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Tris(Cyclopentadienyl)Uranium-t-Butyl: Synthesis, Reactions and Mechanisms

(Ph.D. Dissertation)

by

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Abstract

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Doctor of Philosophy in Chemistry

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The compounds $(RC_5H_4)_3U(t\text{-}Bu)$ were prepared for R = H, Me, Et. Their physical properties are reported. The decomposition of these uranium tertiary alkyl compounds in aromatic solvents was studied in detail. The organometallic decomposition product could not be characterized due to its insolubility. The organic decomposition products, the dependence of their relative ratios upon the identity of the aromatic solvent and the reaction temperature, as well as kinetic studies of the rate of decomposition are consistent with a radical decomposition pathway induced by solvent-assisted uranium-carbon bond homolysis. NMR-spectroscopic studies on the reactions of $(RC_5H_4)_3UCl$ with t-BuLi (R = t-Bu, Me_3Si) showed that a delicate equilibrium exists for these bulkier systems between formation of the reduced $(RC_5H_4)_3U$ species and the tetravalent $(RC_5H_4)_3UH$.

Chapter 2 discusses the reaction chemistry of $(MeC_5H_4)_3U(t\text{-}Bu)$. The compound reacts with σ-donor ligands L to give the trivalent base adducts $(RC_5H_4)_3U(L)$, even with unsaturated ligands (RCN, RNC), capable of inserting into the uranium-carbon bond. The mechanism for the reaction of $(C_5H_5)_3U(t\text{-}Bu)$ with thf was studied in detail. Weak unsaturated ligands such as carbon monoxide and ethylene do insert into the metal-carbon bond of $(MeC_5H_4)_3U(t\text{-}Bu)$. The uranium tertiary alkyl compound also reacts with fluorocarbons under mild conditions and in the presence of hydrocarbon solvents to yield $(MeC_5H_4)_3UF$ and organic products derived from radical pathways.

Chapter 3 discusses analogous reaction chemistry between $(RC_5H_4)_3ThX$ systems and t-BuLi. Reactivity differences between uranium and thorium are highlighted and discussed. The new thorium hydrides $(RC_5H_4)_3ThH$ (R = t-Bu, Me_3Si) were characterized.

Chapter 4 presents a new synthetic approach to the synthesis of sterically crowded $(RC_5H_4)_4U$ compounds. Reaction of the trivalent $(RC_5H_4)_3U$ with $(RC_5H_4)_2Hg$ results in formation of $(RC_5H_4)_4U$. Some aspects of steric congestion, cyclopentadienyl ligand exchange and electron-transfer properties of homoleptic tetravalent uranium cyclopentadienyl compounds are discussed.

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> Although this may seem a paradox, all exact science is dominated by the idea of approximation.
>
> Bertrand Russell

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Introduction

The discovery of the true structure of ferrocene by Wilkinson, Woodward and Fischer in 1952 spurred a rapid development of organometallic chemistry.[1] The field of organoactinide chemistry came into being with the synthesis of Cp_3UCl by Wilkinson in 1956.[2] Not much happened in this area after that, with the exception of the synthesis of Cp_4An (An = U, Th) by Fischer in 1962.[3] The preparation of uranocene $U(C_8H_8)_2$ in 1968 by Streitwieser may be considered to be the discovery that renewed interest in this field.[4] Indeed, in those days, it was noted that the f-orbitals are of the correct symmetry to interact with the E_{2u} and E_{3u} orbitals on the planar cyclooctatetraene dianion. This led to the assumption that the presence of actinide 5f-orbitals, which are relatively accessible in energy in contrast to the lanthanides, combined with the availability of several oxidation states would lead to the discovery of novel behavior without precedent in d-transition metal chemistry. As of this date, however, no clear-cut example of the involvement of f-orbitals in bonding has been presented. On the contrary, variable energy photoelectron spectroscopy by Green has recently shown that the covalent bonding in uranocene is largely due to orbitals of metal 6d and not 5f-parentage.[5]

The discovery of uranocene generated a great deal of interest in organoactinide chemistry. Even though bonding patterns involving f-orbitals remained elusive, a considerable amount of work was accomplished in just a few years. The first π-arene complex was crystallographically characterized in 1971.[6] The first actinide-to-carbon σ-bonds were synthesized in 1973 by several research groups working independently,[7] the first actinide-phosphine coordination compounds were reported by Andersen in 1981,[8] and the first carbon monoxide adduct stable at room temperature was reported in 1985 again by Andersen.[9] The large number of compounds known for the early actinides, particularly thorium and uranium, did indeed reveal some unique reactivity patterns. The peculiar features however should be attributed to the special position occupied by the early actinides in the periodic table and not to f-orbital involvement in bonding. While indications of covalency in early actinide compounds certainly do exist, to a first approximation the bonding is best viewed as ionic.[10] The large ionic radii of the early actinides combined with essentially ionic bonding place them among the more substitutionally-labile metal centers. While this is generally accepted, very few measurements concerning the lability of actinide metal centers actually exist.[11] The bond strengths on the other hand are better compared to the early d-transition metals of the second and third series.[12]

In marked contrast to these early d-transition metals, where 18 electron compounds are the rule, electronic saturation in f-elements is a practical impossibility. Thus the chemistry relies heavily on steric saturation by the use of bulky supporting ligands. Reorganization energies are invariably small as virtually no orbital barriers exist. This may well be the principal way in which f-orbitals participate in determining a unique character of the early actinides. This feature is not often appreciated; even though the importance of f-orbitals in chemical bonding (i.e. in a thermodynamic sense) is minimal, the f-orbitals do significantly influence the chemistry of the early actinides by providing low-lying vacant orbitals that facilitate ligand redistribution reactions and/or coordination of a potential substrate. Hence, the presence of f-orbitals does affect the kinetic properties. As an orbital of appropriate symmetry is virtually always available, the reorganization energy is best viewed as the activation energy due to steric interactions in reaching the transition state. With the rates of ligand substitution at the metal center so fast, these elements provide an obvious attraction as catalysts promising high turnover rates.

The molecular properties of the f-block elements in many cases find parallels to the main-group elements rather than the d-block elements. This is nicely illustrated by the tertiary alkyl compounds of the f-elements. A host of early main-group tertiary alkyl compounds are known. Their reactivity, however, is limited to either transmetallation or acid-base type chemistry as no change in oxidation state is accessible in these compounds. Tertiary alkyl compounds are also known for the soft main-group metals, e.g. Zn, Cd, Hg, Ga, In, etc..[13] Here the chemistry is dominated by homolytic cleavage of a weak metal-carbon bond leading to tertiary radicals and reduced metal. There are, however, only a few d-transition-metal tertiary alkyl compounds. In this case the ubiquitous β-hydrogen elimination mechanism often leads to rapid formation of the corresponding hydrides.[14]

In the few known examples of tertiary alkyl compounds, e.g. $Cr(t\text{-}Bu)_4$, $Cr(1\text{-}norbornyl)_4$, $CpFe(CO)_2(t\text{-}Bu)$, steric or electronic constraints are assumed to render the transition state for β-hydrogen elimination energetically unfavorable.[15] f-Element alkyl compounds generally do not decompose by β-hydrogen elimination and thus isolable tertiary alkyl compounds can be synthesized. The absence of β-hydrogen elimination is thought to be due to the near equivalence of the metal-carbon and metal-hydrogen bond strengths.[16] Indeed, as one goes through the d-transition series from right to left, the metal-hydride bond strength for a given alkyl stays roughly constant, whereas the metal-carbon bond strength increases until it is of comparable magnitude in the early transition-metals. This feature favors β-hydrogen elimination less and less on proceeding towards the early part of the d-transition series. However, the energy gained from the metal-olefin interaction also favors β-hydrogen elimination and this is why β-hydrogen elimination still occurs in the early part of the d-transition series. For the f-elements the metal-olefin interaction is thought to be very weak and this also tends to disfavor β-hydrogen elimination. A number of lanthanide tertiary alkyl compounds have been synthesized by

Evans.[17] They display features related to early main-group compounds. A notable exception is an unsuccessful attempt at preparing Cp^*_2Yb-t-Bu. Interaction of Cp^*_2YbCl with t-BuLi resulted in the isolation of the Yb(II) compound Cp^*_2Yb. This shows that when lower oxidation states are accessible, t-BuLi can be a strong reducing agent.

The early actinides present an obvious attraction for studying the behavior of metal-tertiary alkyl bonds in the absence of β-hydrogen elimination. It has been shown that Cp_3AnR- systems do not decompose by that pathway.[6c] In addition, it is possible to contrast the behavior of analogous uranium and thorium compounds. Uranium has a relatively easily accessible +III oxidation state, whereas the chemistry of thorium is confined to the +IV oxidation state, with one exception.[18] As previous papers on tertiary alkyl metal complexes reported virtually no reactivity studies we decided to explore the reactions of metal-tertiary alkyl bond in uranium and thorium.

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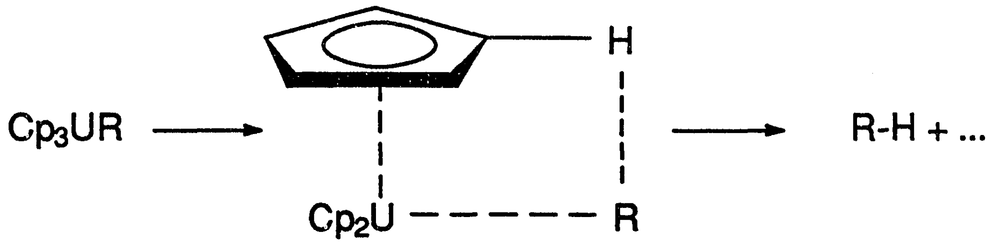
Chapter One:

Tris(Cyclopentadienyl)Uranium-t-Butyl: Synthesis and Decomposition Studies of the Uranium-tertiary Alkyl Bond

Not many isolable compounds containing transition metal tertiary alkyl bonds are known and their reactions have been little explored. Uranium(IV) is a prime candidate for such a study. Since β-hydrogen elimination is generally not the preferred decomposition pathway in organoactinides, a tertiary alkyl compound should be accessible. Furthermore, uranium(IV) can be reduced to uranium(III) and oxidized to uranium(V) in organometallic systems.[1] This should allow for chemistry significantly different from that of early main-group tertiary alkyl compounds.

Marks reported the synthesis of $Cp_3U(t\text{-}Bu)$ among other related alkyl derivatives.[2] Their decomposition pathways were investigated in detail. From mechanistic studies performed primarily on $Cp_3U(n\text{-}Bu)$ the authors concluded that the thermal decomposition proceeds by stereospecific, intramolecular hydrogen-abstraction from the cyclopentadienyl ring, giving an insoluble uranium-containing product and an alkane in high yield (Scheme 1). The tertiary derivative $Cp_3U(t\text{-}Bu)$ was reported to yield 96.5% isobutane and 3% isobutene upon thermolysis. The rates of decomposition in toluene were also measured. The disappearance of uranium-alkyl compound was found to be first order in uranium alkyl and the general order of stability was found to be primary > secondary > tertiary.

Scheme 1



The results obtained by Marks and coworkers showed a remarkably clean process leading to almost exclusive formation of alkane upon thermal decomposition of the uranium alkyl compounds. However, a significantly less selective alkane:alkene ratio was found for thermal decompositions in toluene by Folcher, Fischer and coworkers.[3] They report that the thermal decomposition of Cp_3U(n-Bu) in toluene at 60 °C yielded n-butane and 1-butene in a 75:25 ratio, which differs from the 92:2 ratio reported by Marks for the same solvent, but at 97 °C.

The related methylcyclopentadienyl compound, $(MeC_5H_4)_3U$(t-Bu), was first synthesized by Brennan.[1] The compound was found to decompose slowly in toluene solution leading to what was termed "evolution of various hydrocarbons". This apparent discrepancy in the thermal decomposition results obtained by Marks and Brennan led us to reinvestigate the thermal decomposition of these compounds in aromatic solvents. For the sake of completeness, Bis(indenyl)bis(t-butyl)uranium has been reported, although characterization was meager.[4]

1.1 Synthesis and Characterization of Isolable Tris(cyclopentadienyl)-Uranium-tertiary Alkyl Compounds

The preparation of $(RC_5H_4)_3U(t\text{-}Bu)$ is relatively straightforward in toluene solution as shown in eq 1. Upon addition of t-butyllithium the red-brown $(RC_5H_4)_3UCl$ solution turns dark green. The product is best isolated by crystallization from diethyl ether. The chlorides $(RC_5H_4)_3UCl$ were prepared as described by Brennan, with a slightly modified workup procedure (see experimental section).[1]

$$(RC_5H_4)_3UCl + t\text{-}BuLi \rightarrow (RC_5H_4)_3U(t\text{-}Bu) + LiCl \qquad (1)$$

$$R = H, Me, Et$$

In the methylcyclopentadienyl case, the t-butyl derivative can be prepared with equal convenience starting from tetrakis(methylcyclopentadienyl)uranium instead of the chloride (eq 2). This method of preparation is not convenient for the unsubstituted compound due to the insolubility of tetrakis(cyclopentadienyl)uranium in toluene.

$$(RC_5H_4)_4U + t\text{-}BuLi \rightarrow (RC_5H_4)_3U(t\text{-}Bu) + Li(RC_5H_4) \qquad (2)$$

$$R = Me$$

For best results the stoichiometry has to be carefully controlled in both reaction sequences. The dark-green products are thermally sensitive in the solid state as well as moderately light sensitive. Therefore the reaction is best carried out in the dark in order to maximize the yield, which is usually about 50%. Once isolated the tertiary alkyl compounds are best stored in the dark at low temperature (-20 °C). They are soluble in aromatic hydrocarbon solvents as well as diethyl ether, but they exhibit low solubility in saturated hydrocarbons. Their solid state melting points are quite high (Table 1.1).

Indeed, these high melting points are not indicative of high thermal stability since heating a solid sample to a much more moderate temperature results in irreversible decomposition; the melting points might be the melting point of decomposition products, although no clearly visible change takes place during the melting procedure before reaching the reported melting point.

Table 1.1

$(RC_5H_4)_3U(t\text{-}Bu)$	melting point in °C
R = H	195-200 (dec.)
R = Me	224-228 (dec.)
R = Et	195-200 (dec.)

The solution behavior of these compounds was investigated by variable temperature ^{1}H-NMR spectroscopy. As uranium(IV) is paramagnetic ($5f^2$-electron configuration), the chemical shift of a particular resonance is temperature dependent. The chemical shift usually obeys the Curie law, i.e. δ is directly proportional to 1/T (K). Deviations from linearity are usually interpreted as indicating the presence of a temperature dependent equilibrium in solution, though this is not the only possible explanation for nonlinear behavior.[5] Since the exchange processes in solution are inevitably rapid on the NMR time scale at all temperatures, no mechanistic information is available in the lineshape, other than that Curie law is not obeyed. The spectrum of $(C_5H_5)_3U(t\text{-}Bu)$ appears to follow Curie-Weiss behavior from +30 to -82 °C (Figure 1), although one could make a case that the t-butyl resonance is a curve rather than a straight line. The data points are certainly distributed in a non-random manner around the best linear fit as shown in Figure 1. The effect, however, is tiny and might be due to a systematic error in the data. Therefore the analogous methylcyclopentadienyl compound, $(MeC_5H_4)_3U(t\text{-}Bu)$, was investigated by variable temperature ^1H-NMR spectroscopy. Here, four resonances instead of just two can be followed. The result is shown in Figure 2 and in more detail in Figure 3. It appears that between +46 °C and -78 °C only the resonance for the methyl group of the methylcyclopentadienyl ring follows Curie-Weiss behavior. One of the methylcyclopentadienyl ring proton resonances (labeled a) and the t-butyl group resonance both show a small non-random deviation from linearity analogous to that found for the t-butyl group of $(C_5H_5)_3U(t\text{-}Bu)$. The second ring proton resonance (labeled b) shows a clear nonlinear behavior. Thus in solution, some temperature dependent process is occurring, that changes the averaged population and hence the averaged chemical shift, resulting in nonlinear behavior. Interestingly, the effect is most pronounced in the resonance that is the least temperature dependent. This is counterintuitive since one would expect the resonances with the largest temperature dependence to be the most sensitive to the change in population, since small population changes should change the averaged chemical shifts a lot. This assumes that the chemical shifts of the contributing species are very different. This unusual behavior can be rationalized in two ways. First, a subtle conformational equilibrium may slightly perturb all the resonances in the compound. Such a small perturbation will be most obvious in the least temperature dependent resonance, because it is not overshadowed by a large change in chemical shift with temperature. Second, an equilibrium with a small equilibrium constant may be present, which effects a site exchange for the hydrogen atoms in the molecule with another position of comparable chemical shift. Thus contributions to the averaged chemical shift by the other species present in small quantities will not be detectable, except for one resonance (in this case ring resonance b) for which the exchange takes place between two sites of vastly different chemical shift.

Figure 1: Variable Temperature ^{1}H-NMR of $Cp_3U(t\text{-}Bu)$ in toluene-d_8

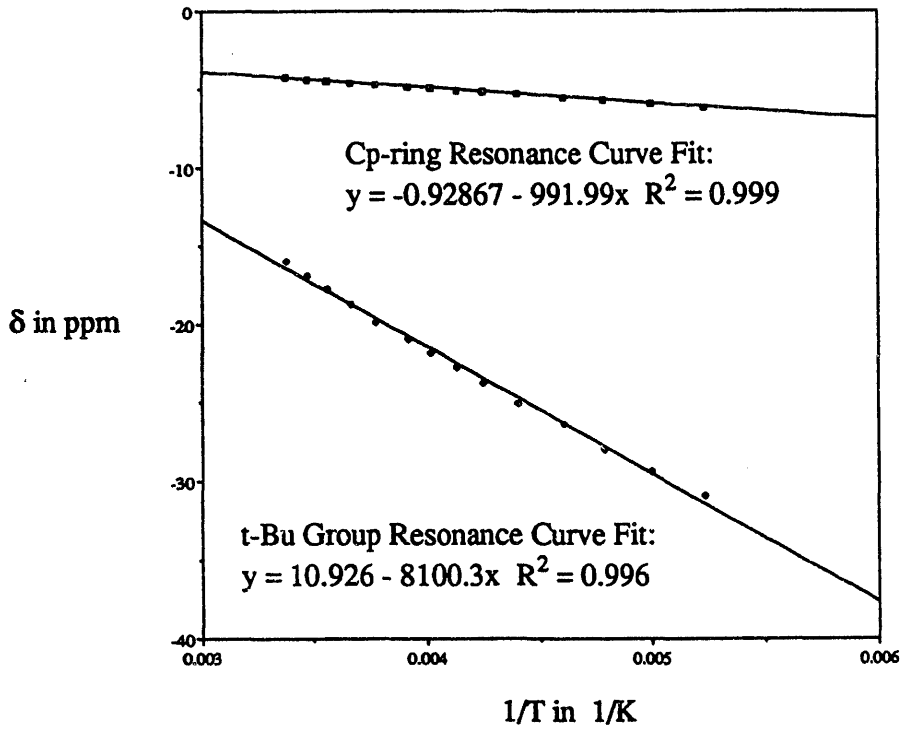


Figure 2: Variable Temperature ^{1}H-NMR of $(MeC_5H_4)_3U(t\text{-}Bu)$ in toluene-d_8

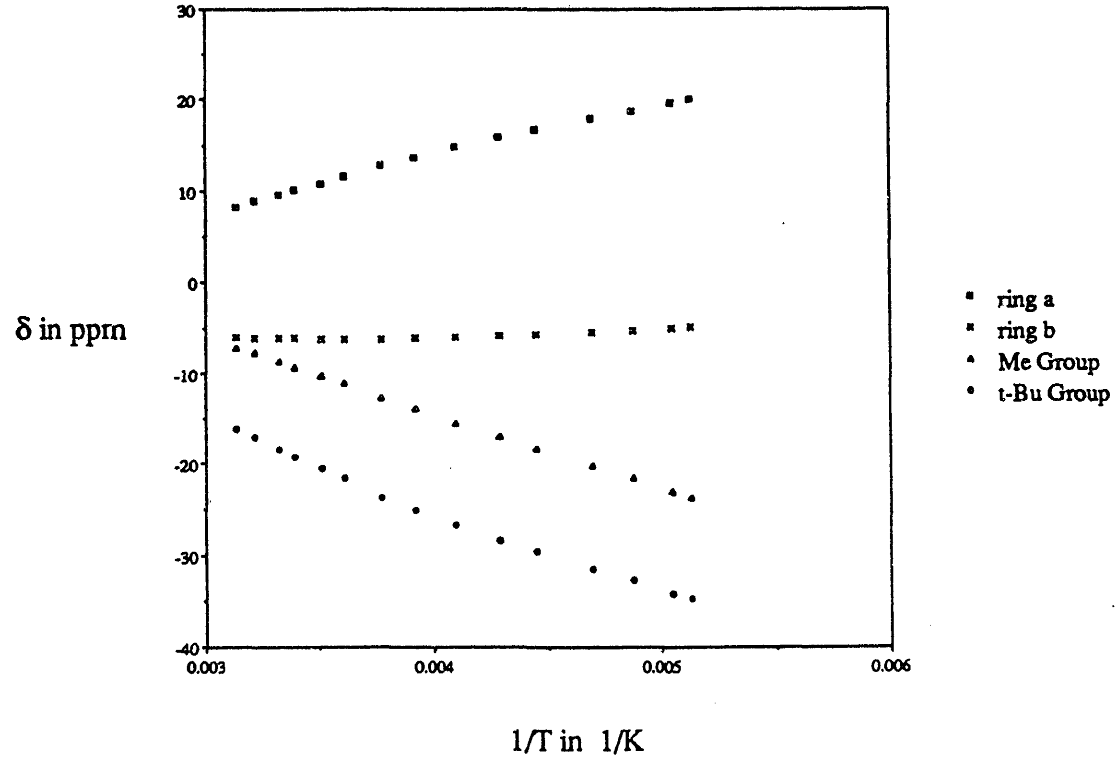
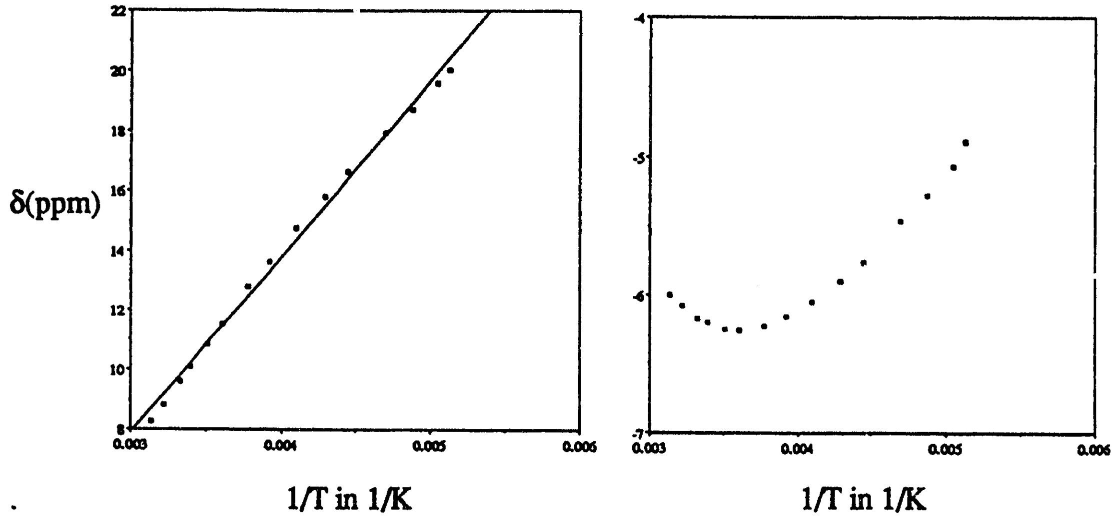


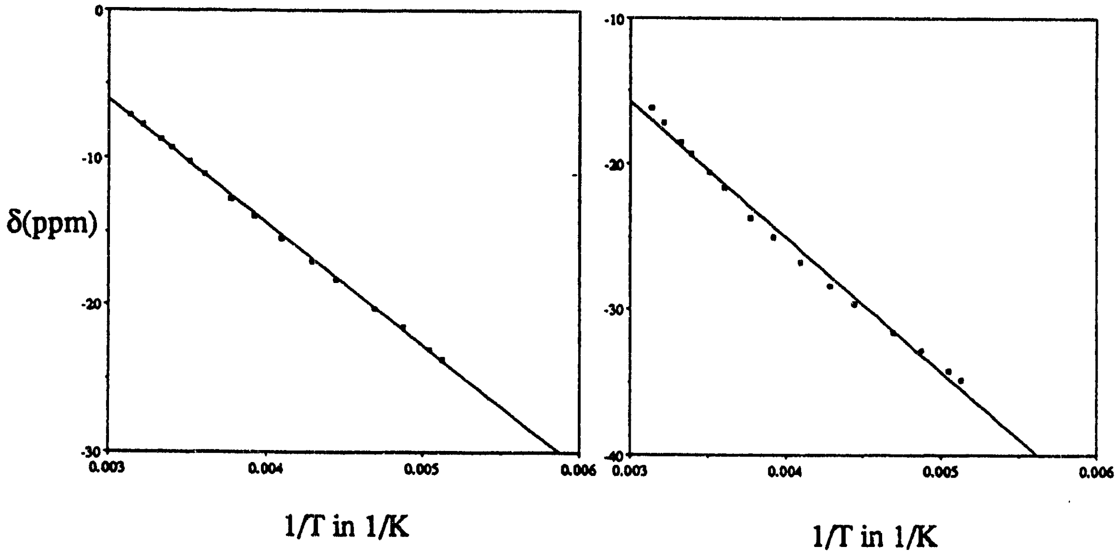
Figure 3: Variable Temperature ^{1}H-NMR of $(MeC_5H_4)_3U(t\text{-}Bu)$



a) MeC_5H_4-Ring Resonance a

b) MeC_5H_4-Ring Resonance b

c) MeC_5H_4-Ring Methyl Group Resonance



d) t-Butyl Group Resonance

One such process could be an η^1-η^5-equilibrium of the cyclopentadienyl group. Indeed, the α-hydrogen ring resonance of the η^1-cyclopentadienyl group should have a chemical shift comparable to that of the α-hydrogens on a σ-alkyl substituent which resonate around -200 ppm at room temperature. In addition, ring resonance b starts to broaden below -60 °C, but none of the other resonances do so. On the basis of these data alone however, one can only speculate as to the nature of the process involved. Similar small deviations from linearity have been observed in a number of tris(cyclopentadienyl)-uranium(IV) compounds and will be discussed in chapter 4. If the variable temperature ^{1}H-NMR spectrum of $(MeC_5H_4)_3U$(t-Bu) is recorded in the presence of several equivalents of diethyl ether in toluene-d_8 solution, the chemical shifts observed are unaffected by the presence of diethyl ether, consistent with diethyl ether coordination to the uranium center being insignificant.

