers; unlike the uranium complexes, the thorium derivatives $[HB(pz)_3]_2ThX_2$ ($X = Cl$, Br) were shown spectoscopically to possess tridentate pyrazolylborate ligands.

Several routes have been identified to produce $[HB(pz)_3]_2UI_2$, including reaction of UI_4 with two equivalents of $K[HB(pz)_3]$ in CH_2Cl_2 (Campello *et al.*, 1994), oxidation of $[HB(pz)_3]_2UI(THF)_2$ with iodine, and reaction of the tetravalent alkyl $[HB(pz)_3]_2U(CH_2SiMe_3)_2$ with iodine (Campello *et al.*, 1993). The reaction of UI_4 with two equivalents of $K[HB(pz)_3]$ in THF does not yield the same compound, however. Instead, the iodobutoxide complex $[HB(pz)_3]_2U(I)[O(CH_2)_4I]$ was isolated, presumably generated by ring-opening of solvent (Collin *et al.*, 1993; Campello *et al.*, 1994). The smaller size of the U(IV) ion, combined with the larger steric size of the $[HB(3,5-Me_2pz)_3]$ ligand, inhibits formation of bis(ligand) complexes of the substituted poly(pyrazolyl)borate; reaction of UCl_4 with two equivalents of $K[HB(3,5-Me_2pz)_3]$ leads to ligand degradation and the formation of $[HB(3,5-Me_2pz)_3]UCl_2(3,5-Me_2pz)$ [equation (25.110)] (Marques *et al.*, 1987a).

$$UCl_4 \ + \ 2K[HB(3,5-Me_2Pz)_3] \ \longrightarrow \qquad\qquad\qquad (25.110)$$
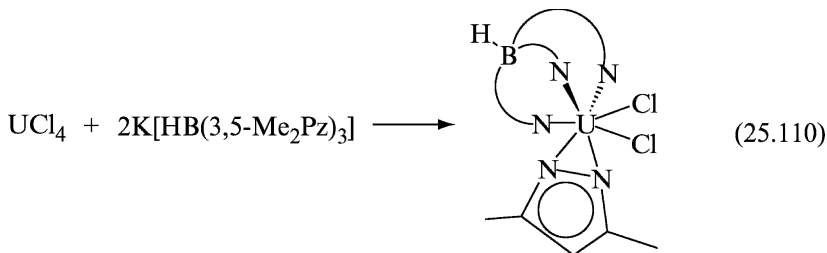
The complex $[HB(3,5-Me_2pz)_3]UCl_3(THF)$ contains a relatively weakly coordinated solvent molecule; the base-free complex can be isolated, and has been crystallographically characterized (Domingos *et al.*, 1990). The THF is also readily replaced by a number of other coordinating bases, permitting comparisons of relative ligand affinity. The relative affinities of a series of bases for $[HB(3,5-Me_2pz)_3]UCl_3$ was found to be

$$O{=}PPh_3 > C_6H_{11}NC > PhCN > MeCN > O{=}P(OEt)_3 >$$
$$O{=}P(O{-}nBu)_3 > C_5H_5N > THF$$
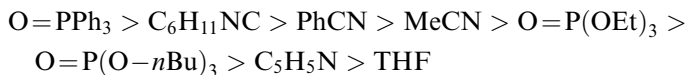
Attempts to introduce a larger poly(pyrazolyl)borate ligand have established the steric limits of this system. Reaction of UCl_4 with one equivalent of the thallium salt of $[HB(3-Mspz)_3]^-$ (Ms = mesityl) generates only the product containing an isomerized ligand, $[HB(3-Mspz)_2(5-Mspz)]UCl_3$ (Silva *et al.*, 2000).