Another noteworthy feature is illustrated by the ^{1}H-NMR spectra shown in Figure 4. If equimolar aliquots of $(MeC_5H_4)_3U$(t-Bu) and $(EtC_5H_4)_3U$(t-Bu) are mixed in benzene-d_6, the first ^{1}H-NMR spectrum recorded after a time lapse of ca. 10 min shows more resonances than can be accommodated by the two individual compounds. Instead one observes the spectrum shown in Figure 4a. As a contrast Figure 5 shows a computer simulation of the expected spectrum of $(MeC_5H_4)_3U$(t-Bu) and $(EtC_5H_4)_3U$(t-Bu) in benzene-d_6 with no interaction between them. The spectrum in Figure 4a looks rather complicated but it can be completely understood. Figure 4b shows the region of the spectrum where one would expect the resonance due to the t-butyl groups bonded to uranium. As can be seen, four distinct resonances are observed. This can be accommodated by the presence of four distinct uranium-t-butyl compounds in solution, which can be rationalized by postulating exchange of the substituted cyclopentadienyl ligands between metal centers. This process seems to be quite fast on a chemical time scale, since the equilibrium mixture is reached by the time the first spectrum can be

Figure 4a: $(MeC_5H_4)_3U(t\text{-}Bu) + (EtC_5H_4)_3U(t\text{-}Bu)$ in Benzene-d_6

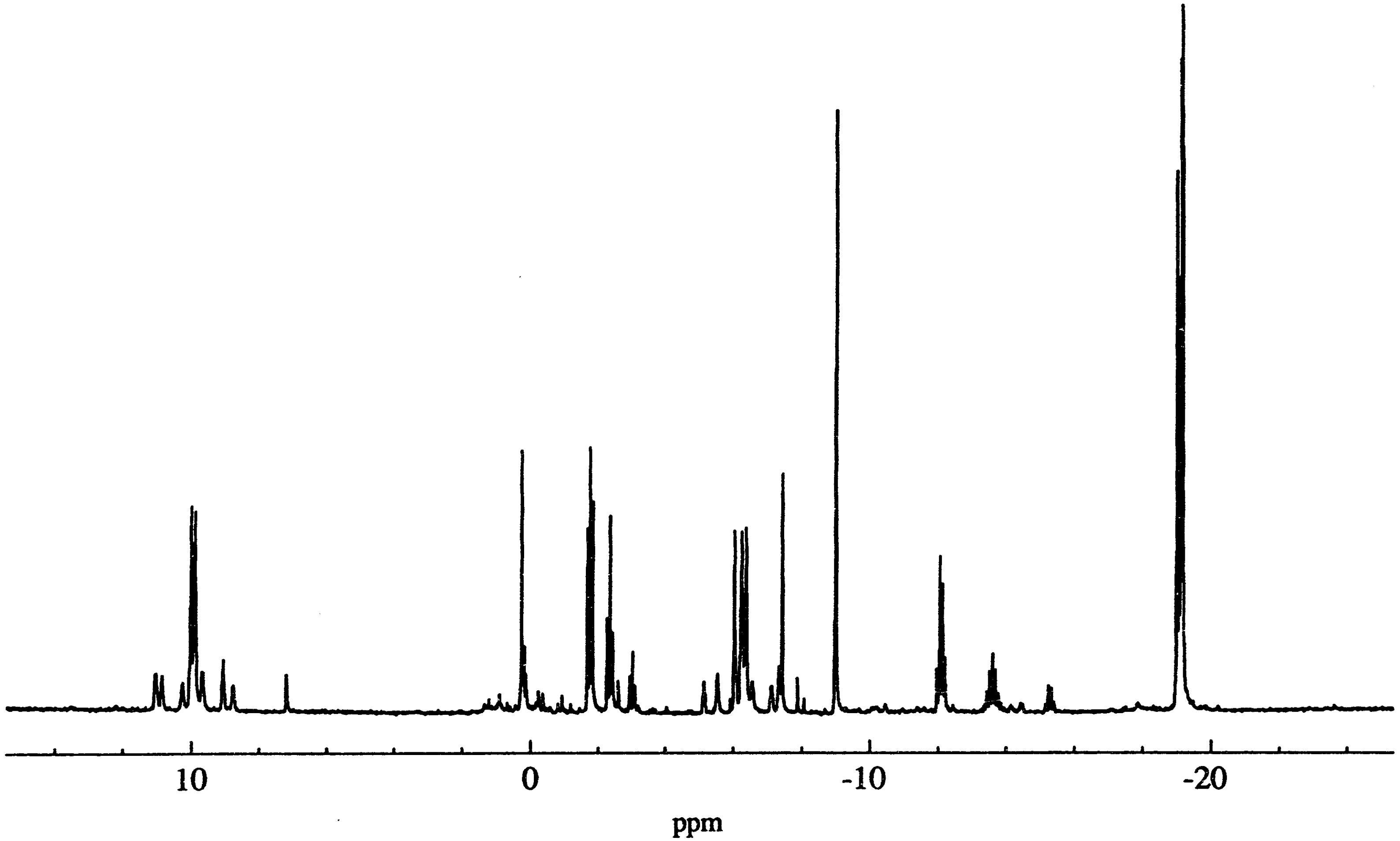


Figure 4b : t-Butyl Region

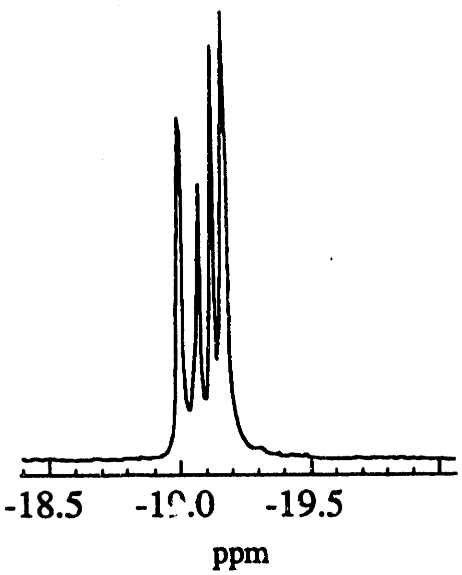


Figure 4c: Methylene Region

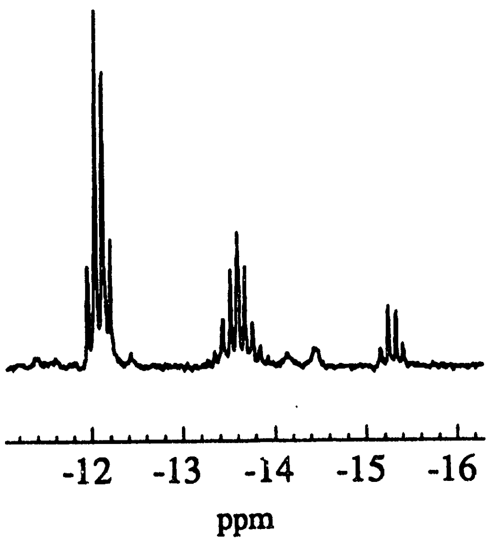


Figure 4d: Ring Resonance a Region

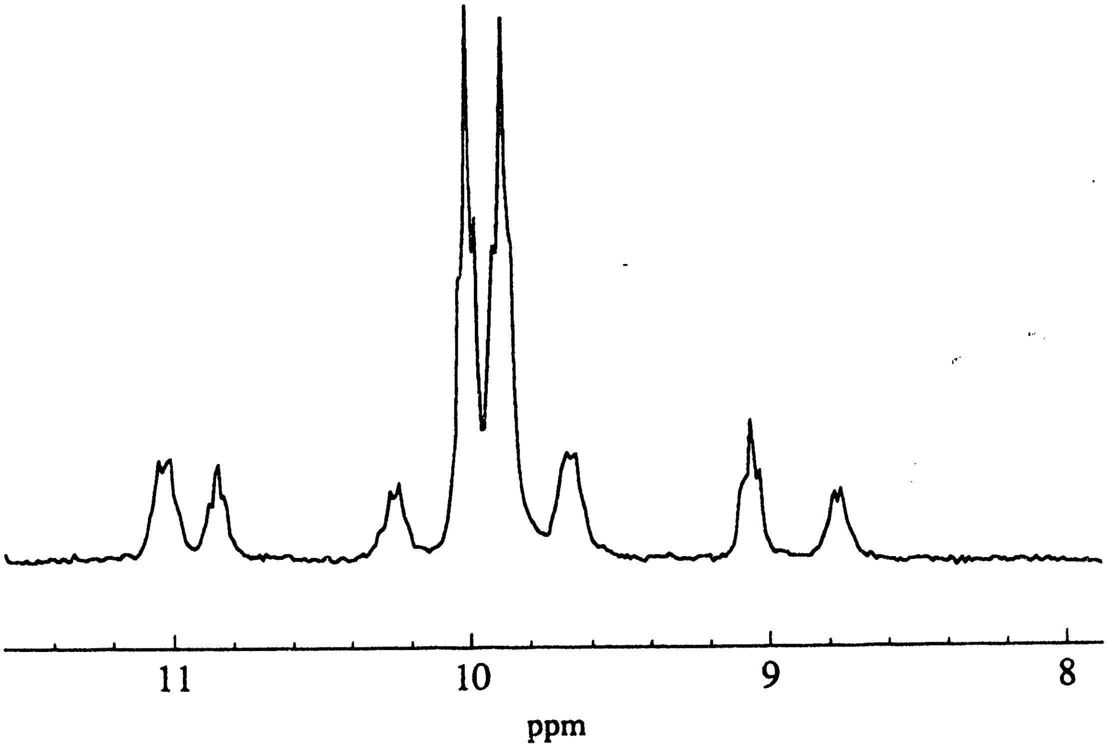
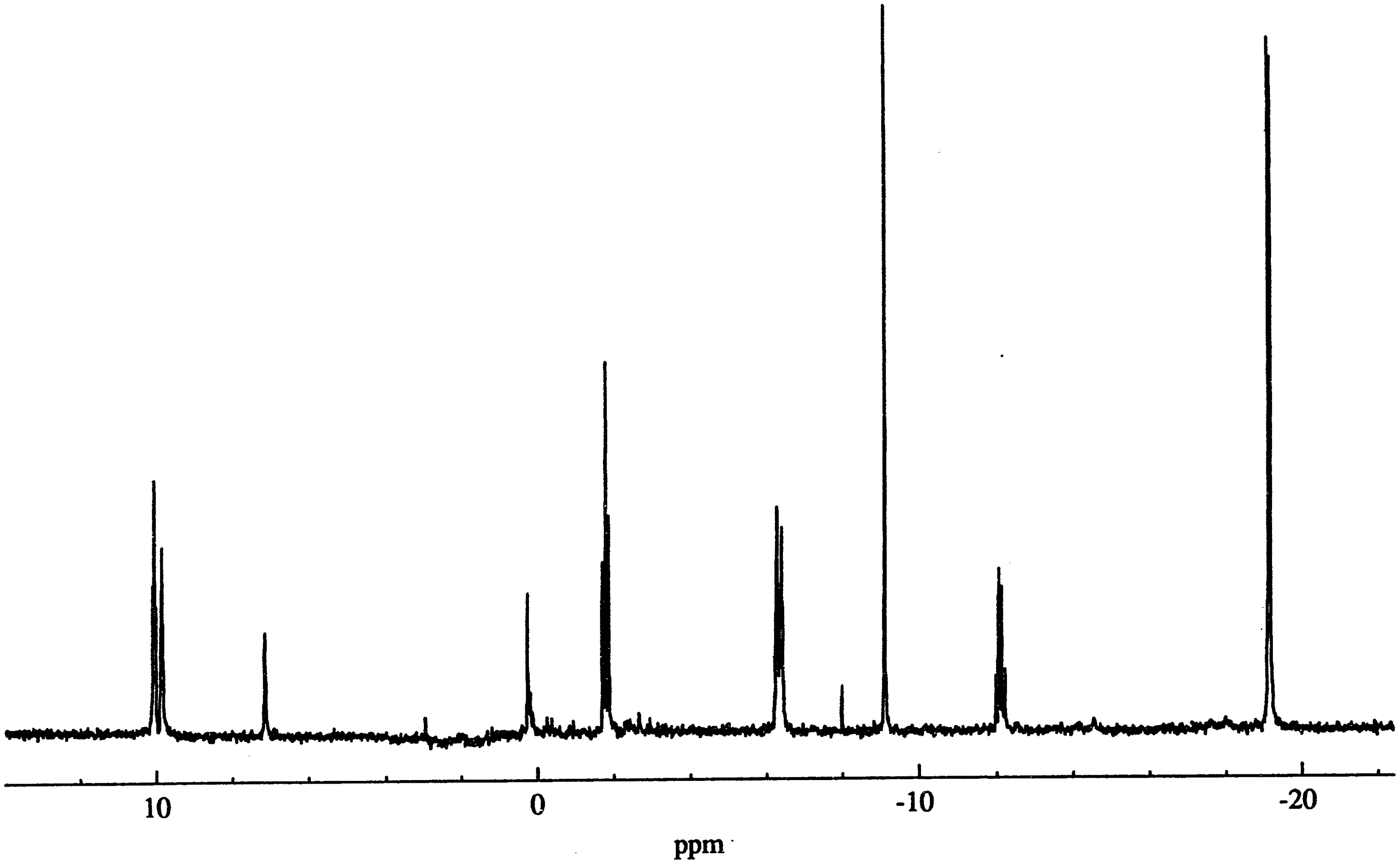


Figure 5: Computer-Generated Superposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ and $(EtC_5H_4)_3U(t\text{-}Bu)$ in Benzene-d_6



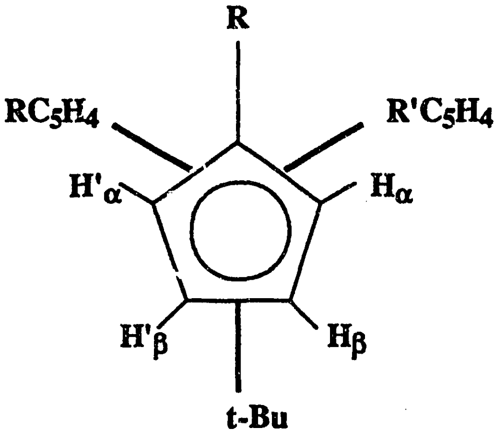
recorded, shown by the fact that the observed spectrum does not change with time.

On the NMR time scale, however, the exchange is slow. The four compounds present in solution would be: $(MeC_5H_4)_3U(t\text{-}Bu)$, $(MeC_5H_4)_2(EtC_5H_4)U(t\text{-}Bu)$, $(MeC_5H_4)(EtC_5H_4)_2U(t\text{-}Bu)$ and $(EtC_5H_4)_3U(t\text{-}Bu)$. With this assumption the spectrum shown in Figure 4a can be assigned completely. It is noteworthy that from Figure 4b it would seem that the ratio of the four compounds is approximately 1:1:1:1, which is different from the statistically expected ratio of 1:3:3:1. However, very small energy differences (< 1 kcal/mol) between the four compounds would be sufficient to perturb the expected statistical ratio.[6]

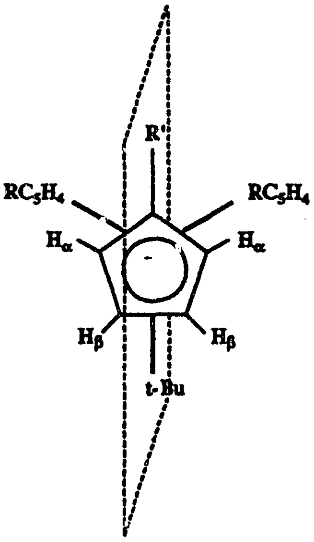
Figure 4d shows the region corresponding to one of the cyclopentadienyl hydrogen ring resonances (labeled a). It is not known whether this resonance around 10 ppm should be assigned to the α- or the β-hydrogen on the ring, since no simple technique allows a straightforward distinction between the two possibilities. NOE experiments would in principle allow us to distinguish between the two possibilities, but such experiments were not attempted. One resonance is expected for each ring resonance a in $(MeC_5H_4)_3U(t\text{-}Bu)$ and $(EtC_5H_4)_3U(t\text{-}Bu)$. In addition two resonances are expected for each of the ring resonances a of the mixed-ring compounds $(RC_5H_4)_2(R'C_5H_4)U(t\text{-}Bu)$. That adds to six resonances, but eight resonances are observed. This feature can be rationalized by realizing that the mixed-ring compounds are prochiral at uranium, as illustrated in Scheme 2.

In Scheme 2, H_α and H'_α (or H_β and H'_β) of an (RC_5H_4)-group are chemically inequivalent in $(RC_5H_4)_2(R'C_5H_4)U(t\text{-}Bu)$ because of the unsymmetrical substitution at uranium. Thus they will give rise to two resonances for one type of ring proton (α or β). Both sides of the $(R'C_5H_4)$-group on the other hand are chemically equivalent as they are

Scheme 2: $(RC_5H_4)_2(R'C_5H_4)U(t\text{-}Bu)$; View down the (RC_5H_4)-Centroid-Uranium Axis



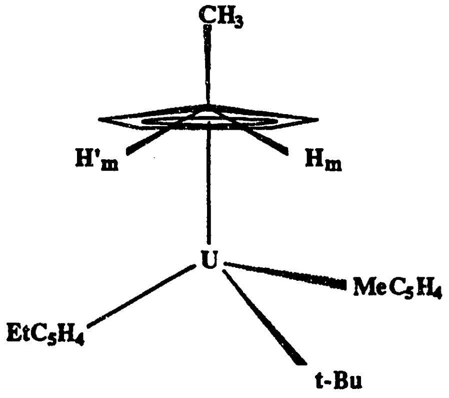
Scheme 3: $(RC_5H_4)_2(R'C_5H_4)U(t\text{-}Bu)$; View down the $(R'C_5H_4)$-Centroid-Uranium Axis



related by a mirror plane (Scheme 3). Thus each mixed cyclopentadienyl compound gives rise to three ring resonances for one type of ring hydrogen. Since there are two mixed compounds and two compounds with only one type of cyclopentadienyl ligand, a total of eight resonances is expected, as observed in Figure 4d for one type of cyclopentadienyl ring hydrogen. The two most intense resonances can be assigned to $(MeC_5H_4)_3U(t\text{-}Bu)$ and $(EtC_5H_4)_3U(t\text{-}Bu)$, respectively.

If this explanation is correct, the prochiral nature of the mixed cyclopentadienyl compounds should be reflected in the methylene resonance of the ethylcyclopentadienyl ligand as well. This is observed. As illustrated in Scheme 4, in $(EtC_5H_4)_2(MeC_5H_4)U(t\text{-}Bu)$ the methylene hydrogens H_m and H'_m are chemically inequivalent. The relevant region of the spectrum is shown in Figure 4c.

Scheme 4: $(EtC_5H_4)_2(MeC_5H_4)U(t\text{-}Bu)$: View down the Methylene-Carbon-Cyclopentadienyl-Carbon Axis



The quartet at $\delta = -12.1$ ppm can be assigned to $(EtC_5H_4)_3U(t\text{-}Bu)$ and the quartet at $\delta = -15.3$ ppm can be assigned to $(MeC_5H_4)_2(EtC_5H_4)U(t\text{-}Bu)$ based on integration. The resonance at $\delta = -13.6$ ppm then is the resonance due to $(EtC_5H_4)_2(MeC_5H_4)U(t\text{-}Bu)$. One can easily see that this resonance is not the quartet expected for simple three bond coupling to the methyl group of the ethyl substituent. Due to the inequivalence one would expect to see two doublets of quartets. The actually observed pattern seems to be a superposition of these two doublets of quartets.

It seems that $(RC_5H_4)_3U$(t-Bu) undergoes intermolecular exchange of cyclopentadienyl rings with remarkable ease. This observation contrasts with the implicit statement by Marks et al. about Cp_3U(n-Bu).[2] These investigators performed crossover experiments between Cp_3U(i-Pr) and (Cp-d_5)$_3$U(n-Bu) in their decomposition studies. They observed only propane and butane-d_1 as the organic products of the decomposition and concluded that the decomposition in toluene is an intramolecular process. The implicit assumption, apparently vindicated by the lack of observed crossover, is that the cyclopentadienyl ligands do not exchange between metal centers.

Cyclopentadienyl ligand exchange is rather rare in transition metal chemistry, but a few examples have been documented in d-transition metal chemistry.[20] A reference to such a process in tris(cyclopentadienyl)uranium chlorides has been made, although no details of the exchange process were reported.[21] It should be noted, however, that few experimental studies have been carried out since it is generally assumed that the ring substitution is inert and therefore there is no point in doing the experiments.

1.2 Thermal Decomposition of $(RC_5H_4)_3U(t\text{-}Bu)$ in Aromatic Solvents

Given the apparent discrepancies between Brennan's and Marks' work (vide supra) the thermal decomposition of the tertiary alkyl compounds in aromatic solvents was reinvestigated.

1.2.1 Product Distribution

Thermal decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ in benzene-d_6 solution gives rise to an insoluble organometallic product or products, as reported in both previous investigations. When the decomposition reaction at 65 °C is followed by ^1H-NMR spectroscopy, new resonances grow in at $\delta = 1.59(s)$, $1.22(s)$, and $0.86(d, J = 5.3\ Hz)$ as the reaction proceeds to completion. Another small resonance at $\delta = 4.71(s)$ grows in as well. This observed product distribution is consistent with the reported observations of Brennan although inconsistent with the results observed by Marks. By comparison to known samples, the resonances at $\delta = 4.71$ and 1.59 ppm could be attributed to isobutene. If the spectrum is observed at higher resolution (data points/Hz), the coupling patterns for the isobutene resonances become resolved. Similarly, the resonance at $\delta = 0.86(d)$ was ascribed to isobutane. The isobutane methyne could not be resolved in the decomposition spectra, probably because of its low intensity and because it is split into a decet by coupling to the methyl groups. In addition, other resonances occur in that region of the spectrum. The resonance at $\delta = 1.22$ was identified as being due to the t-butyl group of t-butyl-benzene-d_5. The presence of these reaction products was confirmed by GC and GC-MS experiments. When the reaction was carried out in toluene-d_8 instead of benzene-d_6, *p*-(t-butyl)toluene-d_7 was formed instead of t-butylbenzene-d_5. No other isomers were detected. A small amount of hexamethylethane was detected in all of the samples. The distribution of the organic products was studied in several aromatic solvents under various conditions. The results obtained mostly with $Cp_3U(t\text{-}Bu)$ are summarized in Tables 1.2 and 1.3.

Table 1.2 illustrates the quantitative behavior of the system. First, the data given in row 1 of the table are percentages of the initial intensity of the t-butyl group resonance of $(C_5H_5)_3U(t\text{-}Bu)$ adjusted for the number of hydrogens in each compound. The sum total amounts to 87%; therefore, these data account for the bulk of the organic products evolved. These quantitative data were determined by condensing the volatile materials in the NMR-tube experiment back into solution at -44 °C and integrating relative to an internal standard (cyclohexane). This procedure showed that at room temperature isobutane is the only product in the gas phase above the solution. Indeed, as the sample is progressively cooled, only the resonance attributed to isobutane grows in to any significant extent. This observation explains the discrepancy with the Marks' investigation.[2] In their experiments only the gases above the solution were sampled in order to determine the product distribution. The entry in row 2 represents another quantitative result, this time determined by ^1H-NMR integration relative to the internal standard (cyclohexane) at room temperature in benzene-d_6. Again the sum total equals 75%, accounting for the bulk of the organic products generated.

The entries in Table 1.3 are only relative amounts, determined by ^1H-NMR integration at 30 °C. Nevertheless, several patterns are apparent. By looking at rows 1 to 5, it can be seen that at a given temperature the product distribution depends on the identity of the aromatic solvent. As the substitution on the aromatic solvent is increased the amount of t-butylarene formed decreases. Rows 2, 6 and 7 illustrate that the amount of t-butylarene decreases with increasing reaction temperature, while the ratio of isobutane:isobutene approaches 1:1, indicating that the product distribution is temperature dependent. Finally, by comparing rows 3 and 8, it can be seen that the

Table 1.2: Decomposition of $(RC_5H_4)_3U(t\text{-}Bu)$ in Aromatic Solvents: Absolute Yields of Organic Products

R =	$[(RC_5H_4)_3U(t\text{-}Bu)]$ (mmol/L)	Aromatic Solvent (ArD)	T (°C)	Isobutane	Isobutene	$(CH_3)_3CC(CH_3)_3$	$(CH_3)_3CAr$
H	25	C_7D_8	50	33.2%	20.3%	ca. 3%	30.4%
H	24	C_6D_6	30	17.1%	8.9%	ca. 3%	46.0%

Table 1.3: Decomposition of $(RC_5H_4)_3U(t\text{-}Bu)$ in Aromatic Solvents: Product Distributions: Relative Ratios

R =	$[(RC_5H_4)_3U(t\text{-}Bu)]$ (mmol/L)	Aromatic Solvent (ArD)	T (°C)	Isobutane	Isobutene	$(CH_3)_3CC(CH_3)_3$	$(CH_3)_3CAr$
H	35	C_6D_6	72	2	1	small	4
H	40	C_7D_8	72	1	1	small	1
H	27	*o*-xylene-d_{10}	72	1	1	small	0
H	22	*p*-xylene-d_{10}	72	1	1	small	0
H	12	mesitylene-d_{12}	72	1	1	small	0
H	25	C_7D_8	50	2	1	small	2
H	28	C_7D_8	30	3	1	small	4
Me	32	C_7D_8	72	10	10	small	1

product distribution depends on the cyclopentadienyl ligand used. The amount of t-butylarene formed decreases with increasing substitution on the cyclopentadienyl ligand and consequently the isobutane:isobutene ratio approaches 1:1.

These rather complicated product distributions are reminiscent of a radical process.[31] However, it has been shown that free t-butyl radicals generated from organic precursors at comparable reaction temperatures do not form significant amounts of t-butylbenzene or *p*-(t-butyl)toluene in benzene or toluene solution, respectively.[7] To further investigate the origin of the t-butylarene formation, its concentration dependence was studied. The results are summarized in Table 1.4.

Table 1.4: t-Butylarene Formation, Concentration Dependence

$[(C_5H_5)_3U(t\text{-}Bu)]$ initial	$[C_6D_5\text{-}t\text{-}Bu]$ final
86.8 mmol/L	25.4 mmol/L (29.3%)
17.4 mmol/L	4.2 mmol/L (24.2%)
3.5 mmol/L	0.4 mmol/L (12.4%)

The data in Table 1.4 were obtained by preparing a solution of $Cp_3U(t\text{-}Bu)$ in 0.5 mL of benzene-d_6. Then a known amount of cyclohexane was added as an internal standard. Part of this solution was placed in an NMR-tube, while 0.1 mL of the solution was diluted to 0.5 ml by addition of more benzene-d_6. Again, part of this second solution was placed in another NMR-tube, while 0.1 mL of solution was diluted to 0.5 mL by addition of more benzene-d_6. Thus three samples from the same batch of starting material at different concentrations were obtained. They were allowed to decompose side-by-side in a constant temperature bath set at 60 °C. The initial and final concentrations were determined by ^{1}H-NMR integration relative to the internal standard. It can be seen that the amount of t-butylbenzene formed as a percentage of the initial intensity of the uranium-t-butyl compound is concentration dependent. Especially at low concentration, the amount of t-butylbenzene formed decreases significantly.

Suspecting a radical-type reaction pathway, the effect of radical traps on the decomposition reaction was investigated. Given the reactive nature of the $(RC_5H_4)_3U$(t-Bu) compounds only a limited number of radical traps could be considered. In a first attempt, $(MeC_5H_4)_3U$(t-Bu) was decomposed in toluene solution in the presence of one equiv of 1,4-cyclohexadiene. This radical trap is an excellent hydrogen atom donor [8] due to its weak carbon-hydrogen bonds in the 1 and 4 positions. Loss of a hydrogen atom in both of these positions allows the compound to aromatize to benzene. In this case, however, 1,4-cyclohexadiene is not an effective radical trap, since the appearance of a red colored mixture suggests that it reacts with the uranium compound. After workup, a red compound was isolated from toluene, which displayed a ^{1}H-NMR resonance at -207 ppm. Since one usually finds resonances for α-hydrogens on alkyl substituents in this region, it would appear that 1,4-cyclohexadiene formed such a σ-alkyl substituent attached to a $(MeC_5H_4)_3U$-fragment. The region between +20 and -20 ppm of the ^{1}H-NMR spectrum was quite complicated, suggesting that the isolated material was not pure. Further characterization was not attempted.

Because 1,4-cyclohexadiene apparently reacts with the uranium-tertiary alkyl compound, we next employed a bulkier radical trap, 9,10-dihydroanthracene. This trap works on the same principle as 1,4-cyclohexadiene, except that substitution of the two double bonds of cyclohexadiene by aromatic rings make it significantly more bulky and thus less able to interact with a metal center. For electronic reasons, the aromatic rings in 9,10-dihydroanthracene also do not bind as well to metal centers as the double bonds in 1,4-cyclohexadiene. When $(MeC_5H_4)_3U$(t-Bu) was allowed to decompose in a benzene-d_6 solution in the presence of seven equiv of 9,10-dihydroanthracene, formation of anthracene was observed. Furthermore, the amounts of t-butylbenzene and isobutene formed were significantly less than in the absence of 9,10 dihydroanthracene (t-butylbenzene:isobutene:isobutane 1:1.5:14.5). Thus it would appear that dihydroanthracene does indeed act as an efficient radical trap, reacting with t-butyl radical to form anthracene and isobutane with high efficiency. However, such a radical trapping experiment is truly valid only if the presence of the radical trap does not affect the rate of reaction. Thus, any conclusion regarding the reaction mechanism is premature before a kinetic investigation is completed. The kinetic aspects of these radical trapping experiments are discussed in section 1.2.2. It should be mentioned that attempts to directly observe radicals by carrying out the reaction in a tube placed in the probe of an EPR-spectrometer at room temperature were unsuccessful.

The organometallic product (or products) of these decomposition reactions is a green pyrophoric material which does not dissolve in common solvents such as tetrahydrofuran. It also does not dissolve in toluene with or without excess trimethylphosphine present. To attempt further characterization of this material, two samples from the same batch of $(MeC_5H_4)_3U$(t-Bu) were decomposed in toluene and toluene-d_8 separately at the same temperature. The infrared spectra of the two solid materials obtained were identical, indicating that deuterium from the solvent is not incorporated. However, the insoluble organometallic product obtained in these decomposition reactions does react with carbon tetrachloride in benzene, giving $(MeC_5H_4)_3UCl$ and another unidentified product that contains resonances attributable to a methylcyclopentadienyl group coordinated to uranium. The ^1H-NMR spectrum shows that no chloroform is formed in this reaction, suggesting that the green material is not a uranium hydride.

1.2.2 Kinetic Investigation

In order to further elucidate the thermal decomposition of $Cp_3U(t\text{-}Bu)$ in aromatic hydrocarbons, the decomposition kinetics were investigated. Marks reported that the rate of decomposition of Cp_3UR compounds in toluene is first-order in Cp_3UR concentration.[2] The reported rate constant for $Cp_3U(t\text{-}Bu)$ at 72 °C in toluene-d_8 was $k_{obs} = 1.42x10^{-3}\ s^{-1}$, corresponding to a half-life ($t_{1/2}$) of 8.2 min. To confirm this observation we followed the disappearance of $Cp_3U(t\text{-}Bu)$ in toluene-d_8 at 72 °C by ^{1}H-NMR spectroscopy for at least three half-lives. It is indeed first-order in $Cp_3U(t\text{-}Bu)$ concentration. The obtained rate constants for several runs are given in Table 1.5.

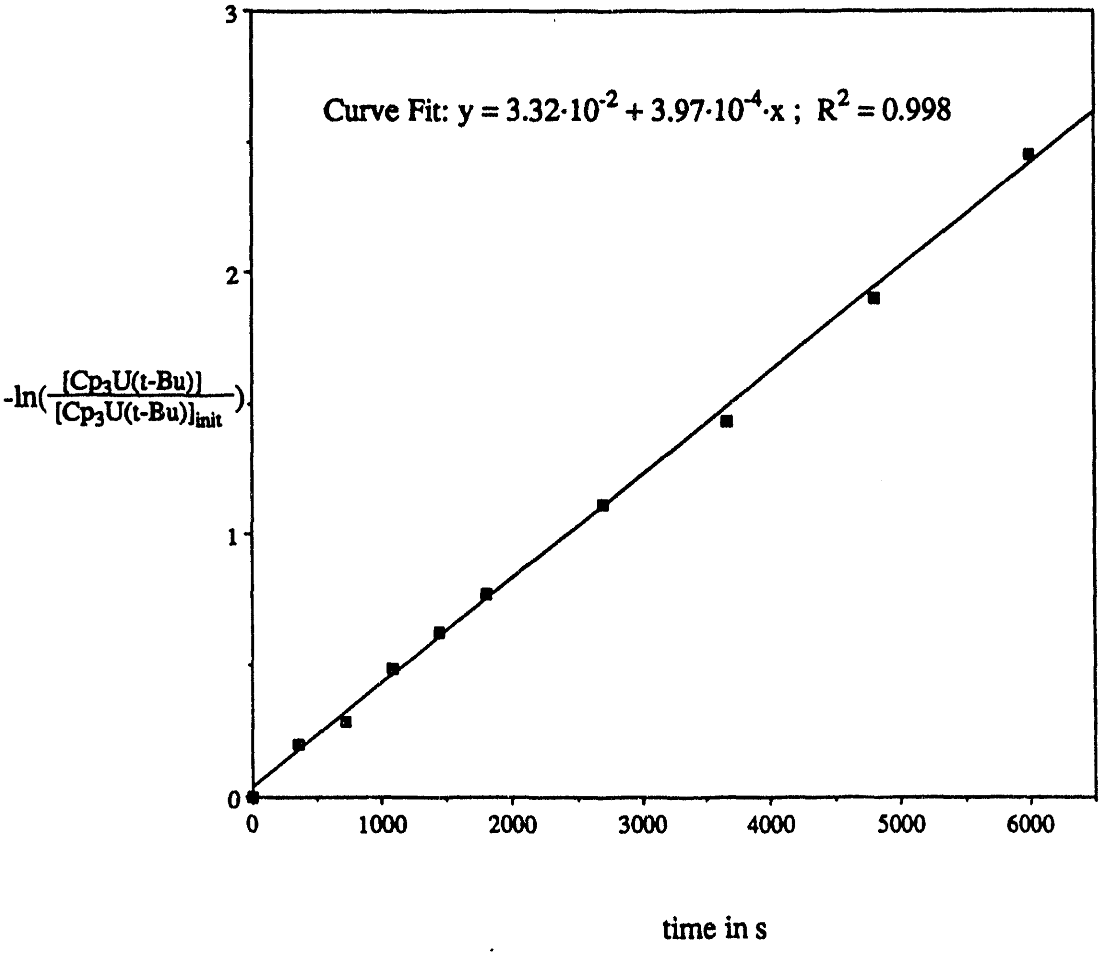
Table1.5: Decomposition of $Cp_3U(t\text{-}Bu)$

solvent	sample origin	T in °C	k_{obs} in s^{-1}	$t_{1/2}$ in min
toluene-d_8	batch 1	72	$3.57x10^{-4}$	32
toluene-d_8	batch 2	72	$3.46x10^{-4}$	33
toluene-d_8	batch 3	72	$3.97x10^{-4}$	29
toluene-d_8	ref. 2	72	$1.42x10^{-3}$	8.2

Estimated Standard Deviation: ± 10%

Figure 6 shows a typical first-order plot. The numerical values of the rate constants are estimated to have a standard deviation of ± 10% based on the reproducibility of the rate constant using different batches of $Cp_3U(t\text{-}Bu)$.

Figure 6: Decomposition of $Cp_3U(t\text{-}Bu)$ in Toluene-d_8 at 72 °C. Kinetics



The rate constant measured by Marks is approximately four times faster than the one obtained here. Since the reported rate constant in the Marks study was based on only three data points, introducing considerable error, we believe that the numbers are in fact rather close and the discrepancy seems not substantial. Furthermore, the observed rate constant suggests that the observed product distributions are not due to catalysis by trace impurities. This would lead to a faster disappearance of $Cp_3U(t\text{-}Bu)$ relative to the previous investigation. Rather the difference in observed rates between the Marks investigation and the present investigation is insufficient to explain a dramatic change in product distribution. It seems that indeed the Marks investigation was misled by only sampling the head gases in order to determine the identity of the organic products.

The presence of t-butylbenzene and *p*-t-butyltoluene in the final products of the thermal decomposition makes it clear that the solvent is involved in the reaction. Monitoring the rate of decomposition as a function of solvent was therefore begun. Unfortunately, $Cp_3U(t\text{-}Bu)$ is insoluble in saturated hydrocarbons. Since $Cp_3U(t\text{-}Bu)$ reacts with most other common deuterated solvents, only aromatic hydrocarbons could be studied. The results are summarized in Table 1.6. Representative plots of the kinetic runs are shown in Figures 7 and 8. As can be seen, the observed rate constant varies quite substantially depending on the deuterated solvent used. The fastest and the slowest rates differ by a factor of 15, which we believe is too large to be due to a classical medium effect. This large solvent dependence of the observed first-order rate constant suggests clearly that the solvent is involved in the rate-determining step of this decomposition reaction. To gain further insight into this possibility the activation parameters for the decomposition process were determined. The kinetic results as a function of temperature and solvent are summarized in Table 1.7.

Table 1.6: Decomposition of $Cp_3U(t\text{-}Bu)$: Observed Rate Constants

Solvent	T (°C)	k_{obs} (s^{-1})	$t_{1/2}$ (min)
benzene-d_6	72	2.65×10^{-3}	4.4
toluene-d_8 *	72	3.67×10^{-4}	32
o-xylene-d_{10}	72	2.21×10^{-4}	52
p-xylene-d_{10}	72	1.79×10^{-4}	65
mesitylene-d_{12}	72	1.83×10^{-4}	63

Estimated Standard Deviation: ± 10%

Table 1.7: Decomposition of $Cp_3U(t\text{-}Bu)$: Temperature Dependence

Solvent	T (°C)	k_{obs} (s^{-1})	$t_{1/2}$ (min)
toluene-d_8	30	3.04×10^{-6}	3806
toluene-d_8	50	2.86×10^{-5}	404
toluene-d_8 *	72	3.67×10^{-4}	32
toluene-d_8	90	2.41×10^{-3}	4.8
p-xylene-d_{10}	30	1.22×10^{-6}	9469
p-xylene-d_{10}	50	1.80×10^{-5}	642
p-xylene-d_{10}	60	4.06×10^{-5}	285
p-xylene-d_{10}	72	1.79×10^{-4}	65
p-xylene-d_{10}	90	1.40×10^{-3}	8.3
benzene-d_6	30	4.25×10^{-5}	272
benzene-d_6	60	9.55×10^{-4}	12
benzene-d_6	72	2.65×10^{-3}	4.4

Estimated Standard Deviation: ± 10%

* : average value for several experiments given

Figure 7: Decomposition of $Cp_3U(t\text{-}Bu)$ in *o*-Xylene-d_{10} at 72 °C, Kinetics

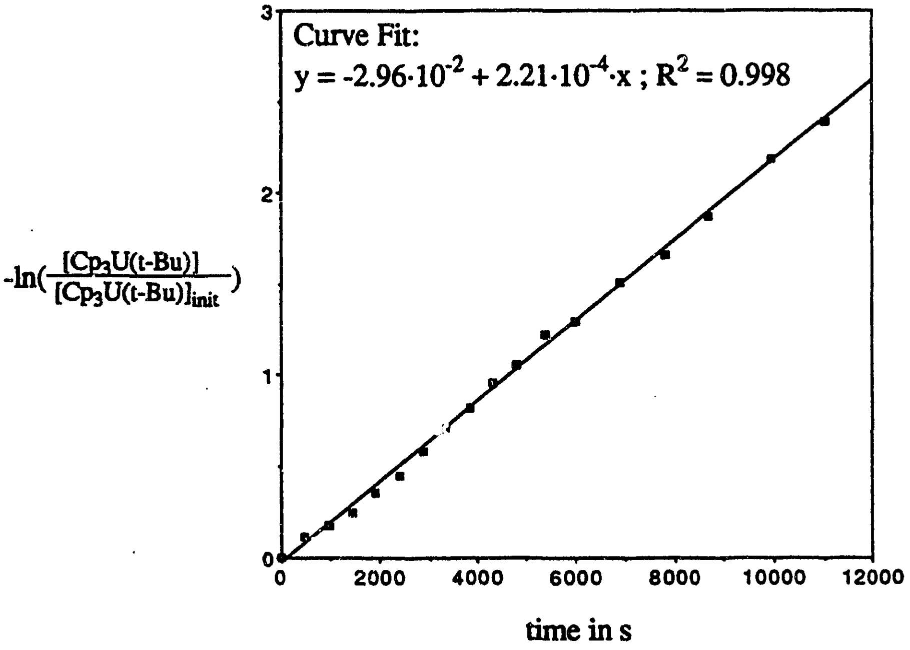
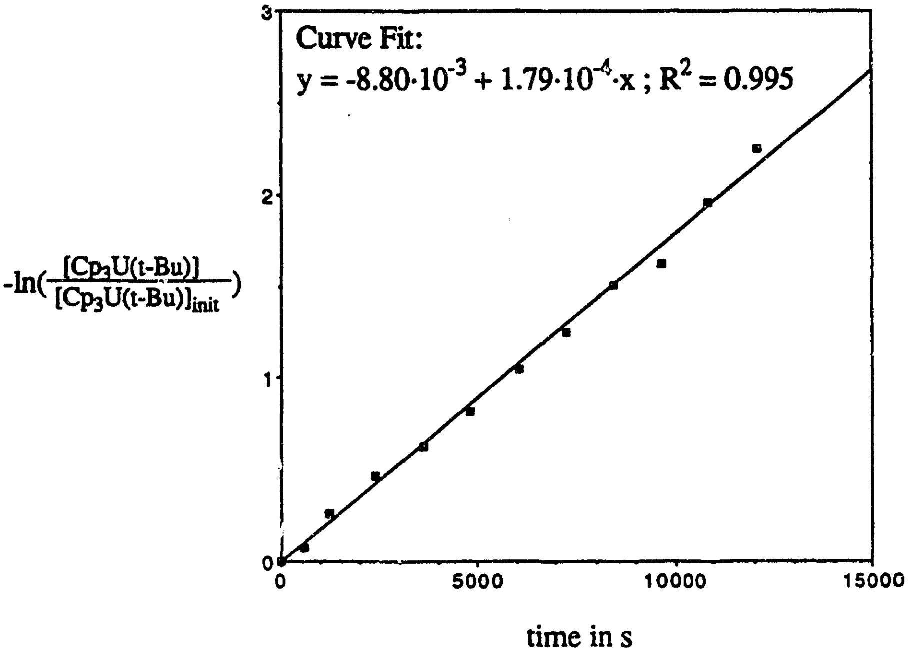


Figure 8: Decomposition of $Cp_3U(t\text{-}Bu)$ in *p*-Xylene-d_{10} at 72 °C, Kinetics



From the rate constants shown in Table 1.7 the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined using eq 3, where k represents the rate constant, k' is Boltzmann's constant and h is Planck's constant:

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\left(\frac{k'}{h}\right) + \frac{\Delta S^{\ddagger}}{R} \qquad (3)$$

The formula in eq 3 is derived from transition-state theory. It is used commonly to describe the temperature dependence of observed rate constants, even for processes in solution that are far more complex than assumed in the original theory. In such a case, it is best to treat $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as experimental parameters useful for comparison of closely related systems.[9] The Eyring plots for toluene-d_8 and p-xylene-d_{10} are shown in Figures 9 and 10. The activation parameters resulting from these Eyring plots are shown in Table 1.8.

Table 1.8: Decomposition of $Cp_3U(t\text{-}Bu)$: Activation Parameters

Solvent	Temp.-range	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal•mol^{-1}•K^{-1})
benzene-d_6	30 - 72 °C	19.9 ± 0.7	-13.0 ± 2.0
toluene-d_8	30 - 90 °C	23.8 ± 0.5	-5.4 ± 1.5
p-xylene-d_{10}	30 - 90 °C	24.6 ± 0.5	-4.6 ± 1.6

The errors given in Table 1.8 were determined by assuming a 10% standard deviation in the values of the observed rate constants. The standard deviations for the activation parameters were then determined from the covariance matrix of the fit.[10]

Figure 9: Eyring Plot for $Cp_3U(t\text{-}Bu)$ Decomposition in Toluene-d_8 (30-90 °C)

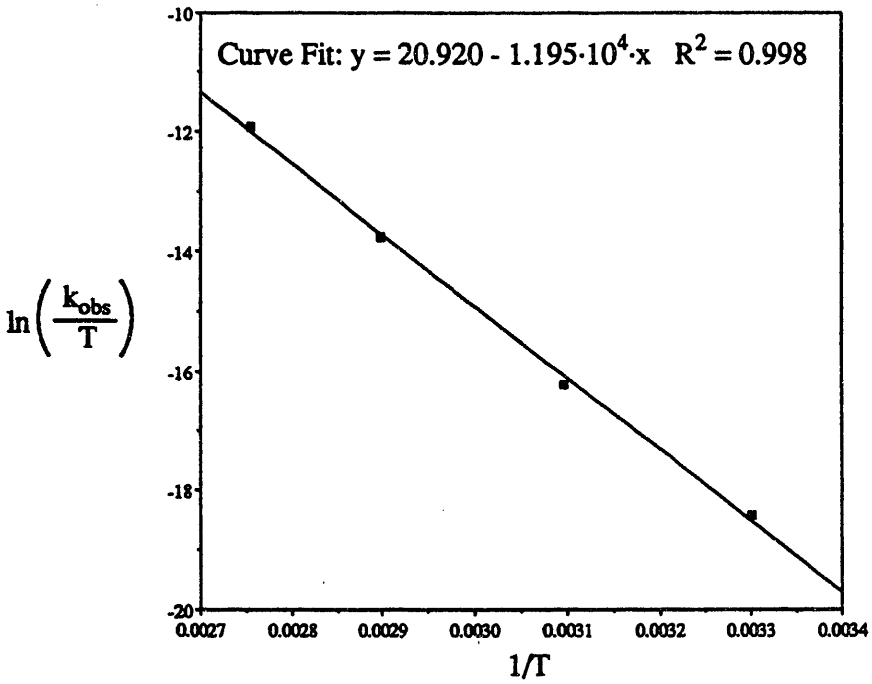
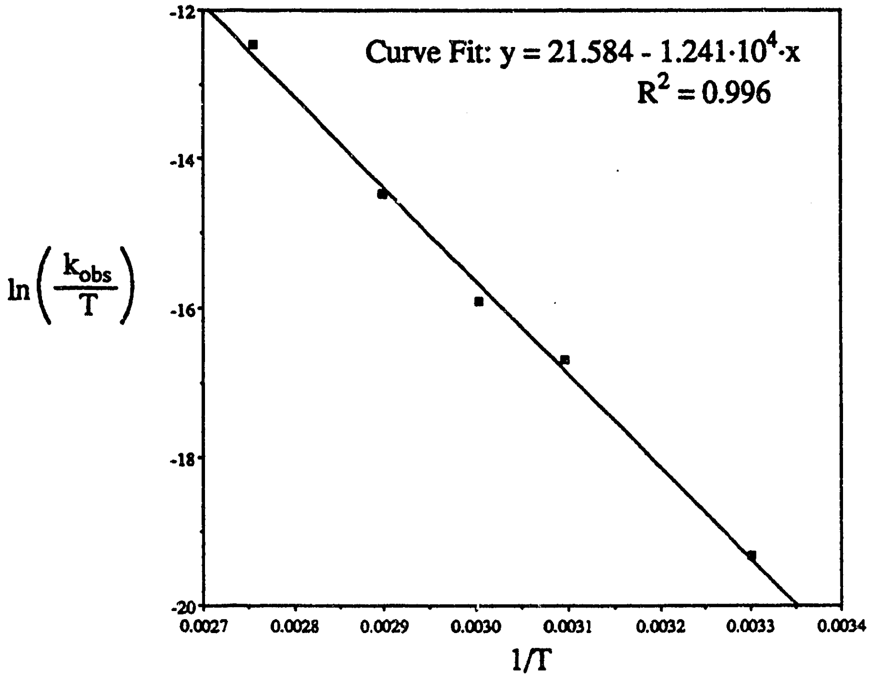


Figure 10: Eyring Plot for $Cp_3U(t\text{-}Bu)$ Decomposition in p-Xylene-d_{10} (30-90 °C)



No striking differences in the activation parameters between the three solvents investigated are apparent. Yet, toluene and benzene both form t-butylarene, whereas *p*-xylene forms no detectable amount of t-butylarene. This marked difference in product distribution is apparently not reflected in the activation parameters. We conclude that the rate-determining step preceedes the step responsible for the formation of the organic products. This, of course, assumes that the mechanism remains unchanged from one aromatic solvent to the next.

The entropy of activation is close to zero though slightly negative. This is certainly not consistent with a simple dissociative pathway like uranium-carbon bond homolysis leading to uranium(III) and a t-butyl radical, since such a process is expected to have a modestly positive entropy of activation. This point is further accentuated by the kinetic investigation of the (presumed) radical trapping experiments with 9,10-dihydroanthracene (vide supra). Significantly, addition of 9,10-dihydroanthracene to the reaction mixture results in an increased rate of decomposition (see Table 1.9). Thus, 9,10-dihydroanthracene does not act as a true radical trap in this system. Rather it seems to interfere with the decompostion reaction, resulting in a rate increase.

This led us to examine experimentally the possibility of a direct reaction between Cp_3U(t-Bu) and the aromatic solvent in the rate-determining step. To determine the order of reaction in arene the decomposition of Cp_3U(t-Bu) under pseudo-first-order conditions in Cp_3U(t-Bu) concentration must be studied with a variety of arene concentrations in an inert solvent. Unfortunately, however, a solvent in which Cp_3U(t-Bu) is both inert and soluble is, so far, unknown. Therefore, the arene concentration dependence of the decomposition reaction was studied using mixed arene solvents. Since the decomposition rate of Cp_3U(t-Bu) is slowest in *p*-xylene-d_{10}, this solvent was chosen

Table 1.9: Decomposition of $Cp_3U(t\text{-}Bu)$: Kinetic Effect of added 9,10-Dihydroanthracene in Toluene-d_8 at 72 °C

[Cp3U(t-Bu)] (mol/L)	[9,10-DHA] (mol/L)	k_{obs} (s^{-1})	$t_{1/2}$ (min)
various *	0	3.67×10^{-4}	32
0.014	0.063	3.68×10^{-3}	3.2
0.048	0.132	3.14×10^{-3}	3.7

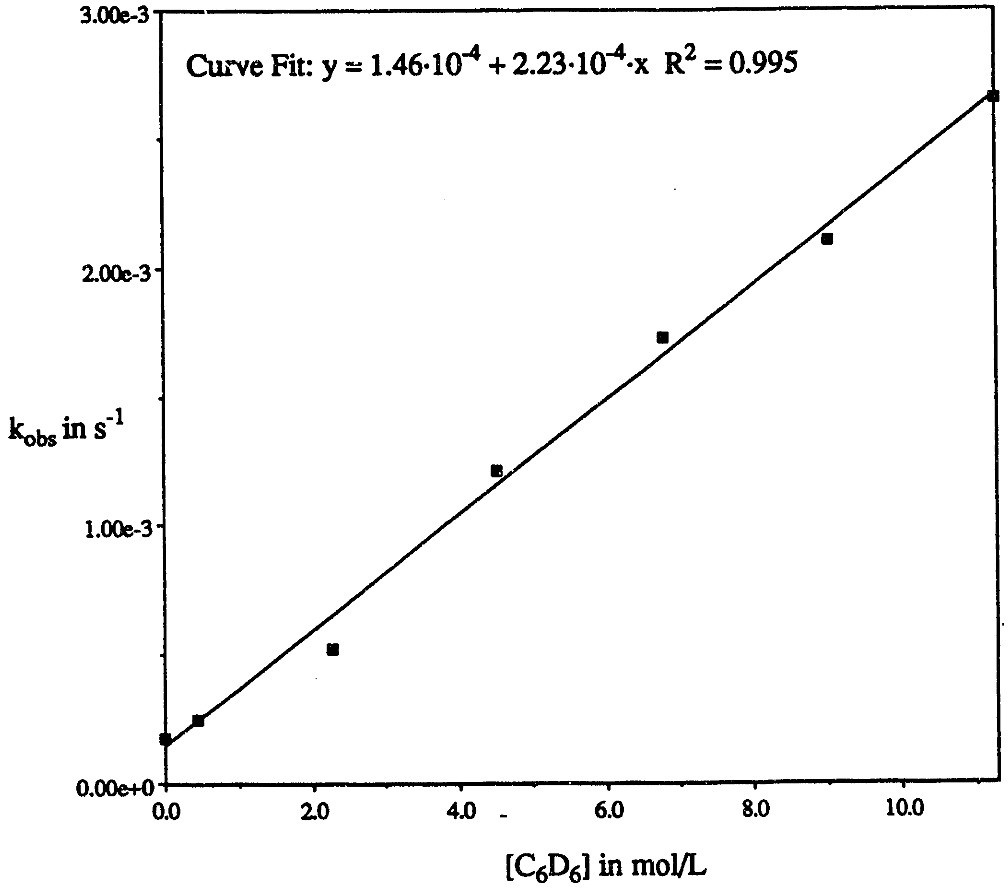
* : average value for several experiments given

as the closest approximation to an inert solvent. The rate of decomposition of $Cp_3U(t\text{-}Bu)$ was measured by varying the concentrations of added benzene-d_6. The observed rate constants for the pseudo-first-order disappearance of $Cp_3U(t\text{-}Bu)$ are shown in Table 1.10. Figure 11 shows a plot of k_{obs} against benzene-d_6 concentration. The relationship is linear to a good approximation. Thus the assumption stated in eq 4, viz., that the observed pseudo-first-order rate constant k_{obs} for the disappearance of $Cp_3U(t\text{-}Bu)$ is in fact composed of two bimolecular rate constants for reaction with each aromatic solvent, is supported by the experimental data.

$$k_{obs} = k_b \cdot [\text{benzene-}d_6] + k_b' \cdot [p\text{-xylene-}d_{10}] \qquad (4)$$

It should be noted, that for the concentration computations of the aromatic solvents, the reported values of the density at 20 °C were used.[11] For an accurate analysis, the density and hence the solvent concentration should be adjusted for the change in temperature. From tabulated values of coefficients of cubical expansion for the non-deuterated equivalents of the aromatic solvents used, we can estimate the error intro-

Figure 11: Decomposition of $Cp_3U(t\text{-}Bu)$: Observed Rate Constants at 72 °C as a Function of Benzene-d_6 Concentration in p-Xylene-d_{10}



duced in this way to be on the order of 5% over the temperature range investigated here.[12] We were unable to locate values for the deuterated solvents, which would have allowed an accurate correction of the concentration factors.

Table 1.10: Decomposition of $Cp_3U(t\text{-}Bu)$: Observed Rate Constants at 72°C in Benzene-d_6/*p*-Xylene-d_{10} Mixtures

[benzene-d_6] (mol/L)	[*p*-xylene-d_{10}] (mol/L)	k_{obs} (s^{-1})	$t_{1/2}$ (min)
0	8.15	1.79×10^{-4}	65
0.45	7.82	2.54×10^{-4}	45
2.26	6.52	5.26×10^{-4}	22
4.52	4.89	1.21×10^{-3}	9.6
6.77	3.26	1.73×10^{-3}	6.7
9.03	1.63	2.11×10^{-3}	5.5
11.29	0	2.65×10^{-3}	4.4

Estimated Standard Deviation: ± 10%

Thus the rate-determining step for the decomposition of $Cp_3U(t\text{-}Bu)$ in an aromatic solvent seems to be bimolecular. The rate law then is given by eq 5, where k_b represents the bimolecular rate constant.

$$-\frac{\partial[Cp_3U(t\text{-}Bu)]}{\partial t} = k_b \cdot [Cp_3U(t\text{-}Bu)] \cdot [\text{Arene}] \tag{5}$$

The relationship between the observed pseudo-first-order rate constant k_{obs} for the decomposition of $Cp_3U(t\text{-}Bu)$ in aromatic solvents and the bimolecular rate constant k_b is given by eq 6:

$$k_{obs} = k_b \bullet [\text{Arene}] \qquad (6)$$

Accordingly, all previously reported k_{obs} values can be divided by arene concentration to yield the corresponding bimolecular rate constants k_b, as listed in Tables 1.11 and 1.12. The laws of error propagation result in the expression given in eq 7 for σ_{k_b}, the standard deviation of k_b.[13]

$$\sigma_{k_b}^2 = \sigma_{k_{obs}}^2 \cdot \left(\frac{1}{[\text{Arene}]}\right)^2 + \sigma_{[\text{Arene}]}^2 \cdot \left(\frac{k_{obs}}{[\text{Arene}]^2}\right)^2 \qquad (7)$$

The standard deviations for k_b given in Tables 1.11 and 1.12 have been derived using eq 7 and assuming, as previously mentioned, a standard deviation of 10% in the observed rate constant, k_{obs}, and a standard deviation of 5% in the determination of the arene concentration. From the values of these bimolecular rate constants we can derive a new set of activation parameters based on the hypothesis of a bimolecular elementary reaction in the rate-determining step. The resulting activation parameters are listed in Table 1.13.

Table 1.11: Bimolecular Rate Constants for the Decomposition of $Cp_3U(t\text{-}Bu)$ at 72 °C

Solvent	$[Solvent]_{neat}$ (mol/L)	k_{obs} (s^{-1})	k_b ($L\bullet mol^{-1}\bullet s^{-1}$)
benzene-d_6	11.29	$2.65x10^{-3}$	$2.35x10^{-4} \pm 2.6x10^{-5}$
toluene-d_8 *	9.41	$3.67x10^{-4}$	$3.90x10^{-5} \pm 4.4x10^{-6}$
o-xylene-d_{10}	8.20	$2.21x10^{-4}$	$2.70x10^{-5} \pm 3.0x10^{-6}$
p-xylene-d_{10}	8.15	$1.79x10^{-4}$	$2.20x10^{-5} \pm 2.5x10^{-6}$
mesitylene-d_{12}	7.16	$1.83x10^{-4}$	$2.56x10^{-5} \pm 2.9x10^{-6}$

* : average value for several experiments given

Table 1.12:Bimolecular Rate Constants for the Decomposition of $Cp_3U(t\text{-}Bu)$ in Aromatic Solvents

Solvent	T (°C)	k_{obs} (s^{-1})	k_b ($L\bullet mol^{-1}\bullet s^{-1}$)
benzene-d_6	30	$4.25x10^{-5}$	$3.76x10^{-6} \pm 4.2x10^{-7}$
benzene-d_6	60	$9.55x10^{-4}$	$8.46x10^{-5} \pm 9.5x10^{-6}$
benzene-d_6	72	$2.65x10^{-3}$	$2.35x10^{-4} \pm 2.6x10^{-5}$
toluene-d_8	30	$3.04x10^{-6}$	$3.23x10^{-7} \pm 3.7x10^{-8}$
toluene-d_8	50	$2.86x10^{-5}$	$3.04x10^{-6} \pm 3.4x10^{-7}$
toluene-d_8 *	72	$3.67x10^{-4}$	$3.90x10^{-5} \pm 4.4x10^{-6}$
toluene-d_8	90	$2.41x10^{-3}$	$2.56x10^{-4} \pm 2.9x10^{-5}$
p-xylene-d_{10}	30	$1.22x10^{-6}$	$1.50x10^{-7} \pm 1.7x10^{-8}$
p-xylene-d_{10}	50	$1.80x10^{-5}$	$2.21x10^{-6} \pm 2.5x10^{-7}$
p-xylene-d_{10}	60	$4.06x10^{-5}$	$4.98x10^{-6} \pm 5.6x10^{-7}$
p-xylene-d_{10}	72	$1.79x10^{-4}$	$2.20x10^{-5} \pm 2.5x10^{-6}$
p-xylene-d_{10}	90	$1.40x10^{-3}$	$1.72x10^{-4} \pm 1.9x10^{-5}$

* : average value for several experiments given

Table 1.13: Decomposition of $Cp_3U(t\text{-}Bu)$: Activation Parameters based on Bimolecular Rate Constants

Solvent	Temp.-range	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ ($cal{\cdot}mol^{-1}{\cdot}K^{-1}$)
benzene-d_6	30 - 72 °C	19.9 ± 0.7	-17.7 ± 2.0
toluene-d_8	30 - 90 °C	23.8 ± 0.6	-9.8 ± 1.8
p-xylene-d_{10}	30 - 90 °C	24.6 ± 0.6	-8.8 ± 1.8

1.2.3 Proposed Mechanism

A mechanistic hypothesis has first and foremost to account for the presence of the observed reaction products. Next in importance is the correct prediction of the observed kinetic behavior of the system. Finally, it should be the simplest model consistent with all of the experimental facts.