A variety of metathesis reactions have been carried out with the bis(ligand) actinide species [HB(pz)₃]₂AnCl₂ (An = Th, U) to generate complexes containing oxygen, nitrogen, or sulfur donors (Santos *et al.*, 1987; Domingos *et al.*, 1989a, 1992b,c), as depicted in Fig. 25.36.
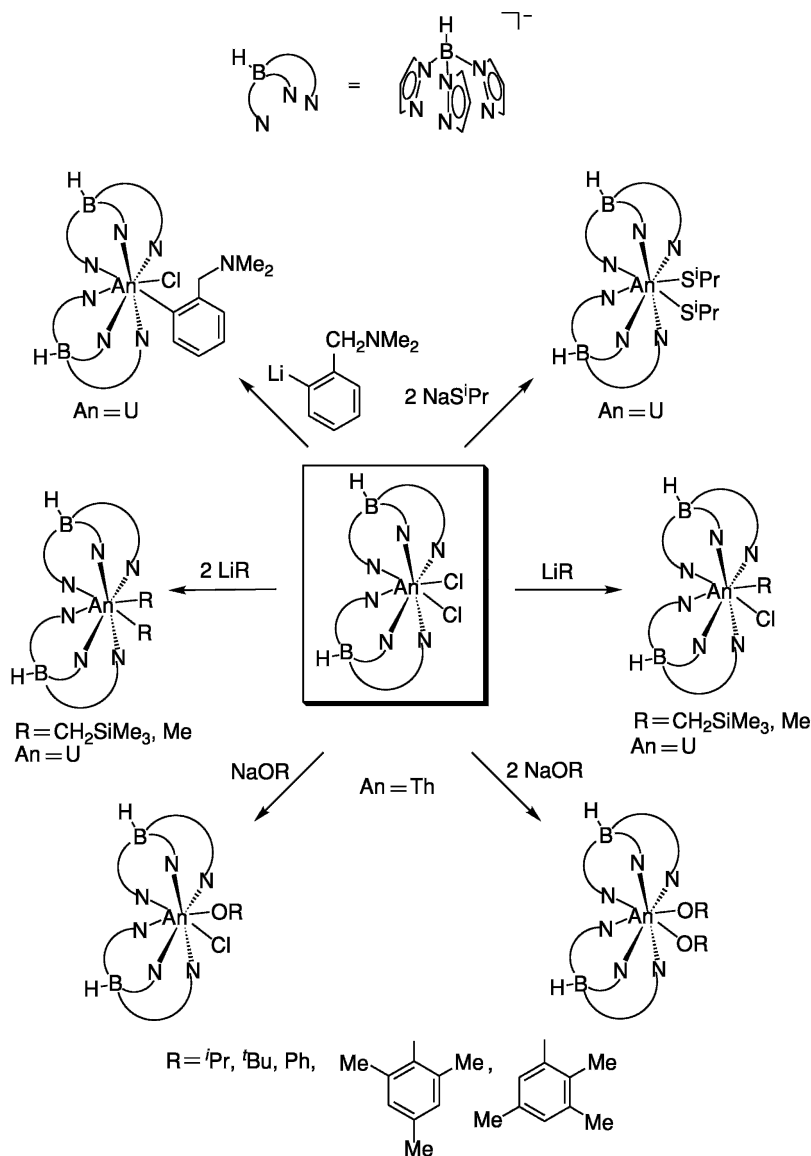
Fig. 25.36   *Chemical reactions of [HB(pz)₃]₂AnCl₂ (An = Th, U).*

Steric factors can be significant in these reactions. For example, reaction of bulky alkylamides with [HB(pz)$_3$]$_2$UCl$_2$ generates only the monoamide complexes [HB(pz)$_3$]$_2$UCl(NR$_2$). These complexes display restricted rotation about the U–N bond at room temperature, indicating a significant degree of steric saturation. Relatively few complexes have been isolated containing alkyl ligands. Many reactions of U(IV) with alkyllithium reagents result in reduction of the metal center. The complexes [HB(pz)$_3$]$_2$Th(CH$_2$SiMe$_3$)$_2$, [HB(pz)$_3$]$_2$U(R) Cl (R = Me, CH$_2$SiMe$_3$, *o*-NMe$_2$CH$_2$C$_6$H$_4$) and [HB(pz)$_3$]$_2$UR$_2$ (R = Me, CH$_2$SiMe$_3$) have been reported (Domingos *et al.*, 1992c; Campello *et al.*, 1997).

In an attempt to reduce the steric constraints of the ancillary ligand, derivatives of the mono(pyrazolylborate) complexes [HB(3,5-Me$_2$pz)$_3$]AnCl$_3$(THF) (An = Th, U) have also been prepared (Marques *et al.*, 1987b; Domingos *et al.*, 1989b, 1992d; Leal *et al.*, 1992). As before, the degree of substitution is often dependent on the size of the ligand introduced; tris(amide) derivatives such as [HB(3,5-Me$_2$pz)$_3$]An(NR$_2$)$_3$ can be produced for R = Et, Ph, whereas for the larger ligand [N(SiMe$_3$)$_2$]$^-$, only a monoamide complex can be isolated. The monoalkoxide and monoaryloxide complexes of thorium have been reported to be unstable; uranium mono(phenoxide) and bis(phenoxide) complexes are only stable in the presence of a coordinating molecule of THF (Domingos *et al.*, 1989b). The complex [HB(3,5-Me$_2$pz)$_3$]UCl$_3$(THF) is also susceptible to reduction by alkyllithium reagents; the full range of [HB(3,5-Me$_2$pz)$_3$]U(Cl)$_{3-x}$(R)$_x$ complexes have been prepared only for R = CH$_2$SiMe$_3$. Reaction of [HB(3,5-Me$_2$pz)$_3$]UCl$_3$(THF) with phenyllithium results in the formation of U(III) species (Silva *et al.*, 1995), but the use of aryllithium reagents with bulky ortho-substituents permits isolation of mono(aryl) products, [HB (3,5-Me$_2$pz)$_3$]UCl$_2$R. The reactivity of [HB(3,5-Me$_2$pz)$_3$]UCl$_2$(CH$_2$SiMe$_3$) and [HB(3,5-Me$_2$pz)$_3$]UCl$_2$[CH(SiMe$_3$)$_2$] toward unsaturated substrates has been investigated (Domingos *et al.*, 1994); insertion similar to that reported in other alkyl complexes is observed. As an example, [HB(3,5-Me$_2$pz)$_3$]UCl$_2$(CH$_2$-SiMe$_3$) reacts with stoichiometric amounts of aldehydes, ketones, nitriles, and isonitriles to yield the corresponding secondary and tertiary alkoxide, azomethine, and iminoalkyl products.

The neptunium derivatives [HB(pz)$_3$]$_2$NpCl$_2$ and [HB(3,5-Me$_2$pz)$_3$] NpCl$_3$(THF) have been produced from NpCl$_4$ (Apostolidis *et al.*, 1990).