We first discuss the mechanistic implications of the observed product distributions. In the present case, the organometallic decomposition product unfortunately could not be characterized, consistent with the Marks' study.[2] The organometallic decomposition product is not Cp_3U, nor is it a polymeric form thereof, as Cp_3U would be expected to react with Lewis bases such as thf or trimethylphosphine to yield a base adduct,[14] and it does not. The reaction of the decomposition product with carbon tetrachloride is inconclusive as well; it does not even allow the conclusion that the organometallic product is a uranium(III) species, because uranium(IV) species are also known to react with alkyl chlorides to yield Cp_3UCl.[15]

Thus, the major aspects of the product distribution that a mechanistic hypothesis will have to explain are:

(a) the presence of isobutane, isobutene, hexamethylethane and t-butylarene,
(b) the dependence of the product distribution on reaction temperature, solvent and [Cp_3U(t-Bu)]-concentration, and
(c) the dependence on the cyclopentadienyl ligand used.

The presence of isobutane, isobutene and hexamethylethane can be rationalized satisfactorily by invoking the presence of t-butyl radicals. Indeed, free t-butyl radicals are known to yield isobutane and isobutene by disproportionation and hexamethylethane by radical recombination.[16] However, the presence of significant amounts of t-butylarene in the case of benzene and toluene cannot be due to reaction of free t-butyl radicals with the aromatic solvent. A detailed study by Pryor has shown that free t-butyl radicals do not add to benzene or toluene to any appreciable extent at comparable reaction temperatures.[7] Thus, the formation of t-butylarene has to be mediated by the metal center in some fashion.

The observation of a temperature dependent product distribution rules out a single concerted mechanism. The temperature dependence is consistent with a stepwise mechanism that has a branching point, where part of an intermediate reacts in one way and part of the same intermediate reacts in another way. One can assume a temperature dependence for the branching ratio and thus the product distribution will be temperature dependent. Alternatively, two or more concerted mechanisms operating in parallel and with different temperature dependences will also lead to a temperature dependent product distribution.

The formation of t-butylarene clearly implies that the product distribution is solvent dependent. Because the formation of t-butylarene has to be metal mediated, one can postulate that the initial step of the mechanism involves direct coordination of the aromatic solvent to the uranium center. Another important fact is illustrated by Table 1.4: The final yield of t-butylarene depends on the initial concentration of Cp_3U(t-Bu) at a given temperature. This implies that t-butylarene is formed in a bimolecular step rather than in a unimolecular step, in which case the amount of t-butylarene formed should be independent of the initial Cp_3U(t-Bu) concentration.

The dependence of the product distribution on the cyclopentadienyl ligand used (RC_5H_4 ; R = H, Me, Et) indicates that steric interactions at the metal center play a significant role in this reaction (electron density at the metal will also change with cyclopentadienyl-substitution, but the effect is likely to be minor). This idea is reinforced by the dependence of the product distribution on the nature of the aromatic solvent. Whereas use of benzene or toluene results in the formation of significant amounts of t-butylarene, no detectable t-butylarene is formed in the case of the sterically more demanding xylenes and mesitylene. It may seem difficult to imagine an aromatic hydrocarbon molecule coordinating to an already crowded metal center. After all, the high degree of steric congestion around the uranium metal fragment is supposedly responsible for the weakness of the uranium-tertiary alkyl bond in the first place. Yet, the decomposition mechanism clearly involves coordination of an aromatic substrate. This apparent contradiction can be resolved by separating the thermodynamic from the kinetic aspects of this system. The weakness of the uranium-tertiary alkyl bond is indeed best ascribed to steric congestion around the metal center, as well as to the relatively high stability of a tertiary alkyl radical. In other words, the left side of eq 8 is energetically raised by steric congestion, whereas the right side is lowered by the stability of a tertiary radical relative to a primary radical. The net result is a weak metal-carbon bond, a thermodynamic statement.

$$Cp_3UR \rightarrow \quad Cp_3U\bullet + R\bullet \tag{8}$$

The kinetic aspects and how they relate to steric effects will be described in detail below. As a prelude, it is meaningful to note the remarkable ease with which cyclopentadienyl ligand exchange (much faster than decomposition) between metal centers occurs in this system, indicating that low energy pathways are accessible. A bimolecular (and hence associative) pathway seems to be the most plausible pathway for cyclopentadienyl ligand exchange. In this light, coordination of an aromatic substrate to the metal center seems more plausible. Further evidence comes from the fact that a whole host of substrates react with Cp_3U(t-Bu) in a bimolecular fashion (see Chapter 2).

To summarize, we have either several concerted mechanisms operating simultaneously, or more simply a stepwise mechanism. This latter mechanism would involve interaction between the metal center and the aromatic solvent leading to an intermediate, which can then decompose in several ways. At least one pathway involves t-butyl radicals. Another path results in the formation of t-butylarene in a bimolecular process.

The most important results of the kinetic investigation can be summarized as follows:

(a) The rate of decomposition is first-order in Cp_3U(t-Bu) concentration.

(b) The rate of decomposition depends on the nature of the aromatic solvent (see Table 1.6).

(c) The activation parameters derived from k_{obs}-values indicate a slightly negative entropy of activation (see Table 1.8).

(d) The mixed solvent kinetics are consistent with a first-order rate dependence on arene concentration (see Figure 11).

The first point on this list is an experimental observation. All kinetic runs were followed over at least three half-lives. The observed rate constants are independent of the initial concentration of Cp_3U(t-Bu). Marks also found the decomposition of Cp_3U(t-Bu) to be first-order in Cp_3U(t-Bu) concentration.[2]

The results in Table 1.6 indicate that the rate of decomposition depends on the nature of the aromatic solvent. This result is consistent with the mechanistic hypothesis derived from the observed product distributions; the aromatic solvent and the metal center interact with each other in a bimolecular fashion. The reaction is thus first-order in both Cp_3U(t-Bu) and arene concentration. Could this rate dependence on the nature of the aromatic solvent be rationalized as a solvent effect? Relevant solvent properties are listed in Table 1.14 for the non-deuterated aromatic solvents in question. Tabulated values for the deuterated solvents actually used could not be located, but it seems

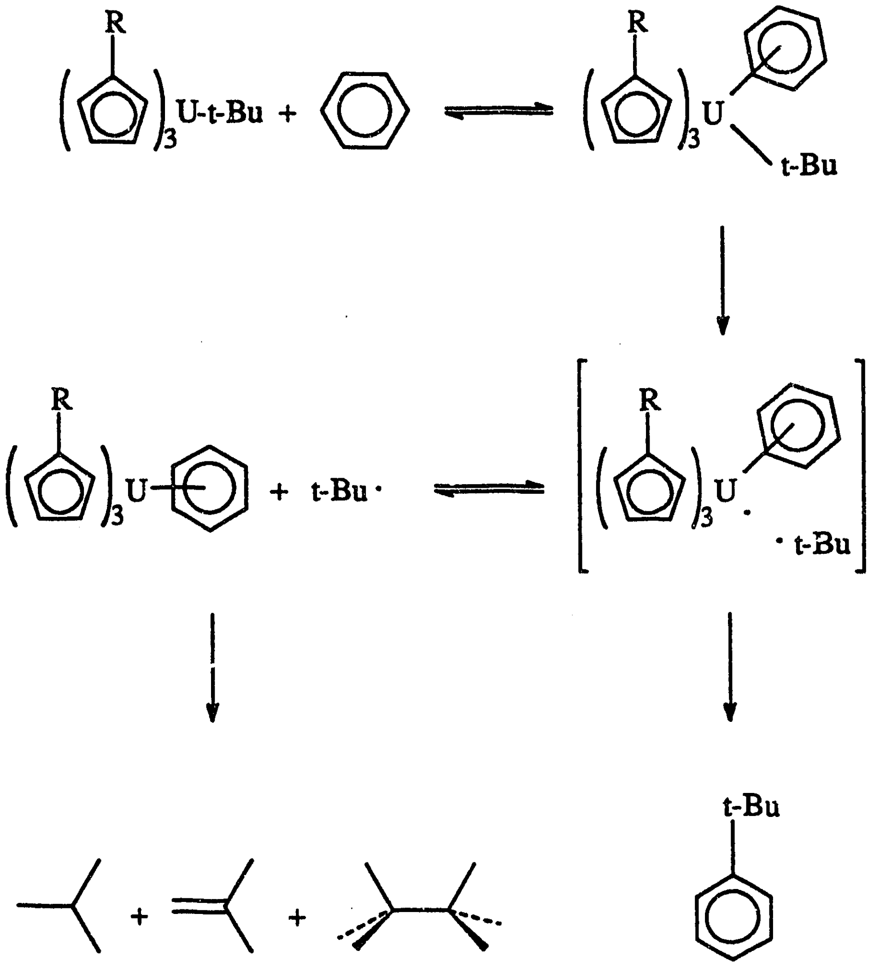
Table 1.14: Aromatic Solvent Properties

Solvent	Dielectric Constant (at °C) [17]	Dipole Moment in D [17]	Viscosity [18] in Centipoises at 40 °C
benzene	2.3 (20)	0	0.503
toluene	2.4 (25)	0.39	0.471
o-xylene	2.6 (20)	0.62	0.627
p-xylene	2.3 (20)	0	0.513
mesitylene	2.3 (20)	0	----

reasonable to assume that a similar trend will be followed by both non-deuterated and deuterated solvents. From the values in Table 1.14, no trend correlating any of these properties with the observed reactivity differences is immediately apparent. Therefore in light of the much more straightforward correlation between rate of reaction and steric bulk of the arene solvent, a bimolecular reaction mechanism offers the best explanation of the observed rate data. The arene solvent attacks the uranium metal center directly and decomposition proceeds therefrom. This point is further emphasized by the negative entropies of activation and the mixed solvent kinetics (Figure 11).

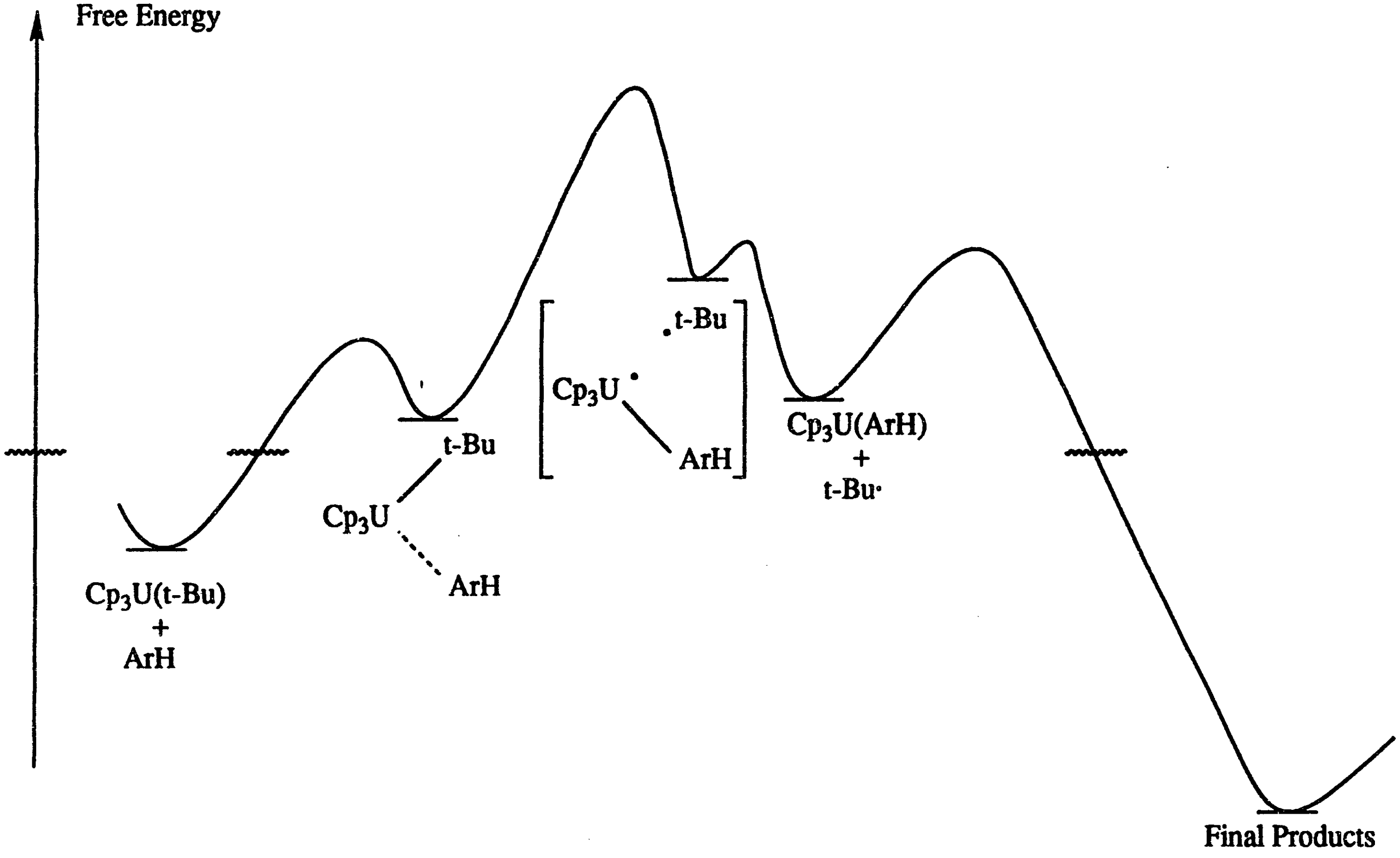
Coordination of a non-classical ligand such as an arene to a hard metal center like uranium may seem to be an unusual proposition but isolated examples of such compounds in both the uranium(IV) and uranium(III) oxidation states clearly document that such an interaction is feasible, at least in the solid state.[19] As shown in Scheme 5, we propose that coordination of arene weakens the metal tertiary alkyl bond sufficiently for it to be broken in a homolytic fashion. At this point one is left with two fragments, a tris(cyclopentadienyl)uranium arene complex and a tertiary alkyl radical. The t-butyl radical can then either react with itself to disproportionate or recombine, giving rise to isobutane, isobutene and hexamethylethane. t-Butylarene can also be formed by reaction of the t-butyl radical with the tris(cyclopentadienyl)uranium arene complex, i.e. the radical pair dissociation is reversible. The dependence of the amount of t-butylarene formed on the initial concentration of $Cp_3U(t\text{-}Bu)$ is accounted for by such a bimolecular process. As unimolecular decomposition pathways almost certainly do exist, e.g. loss of arene from tris(cyclopentadienyl)uranium arene, these will be less affected by a reduction in the overall concentration of the system. Thus the amount of t-butylarene formed will be less at lower overall concentrations.

Scheme 5: Proposed Mechanism for the Decomposition of $(RC_5H_4)_3U(t\text{-}Bu)$ in Aromatic Solvents (R= H,Me,Et)



A bimolecular rate-determining step that involves the aromatic solvent is further supported by the decomposition kinetics in mixtures of benzene-d_6 and *p*-xylene-d_{10}. The linear relationship of the observed rate constant with increasing benzene concentration strongly suggests this. Unfortunately no inert solvent could be found such that the rate dependence on a particular arene could be studied without the presence of competing side reactions. Scheme 5 outlines the proposed mechanism and Figure 12 shows a free energy diagram.

Figure 12: Free Energy Diagram for $Cp_3U(t\text{-}Bu)$ Decomposition in Aromatic Solvents



The reaction is initiated by reversible coordination of the arene to the uranium metal center. In the transition state the uranium-tertiary alkyl bond is broken homolytically. The t-butyl radical formed escapes from the solvent cage, leaving behind a tris(cyclopentadienyl)uranium(III)arene complex. This arene complex can now react with a t-butyl radical to give t-butylarene or decompose on its own by loss of arene. The tertiary butyl radical formed can also react with another one of its kind to give either radical disproportionation or recombination products characteristic for free t-butyl radicals. The crucial step, coordination of arene to the metal center could involve a cyclopentadienyl ligand that is slipped off of its pseudo-C_5 axis. This is not unreasonable given the ease of intermolecular cyclopentadienyl ligand exchange, but we cannot offer proof of this possibility.

The mechanistic proposal made here is formally similar to the well-known S_N2-process in organic chemistry or classical coordination chemistry. The big difference is that a two-electron ligand (an arene can be a 2, 4 or 6-electron donor, but in any case an even number of electrons) replaces not another two-electron ligand but a one-electron ligand, namely an alkyl radical. This corresponds to a one-electron reduction of the metal center. Thus this process can be referred to as a solvent-assisted uranium-carbon bond homolysis. The coordination of the arene solvent provides enough weakening of the uranium-carbon bond to significantly enhance the rate of bond homolysis.

It is attractive to interpret the slight nonlinear behavior of the variable temperature ^{1}H-NMR spectra as a result of temperature dependent reversible arene coordination to the metal center. However, diethyl ether has no effect on the variable temperature ^{1}H-NMR spectrum of $(MeC_5H_4)_3U(t\text{-}Bu)$. Therefore, it is more prudent to ascribe the observed nonlinear behavior to some other property such as an intramolecular conformational equilibrium.

Finally, the observation of CIDNP in the ^{1}H-NMR spectra of the thermal decomposition of $(t\text{-Bu})_2Mg$, $(t\text{-Bu})_2Zn$ and $(t\text{-Bu})_2Hg$ by Benn should be mentioned.[32] The author observed polarization in the organic decomposition products isobutane and isobutylene, but not in hexamethylethane. Based on this, radical mechanisms were proposed for these decomposition reactions. In the thermal decomposition of $(t\text{-Bu})_2Mg$ in benzene-d_6, a side product was observed at $\delta = 1.26$, representing always less than 20% of the total products. Its identity was not clarified, other than that it does not show polarization. It was ignored in the interpretation of the results. This chemical shift of $\delta = 1.26$ is disturbingly reminiscent of t-butylbenzene-d_5, as established by the present investigation. Hence if this unidentified product should indeed be t-butylbenzene-d_5, the type of solvent-assisted metal-carbon bond homolysis mechanism described previously may well be more general than just a curiosity in uranium chemistry.

1.3 Tertiary Alkyl Compounds as Intermediates in the Reduction of Uranium(IV) to Uranium(III) Compounds?

The use of t-butyllithium as a reducing agent for converting uranium(IV) halide compounds into uranium(III) compounds is a well-established synthetic methodology. Marks reported the reduction of $Cp^*{}_2UCl_2$ to $[Cp^*{}_2UCl]_3$ by t-butyllithium.[22] This approach was successfully applied to both tris(cyclopentadienyl)- and bis(cyclopentadienyl) compounds (eqs 9 and 10).

$$(RC_5H_4)_3UCl + t\text{-}BuLi \rightarrow (RC_5H_4)_3U \qquad (9)$$

R = SiMe3 ref. 23

t-Bu ref. 24

$$(R_2C_5H_3)_2UCl_2 + t\text{-}BuLi \rightarrow [(R_2C_5H_3)_2UCl]_2 \qquad (10)$$

R = SiMe3 ref. 25

t-Bu ref. 26

The method is not limited to uranium. Evans and Atwood have reported the reduction of Cp2YbCl by t-BuLi (eq 11).[27]

$$Cp_2YbCl + t\text{-}BuLi \rightarrow Cp_2Yb \qquad (11)$$

The analogous reaction with lutetium or erbium instead of ytterbium however, does not lead to reduction, but instead a lanthanide(III) tertiary alkyl compound is isolated (eq 12).

$$Cp_2LnCl + t\text{-}BuLi \rightarrow Cp_2Ln(t\text{-}Bu) \qquad (12)$$

$$Ln = Lu,Er$$

The reason for this differential reactivity must reside in the reduction potentials of these lanthanides. Ytterbium(III) is the most easily reduced to ytterbium(II). The reducing power of t-BuLi is apparently high enough to overcome the -1.4 V electrochemical barrier for ytterbium, but not so for lutetium and erbium.[28]

The synthetic reports of the reduction of uranium(IV) to uranium(III) organometallic compounds suggest that these reactions might proceed through intermediate uranium-t-butyl compounds. Therefore an attempt was made to observe these intermediates by NMR spectroscopy and identify the organic reaction products.

The reaction of $(Me_3SiC_5H_4)_3UCl$ with t-BuLi was investigated initially (eq 9). The synthetic scale reaction is usually done in hexane solvent. For the purpose of following the reaction by ^{1}H-NMR spectroscopy the reaction was carried out stoichiometrically in benzene-d_6. At room temperature the reaction proceeds to completion (i.e. no t-BuLi was left) within a couple of hours. Surprisingly, $(Me_3SiC_5H_4)_3U$ is not the only reaction product. A substantial amount of $(Me_3SiC_5H_4)_3UH$ is formed as well. This compound was identified by its ^{1}H-NMR spectrum, which features a characteristic hydride resonance at 293 ppm (C_6D_6; 30 °C).[29] At no point during the reaction could an intermediate be observed by ^{1}H-NMR spectroscopy. The organic products include isobutane, isobutene and t-butylbenzene-d_5. Thus it seems that a mechanism similar to the one operating in the decomposition of the isolable tertiary butyl compounds discussed in Section 1.2 is operating. This would suggest that the present reaction is initiated by aromatic solvent attack on the presumed intermediate t-butyl compound. The approximate relative amounts are given in Table 1.14.

Table 1.14: Product Distribution from the Reaction of $(Me_3SiC_5H_4)_3UCl$ with t-BuLi in Benzene-d_6 at 30 °C: Approximate Relative Ratios

$(Me_3SiC_5H_4)_3U$	$(Me_3SiC_5H_4)_3UH$	Isobutane	Isobutene	$t\text{-}BuC_6D_5$	Hexamethylethane
5	2	3	3	1	small

The amount of $(Me_3SiC_5H_4)_3UH$ formed seems to be much less in a synthetic scale reaction performed in hexane, consistent with a solvent effect. Presumably, the amount of $(Me_3SiC_5H_4)_3UH$ formed depends on the overall concentration of the system as well.

Another interesting question is the fate of the deuterium atom that was originally on the benzene ring from which t-butylbenzene-d_5 was formed. By GC-MS no evidence for deuterium incorporation into the isobutane was detected. A ^2H-NMR spectrum of the organometallic reaction products showed no detectable deuterium incorporation either. This question thus remains unresolved. The hydride bound to uranium does not seem to originate from solvent. One possibility is that a β-hydrogen elimination mechanism may be competitive with homolysis, giving rise to $(Me_3SiC_5H_4)_3UH$.

The related system with the t-butylcyclopentadienyl ligand was investigated also. Again, stoichiometric amounts of t-BuLi and $(t\text{-}BuC_5H_4)_3UCl$ were allowed to react in benzene-d_6 at room temperature. Again, the reaction proceeded to completion within a couple of hours. As for the trimethylsilylcyclopentadienyl system, $(t\text{-}BuC_5H_4)_3U$ was not the only reaction product. A small amount of $(t\text{-}BuC_5H_4)_3UH$ was formed as well. This compound was identified by its ^{1}H-NMR spectrum, which features a characteristic hydride resonance at 276 ppm (C_6D_6; 30 °C).[30] Again, at no point during the reaction could an intermediate be observed by ^{1}H-NMR spectroscopy. The organic products include isobutane, isobutene and t-butylbenzene-d_5. The approximate relative ratios of the observed reaction products are given in Table 1.15.

Table 1.15: Product Distribution from the Reaction of $(t\text{-}BuC_5H_4)_3UCl$ with t-BuLi in Benzene-d_6 at 30 °C: Approximate Relative Ratios

$(t\text{-}BuC_5H_4)_3U$	$(t\text{-}BuC_5H_4)_3UH$	Isobutane	Isobutene	$t\text{-}BuC_6D_5$	Hexamethylethane
6	1	3	3	small	small

As can be seen, the relative amount of uranium hydride formed in the t-butylcyclopentadienyl system is significantly less than in the trimethylsilylcyclopentadienyl system. This may be a manifestation of greater steric congestion in the t-butylcyclopentadienyl compounds. Also, the amount of t-butylbenzene-d_5 formed is very small, indicative of less arene coordination to the metal center. On a continuum between solvent-assisted uranium-carbon bond homolysis and unassisted uranium-carbon bond homolysis, the t-butylcyclopentadienyl system tends toward unassisted uranium-carbon bond homolysis because of its greater steric congestion. The enhanced steric congestion now provides enough driving force on its own for metal-carbon bond homolysis by weakening the metal-tertiary alkyl bond.

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Chapter Two

Reactions of Tris(Cyclopentadienyl)Uranium-t-Butyl with Lewis Bases and Fluorocarbons

Brennan first synthesized $(MeC_5H_4)_3U(t\text{-}Bu)$ from the reaction of $(MeC_5H_4)_3UCl$ with t-BuLi in an unsuccessful attempt to reduce $(MeC_5H_4)_3UCl$ to base-free $(MeC_5H_4)_3U$.[1] He also examined some reactions of $(MeC_5H_4)_3U(t\text{-}Bu)$. He found that reaction of the tertiary alkyl compound with trimethylphosphine results in immediate reduction and formation of the uranium(III) base-adduct $(MeC_5H_4)_3U(PMe_3)$ (eq 1).

$$(MeC_5H_4)_3U(t\text{-}Bu) + PMe_3 \longrightarrow (MeC_5H_4)_3U(PMe_3) \qquad (1)$$

Furthermore, $(MeC_5H_4)_3U(t\text{-}Bu)$ reacts with carbon monoxide to yield an η^2-acyl complex (eq 2). A similar reaction has been reported for the analogous $Cp_3U(t\text{-}Bu)$.[2]

$$(MeC_5H_4)_3U(t\text{-}Bu) + CO \longrightarrow (MeC_5H_4)_3U-\overset{\overset{O}{\|}}{C}\text{-t-Bu} \qquad (2)$$

Finally, Brennan showed that $(MeC_5H_4)_3U(t\text{-}Bu)$ reacts with trifluorophosphine to yield $(MeC_5H_4)_3UF$ (eq 3).

$$(MeC_5H_4)_3U(t\text{-}Bu) + PF_3 \longrightarrow (MeC_5H_4)_3UF + \ldots \qquad (3)$$

Brennan also remarked that while the reaction of PMe_3 with $(MeC_5H_4)_3U(t\text{-}Bu)$ results in immediate quantitative formation of $(MeC_5H_4)_3U(PMe_3)$, the thermal decomposition product of $(MeC_5H_4)_3U(t\text{-}Bu)$ in toluene solution does not redissolve in the presence of excess trimethylphosphine. Thus, he concluded that the the thermal decomposition product of $(MeC_5H_4)_3U(t\text{-}Bu)$ in toluene is not an intermediate in the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with PMe_3.

We decided to further explore these three reactivity patterns, (a) reduction to uranium(III) in the presence of a donor ligand, (b) insertion of small unsaturated organic molecules into the metal-tertiary alkyl bond and (c) atom abstraction.

2.1 Reactions of Tris(Cyclopentadienyl)Uranium-t-Butyl with Lewis Bases

2.1.1 Synthetic Studies

The first question that we addressed was how good a ligand towards uranium(III) does L have to be for reduction to proceed according to eq 4.

$$Cp_3U(t\text{-}Bu) + L \longrightarrow Cp_3U(L) \qquad (4)$$

Brennan has established a series for the relative basicity of various ligands towards the tris(methylcyclopentadienyl)uranium fragment.[3] The series is shown in eq 5. This ligand substitution series was established by competition experiments under thermodynamic control where two bases are allowed to compete for the $(MeC_5H_4)_3U$ fragment. These experiments showed that thf is one of the weakest ligand towards $(MeC_5H_4)_3U$ for which an isolable base adduct $(MeC_5H_4)_3U(L)$ is known.

$$PMe_3 > P(OCH_3)_3 > NC_5H_5 > SC_4H_8 \sim OC_4H_8 \sim N(CH_2CH_2)_3CH > CO \quad (5)$$

Trimethylphosphine on the other hand binds rather strongly to $(MeC_5H_4)_3U$. Yet the ease with which the reduction of $(MeC_5H_4)_3U(t\text{-}Bu)$ to the uranium(III) base adduct takes place is quite astounding given that the uranium(IV)/uranium(III) reduction potential in these types of organometallic compounds is generally rather high (see Table 2.1).

Table 2.1: Uranium(IV)/Uranium(III) Reduction Potentials

Compound	$E_{1/2}$ (V) [4] (reversible half-wave potential vs. NHE)
Cp_4U	-1.54
Cp_3UCl	-1.40
$Cp^*{}_2UCl_2$	-1.68

We therefore investigated the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with thf, the weakest ligand that gives an easily-accessible isolable $(MeC_5H_4)_3U(L)$ base adduct. When $(MeC_5H_4)_3U(t\text{-}Bu)$ is treated with an excess of thf in toluene solution, formation of $(MeC_5H_4)_3U(thf)$ is observed. The organic products of this reaction are isobutane and isobutene in approximately a 1:1 ratio, as well as a small amount of hexamethylethane (eq 6). The identities of these compounds were confirmed by ^1H-NMR spectroscopy and gas chromatography. These products can be ascribed as arising from free t-butyl radicals in aromatic hydrocarbon solution [5]

$$(MeC_5H_4)_3U(t\text{-}Bu) + thf \rightarrow (MeC_5H_4)_3U(thf) + Me_3CH + Me_2C{=}CH_2 + Me_3CCMe_3 \qquad (6)$$

Monitoring the reaction by ^{1}H-NMR spectroscopy in the presence of an internal standard (cyclohexane) demonstrated that the conversion to $(MeC_5H_4)_3U(thf)$ was essentially quantitative. This contrasts markedly with the behavior of the analogous primary alkyl compounds Cp_3UMe and $Cp_3U(n\text{-}Bu)$. Both of these compounds are soluble in thf and no reduction reaction occurs at room temperature. Even upon photolysis, formation of $Cp_3U(thf)$ from Cp_3UMe or $Cp_3U(n\text{-}Bu)$ is slow.[6] The reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with thf is slower than its reaction with PMe_3. With one equivalent of thf in toluene solution, the reaction is no longer instantaneous, but goes to completion in ca. 1 day. The implication is that the rate of reaction for equation 4 depends on the σ-donor ability of the incoming ligand L. Upon attempted dissolution of $(MeC_5H_4)_3U(t\text{-}Bu)$ in neat thf, the donor complex $(MeC_5H_4)_3U(thf)$ was formed within minutes, although side products were formed as well, which presumably arise from reaction of t-butyl radicals with thf. No attempts were made to characterize these side products. If several equivalents of thf are used in toluene or benzene solution the rate of reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with thf qualitatively increases with increasing thf concentration. The reactivity of $Cp_3U(t\text{-}Bu)$ and $(EtC_5H_4)_3U(t\text{-}Bu)$ towards thf is qualitatively similar to that of $(MeC_5H_4)_3U(t\text{-}Bu)$.

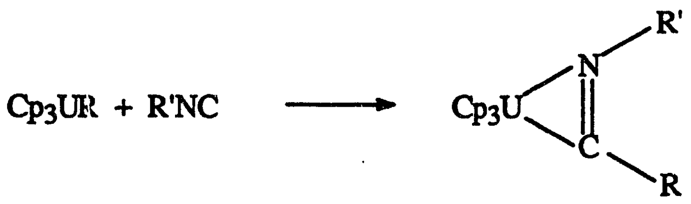
In order to gain some insight into the preferred oxidation state in this system (eq 4), the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ was investigated with ligands L known to form isolable trivalent $(MeC_5H_4)_3U(L)$ complexes [1,7], but which would also be capable of inserting into the metal-carbon bond and thus maintaining the tetravalent oxidation state of the metal center. The reaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and t-butylnitrile resulted in formation of the reduced uranium(III) base adduct (eq 7).

$$(MeC_5H_4)_3U(t\text{-}Bu) + t\text{-}BuCN \longrightarrow (MeC_5H_4)_3U(NC\text{-}t\text{-}Bu) \qquad (7)$$

This may seem not too surprising as insertions of nitriles into metal-carbon bonds are rare.[8] More significantly, t-butylisocyanide also formed the uranium(III) base adduct (eq 8), in spite of the fact that many examples of isocyanide insertions into metal-carbon bonds are known.[9]

$$(MeC_5H_4)_3U(t\text{-}Bu) + t\text{-}BuNC \longrightarrow (MeC_5H_4)_3U(CN\text{-}t\text{-}Bu) \qquad (8)$$

Isocyanides have been reported to insert into the metal-carbon bond of Cp_3UMe and $Cp_3U(n\text{-}Bu)$ (eq 9),[10] reinforcing the unique reactivity of the tertiary alkyl compound. Analogous reactions of nitriles with Cp_3UR don't appear to have been studied.



(9)

$R = n\text{-}Bu;\ R' = t\text{-}Bu,\ C_6H_{11},\ 2,6\text{-}Me_2C_6H_3$
$R = Me;\ R' = C_6H_{11},\ n\text{-}Bu$

In addition, ethylisocyanide also reacted with $(MeC_5H_4)_3U(t\text{-}Bu)$ to give $(MeC_5H_4)_3U(CNEt)$. The combined results suggest that the intrinsically preferred product is the uranium(III) base adduct. At least, it seems that the substitution of the t-butyl group in t-butylisocyanide for the sterically much less demanding primary ethyl substituent does not affect the outcome of the reaction. Thus steric effects seem to be of secondary importance in the isocyanide examples.

It is also worth mentioning that for these compounds the isocyanide stretching frequencies increase upon coordination rather than decrease, as shown in Table 2.2. This observation is not uncommon in f-element isocyanide complexes.[1,15] This increase has been ascribed to the C-N antibonding character of the $7a_1$ orbital, the carbon "lone pair" in the isocyanide. σ-Donation from this orbital to the metal removes C-N antibonding character from the isocyanide and thus results in an increased isocyanide stretching frequency. Conventional π-backbonding from the metal to the isocyanide increases the C-N antibonding character by populating empty C-N antibonding orbitals. This results in a decrease of the isocyanide stretching frequency. The relative magnitude of these two opposite effects determines whether an increase or a decrease in C-N stretching frequency is observed for the coordinated isocyanide.[16]

Table 2.2: Infrared Stretching Frequencies for the Isocyanide and Nitrile Base Adducts

R-X≡Y	ν(X≡Y) (cm^{-1}) for free R-X≡Y	ν(X≡Y) (cm^{-1}) for $(MeC_5H_4)_3U(Y\equiv XR)$
t-Bu-C≡N	2232	2220
t-Bu-N≡C	2131	2140
Et-N≡C	2151	2155

Clearly, exploitation of the reaction shown in eq 4 should allow us to prepare uranium(III) base adducts with weak metal-ligand bonds. One should keep in mind though that the results discussed in chapter one indicate that aromatic solvents do coordinate to the tris(cyclopentadienyl)uranium fragment, although the arene adduct is not stable to the reaction conditions. Thus the ideal "weak" ligand L would have to be able to compete with the arene solvent for coordination and not be able to undergo any subsequent decomposition reactions.

Diethyl ether would be expected to be a worse ligand than thf towards the tris-(cyclopentadienyl)uranium fragment, yet a better ligand than arene towards an oxophilic metal center. However, when one equivalent of diethyl ether is added to a solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ in benzene-d_6, no reaction occurs over ca. 16 h. Rather it seems that the presence of diethyl ether in the reaction mixture inhibits the decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ in benzene at room temperature. Thus the hypothesis that diethyl ether would be a better ligand than arene seems to be confirmed; diethyl ether does not allow the arene-induced decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ to proceed. However, diethyl ether is not a potent enough ligand to displace a t-butyl radical from $(MeC_5H_4)_3U(t\text{-}Bu)$ at any appreciable rate at room temperature. Upon heating the benzene solution to 65 °C, decomposition proceeded in the same way as in the absence of diethyl ether. Presumably, at this temperature most of the diethyl ether will be found in the gas phase above the solution. Thus it is effectively removed from the reaction mixture.

A tris(cyclopentadienyl)uranium(III) complex of diphenylacetylene was claimed in solution on the basis of shifts in the ^{1}H-NMR spectrum.[12] In a later paper the authors, stopping short of retraction, admitted in a footnote that the starting material they had used for these solution studies was not what they had claimed it to be, but instead was a uranium(III) hydride.[13] This allows for a rational explanation of the observed formation of stilbene from diphenylacetylene. The reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with acetylenes was investigated in the hope of isolating a uranium(III) acetylene complex. However, no interaction could be detected by ^{1}H-NMR spectroscopy between $(MeC_5H_4)_3U(t\text{-}Bu)$ and bis(trimethylsilyl)acetylene in benzene-d_6 solution. On a synthetic scale, reaction of

$(MeC_5H_4)_3U(t\text{-}Bu)$ with diethylacetylene in toluene solution did not give rise to a color change as the solution was stirred at room temperature and no tractable uranium-containing products could be isolated from this reaction mixture.

The reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with an excess of diphenylacetylene in benzene-d_6 solution gave rise to a gradual color change from deep green to red. Monitoring the reaction by ^{1}H-NMR spectroscopy showed that no resonances attributable to a new uranium-containing species became apparent (spectra recorded at 30-60 °C). Most interestingly however, no significant resonances due to decomposition products of $(MeC_5H_4)_3U(t\text{-}Bu)$ in benzene-d_6 solution (isobutane, isobutene, t-butylbenzene-d_5) could be detected, despite the complete disappearance of the resonances due to $(MeC_5H_4)_3U(t\text{-}Bu)$. The resonances due to the excess of diphenylacetylene present in solution were broadened and shifted slightly upfield, relative to free diphenylacetylene. Thus an interaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and diphenylacetylene is probably occurring in solution. On a preparative scale however, no tractable uranium containing products could be isolated from the reaction mixture. Given the precedent, in the absence of any irrefutable evidence, it seems prudent not to speculate on the nature of the interaction.

2.1.2 Mechanistic Investigation

The initial reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with a σ-donor ligand L is given below (eq 10).

$$(MeC_5H_4)_3U(t\text{-}Bu) + L \longrightarrow (MeC_5H_4)_3U(L) + t\text{-}Bu\cdot \qquad (10)$$

Formally at least, the reaction can be viewed as a substitution at the metal center, in which a 2-electron ligand displaces a 1-electron ligand, or alternatively as a ligand-assisted metal-carbon bond homolysis. As such processes are rather uncommon, we decided to investigate the mechanism more closely.[20] The qualitative observations made with various ligands L are

(a) the rate of reaction depends on the σ-donor ability of the incoming ligand L,

(b) the rate of reaction depends on the concentration of the incoming ligand L,

(c) the rate of reaction is much faster than the rate of decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ in the same solvent in the absence of L.

It seemed straightforward to postulate a bimolecular reaction pathway involving the incoming ligand L in the rate-determining step. Hence, a kinetic study of the rate dependence on the concentration of the incoming ligand seemed appropriate. Unfortunately, reaction with most ligands is too fast even at room temperature to be amenable to a kinetic study by ^{1}H-NMR spectroscopy. In fact, thf is the only ligand whose rate of reaction is slow enough. Thus we were not able to study the rate of reaction as a function of various ligands, but the investigation had to be confined to thf.

Several technical problems had to be solved before this kinetic investigation could be done. First, just as in Chapter 1, $Cp_3U(t\text{-}Bu)$ was chosen for the kinetic study rather than $(MeC_5H_4)_3U(t\text{-}Bu)$. The single resonance for the equivalent cyclopentadienyl ring protons in $Cp_3U(t\text{-}Bu)$ is close to the diamagnetic region of the ^{1}H-NMR spectrum and thus provides a strong signal that can be integrated easily against a diamagnetic standard. It is desirable to measure the rate of disappearance of $Cp_3U(t\text{-}Bu)$ as a function of time at a given concentration of thf under pseudo-first-order conditions. This means that the thf has to be in at least a ten-fold excess relative to $Cp_3U(t\text{-}Bu)$. Such a large excess of thf at the early stages of the reaction would produce strong sharp resonances in the NMR spectrum that would obscure a significant part of the diamagnetic region. Furthermore, as the reaction progresses, more and more $Cp_3U(thf)$ will be present in solution. The coordinated thf in this compound exchanges quickly on the NMR time scale with free thf at room temperature. Thus only an averaged signal would be observed that gradually moves to higher field and broadens because the contribution of $Cp_3U(thf)$ to the time-averaged resonance increases as the reaction progresses. With thf in at least a tenfold excess, this would most definitely obscure the resonance of cyclohexane, the internal standard. To avoid these problems, thf-d_8 rather than thf was used as a ligand. The residual proton resonances of even a large excess of thf-d_8 are manageable in size and position in the ^{1}H-NMR spectrum. Clearly, it would be desirable to study this reaction in an inert solvent. However, since we were not able to find a solvent that is inert towards $Cp_3U(t\text{-}Bu)$, the kinetics were studied in *p*-xylene-d_{10}, the solvent in which decomposition of $Cp_3U(t\text{-}Bu)$ is slowest (see Chapter 1). Thus the kinetics were run at 30 °C in *p*-xylene-d_{10} under pseudo-first-order conditions in thf concentration.

A typical individual kinetic run is shown in Figure 1. It can be seen that once again the decay of $Cp_3U(t\text{-}Bu)$ was followed for at least three half-lives. All runs showed the expected pseudo-first-order decay of $Cp_3U(t\text{-}Bu)$. The standard deviation in k_{obs} can again be estimated to be on the order of ±10%, based on the results of Chapter 1. Figure 2 shows a plot of the observed rate constant k_{obs} as a function of thf-d_8 concentration. The data shown in Figure 2 are given in Table 2.3. Table 2.3 and Figure 2 both show that a simple linear relationship between thf-d_8 concentration and the observed rate constant k_{obs} does not hold. It seems that at low thf-d_8 concentration, there is a marked drop-off in the observed rate constant by two orders of magnitude, while the other data points ([thf-d_8] from 0.098M to 4.24M) fall reasonably well on a straight line.

Table 2.3: Observed Rate Constants for the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in *p*-xylene-d_{10} at 30 °C as a Function of thf-d_8 Concentration

[thf-d_8] (mol/L)	k_{obs} (s^{-1})	$t_{1/2}$ (min.)
0	$1.22x10^{-6}$	9469
0.098	$1.79x10^{-4}$	64
0.47	$2.33x10^{-4}$	50
0.95	$3.03x10^{-4}$	38
1.37	$3.95x10^{-4}$	29
1.89	$4.33x10^{-4}$	27
2.54	$4.20x10^{-4}$	27
4.24	$6.59x10^{-4}$	18

Estimated Standard Deviation: ± 10%

Thus, the initial working model of a simple bimolecular reaction between $Cp_3U(t\text{-}Bu)$ and thf-d_8 obeying second-order kinetics had to be abandoned. As an alternative, a model involving a fast preequilibrium was considered (Scheme 1).[14] The rate expression for this model is given in eq 11.

Scheme 1: Fast Preequilibrium Mechanistic Model

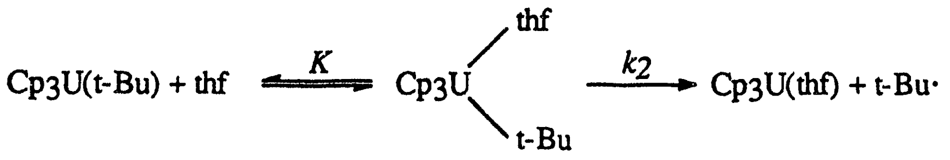
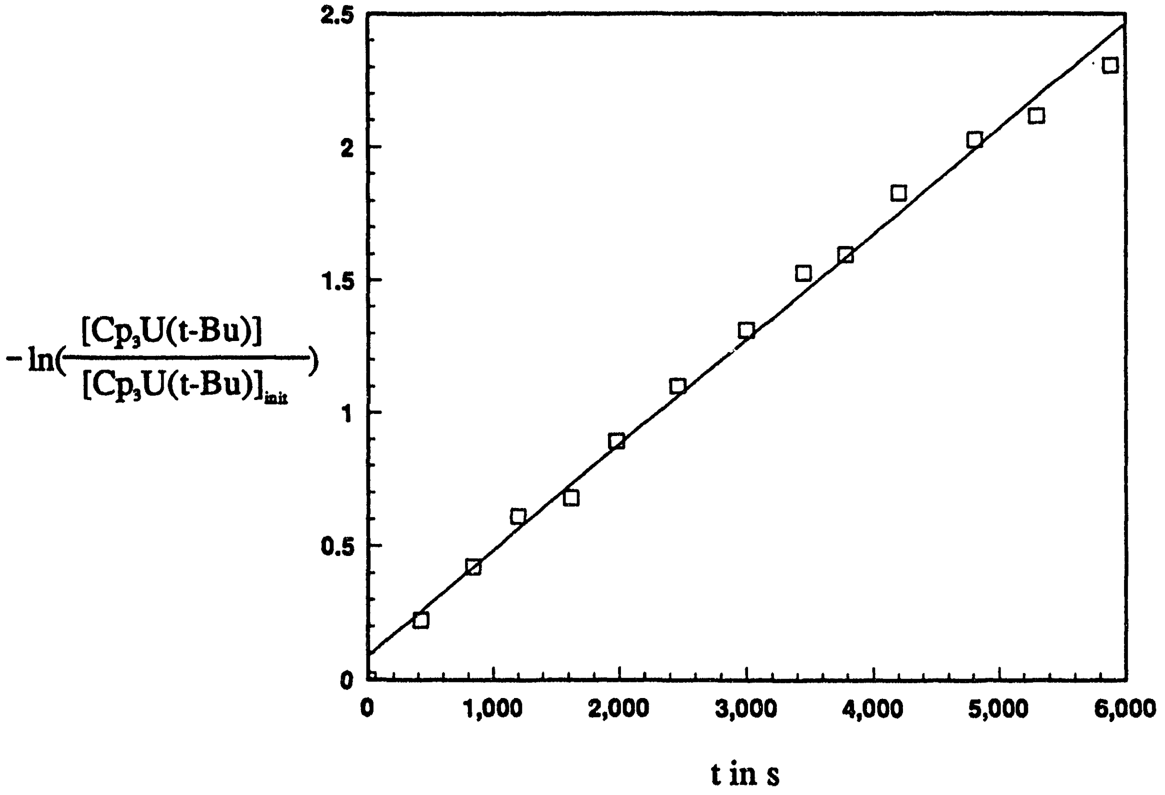
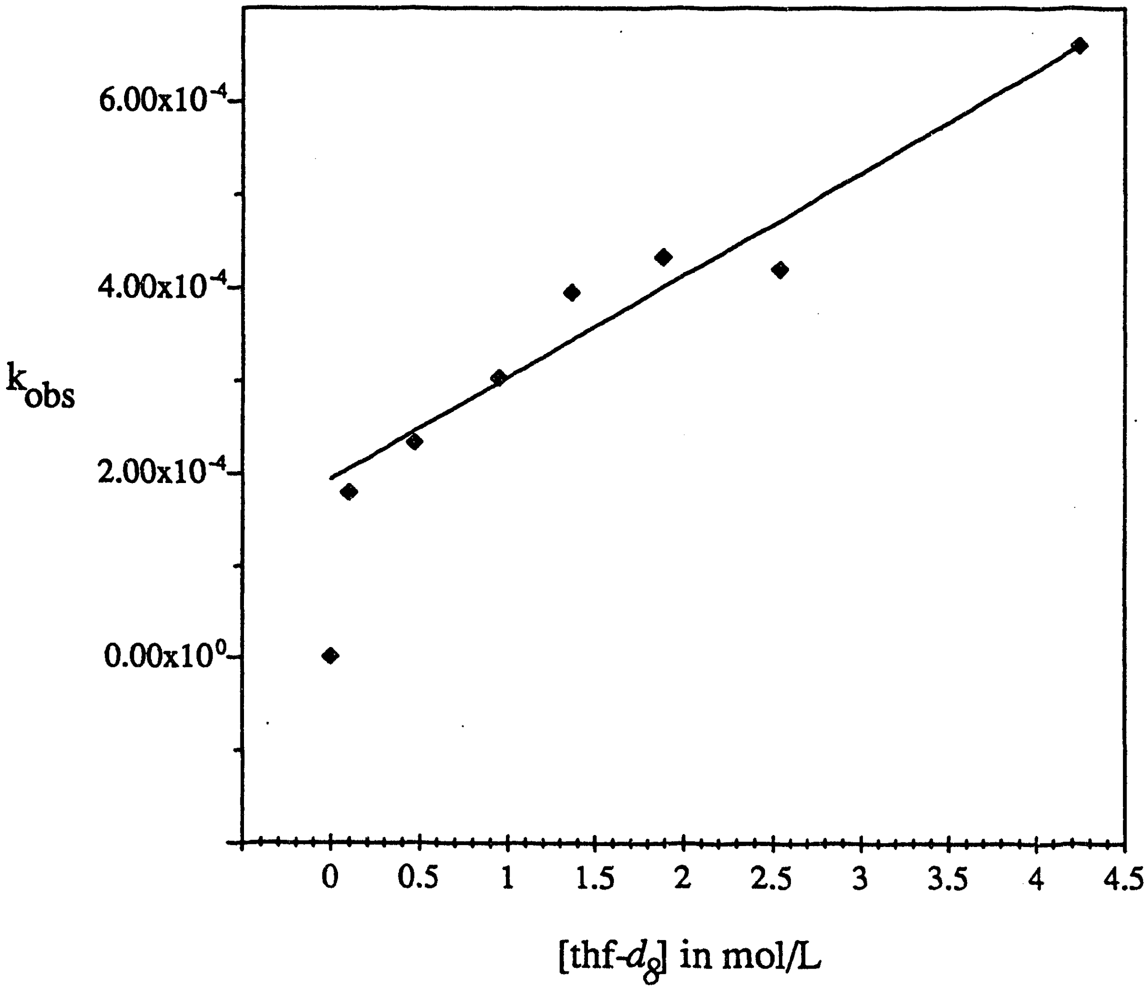


Figure 1: Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in *p*-Xylene-d_{10} at 30 °C: Kinetic Run at 1.37M in thf-d_8



Curve Fit: $y = 3.95e\text{-}04 \cdot x + 8.85e\text{-}02 \quad R^2 = 0.993$

Figure 2: Observed Rate Constant as a Function of thf-d_8 Concentration for the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in p-Xylene-d_{10} at 30 °C

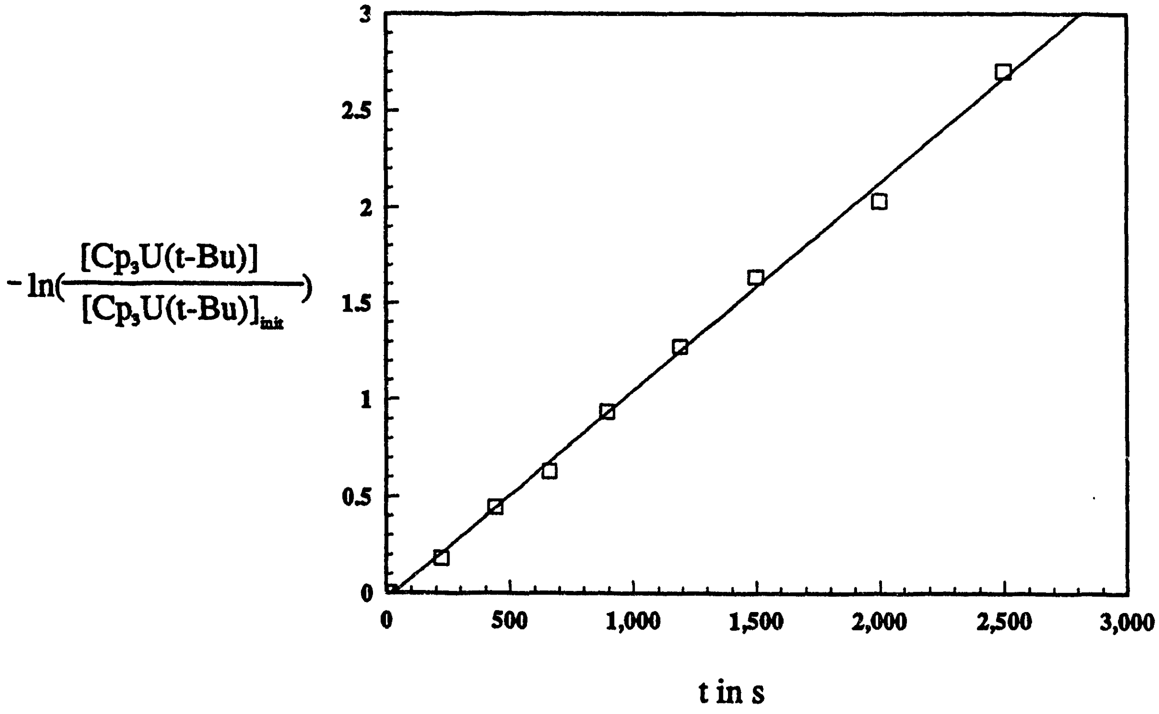


$$-\frac{\partial[\mathrm{Cp_3U(t-Bu)}]}{\partial t} = \frac{k_2K[\mathrm{Cp_3U(t-Bu)}][\mathrm{thf}]}{1 + K[\mathrm{thf}]} \tag{11}$$

However, attempts to fit the data according to this model gave unsatisfactory results. Optimization of the parameters K and k_2 using a non-linear least squares fitting procedure leads to a poor fit. More importantly, the preequilibrium constant K obtained from the fit would be so large that a significant percentage of the species with both thf and the t-butyl group coordinated to the uranium center would be present in solution. Because this equilibrium would by definition be fast on the NMR time scale, only an averaged resonance would be observed for the base-free Cp_3U(t-Bu) and the Cp_3U fragment with both the t-butyl group and thf coordinated. As the reaction is run at varying concentrations of thf, one would expect a shift in the relative concentrations of these two species in order to maintain the equilibrium. This would then be reflected in the chemical shift of both the cyclopentadienyl group resonance and the t-butyl group resonance. This is not observed, hence this mechanism is not a satisfactory model for the system.

The kinetic data collected in *p*-xylene-d_{10} and shown in Figure 2 look similar to the superposition of a saturation kinetics plot and a second-order kinetics plot. This would imply a mechanism involving two distinct pathways. Given the results obtained in Chapter 1, we suspected the possibility of solvent participation in this reaction. In order to test that hypothesis, the reaction of Cp_3U(t-Bu) with thf was reinvestigated in benzene-d_6 solution. The kinetics were run at 30 °C in benzene-d_6 under pseudo-first-order conditions in thf concentration. A typical individual kinetic run is shown in Figure 3. Once again the decay of Cp_3U(t-Bu) was followed for at least three half-lives. All runs showed the expected pseudo-first-order decay of Cp_3U(t-Bu).