The reaction of uranium tetrachloride with two equivalents of the bulky ligand [B(pz)$_4$]$^-$ as the potassium salt yields the complex [B(pz)$_4$]$_2$UCl$_2$ (Campello *et al.*, 1999). Although a limited number of derivatives of this compound could be produced, in general the ligand set provided less thermal stability than comparable complexes of the '[HB(pz)$_3$]$_2$U' fragment. The complex [B(pz)$_4$]$_2$UCl$_2$ displays eight-coordinate geometry in the solid state, in a distorted square antiprismatic arrangement of ligands (Fig. 25.37).

The complex is fluxional in solution; ^{1}H NMR spectra demonstrate that all coordinated pyrazolylborate rings are equivalent. For the derivatives [B(pz)$_4$]$_2$UCl(O^{t}Bu), [B(pz)$_4$]$_2$UCl(O-2,4,6-Me$_3$C$_6$H$_2$), [B(pz)$_4$]$_2$U(S^{i}Pr)$_2$, and
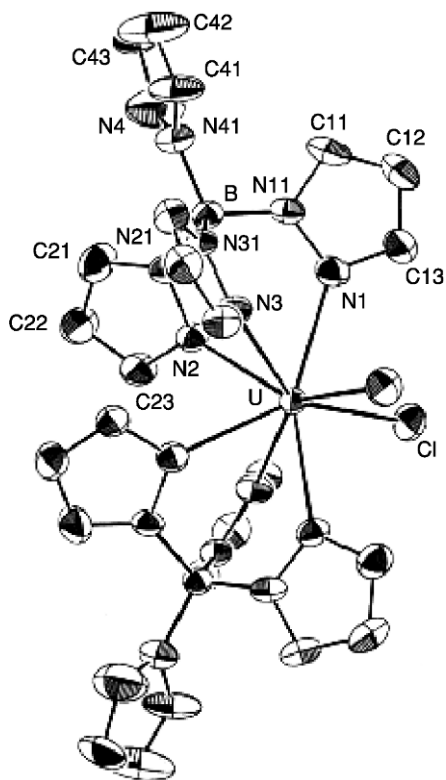
Fig. 25.37 *Molecular structure of* $[B(pz)_4]_2 UCl_2$ *(Campello* et al., *1999). (Reprinted with permission from Elsevier.)*

$[B(pz)_4]_2U(O^tBu)_2$, it is possible to slow down the interconversion of the typical eight-coordinate polyhedra (square antiprism ↔ dodecahedron ↔ bicapped trigonal prism). At higher temperatures, it was possible for some of these compounds to reach a regime where all pyrazolyl groups were equivalent on the NMR timescale, indicating dissociative exchange of free and coordinated rings.

25.4.3 Tris(amidoamine)

As in the case of early transition metals, the tris(amido)amine class of ligands, $[N(CH_2CH_2NR)_3]^{3-}$ (R = trialkylsilyl), has proven to be a versatile ligand set that supports unusual reactivity in the early actinides. Complexes of both thorium and uranium have been generated by metathesis reactions involving both the ligands $[N(CH_2CH_2NSiMe_3)_3]^{3-}$ and $[N(CH_2CH_2NSi^tBuMe_2)_3]^{3-}$. The complexes $[\{N(CH_2CH_2NSiMe_3)_3\}AnCl]_2$ (An = Th, U) were the first to be reported (Scott and Hitchcock, 1994); the molecular structure of the uranium complex demonstrated it was dimeric in the solid state. The chloride ligand may

be substituted, and derivatives incorporating cyclopentadienyl, borohydride, alkoxide, amide, and diazabutadiene derivatives have been characterized (Scott and Hitchcock, 1995a,b; Roussel *et al.*, 1997a, 1999). Attempts to alkylate the complex [N(CH$_2$CH$_2$NSi^{t}BuMe$_2$)$_3$]UI with alkyllithium or alkylpotassium reagents resulted in the isolation of a metallacyclic product resulting from intramolecular activation of a methyl group, as shown in equation (25.111) (Boaretto *et al.*, 1999).

$$\text{R} = \text{Si}^t\text{BuMe}_2$$
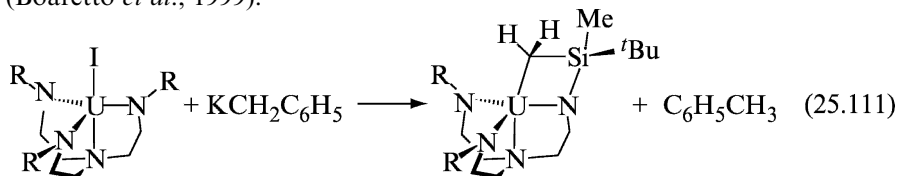
The U–C bond length in the metallacyclic unit is unusually long [2.752(11) Å], and is susceptible to protonation by alcohols, amines, and terminal alkynes; reaction with pyridine leads to the generation of a η^2-pyridyl complex.