Figure 3: Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in Benzene-d_6 at 30 °C: Kinetic Run at 3.69M in thf-d_8



Curve Fit: y := 1.08e-03•x -3.67e-02 $R^2 = 0.996$

Figure 4: Observed Rate Constant as a Function of thf-d_8 Concentration for the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in Benzene-d_6 at 30 °C

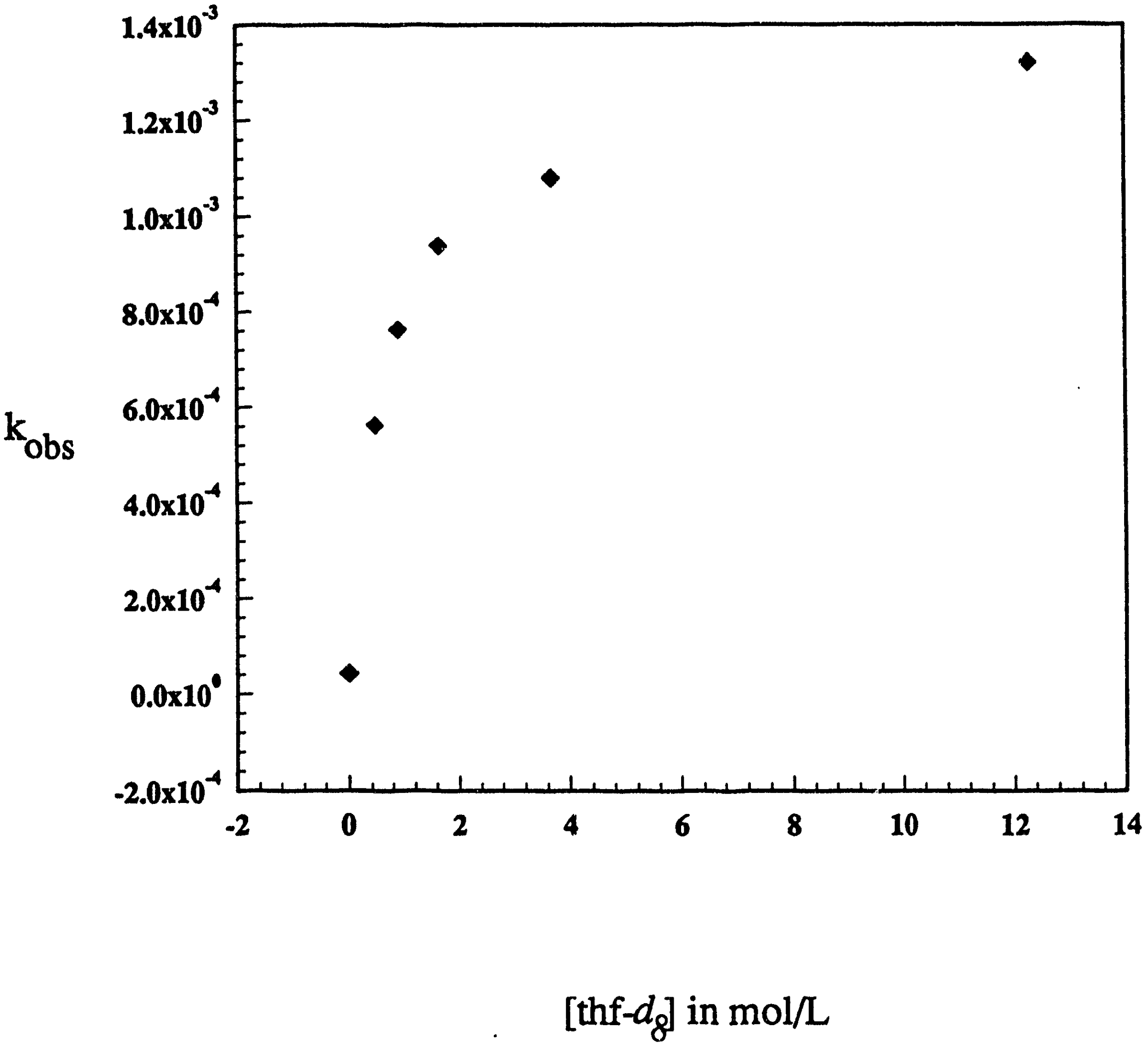


Table 2.4: Observed Rate Constants for the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in Benzene-d_6 at 30 °C as a Function of thf-d_8 Concentration

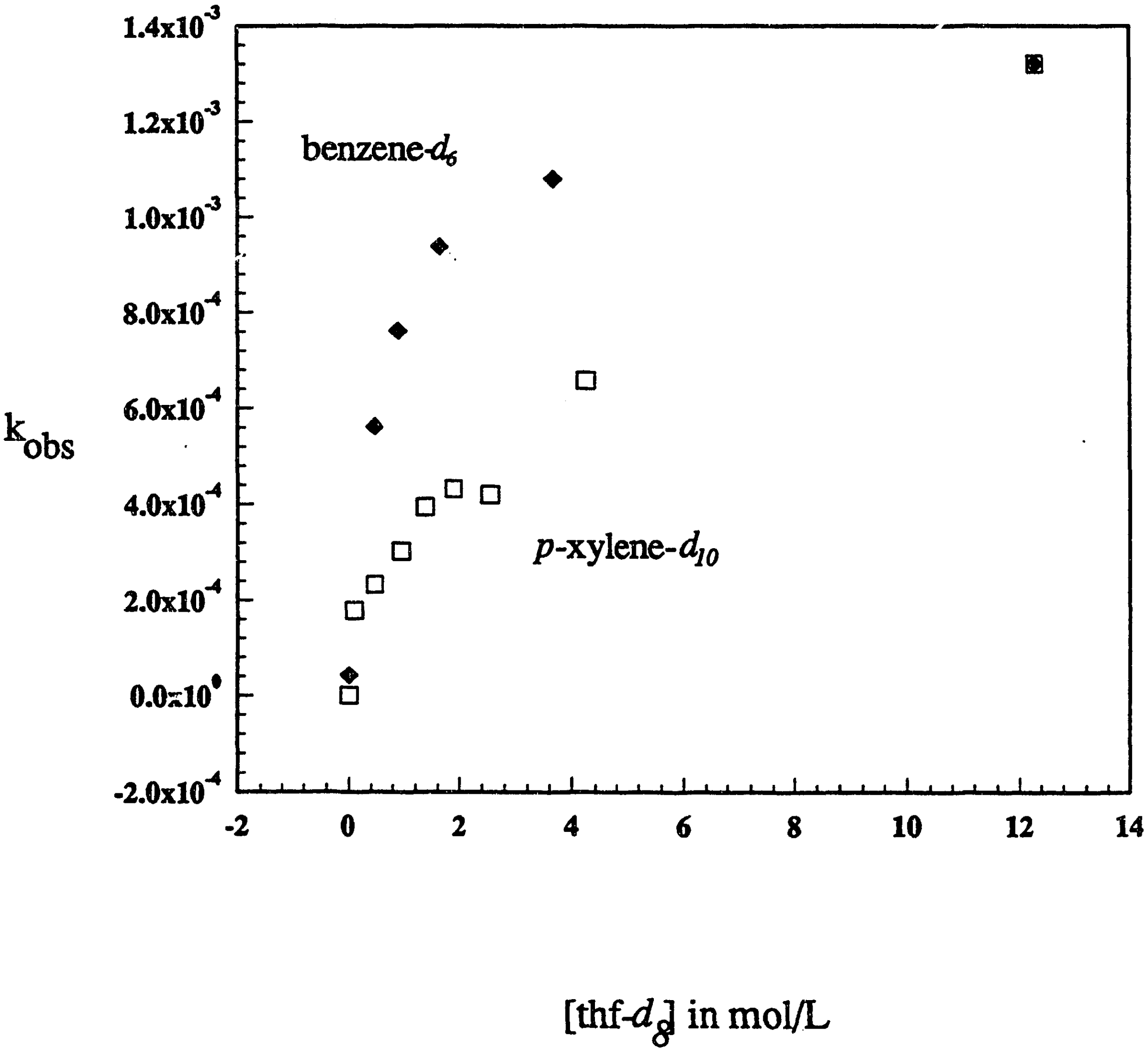
[thf-d_8] (mol/L)	k_{obs} (s^{-1})	$t_{1/2}$ (min.)
0	4.25×10^{-5}	272
0.47	5.62×10^{-4}	21
0.90	7.62×10^{-4}	15
1.64	9.38×10^{-4}	12
3.69	1.08×10^{-3}	11
12.29	1.32×10^{-3}	8.8

Estimated Standard Deviation: ± 10%

Figure 4 shows a plot of the observed rate constant k_{obs} as a function of thf-d_8 concentration. The data shown in Figure 4 are given in Table 2.4. The last data point in Table 2.4 ([thf-d_8] = 12.29M) corresponds to neat thf-d_8. The reaction is apparently also first-order in $Cp_3U(t\text{-}Bu)$ in neat thf, although as mentioned earlier, the reaction is no longer clean. Side-products presumably arising from reaction of t-butyl radicals with thf are formed. Nevertheless, it seems that the rate-determining step is still the same and hence we find it useful to include this data point in the subsequent discussion.

Figure 5 shows the kinetics in *p*-xylene-d_{10} and benzene-d_6 in the same plot. It appears that there is indeed a solvent effect on the reaction kinetics, although not as pronounced as for the decomposition of $Cp_3U(t\text{-}Bu)$ in aromatic solvents.

Figure 5: Observed Rate Constant as a Function of thf-d_8 Concentration for the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 at 30 °C



A further observation is illustrated in Figure 6. In some, but not all, of the kinetic runs, the resonances due to isobutane and isobutene show unusual lineshape in the initial stages of the reaction. Figure 6 shows that while the spectrum is properly phased for a normal absorption spectrum, the resonances due to isobutane and isobutene are not. Figure 7 shows a blowup of the region of interest. This unusual lineshape observed for the reaction products isobutane and isobutene does dissipate progressively as the reaction proceeds and toward the end of the reaction a normal absorption spectrum is observed for isobutane and isobutene. We believe this effect to be due to chemically-induced dynamic nuclear polarization (CIDNP), which gives rise to stimulated NMR emission.[17] CIDNP can be detected in the NMR spectra of products arising from reactions of free radicals performed in a magnetic field. The resulting nuclear polarizations are indicated in emission lines and anomalous enhancement of absorption signals due to dynamic coupling at some time during the reaction of the nuclear spins under observation to an electron spin system in the presence of a magnetic field. They are observed exclusively in those reaction products formed from radical intermediates.

While more involved conclusions have been drawn from CIDNP by experts,[18] relating the observed peak shape to the nature of the recombining spin system, we are content with stating that isobutane and isobutene are formed from radical precursors. The CIDNP patterns observed here for isobutane and isobutene in the reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 are qualitatively quite similar to the patterns observed for isobutane and isobutene by Benn in the decomposition of $(t\text{-}Bu)_2Mg$ in benzene solution.[19]

Figure 6: CIDNP observed in the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in benzene-d_6

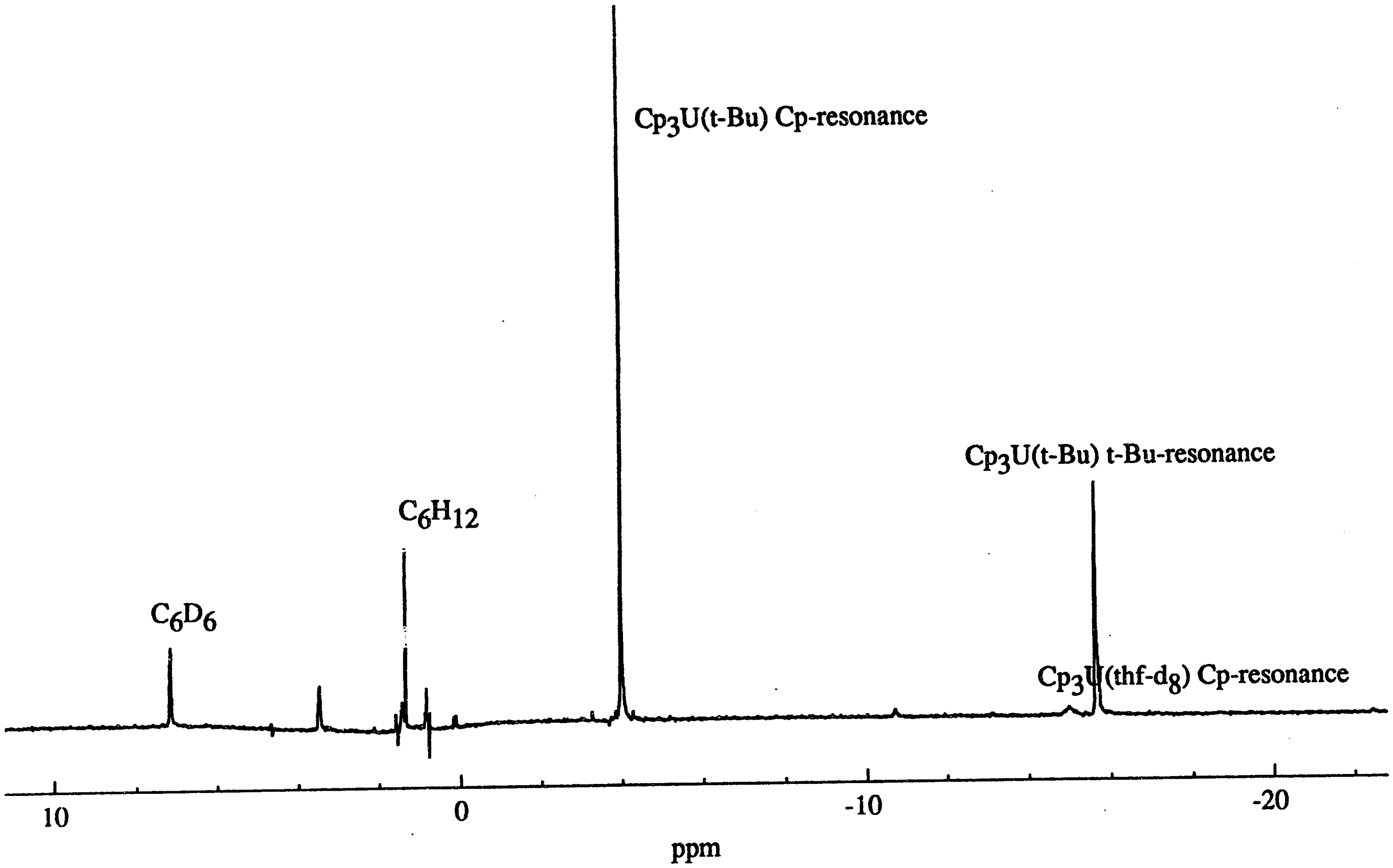
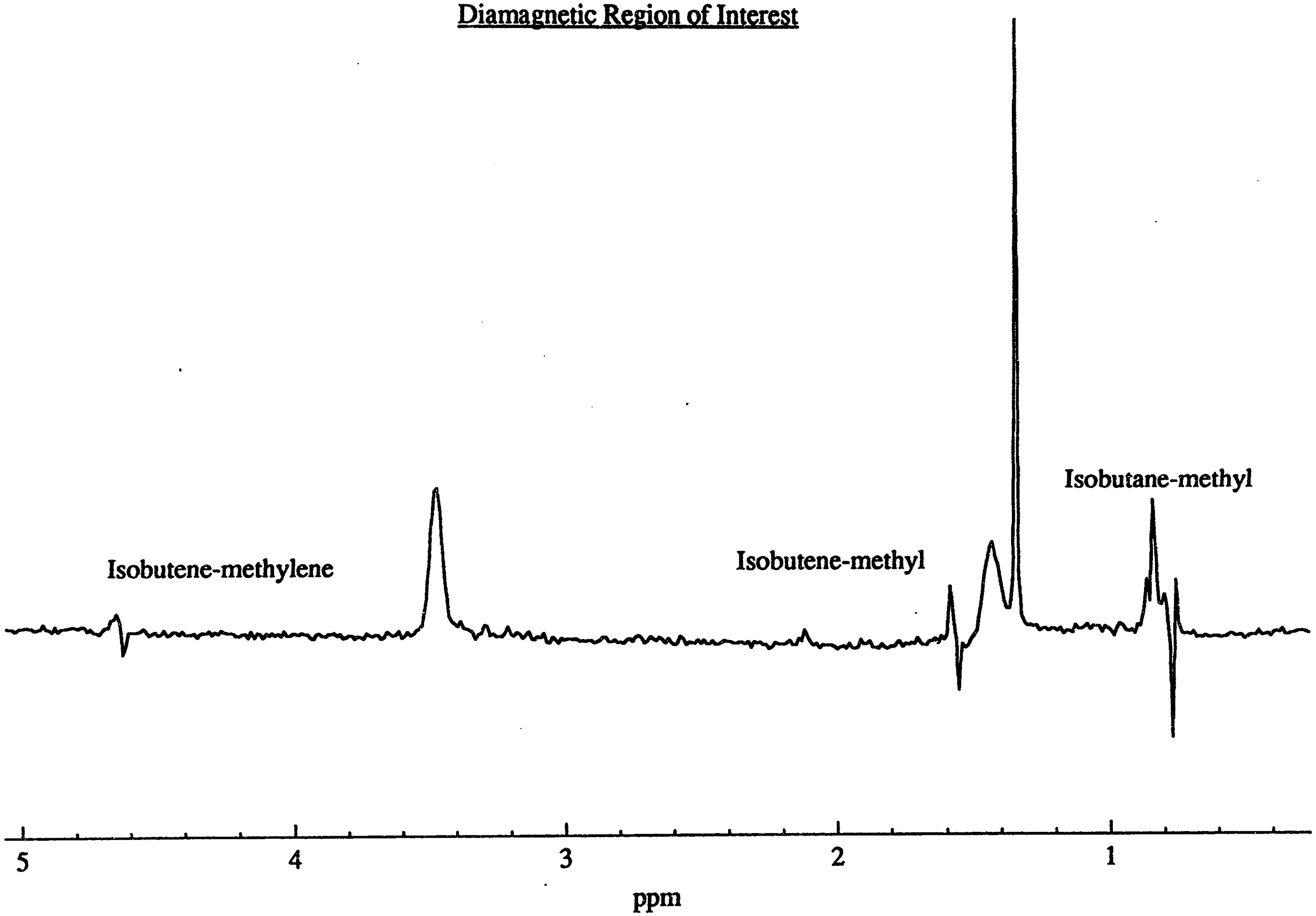


Figure 7: CIDNP observed in the Reaction of $Cp_3U(t\text{-}Bu)$ with thf-d_8 in benzene-d_6

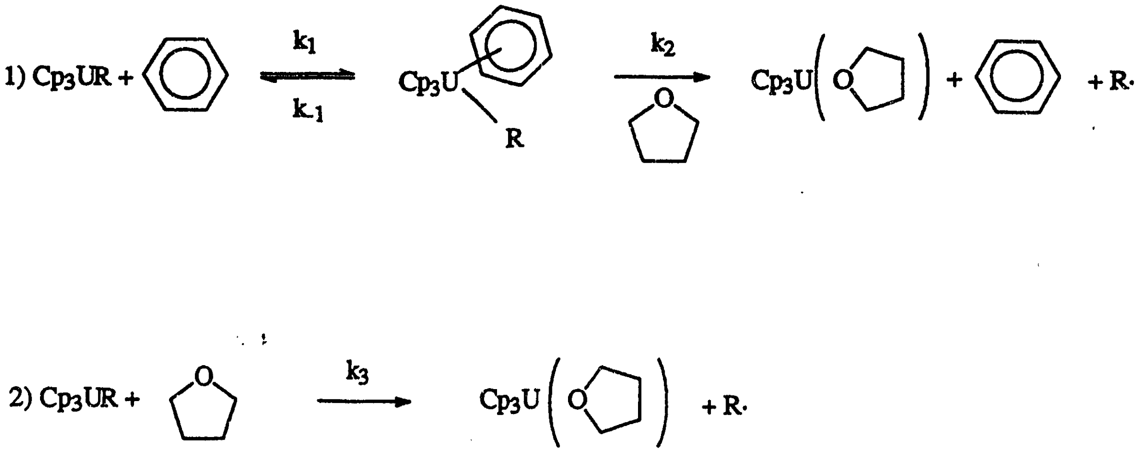
Diamagnetic Region of Interest



Proposed Mechanism:

The unambiguous identification of the organic reaction products isobutane and isobutene in addition to the observation of CIDNP in these two reaction products indicate that a t-butyl radical is displaced not only formally but in actual fact from the uranium center. In order to account for the observed dependence of the reaction rate on thf concentration and $Cp_3U(t\text{-}Bu)$ concentration, we propose that the reaction is occuring by two distinct pathways; the first involving a solvated intermediate and obeying saturation kinetics, and a second pathway that involves direct second-order displacement of a t-butyl radical from the uranium center by thf. The reaction pathway is outlined in Scheme 2.

Scheme2: Proposed Reaction Sequence



The rate law for this reaction sequence can be derived in the following way, in which ArH represents an aromatic solvent, [thf] represents the concentration of thf-d_8 in solution and R represents a t-butyl group.

The rate law for pathway 1) is given by:

$$-\frac{\partial[Cp_3UR]}{\partial t} = k_1[Cp_3UR][ArH]-k_{-1}[Cp_3U(ArH)(R)] \qquad (a)$$

Applying the steady state approximation to the intermediate $Cp_3U(ArH)(R)$ gives:

$$\frac{\partial[Cp_3U(ArH)(R)]}{\partial t} = k_1[Cp_3UR][ArH]-(k_{-1}+k_2[thf])[Cp_3U(ArH)(R)]$$

$$\frac{\partial[Cp_3U(ArH)(R)]}{\partial t} = 0$$ Steady State. Solving for $[Cp_3U(ArH)(R)]$ gives:

$$[Cp_3U(ArH)(R)] = \frac{k_1[Cp_3UR][ArH]}{k_{-1}+k_2[thf]} \qquad (b)$$

Substituting (b) into (a) gives:

$$-\frac{\partial[Cp_3UR]}{\partial t} = k_1[Cp_3UR][ArH](1-\frac{k_{-1}}{k_{-1}+k_2[thf]}) \qquad (c)$$

For pathway 2):

$$-\frac{\partial[Cp_3UR]}{\partial t} = k_3[Cp_3UR][thf] \qquad (d)$$

The overall rate expression for the disappearance of Cp_3UR is then given by combining expressions (c) + (d):

$$-\frac{\partial[Cp_3UR]}{\partial t} = \{k_1(1-\frac{k_{-1}}{k_{-1}+k_2[thf]})[ArH]+k_3[thf]\}[Cp_3UR] \qquad (e)$$

Expression (e) still contains two variables ([thf] and [ArH]). Since the goal is to arrive at an expression relating the observed rate constant for the first-order disappearance of CpU(t-Bu) to the thf concentration, one variable has to be eliminated in order to determine the parameters k_1, k_{-1}, k_2 and k_3. Indeed, the non-linear least squares fitting program used admits only one variable. However, it can be seen that the two variables in expression (e) are not independent: Assuming that thf and the arene ArH form an ideal solution, the following relationship stands:

$[\mathrm{ArH}] = a + b \cdot [\mathrm{thf}]$ where a,b are known constants

Introducing the ideal solution hypothesis into the overall rate expression (e) gives:

$$-\frac{\partial[\mathrm{Cp_3UR}]}{\partial t} = \{k_1(1-\frac{k_{-1}}{k_{-1}+k_2[\mathrm{thf}]})(a+b[\mathrm{thf}])+k_3[\mathrm{thf}]\}[\mathrm{Cp_3UR}] \qquad (f)$$

Expression (f) can be fitted, but it does not result in sensible values for k_{-1} and k_2, because the errors are very large in these two parameters. Instead, the slightly rearranged expression (g) below, which gives the ratio of k_2/k_{-1} as one of the parameters can be fitted with reasonable error limits:

$$\begin{aligned}-\frac{\partial[\mathrm{Cp_3UR}]}{\partial t} &= \{k_1(1-\frac{1}{1+\frac{k_2}{k_{-1}}[\mathrm{thf}]})(a+b[\mathrm{thf}])+k_3[\mathrm{thf}]\}[\mathrm{Cp_3UR}] \\ &= k_{obs}[\mathrm{Cp_3UR}]\end{aligned} \qquad (g)$$

This model can then be applied to the data obtained in *p*-xylene-d_{10} and benzene-d_6 solution. A detailed description of the algorithms used by the Passage II data analysis program (©1988 Passage Software Inc., Fort Collins, CO) can be found in ref. 32. The result of a non-linear least squares fit is shown in Figure 8. The best fitting parameters are given in Table 2.5.

Table 2.5: Best Non-Linear Least Squares Fit Parameters for the Proposed Mechanism

Solvent	$k_1(M^{-1} \cdot s^{-1})$	k_2/k_{-1}	$k_3(M^{-1} \cdot s^{-1})$
benzene-d_6	$1.01 \times 10^{-4} \pm 0.17 \times 10^{-4}$	1.86 ± 0.80	$1.07 \times 10^{-4} \pm 0.11 \times 10^{-4}$
p-xylene-d_{10}	$2.99 \times 10^{-5} \pm 0.33 \times 10^{-5}$	29.6 ± 19.5	$1.12 \times 10^{-4} \pm 0.09 \times 10^{-4}$

The standard deviation of the individual rate constants k_{obs} was estimated to be ±10% in accordance with the results in Chapter 1. This standard deviation was then used as the error associated with each data point. On this basis, the standard deviations of the fitting parameters (k_1, k_2/k_{-1}, k_3) were obtained from the covariance matrix of the non-linear least squares fit.[32]

As can be seen, the model does fit the experimental data reasonably well. Figure 9 shows a free energy diagram for the proposed reaction sequence. Inspection of the values for k_1 shows that benzene-d_6 reacts more rapidly with $Cp_3U(t\text{-}Bu)$ to form the solvated species than does *p*-xylene-d_{10}, as expected. The large error associated with the partitioning ratio k_2/k_{-1} for *p*-xylene-d_{10} is caused by the sharp change in slope for that

Figure 8: Non-Linear Least Squares Fit

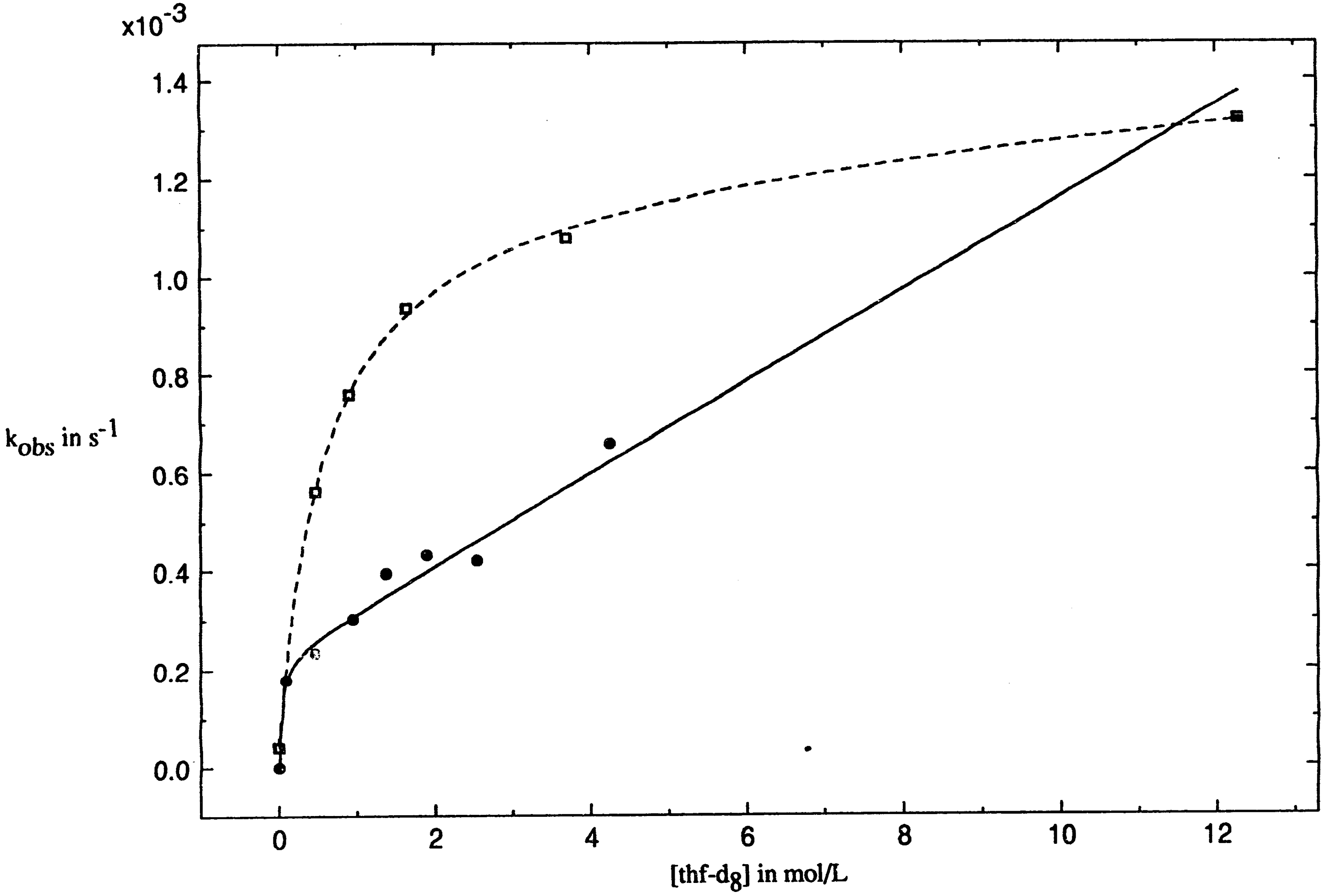
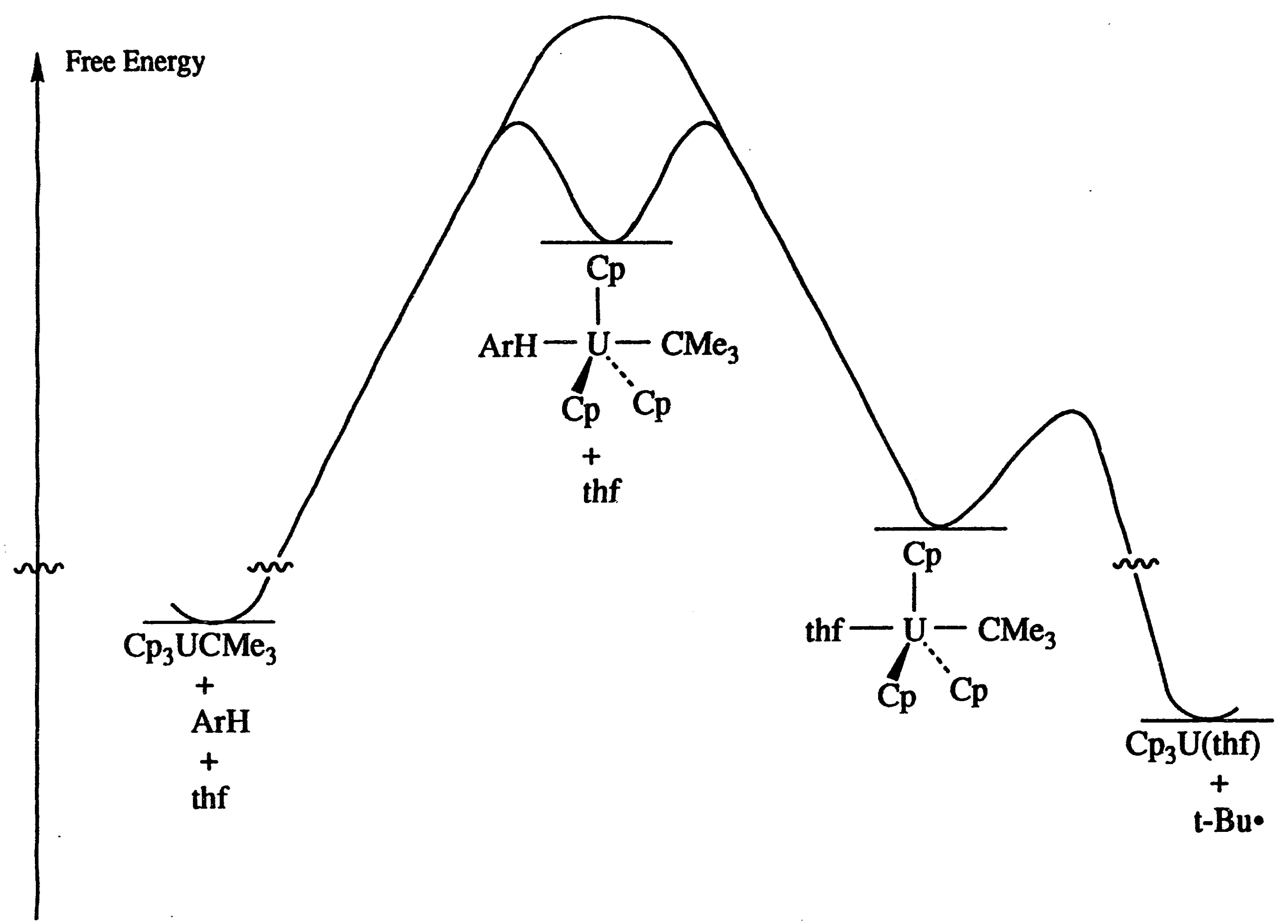


Figure 9: Free Energy Diagram for the Proposed Reaction Sequence of $Cp_3U(t\text{-}Bu)$ with thf



curve. This, unfortunately, makes comparison of k_2/k_{-1} for benzene-d_6 and *p*-xylene-d_{10} meaningless.

Formally, this mechanism is very similar to the well-established substitution mechanism at square-planar d^8-metal centers in classical coordination chemistry.[33] But these substitutions deal with either a 2-electron-donor entering ligand and a 2-electron-donor leaving group or a 1-electron-donor entering ligand and a 1-electron-donor leaving group. Here, we have the more unusual case of a 2-electron-donor entering ligand and a 1-electron-donor carbon-based radical leaving group. In organometallic chemistry 17-electron transition metal complexes have been shown to undergo substitution with 2-electron-donor ligands by associative pathways, resulting in a $17e^- \rightarrow 19e^- \rightarrow 17e^-$ transformation.[31] Intermediate 17-electron transition metal complexes have been postulated to undergo associative substitution of a 1-electron-donor ligand by a 2-electron-donor ligand, resulting in a $17e^- \rightarrow 19e^- \rightarrow 18e^-$ transformation.[20] But, to the best of our knowledge, no mechanistic information is available on such processes, and hence, the present study is the first detailed mechanistic investigation of ligand- or solvent-assisted metal-carbon bond homolysis.

2.2 Insertion Reactions into the Metal-Carbon Bond of Tris(Cyclopentadienyl)Uranium-t-Butyl

The insertion of carbon monoxide into the metal-tertiary alkyl bond of $(MeC_5H_4)_3U$(t-Bu) was observed by Brennan.[1] He isolated the η^2-acyl compound $(MeC_5H_4)_3U$(C(O)-t-Bu) from this reaction (eq 2). We prepared the acyl by a slightly modified procedure in order to investigate its variable temperature ^{1}H-NMR behavior. The compound exhibits four ^{1}H-NMR resonances at room temperature, two resonances integrating to six protons each for the methylcyclopentadienyl ring protons and two resonances integrating to nine protons each for the methylcyclopentadienyl methyl group and the acyl t-butyl group. These latter two resonances cannot be assigned unambiguously, but based on the much narrower line-width for the downfield resonance, as well as its shorter longitudinal relaxation time, the downfield resonance is tentatively assigned to the t-butyl group.

Figure 10 shows a plot of δ versus 1/T from +95 to -88 °C in toluene-d_8. No coalescence behavior is observed over the temperature range examined. Figure 11 shows the data in more detail. The plots show a slight deviation from linearity and hence Curie-Weiss behavior is not followed. As observed previously (see Chapter 1), this effect is most pronounced in the overall least temperature-dependent resonance (ring resonance a). One might be tempted to ascribe this behavior to the presence of a temperature-dependent η^1-η^2-equilibrium for the acyl group. However, given that a similar perturbation has been observed for a number of unrelated compounds (see Chapter 1 and 4), we ascribe this behavior to the presence of temperature-dependent conformational equilibria. This point is further illustrated by Figure 12. Here, a superposition of the variable temperature ^{1}H-NMR spectra of $(MeC_5H_4)_3U$(C(O)-t-Bu) in toluene-d_8 and methylcyclohexane-d_{14} is shown. The light symbols represent the data in toluene, while the dark symbols represent the data in methylcyclohexane. The curves follow the same

Figure 10: Variable Temperature ^{1}H-NMR Spectrum of $(MeC_5H_4)_3U(C(O)\text{-}t\text{-}Bu)$ in toluene-d_8 from +95 to -88 °C

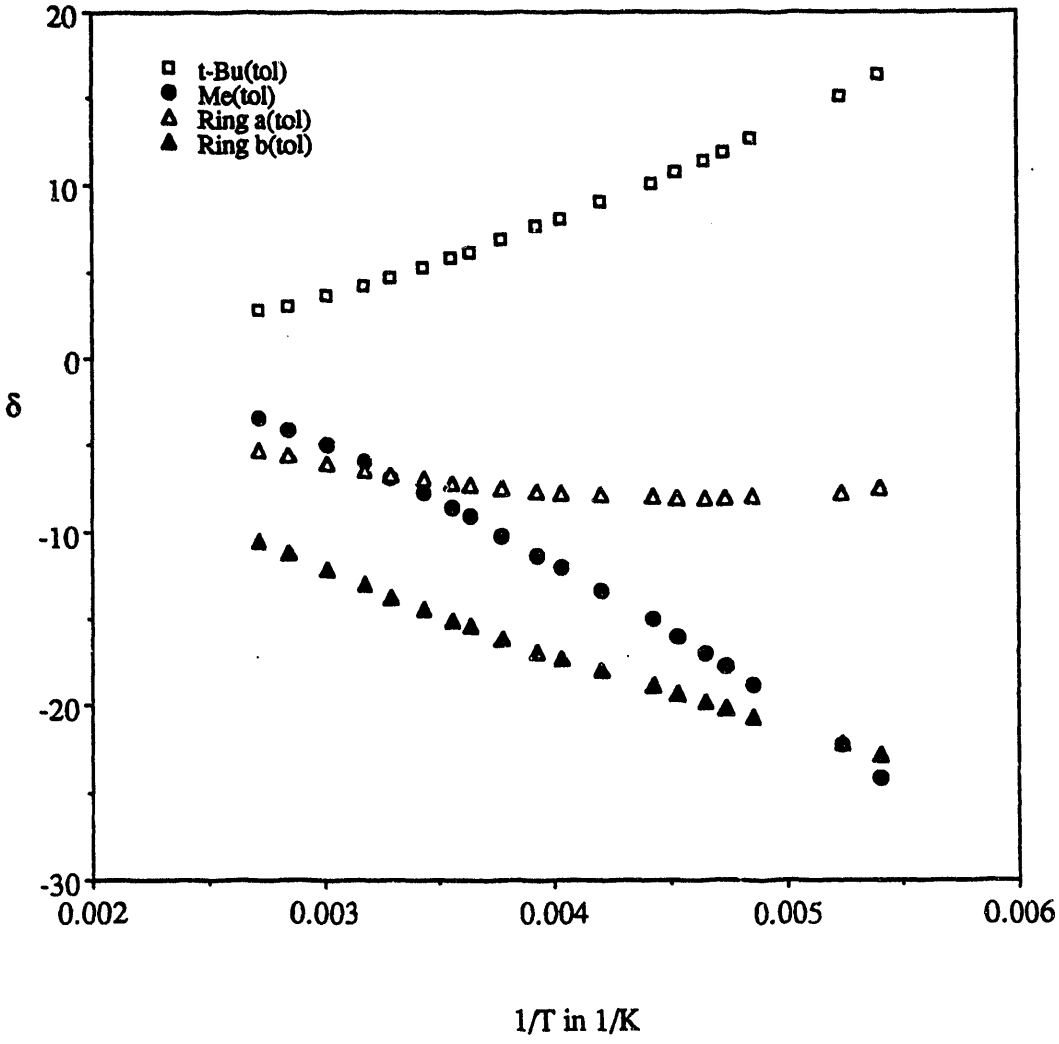


Figure 11: Variable Temperature ^{1}H-NMR Spectrum of $(MeC_5H_4)_3U(C(O)\text{-t-Bu})$ in toluene-d_8 from +95 to -88 °C

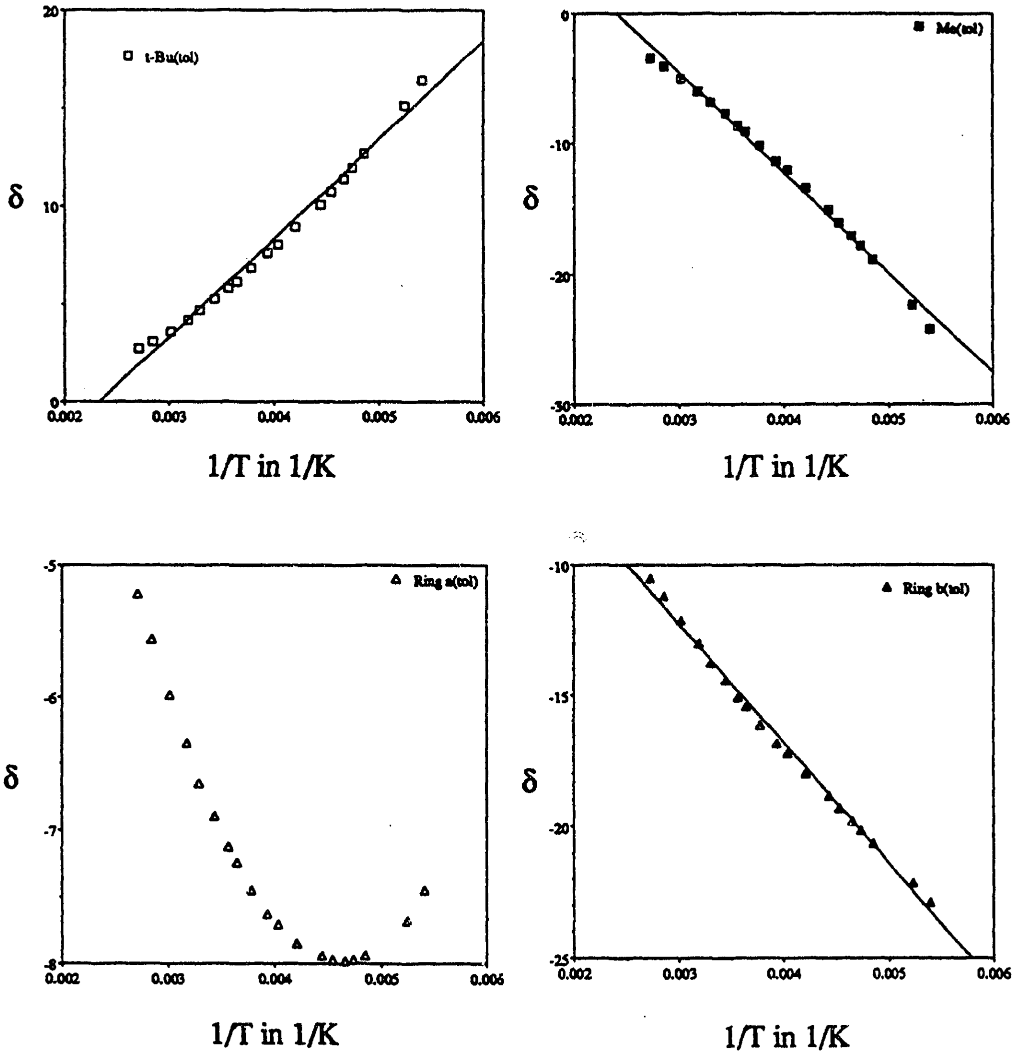
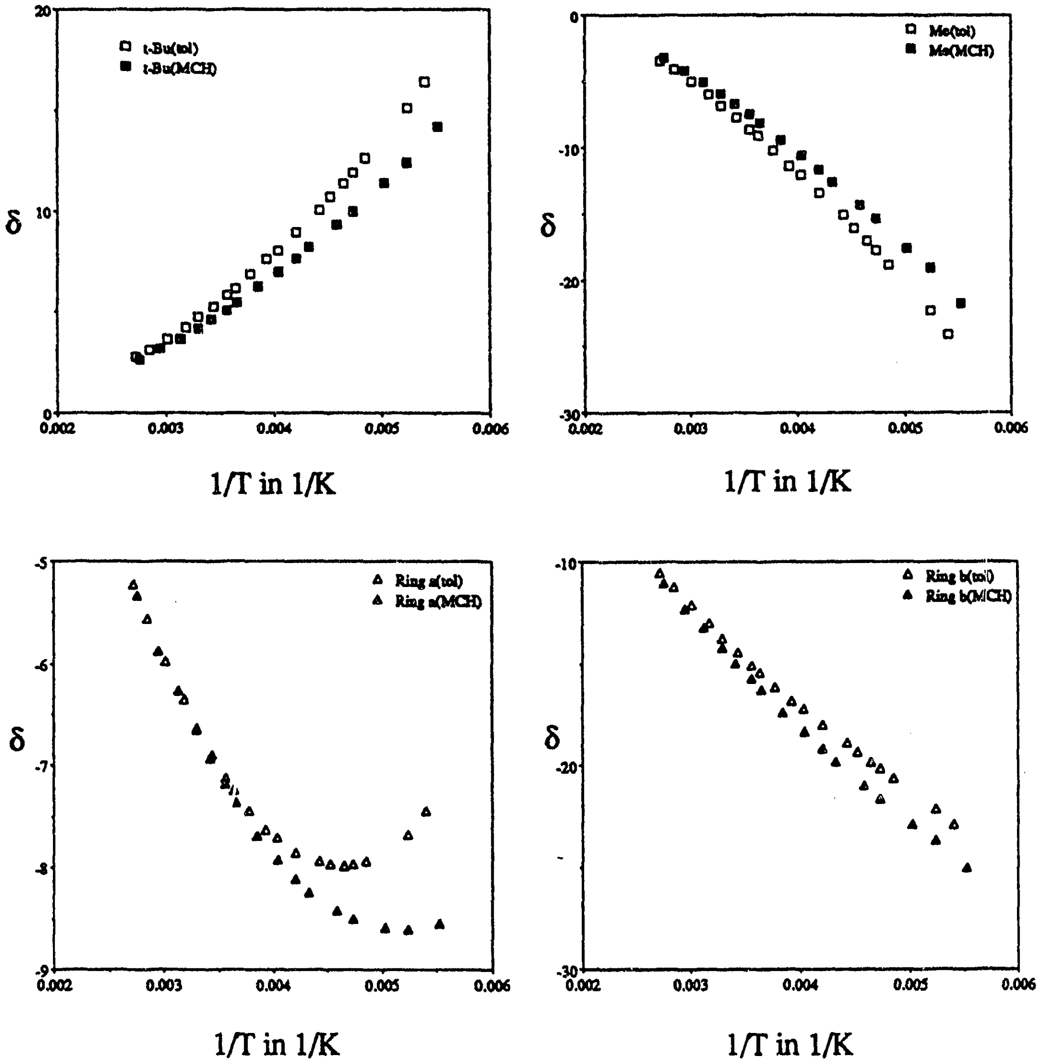


Figure 12: Variable Temperature ^{1}H-NMR Spectrum of $(MeC_5H_4)_3U(C(O)\text{-}t\text{-}Bu)$ in toluene-d_8 from +95 to -88 °C and in methylcyclohexane-d_{14} from +90 to -92 °C



qualitative behavior in both solvents, although a solvent effect on the chemical shift is clearly visible. Looking at ring resonance a (lower left graph), it should be noted that the point at which the curve bottoms out is shifted to lower temperature in methylcyclohexane relative to toluene. We ascribe this behavior to the greater viscosity of toluene relative to methylcyclohexane at low temperatures. Higher viscosity will result in higher internal pressure, which in turn will tend to favor the low energy conformations of the molecule over the high energy ones.

When samples of $(MeC_5H_4)_3U(C(O)\text{-t-Bu})$ in toluene-d_8 or methylcyclohexane-d_{14} solution were heated to 90 °C for 1 h complete decomposition of the compound occurred. The only soluble product of these decomposition reactions was t-butyltoluene. A similar reaction has recently been reported by Ephritikhine and coworkers for the analogous $Cp_3U(C(O)R)$ compounds (eq 12).[34] The authors report that the reaction is promoted by the presence of a classical σ-donor ligand. They also established that the aromatic moiety originates from the cyclopentadienyl ligand by incorporation of the acyl carbon into the six-membered ring. They attribute this peculiar reactivity to the oxycarbenoid character of the $Cp_3U(C(O)R)$ complexes.

$$Cp_3U(C(O)R) \xrightarrow{\text{thf}} PhR + \ldots\ldots \qquad (12)$$

$$R = Me,\ n\text{-}Bu,\ i\text{-}Pr,\ t\text{-}Bu$$

The present results indicate that, although this reaction may be accelerated by the presence of classical donor ligands, their presence is not required for the reaction to proceed. The use of methylcyclopentadienyl ligands on uranium rather than cyclopentadienyl ligands leads to formation of alkyltoluenes rather than alkylbenzenes. Hence the regiochemistry of the reaction becomes an issue. In the case of $(MeC_5H_4)_3U(C(O)\text{-t-}$

Bu) decomposition in toluene-d_8 at 90 °C a mixture of t-butyltoluenes is obtained. By GC, two products were found in a 5:1 ratio. The minor product was identified as being 4-t-butyltoluene by comparison to known a commercial sample. For the decomposition of $(MeC_5H_4)_3U(C(O)\text{-t-Bu})$ in methylcyclohexane-d_{14} at 90 °C the same two products were found in a 10:1 ratio. Again, 4-t-butyltoluene was the minor reaction product. Thus it appears that the product distribution is solvent dependent. Further experiments are required to ascertain the identity of the major reaction product, either 2- or 3-t-butyltoluene.

Finally, it should be noted that carbon monoxide insertion was reported to be reversible in the Cp_3UR series (R = Me, Et, i-Pr, n-Bu, t-Bu) at temperatures above 60 °C.[2] The reported ^1H-NMR spectra are clearly consistent with this conclusion. In the present case, however, we see no evidence of reversibility for carbon monoxide insertion into the metal-carbon bond of $(MeC_5H_4)_3U(\text{t-Bu})$. We can offer no explanation for this apparent difference between the $(MeC_5H_4)_3UR$ series and the Cp_3UR series.

Under ethylene (210 psi), a toluene solution of $(MeC_5H_4)_3U(\text{t-Bu})$ reacted over a period of ca. 5 h to yield the monoinsertion product (eq 13).

$$(MeC_5H_4)_3U(\text{t-Bu}) + CH_2CH_2 \longrightarrow (MeC_5H_4)_3U(CH_2CH_2\text{-t-Bu}) \quad (13)$$

The resulting neohexyl derivative, $(MeC_5H_4)_3U(CH_2CH_2\text{-t-Bu})$, is stable under 210 psi of ethylene for up to one week. No evidence of further insertion into the uranium-neohexyl bond was observed by ^1H-NMR spectroscopy. This behavior is quite unusual for transition metal-carbon bonds since they normally either polymerize ethylene or do not react with it at all.[21] It is reasonable to postulate that the driving force for this insertion reaction is the relief of steric congestion around the uranium center in going from a tertiary to a primary alkyl group, which results in the formation of a somewhat stronger primary versus tertiary uranium-alkyl bond. For subsequent insertions, these driving forces are essentially lost, leading to a large difference between the rate of the first insertion step and the rate of chain growth therefrom. One might also speculate that the reaction mechanism for ethylene insertion is novel. In keeping with other reactions of $(MeC_5H_4)_3U(t\text{-}Bu)$, initial attack of ethylene on the tertiary alkyl complex would lead to uranium-carbon bond homolysis and formation of a caged radical pair consisting of a uranium(III) ethylene complex and a t-butyl radical. Subsequent attack of the t-butyl radical on the coordinated olefin would lead to the observed insertion product. This mechanism would also explain why no further insertion of ethylene is observed, since ethylene can be viewed as trapping a radical pair.

2.3 Reactions of Tris(Cyclopentadienyl)Uranium-t-Butyl with Fluorocarbons

The reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with PF_3 resulting in formation of $(MeC_5H_4)_3UF$ reported by Brennan (eq 3) [1] prompted us to investigate the possibility of abstracting fluorine from other substrates, in particular fluorocarbons. Only a few examples of intermolecular carbon-fluorine bond activation have been reported.[22] The pronounced inertness of perfluorocarbons is undoubtedly caused by the high carbon-fluorine bond dissociation energies [23] and by the weakness of metal-fluorocarbon interactions.[24] Thus both thermodynamic and kinetic factors generally disfavor carbon-fluorine bond activation.

Based upon previous experience, the presence of a functional group in the fluorocarbon molecule is often a requirement for reaction.[22] Therefore, we first investigated the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with hexafluorobenzene, a fluorocarbon with a very strong carbon-fluorine bond (154 kcal/mol).[23] Hexafluorobenzene possesses π-electron density which can allow it to coordinate to a metal center. Indeed, $(MeC_5H_4)_3U(t\text{-}Bu)$ reacts with hexafluorobenzene in benzene or toluene solution to form $(MeC_5H_4)_3UF$ (eq 14). $(MeC_5H_4)_3UF$ has been prepared previously by reaction of $(MeC_5H_4)_3U(thf)$ with PF_3.[25]

$$(MeC_5H_4)_3U(t\text{-}Bu) + C_6F_6 \xrightarrow[12\text{-}24\ h]{RT} (MeC_5H_4)_3UF + \ldots\ldots \qquad (14)$$

The rate of this reaction increases with increasing concentration of hexafluorobenzene. By ^1H- and ^{19}F-NMR spectroscopy, and GC and GC-MS techniques, the organic products of this reaction were found to be isobutane, isobutene, pentafluorobenzene and t-butylpentafluorobenzene. Note that by GC, the hexafluorobenzene used as a starting material in these reactions was shown to be free of pentafluorobenzene. The identity of these products was confirmed by comparison with authentic commercial samples. A sample of t-butylpentafluorobenzene was synthesized independently from hexafluorobenzene and t-butyllithium (eq 15).

$$C_6F_6 + \text{t-BuLi} \longrightarrow \text{t-Bu}C_6F_5 + \text{LiF} \qquad (15)$$

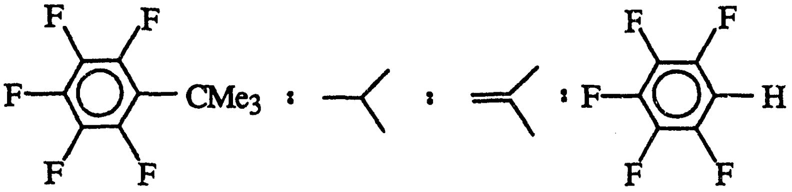
In addition, small amounts of 2,3,4,5,6-pentafluoro-4'-methylbiphenyl were isolated from the reaction mixture by sublimation, when the reaction between hexafluorobenzene and $(MeC_5H_4)_3U(\text{t-Bu})$ was carried out in toluene. This compound was identified by comparison to reported literature data.[26] Small quantities of bibenzyl were detected by GC. Traces of hexamethylethane, the coupling product of two t-butyl radicals, were found in all samples as well. Other products present in trace amounts were not characterized. The relative amounts of these organic products as determined by GC are given in Scheme 3. When the reaction was carried out in benzene-d_6 solution at 25 °C, the amounts of t-butylpentafluorobenzene, isobutane and isobutene formed accounted for 25%, 40% and 15%, respectively, of the initial intensity of $(MeC_5H_4)_3U(\text{t-Bu})$ by ^{1}H-NMR integration at 30 °C.

This product distribution is temperature dependent. When the reaction is run at higher temperature, the amount of coupled product, t-butylpentafluorobenzene, decreases with respect to the other reaction products, and the ratio of isobutane and isobutene approaches 1:1. The fact that the rate of reaction depends on the concentration of hexafluorobenzene is suggestive of a bimolecular reaction mechanism, rather than a free-radical mechanism initiated by uranium-carbon bond homolysis. Thus, coordination of hexafluorobenzene followed by ligand-induced uranium-carbon bond homolysis is

Scheme 3: Product Distribution

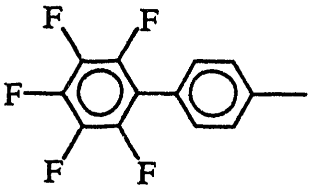
$$(MeC_5H_4)_3UCMe_3 + C_6F_6 \xrightarrow[25\,°C]{toluene} (MeC_5H_4)_3UF$$

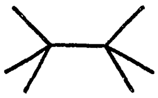
Organic Products: Relative Amounts at 25 °C

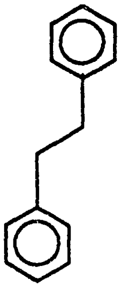


1 : 2 : 1 : 2

Minor Products Present in Small Quantities:

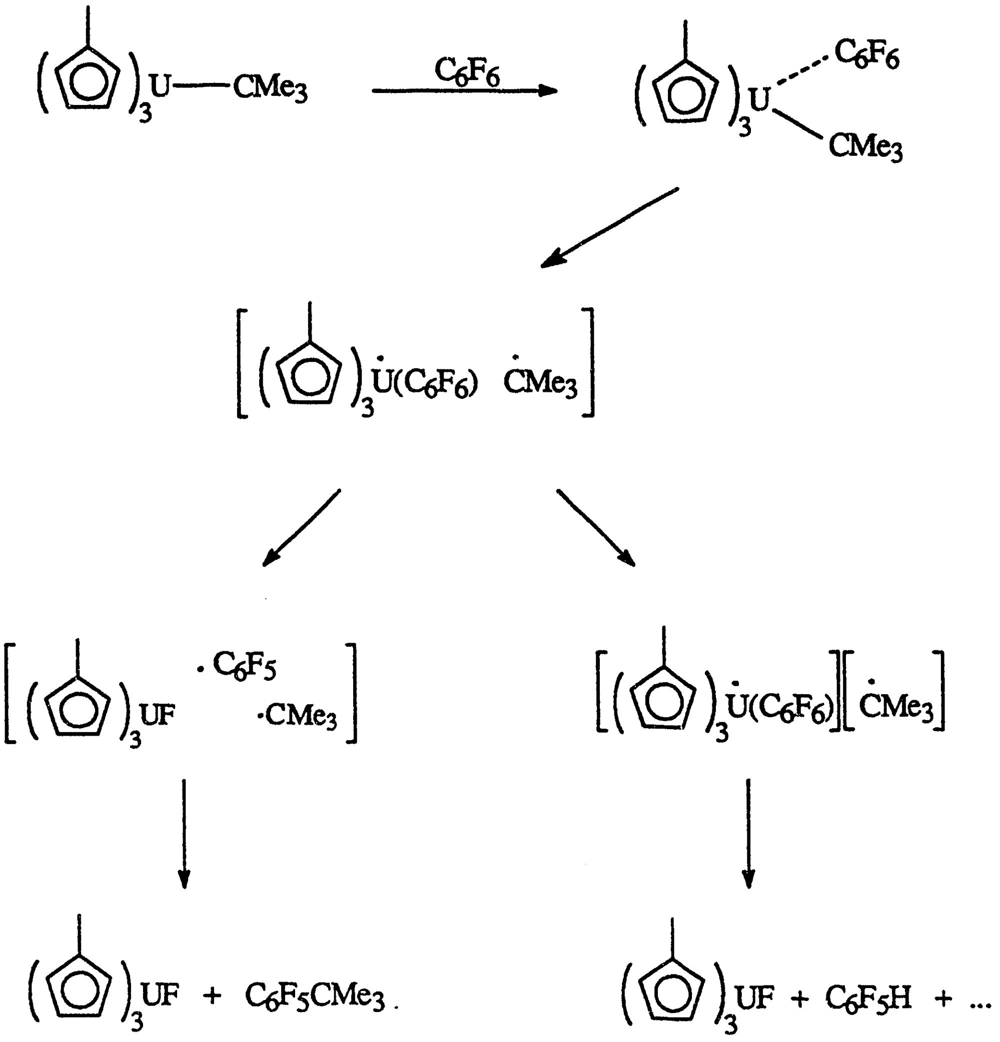






expected to initiate the reaction, similar to the reaction of the more conventional Lewis-bases with $(MeC_5H_4)_3U(t\text{-}Bu)$ (see Section 2.1). We believe that t-butylpentafluorobenzene arises from a caged radical pair as shown in Scheme 4. When the t-butyl radical escapes from this solvent cage, pentafluorobenzene and isobutane/isobutene are expected to be the organic products. But if the t-butyl radical remains in the solvent cage, radical coupling is expected to yield t-butylpentafluorobenzene. From this model the product distribution is expected to be temperature dependent, since at a higher temperature more radical escape from the solvent cage should take place. Thus the amount of t-butylpentafluorobenzene should decrease at higher reaction temperatures. This was indeed observed experimentally.