Initial attempts to reduce the complex [N(CH$_2$CH$_2$NSi^{t}BuMe$_2$)$_3$]UCl resulted in the formation of a mixed-valence complex [{N(CH$_2$CH$_2$NSi^t-BuMe$_2$)$_3$}U]$_2$(μ-Cl) (Roussel *et al.*, 1996, 1997b). The complex is thought to possess electronically distinct U(III) and U(IV) centers. Fractional sublimation results in the isolation of a purple species, identified as the trivalent [N(CH$_2$CH$_2$NSi^{t}BuMe$_2$)$_3$]U (Roussel *et al.*, 1997b). This complex can also be produced by reduction of [N(CH$_2$CH$_2$NSi^{t}BuMe$_2$)$_3$]UI by potassium in pentane. A variety of base adducts of this complex have been reported (Roussel *et al.*, 2002). The U(III) complex can similarly be oxidized by trimethylamine N-oxide, trimethylsilyazide, and trimethylsilyldiazomethane to yield μ-oxo, imido, and hydrazido derivatives, respectively (Roussel *et al.*, 2002). One of the most unusual adducts isolated in this system is prepared by the reaction of the U(III) complex with dinitrogen [equation (25.112)].

$$\text{R} = \text{Si}^t\text{BuMe}_2$$
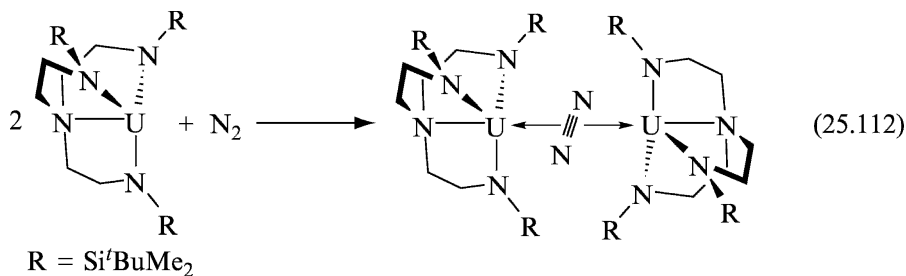
The molecular structure of the complex has been reported (Roussel and Scott, 1998) (Fig. 25.38). The N–N distances in the dinitrogen unit are essentially unperturbed. Metrical data, along with magnetic data, suggest that the complex
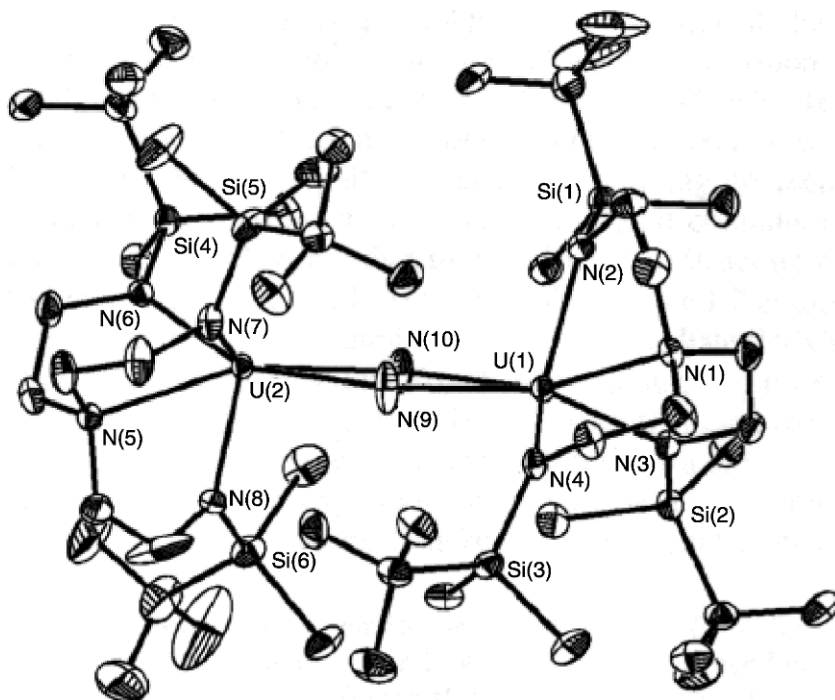
Fig. 25.38 *Molecular structure of* $[\{N(CH_2CH_2NSi^tBuMe_2)_3\}U](\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$. *(Reprinted with permission from Roussel and Scott (1998). Copyright 1998 American Chemical Society.)*

may be best formulated as a U(III) species. The electronic structure of this complex has been investigated; the only significant U–N$_2$–U interaction was found to consist of U→N$_2$ π-backbonding (Kaltsoyannis and Scott, 1998).

25.4.4 Other

Few other ligands have been developed with the steric bulk and solubility to stabilize mononuclear actinide complexes and support organometallic chemistry. A bulky amide ligand set has been developed for uranium that supports novel coordination complexes of lower valent uranium. Complexes of the formula (NRAr)$_3$UI (R = ^{t}Bu, adamantyl; Ar = 3,5-Me$_2$C$_6$H$_3$) may be prepared by the reaction of UI$_3$(THF)$_4$ with Li[NRAr] (Odom *et al.*, 1998); oxidation of the uranium center is presumed to be accompanied by sacrificial generation of U(0). A limited number of tetravalent derivatives of this ligand set have been reported, including the silyl complex (N^{t}BuAr)$_3$U[Si(SiMe$_3$)$_3$] (Diaconescu *et al.*, 2001) and the bridging cyanoimide complex (N^{t}BuAr)$_3$U= N=C=N=U(N^{t}BuAr)$_3$ (Ar = 3,5-Me$_2$C$_6$H$_3$) (Mindiola *et al.*, 2001).

Reduction of the uranium (IV) complex by sodium amalgam results in the isolation of (N^{t}BuAr)$_3$U(THF) (Ar = 3,5-Me$_2$C$_6$H$_3$). Reaction of the trivalent complex with Mo[N(Ph)(R$'$)]$_3$ (R$'$ = ^{t}Bu, adamantyl) under dinitrogen results in the formation of [N^{t}BuAr]$_3$U(μ-N$_2$)Mo[N(Ph)(R$'$)]$_3$, which contains a linear Mo–N–N–U unit. It is suggested that both metals are best regarded as tetravalent. As previously mentioned, reduction of (N^{t}BuAr)$_3$UI also provides entry into an interesting class of μ-arene complexes (*vide supra*).

25.5 BIMETALLIC COMPLEXES

One of the least explored aspects of the non-aqueous chemistry of the actinides is that of complexes containing other metals. Bimetallic complexes have been studied with the intent of creating complexes with two centers of reactivity for effecting chemical transformations. In addition, interest has grown in creating true metal–metal bonds. These complexes are rare; metal–metal bonding is disfavored in the f-elements with respect to d-transition metals, perhaps due to the limited radial extent of valence d- and f-orbitals most likely to be employed in bonding between two metal centers.

Many of the early attempts to generate bimetallic complexes focused on metathesis reactions involving the introduction of anionic metal carbonylate ligands onto actinide cations (Bennett *et al.*, 1971; Dormond and Moise, 1985). These reactions invariably resulted in the isolation of isocarbonyl species in which the actinide was bound by the oxygen atom of one or more carbonyl ligands [equation (25.113)].

$$UCl_4 + 4Na[Mn(CO)_5] \xrightarrow{\text{THF}} U[Mn(CO)_5]_4 + 4NaCl \qquad (25.113)$$

More recently, synthetic efforts have been further expanded to include several classes of compounds in which bridging ligands hold two metal centers in close proximity, but no evidence exists for a metal–metal interaction. Bridging hydride complexes (η^5-C$_5$H$_5$)$_3$UH$_6$ReL$_2$ (L = PPh$_3$, P(*p*-F-C$_6$H$_4$)$_3$) have been prepared by the reaction of (η^5-C$_5$H$_5$)$_3$UCl with [K(THF)$_2$][L$_2$ReH$_6$] in THF (Baudry and Ephritikhine, 1986). The compounds are fluxional at room temperature in solution, judging from the equivalence of all hydride ligands in the ^{1}H NMR spectrum, but it has been hypothesized that the Re and U centers are bridged by multiple hydride ligands. Ring-substituted analogs (η^5-C$_5$H$_4$R)$_3$UH$_6$Re(PPh$_3$)$_2$ could not be prepared directly from (η^5-C$_5$H$_4$R)$_3$UCl; rather, the cationic reagent [(η^5-C$_5$H$_4$R)$_3$U][BPh$_4$] was employed (Cendrowski-Guillaume and Ephritikhine, 1996). Reaction of (η^5-C$_5$Me$_5$)$_2$UCl(THF) with [K(THF)$_2$][(PPh$_3$)$_2$ReH$_6$] does not result in simple metathesis. Instead, an anionic product of the formula [K(THF)$_2$][(η^5-C$_5$Me$_5$)$_2$U(Cl)H$_6$Re(PPh$_3$)$_2$] is obtained (Cendrowski-Guillaume *et al.*, 1994; Cendrowski-Guillaume and Ephritikhine, 1996). NMR data suggest that three hydride ligands bridge the two metal centers.

Other examples of bimetallic complexes are generated using ligands on the actinide center that have pendant phosphine groups capable of binding transition metal centers. The diphenylphosphidocyclopentadienyl ligand acts as an electron-poor carbocyclic ligand in the synthesis of bis- and tris-cyclopentadienyl uranium complexes $(\eta^5\text{-}C_5H_4PPh_2)_3UX$ and $(\eta^5\text{-}C_5H_4PPh_2)_2UX_2$ (X = Cl, OR, R, NEt$_2$, BH$_4$) (Dormond *et al.*, 1990; Baudry *et al.*, 1993). In reactions with suitable transition metal reagents, complexes can be prepared in which the diphenylphosphide group binds to a second metal center (Dormond *et al.*, 1990; Baudry *et al.*, 1993; Hafid *et al.*, 1994) (equation (25.114)).

$$(\eta^5\text{-}C_5H_4PPh_2)_3U\text{---}X + \text{[norbornadiene]}Mo(CO)_4 \longrightarrow$$

X = Cl, BH$_4$, NEt$_2$

$$(25.114)$$
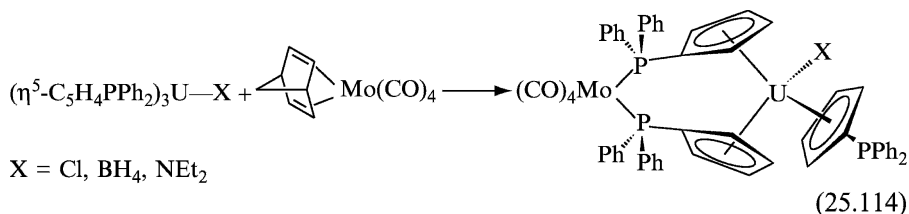
A second approach involves the use of cyclopentadienyl complexes in which the other substituents have pendant phosphine groups. A series of alkoxyphosphido complexes of uranium have been prepared for both bis- and tris-cyclopentadienyl frameworks: $(\eta^5\text{-}C_5Me_5)_2UCl[O(CH_2)_nPPh_2]$, $(\eta^5\text{-}C_5Me_5)_2U[O(CH_2)_nPPh_2]_2$, and $(\eta^5\text{-}C_5H_5)_3U[O(CH_2)_nPPh_2]$ (*n* = 0,1) (Dormond *et al.*, 1994). These species react with (norbornadiene)M(CO)$_4$ (M = Mo, W) to yield bimetallic compounds. The complexes $(\eta^5\text{-}C_5Me_5)_2U[O(CH_2)_nPPh_2]_2$ generate 1:1 (U:M) products in which both phosphorus atoms are bound to a single transition metal. As illustrated in equation (25.115), the complexes $(\eta^5\text{-}C_5Me_5)_2UCl[O(CH_2)_nPPh_2]$ and $(\eta^5\text{-}C_5H_5)_3U[O(CH_2)_nPPh_2]$ react to form 2:1 (U:M) adducts in which the metal carbonyl fragment is bound to one 'arm' of each of the uranium units:

$$2(\eta^5\text{-}C_5Me_5)_2U\begin{smallmatrix}Cl\\OCH_2PPh_2\end{smallmatrix} + \text{[norbornadiene]}Mo(CO)_4 \longrightarrow$$

$$(25.115)$$
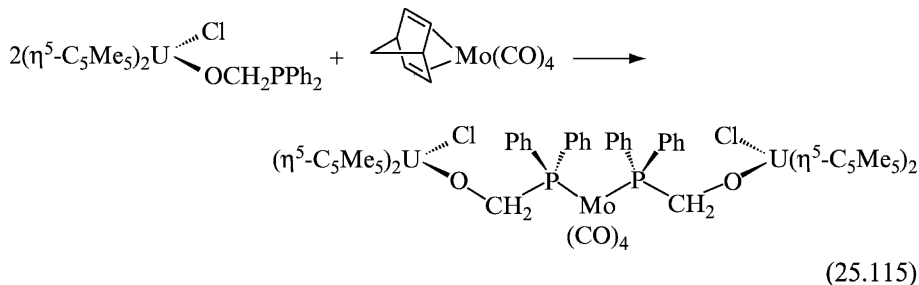
The compounds containing the sterically less hindered OCH$_2$PPh$_2$ ligand react more quickly in substitution reactions that their counterparts containing OPPh$_2$.

The phospholyl ligand has also demonstrated the ability to bridge two metal centers in a $\mu\text{-}\eta^5,\eta^1$ manner. Reduction of NiCl$_2$ in the presence of the previously mentioned uranium phospholyl compound $(\eta^5\text{-}C_5Me_4P)_2UCl_2$ yields the complex $Cl_2U(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2Ni(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2UCl_2$ in which the

central nickel atom is bound in a near-tetrahedral fashion by four phosphorus atoms from the four phospholyl ligands (Arliguie *et al.*, 1996).
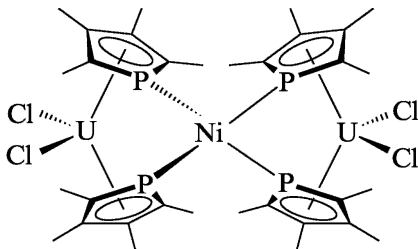
The dimeric nickel phospholyl complex $(\eta^5\text{-}C_5Me_4P)Ni(\mu\text{-}\eta^1\text{-}C_5Me_4P)_2Ni$ $(\eta^5\text{-}C_5Me_4P)$ can also be prepared; reduction of this in the presence of two equivalents of $(\eta^5\text{-}C_5Me_4P)_2UCl_2$ yields a tetrametallic complex $[Cl_2U(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2Ni(\mu\text{-}\eta^1\text{-}C_5Me_4P)_2Ni(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2UCl_2]$ (Fig. 25.39). In these complexes, long U···Ni distances (>3.3 Å) preclude direct metal–metal interaction.

Select compounds have been prepared in which the bridging ligands appear to coexist with a direct metal–metal interaction. The phosphido-bridged complexes $(\eta^5\text{-}C_5Me_5)_2Th(\mu\text{-}PPh_2)_2ML_n$ $[ML_n = Ni(CO)_2, Pt(PMe_3)]$ are prepared by the reaction of the thorium phosphide precursor, $(\eta^5\text{-}C_5Me_5)_2Th$ $(PPh_2)_2$ with an olefin complex of the appropriate transition metal species in the presence of additional ligand [equations (25.116) and (25.117)] (Ritchey *et al.*, 1985; Hay *et al.*, 1986).

$$(\eta^5\text{-}C_5Me_5)_2\,Th(PPh_2)_2 + Ni(COD)_2 + 2CO \longrightarrow (\eta^5\text{-}C_5Me_5)_2Th \overset{\overset{\displaystyle Ph_2}{\displaystyle P}}{\underset{\underset{\displaystyle Ph_2}{\displaystyle P}}{<}} Ni(CO)_2$$

$$(25.116)$$

$$(\eta^5\text{-}C_5Me_5)_2Th(PPh_2)_2 + Pt(COD)_2 + PMe_3 \longrightarrow (\eta^5\text{-}C_5Me_5)_2Th \overset{\overset{\displaystyle Ph_2}{\displaystyle P}}{\underset{\underset{\displaystyle Ph_2}{\displaystyle P}}{<}} Pt\text{---}PMe_3$$

$$(25.117)$$
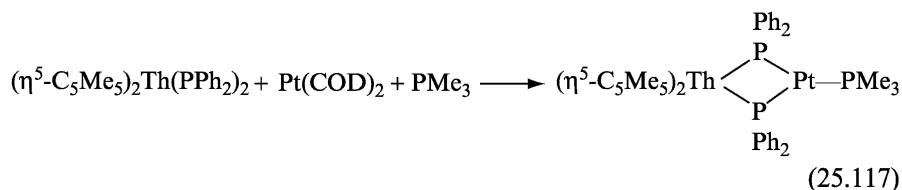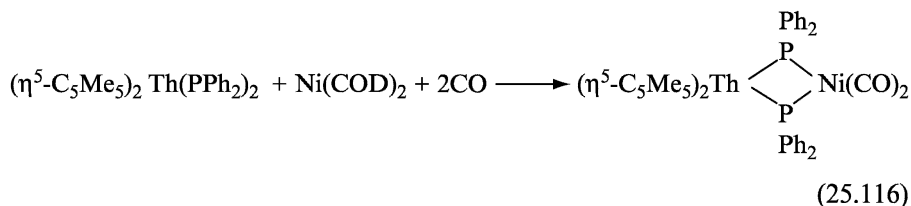
Calculations performed on both complexes suggest the presence of a direct M–Th interaction (Hay *et al.*, 1986; Ortiz, 1986). This contention appears to be supported both by ^{31}P NMR and structural evidence. The thorium–metal distance in each compound is shorter than that expected on the basis of metal radii derived from related structures without metal–metal nonbonded distances [Th–Ni = 3.206(2) Å, Th–Pt = 2.984(1) Å]. Furthermore, the Th–M–P$_2$ unit is 'folded' about the phosphide ligands in each case to bring the two metal atoms
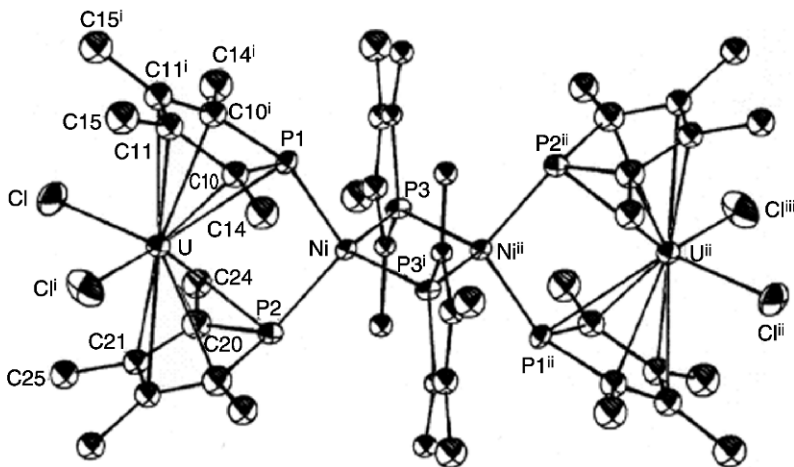
Fig. 25.39 *Molecular structure of* $[Cl_2U(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2Ni(\mu\text{-}\eta^1\text{-}C_5Me_4P)_2Ni(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4P)_2UCl_2]$ *(Arliguie* et al.*, 1996). (Reprinted with permission from Elsevier.)*

in closer proximity. Theoretical examination of these compounds suggest that the interaction is essentially a M→Th (M = Ni, Pt) dative donor–acceptor bond, involving principally metal d-orbitals.

One class of compounds exist which possess an unsupported metal–metal interaction. Reaction of $(\eta^5\text{-}C_5Me_5)_2ThX_2$ (X = Cl, I) with $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$ produces the complexes $(\eta^5\text{-}C_5Me_5)_2Th(X)Ru(\eta^5\text{-}C_5H_5)(CO)_2$ [equation (25.118)] (Sternal *et al.*, 1985). This synthetic methodology has also been extended to include derivatives of the tris(cyclopentadienyl) framework [equation (25.119)] (Sternal and Marks, 1987).

$$(\eta^5\text{-}C_5Me_5)_2ThX_2 + Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2] \longrightarrow (\eta^5\text{-}C_5Me_5)_2Th \overset{X}{\underset{OC \quad CO}{\diagup Ru \diagdown}} + NaX$$

X = Cl, I

$$\text{(25.118)}$$

$$(\eta^5\text{-}C_5H_5)_3AnCl + Na[(\eta^5\text{-}C_5H_5)M(CO)_2] \longrightarrow (\eta^5\text{-}C_5H_5)_3An \longrightarrow M \underset{OC \quad CO}{} + NaX$$

An = Th, U   M = Fe, Ru

$$\text{(25.119)}$$
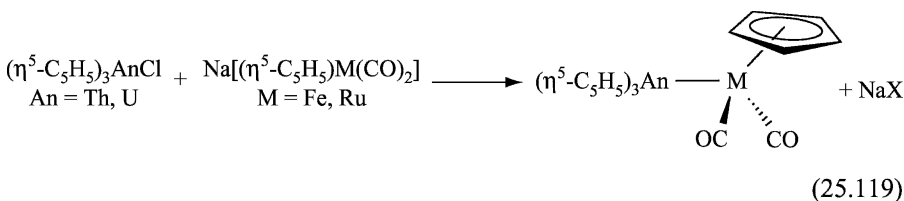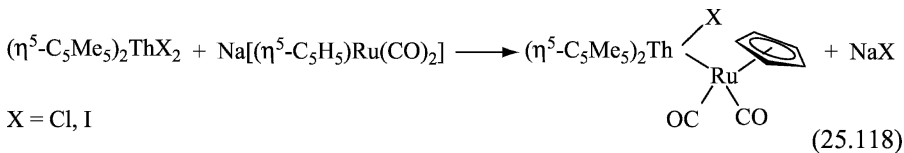
The molecular structure of $(\eta^5\text{-}C_5Me_5)_2Th(I)Ru(\eta^5\text{-}C_5H_5)(CO)_2$ has been determined (Fig. 25.40); it confirms the presence of a direct metal–metal interaction, with a Th–Ru bond length of 3.0277(6) Å.
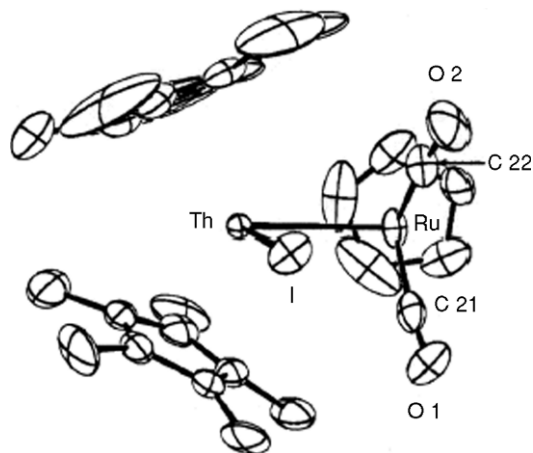
Fig. 25.40   *Molecular structure of $(\eta^5\text{-}C_5Me_5)_2Th(I)Ru(\eta^5\text{-}C_5H_5)(CO)_2$. (Reprinted with permission from Sternal et al. (1985). Copyright 1985 American Chemical Society.)*

The bond distance is sensitive to the identity of the metal; the Th–Fe distance in the complex $(\eta^5\text{-}C_5H_5)_3ThFe(\eta^5\text{-}C_5H_5)(CO)_2$ is 2.940(5) Å. Variable temperature NMR data for the complexes $(\eta^5\text{-}C_5H_5)_3AnM(\eta^5\text{-}C_5H_5)(CO)_2$ (M = Fe, Ru) suggest rotation about the metal–metal bond is hindered in solution at room temperature. Thermochemical measurements have determined U–M bond disruption enthalpies for the derivatives $(\eta^5\text{-}C_5H_5)_3UM(\eta^5\text{-}C_5H_5)(CO)_2$ [M = Fe, 30.9 (3.0) kcal/mol; M = Ru, 40.4 (4.0) kcal/mol], indicating relatively weak metal–metal interactions (Nolan *et al.*, 1991). Consistent with this observation, the An–M interactions are easily disrupted by protic reagents. In addition, reaction of $(\eta^5\text{-}C_5Me_5)_2Th(Cl)Ru(\eta^5\text{-}C_5H_5)(CO)_2$ with coordinating bases (such as ketones or acetonitrile) generates $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$, along with thorium products arising from C–H activation of the Lewis base substrate, followed by insertion of a second (and third) equivalent of the Lewis base (Sternal *et al.*, 1987). Theoretical examination of the bonding $(\eta^5\text{-}C_5Me_5)_2Th(I)Ru(\eta^5\text{-}C_5H_5)(CO)_2$ (Bursten and Novo-Gradac, 1987) demonstrates that once again, the bonding is best described as a Ru→Th dative donor–acceptor bond, involving principally Th 6d and Ru 4d orbitals.

25.6   NEUTRAL CARBON-BASED DONOR LIGANDS

One of the most common ligands in d-transition metal organometallic chemistry, the carbonyl ligand, is virtually unknown in actinide chemistry. Aside from the carbon monoxide adducts of tris(cyclopentadienyl)uranium previously described (see Section 25.2.1.1), there are no actinide carbonyl complexes that are

isolable at room temperature and pressure. Uranium carbonyl complexes U $(CO)_n$ ($n = 1$–6) were first reported to form in matrix isolation experiments and were produced by the condensation of thermally generated uranium vapor with carbon monoxide in an argon matrix at 4 K (Slater *et al.*, 1971; Sheline and Slater, 1975). More recent studies indicate that thermal and pulsed-laser evaporated uranium atoms undergo reaction with CO in argon matrices to generate the linear triatomic species CUO (Tague *et al.*, 1993). Tague *et al.* (1993) indicate that higher uranium carbonyls ($n > 2$) are only produced upon subsequent annealing of the matrices to 15—30 K. Photolysis was reported to regenerate CUO from the carbonyls.

The most recent class of Group 14 donor ligands to be employed in actinide chemistry is that of *N*-heterocyclic carbenes. These ligands act as σ-donor bases toward a number of metals in coordination chemistry. Reaction of $[UO_2Cl_2(THF)_2]_2$ with 1,3-dimesitylimidazole-2-ylidene and its 4,5-dichloro-substituted derivative generate 1:2 (uranium:carbene) adducts $UO_2Cl_2(L)_2$ (Oldham *et al.*, 2001). Crystallographic characterization reveals an octahedral metal center with *trans* oxo, chloro, and carbene ligands. The uranium–carbon bond distances in these species are long at 2.626(7) and 2.609(4) Å, consistent with the formulation of the C–U bond as a dative interaction.

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