Scheme 4: Proposed Mechanism



It is reasonable to postulate that the principal driving force for the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with hexafluorobenzene is thermodynamic. A weak uranium-carbon bond and a strong carbon-fluorine bond have to be broken. This is offset by the formation of a uranium-fluorine bond and either a carbon-carbon bond (t-butylpentafluorobenzene), a carbon-hydrogen bond (isobutane and pentafluorobenzene) or a carbon-carbon double bond (isobutene). The U-F bond energy can be estimated as ca. 150 kcal/mol based on known thermochemical data for uranium fluorides.[27] Its strength offsets the C-F bond dissociation energy of hexafluorobenzene which is reported to be 154 kcal/mol.[23] The U-C bond strength can be estimated as ca. 80 kcal/mol based on thermochemical measurements on primary actinide alkyl compounds.[28] Because a tertiary alkyl-uranium bond is likely to be significantly weaker than 80 kcal/mol, its dissociation energy is more than compensated for by the successive reactions of the organic radical intermediates formed in the reaction. Hence, the overall reaction is exergonic.

In order to expand this study to aliphatic fluorocarbons, benzotrifluoride was investigated next. This substrate possesses an aromatic phenyl ring that can potentially coordinate to the metal center and perhaps facilitate C-F bond activation. As expected, $(MeC_5H_4)_3U(t\text{-}Bu)$ reacts with benzotrifluoride to form $(MeC_5H_4)_3UF$ in essentially quantitative yield (eq 16).

$$(MeC_5H_4)_3U(t\text{-}Bu) + PhCF_3(\text{neat}) \xrightarrow[20\text{ min}]{65\,^\circ C} (MeC_5H_4)_3UF + PhCF_2(t\text{-}Bu) + \ldots \quad (16)$$

In neat benzotrifluoride, 1,1-difluoro-2,2-dimethylpropylbenzene was identified among the volatile reaction products by GC-MS. Since isobutane and isobutene are also present, it seems likely that the radical recombination product, tetrafluoro-1,2-diphenylethane, should be present as well. However, it was not detected. If the reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with benzotrifluoride is run in an aromatic solvent such as *p*-xylene-d_{10}, no 1,1-difluoro-2,2-dimethylpropylbenzene was detected by GC-MS.

Extension of the C-F activation process to saturated perfluorocarbons was considered next. The choice of a suitable substrate is more difficult because of the physical and chemical properties of perfluorocarbons.[35] They are poor solvents as well as being poorly soluble themselves in hydrocarbon solvents. We therefore attempted a heterogeneous reaction between perfluoromethylcyclohexane and $(MeC_5H_4)_3U(t\text{-}Bu)$ (eq 17). Over a period of 4 h at 65 °C, formation of $(MeC_5H_4)_3UF$ was observed, although the conversion was not quantitative (ca. 70%).

$$(MeC_5H_4)_3U(t\text{-}Bu) + C_7F_{14} \xrightarrow[4\ h]{65\ ^\circ C} (MeC_5H_4)_3UF + ... \qquad (17)$$

Since the incomplete conversion in the above reaction might have been a consequence of working with a heterogeneous system, it was desirable to investigate a homogeneous system. Perfluorocyclohexane, in contrast to most other saturated perfluorocarbons, is reasonably soluble in aromatic solvents.[36] When the reaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and perfluorocyclohexane was carried in toluene solution at room temperature for 12 h with a 5-fold excess of perfluorocyclohexane, a 1:1 mixture of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$ was obtained (eq 18).

$$(MeC_5H_4)_3U(t\text{-}Bu) + C_6F_{12} \xrightarrow[12\ h;\ RT]{toluene} (MeC_5H_4)_3UF + (MeC_5H_4)_3U(CH_2Ph) + ... \qquad (18)$$

Among the organic products undecafluorocyclohexane, isobutane and isobutene were detected by GC and GC-MS. The identity of $(MeC_5H_4)_3U(CH_2Ph)$ was confirmed by its independent synthesis from benzylpotassium and $(MeC_5H_4)_4U$ or $(MeC_5H_4)_3UCl$ (eq 19). Since the investigation described in Chapter 1 established that the thermal decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ in toluene solution does not lead to formation of $(MeC_5H_4)_3U(CH_2Ph)$ in the absence of perfluorocyclohexane, the fluorocarbon must be involved in the formation of the uranium benzyl species. These observations can be rationalized by a radical reaction sequence as outlined in Scheme 5.

$$(MeC_5H_4)_3UX + KCH_2Ph \longrightarrow (MeC_5H_4)_3U(CH_2Ph) \qquad (19)$$

$$X = MeC_5H_4, Cl$$

Scheme 5: Proposed Reaction Sequence for the Reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with C_6F_{12} in Toluene Solution

a) $(MeC_5H_4)_3U(t\text{-}Bu) + C_6F_{12} \longrightarrow (MeC_5H_4)_3UF + C_6F_{11}\cdot + t\text{-}Bu\cdot$

b) $C_6F_{11}\cdot + PhCH_3 \longrightarrow C_6F_{11}H + PhCH_2\cdot$

c) $(MeC_5H_4)_3U(t\text{-}Bu) + PhCH_2\cdot \longrightarrow (MeC_5H_4)_3U(CH_2Ph) + t\text{-}Bu\cdot$

The reaction of a $C_6F_{11}\bullet$ radical with toluene to yield $C_6F_{11}H$ and a benzyl radical has been documented.[37] The benzyl radical then attacks another molecule of $(MeC_5H_4)_3U$(t-Bu) to yield $(MeC_5H_4)_3U(CH_2Ph)$ and a t-butyl radical. To test this hypothesis, the reaction was carried out in toluene in the presence of a three-fold excess of 9,10-dihydroanthracene, a radical trap, and a five-fold excess of perfluorocyclohexane. After stirring for 12 h at room temperature, a 20:1 mixture of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$ was obtained and anthracene was detected by GC among the volatile organic products. Given this high trapping efficiency, it seems likely that the dihydroanthracene is trapping primarily the relatively stable benzyl radical rather than the reactive $C_6F_{11}\bullet$ radical. The conversion in these reactions is essentially quantitative based on uranium. If the reaction is carried out in *o*-xylene-d_{10} as a solvent, conversion to $(MeC_5H_4)_3UF$ is essentially quantitative. Apparently, the *o*-xylyl radical, that is presumably formed in this reaction, is too hindered to displace a t-butyl group from the uranium center at an appreciable rate.

The organometallic product $(MeC_5H_4)_3UF$ of the preceeding reactions of $(MeC_5H_4)_3U(t\text{-}Bu)$ with fluorocarbons is of interest as well. Indeed, the analogous Cp_3UF has been reported to possess peculiar physical properties.[29] Specifically, the temperature dependent ^1H-NMR spectrum of Cp_3UF in toluene or thf solution was claimed to not follow the Curie law. The resulting "S" shaped curves of the δ vs. 1/T plots were interpreted to be due to a temperature dependent equilibrium between a solvated monomer and a base-free dimer.

We therefore investigated the variable temperature ^1H-NMR spectra of $(MeC_5H_4)_3UF$ both in toluene-d_8 and in thf-d_8 solution. The resulting plots of δ vs. 1/T are shown in Figures 13 and 14. Within experimental error all three resonances for the methylcyclopentadienyl groups follow the Curie law in both solvents. Furthermore, both plots are virtually superimposable, indicating that no solvent effect on the ^1H-NMR spectra can be detected. This result suggests that either the earlier experimental results on Cp_3UF are in error (as might be inferred from the X-ray crystal structure, which has shown Cp_3UF to be monomeric in the solid state [30]) or the small change in substituent on the cyclopentadienyl ring modifies the behavior of the resulting metallocene.

Figure 13: Variable Temperature ^{1}H-NMR-Spectrum of $(MeC_5H_4)_3UF$ in toluene-d_8

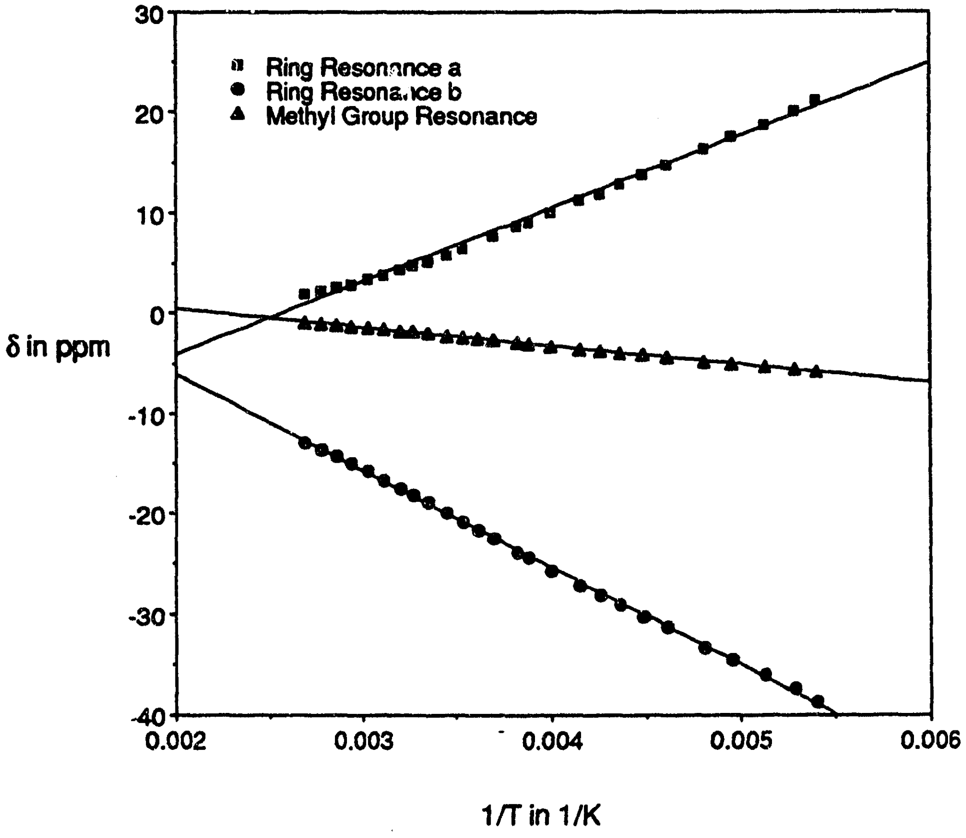
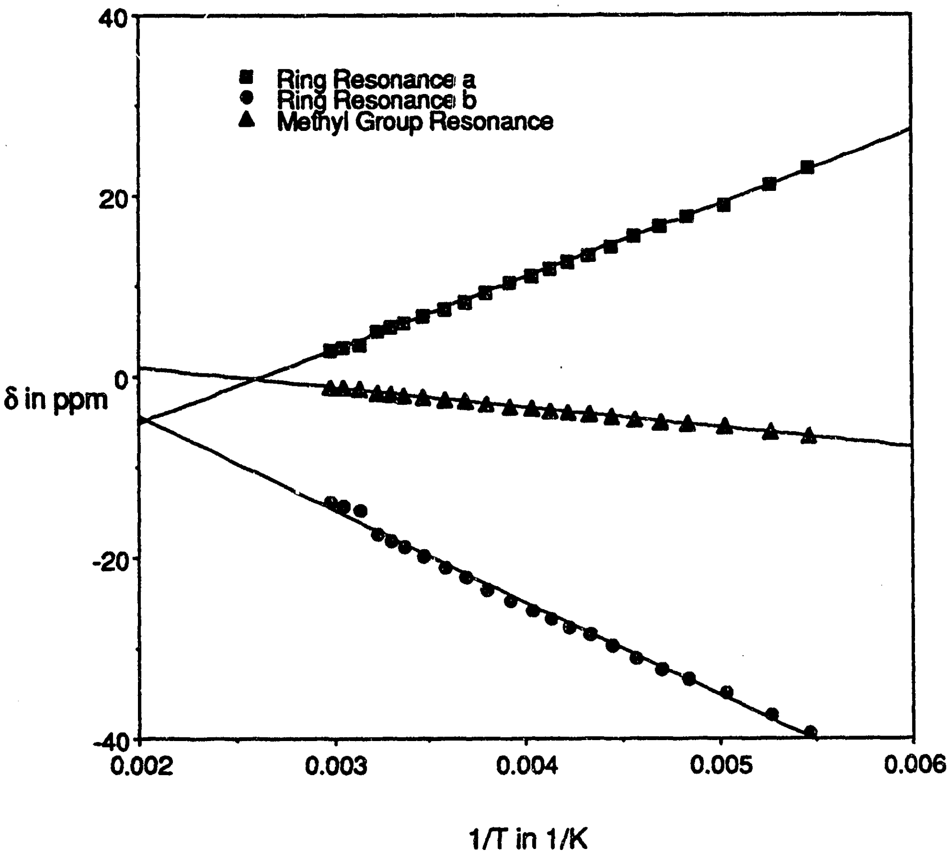


Figure 14: Variable Temperature ^{1}H-NMR-Spectrum of $(MeC_5H_4)_3UF$ in thf-d_8



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Chapter Three

Reactions of Tris(Cyclopentadienyl)Thorium Compounds with tertiary Butyllithium

The results obtained with $(MeC_5H_4)_3U(t\text{-}Bu)$ (see Chapters 1 and 2) encouraged us to attempt the preparation of the analogous thorium compound $(MeC_5H_4)_3Th(t\text{-}Bu)$. Since tetravalent thorium is much more difficult to reduce to trivalent thorium than is uranium,[1] it is expected that major differences in the reactivity between these two compounds would be observed. Ligand-assisted thorium-carbon bond homolysis, compared to the uranium system, should be less favorable than in the uranium case, and it is likely that insertions into the thorium-tertiary alkyl bond with unsaturated substrates would be observed, rather than reduction. The thorium-carbon bond would also be expected to be somewhat more stable than the uranium analogue, as thorium-carbon bond strengths are generally ca. 5 kcal/mol higher than the analogous uranium-carbon bond strengths.[2] In addition, tetravalent thorium is somewhat bigger than tetravalent uranium,[3] and the increased ionic radius of tetravalent thorium vs. uranium would tend to reduce steric congestion around the metal center in sterically crowded thorium compounds relative to the uranium analogues. While all these factors are interrelated, they certainly give credence to the prediction that tris(cyclopentadienyl)thorium tertiary alkyl compounds will be more stable than the analogous uranium compounds.

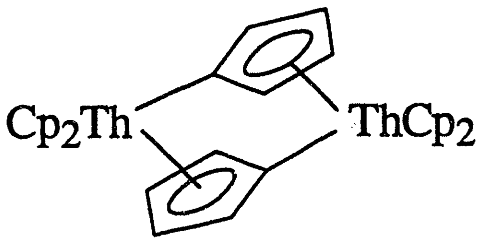
The first compounds containing thorium-alkyl σ-bonds were reported in 1976 by Marks.[4] A number of Cp_3ThR compounds were obtained according to eq 1.

$$\mathrm{Cp_3ThCl} \xrightarrow[\mathrm{RMgX}]{\mathrm{RLi\ or}} \mathrm{Cp_3ThR} \qquad (1)$$

R = allyl; i-Pr; 2-*cis*-2-butenyl; 2-*trans*-2-butenyl; n-Bu; neopentyl

The authors report that in general reaction conditions are somewhat more critical than in the analogous uranium series. Considerable reduction to thorium metal supposedly competes with alkylation. The authors also mention that it was not possible to synthesize either the phenyl or t-butyl derivative in a pure state. No additional details on these two compounds were given. The thermal decomposition of the isolable Cp_3ThR compounds was reported to yield predominantly the alkane RH. The organometallic product of the thermal decomposition, $[Cp_2Th(C_5H_4)]_2$, exhibits a double η^1:η^5-C_5H_4-bridge (Figure 1) as shown by X-ray crystallography.[5] Based on labeling experiments, the thermolysis was proposed to occur via intramolecular, stereospecific hydrogen abstraction from the cyclopentadienyl ligand.

Figure 1: Thermal Decomposition Product of $Cp_3Th(n\text{-}Bu)$



A later paper reported an investigation of the photochemistry of Cp_3ThR compounds.[6] The authors noted that, while the thermal stability of these compounds is quite high, photochemical decomposition induced by UV irradiation proceeds quite easily. The predominant decomposition pathway seems to be photochemically induced β-hydrogen elimination (eq 2).

$$2\ Cp_3Th(CHRCH_2R') \xrightarrow{h\nu} 2\ Cp_3Th + RCH_2CH_2R' + RCH{=}CHR' \qquad (2)$$

The organometallic product, Cp_3Th, was described as a dark-green paramagnetic extremely air-sensitive and insoluble compound. While the characterization of Cp_3Th was incomplete, the reported reactivity is certainly consistent with this formulation. In contrast to the alkyl derivatives containing β-hydrogens, irradiation of Cp_3ThMe resulted in significantly slower decomposition. The identified products were Cp_4Th and methane. Thus it appears that under photochemical conditions β-hydrogen elimination (where it is possible) becomes the favored decomposition pathway for Cp_3ThR compounds.

3.1 Tris(Methylcyclopentadienyl)Thorium Compounds

Our initial strategy for synthesizing $(MeC_5H_4)_3Th(t\text{-}Bu)$ was to follow a procedure analogous to the successful methods used in uranium chemistry. This would involve a metathesis reaction of $(MeC_5H_4)_3ThCl$ with t-BuLi. The first problem was encountered in the preparation of $(MeC_5H_4)_3ThCl$. While tris(methylcyclopentadienyl)-thorium chloride can indeed be prepared analogously to the corresponding uranium compound according to eq 3, the yield is low. Furthermore, the product is contaminated by an impurity that is difficult to remove by crystallization. This impurity was later identified as $(MeC_5H_4)_4Th$.

$$ThCl_4 + 3\ Na(MeC_5H_4) \xrightarrow{thf} (MeC_5H_4)_3ThCl + 3\ NaCl \qquad (3)$$

The analogous reaction with uranium proceeds easily to yield $(MeC_5H_4)_3UCl$ in high yield. No problems with contamination by $(MeC_5H_4)_4U$ are encountered. This difference must reside in the properties of the actinide tetrahalides. Whereas UCl_4 is soluble in thf,

$ThCl_4$ is not. Hence, the surface of the insoluble $ThCl_4$ can become covered with sodium chloride as the reaction proceeds. This would tend to shut down the reaction by effectively removing the additional $ThCl_4$ from the reaction. The excess of sodium methylcyclopentadienyl now present in solution will react with $(MeC_5H_4)_3ThCl$ to yield $(MeC_5H_4)_4Th$. To test this hypothesis, the reaction was carried out in the presence of a large amount of crushed glass. By stirring the reaction mixture vigorously, it was hoped that the glass pieces would polish the surface of the thorium tetrachloride. This method did result in a marginal increase of the yield, but it was clear that a new approach was needed to synthesize $(MeC_5H_4)_3ThCl$ efficiently.

Since the insolubility of thorium tetrachloride was perceived to be the main problem, a soluble source of thorium tetrachloride was desirable. The known complex, $ThCl_4(tmeda)_2$, is soluble in aromatic hydrocarbons.[7] It is easily prepared in high yield by stirring thorium tetrachloride in toluene in the presence of an excess of tmeda (N,N,N',N'-tetramethylethylenediamine) as outlined in eq 4.

$$ThCl_4 + \text{excess tmeda} \xrightarrow{\text{toluene}} ThCl_4(tmeda)_2 \qquad (4)$$

This material reacts cleanly with sodium methylcyclopentadienyl in thf solution to give $(MeC_5H_4)_3ThCl$ in high yield (eq 5). More importantly, because the product is no longer contaminated with $(MeC_5H_4)_4Th$ no tedious separation is required in the workup.

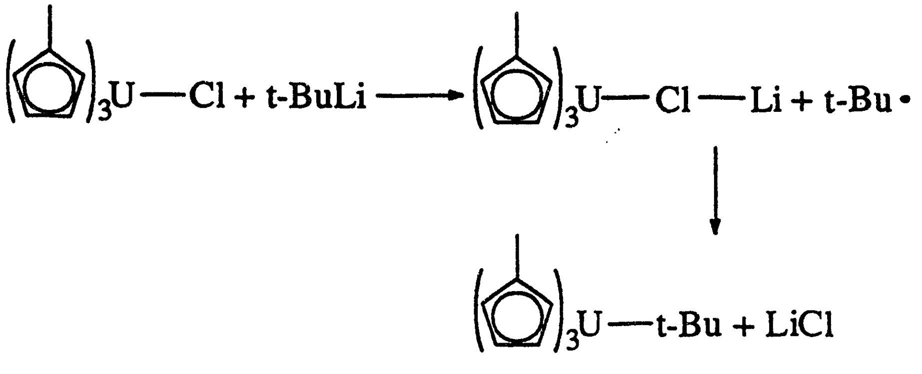
$$ThCl_4(tmeda)_2 + 3\ Na(MeC_5H_4) \longrightarrow (MeC_5H_4)_3ThCl \qquad (5)$$

The next step was to react $(MeC_5H_4)_3ThCl$ with t-BuLi. Surprisingly, no reaction is observed upon addition of one equiv of t-BuLi to a toluene solution of $(MeC_5H_4)_3ThCl$. Over short periods of time (ca. 1 h), only unreacted starting material was recovered. When the reaction mixture was stirred at room temperature for ca. 24 h, slow formation of a white precipitate was observed. However, upon workup, only starting material was recovered in ca. 35% isolated yield. Presumably, the white precipitate observed is due to reaction of t-BuLi with toluene and/or the cyclopentadienyl rings, resulting in intractable materials. In marked contrast, a toluene solution of $(MeC_5H_4)_3ThCl$ reacted instantaneously with MeLi to give $(MeC_5H_4)_3ThMe$ in good yield (eq 6).

$$(MeC_5H_4)_3ThCl + MeLi \longrightarrow (MeC_5H_4)_3ThMe + LiCl \qquad (6)$$

This difference in reactivity between uranium and thorium on the one hand and methyllithium and t-butyllithium on the other is quite striking. The causes are hard to rationalize. The thorium-chlorine bond is expected to be somewhat stronger than the uranium-chlorine bond and the metal-methyl bond can be expected to be stronger than the metal-t-butyl bond.[8] So, overall, the reaction of $(MeC_5H_4)_3ThCl$ with t-BuLi is the least favored reaction thermodynamically. However, this is likely not to be of crucial importance, since these reactions presumably are driven by the formation of insoluble and highly stable lithium chloride.[9] Hence, the lack of an observed metathesis reaction between $(MeC_5H_4)_3ThCl$ and t-BuLi is probably due to a transition state that is energetically inaccessible, i.e. the reaction is kinetically unfavorable. However, the transition state for the reaction of $(MeC_5H_4)_3ThCl$ with t-BuLi is likely to be less sterically crowded than for the analogous reaction of $(MeC_5H_4)_3UCl$ with t-BuLi, because of the somewhat bigger ionic radius of tetravalent thorium vs. uranium. One might then speculate that the difference is electronic in nature. The reaction in the uranium system can be initiated by single-electron transfer from t-BuLi to $(MeC_5H_4)_3UCl$. Subsequent or simultaneous chlorine abstraction from the trivalent uranium species by the lithium cation and trapping of the $(MeC_5H_4)_3U$ fragment by the t-butyl radical would lead to the observed reaction (Scheme 1). Clearly, single-electron transfer from t-BuLi to $(MeC_5H_4)_3ThCl$ would be much more unfavorable, given the Th(IV)/Th(III) reduction potential. Circumstantial evidence for such a mechanism operating in the uranium system comes from the observation that t-BuLi does react with tetravalent uranium compounds to yield trivalent uranium species. Although it has generally been postulated that these reactions proceed via an intermediate tetravalent uranium-t-butyl compound, followed by uranium-carbon bond homolysis, no such intermediate has ever been observed (see Chapter 1, Section 1.3). The reactions of $(MeC_5H_4)_3AnCl$ with MeLi on the other hand are likely to proceed by a metathesis pathway. Methyl radical is significantly more unstable than t-butyl radical and thus more unlikely to participate in a single-electron transfer process. Furthermore, the transition state for a metathesis reaction with methyllithium vs. t-butyllithium is likely to be less sterically crowded. With the presently available information, however, this mechanism (Scheme 1) can at best be considered a working hypothesis.

Scheme 1: Reaction of t-BuLi with $(MeC_5H_4)_3UCl$, Proposed Single-Electron Transfer Mechanism



In order to successfully prepare $(MeC_5H_4)_3Th(t\text{-}Bu)$, we reasoned that we needed a better leaving group than chloride on the tris(methylcyclopentadienyl)thorium fragment. We therefore prepared $(MeC_5H_4)_3ThI$ by reaction of $(MeC_5H_4)_3ThCl$ with trimethylsilyliodide (eq 7).

$$(MeC_5H_4)_3ThCl + Me_3SiI \longrightarrow (MeC_5H_4)_3ThI \qquad (7)$$

When a toluene solution of $(MeC_5H_4)_3ThI$ was treated with t-BuLi, again no reaction was observed over short periods of time. As previously observed, over longer periods of time, only starting material was recovered, although intractable materials had formed, presumably by reaction of t-BuLi with toluene and/or the methylcyclopentadienyl rings. As in the chloride case, $(MeC_5H_4)_3ThI$ reacted instantaneously with MeLi to give $(MeC_5H_4)_3ThMe$ (eq 8). In order to eliminate at least the possibility that t-BuLi reacts with the solvent toluene, we sought a hexane soluble starting material that would be capable of undergoing the desired substitution reaction.

$$(MeC_5H_4)_3ThI + MeLi \longrightarrow (MeC_5H_4)_3ThMe \qquad (8)$$

Because $(MeC_5H_4)_4U$ reacts with t-butyllithium to give $(MeC_5H_4)_3U(t\text{-}Bu)$ and the former is also moderately soluble in hexane, $(MeC_5H_4)_4Th$ was investigated. This compound is easily prepared in high yield by reaction of $ThCl_4(tmeda)_2$ with 4 equiv of sodium methylcyclopentadienyl in thf solution (eq 9). Like its uranium analogue, $(MeC_5H_4)_4Th$ is moderately soluble in hexane. However, when a hexane or benzene solution of $(MeC_5H_4)_4Th$ was treated with t-BuLi, no reaction was observed over several hours. Some intractable material was formed over a longer time, presumably by

$$ThCl_4(tmeda)_2 + 4\ Na(MeC_5H_4) \xrightarrow{thf} (MeC_5H_4)_4Th \qquad (9)$$

reaction of t-BuLi with the methylcyclopentadienyl rings, and only $(MeC_5H_4)_4Th$ was recovered from the reaction mixture in lower yield. Again, $(MeC_5H_4)_4Th$ reacted instantaneously with MeLi to give $(MeC_5H_4)_3ThMe$ in high yield (eq 10). This reaction is of equal convenience as the reaction of $(MeC_5H_4)_3ThCl$ with MeLi for the preparation of $(MeC_5H_4)_3ThMe$.

$$(MeC_5H_4)_4Th + MeLi \longrightarrow (MeC_5H_4)_3ThMe + Li(MeC_5H_4) \qquad (10)$$

We also attempted the reaction of $(MeC_5H_4)_3ThMe$ with t-BuLi in hexane solution. Since $(MeC_5H_4)_3ThMe$ is moderately soluble in hexane and methyllithium is insoluble, we hoped to exchange alkyl groups with the precipitation of insoluble methyllithium being the driving force. However, no immediate reaction occurred and only $(MeC_5H_4)_3ThMe$ (60%) was recovered from the reaction mixture over 24 h. We conclude that alkyl group metathesis does not appear to be a viable synthetic approach. This is confirmed by the analogous reaction of $(MeC_5H_4)_3UMe$ with t-BuLi in hexane, which also does not result in formation of $(MeC_5H_4)_3U(t\text{-}Bu)$.

We then undertook the preparation of tris(methylcyclopentadienyl)thorium aryloxides, because these compounds are expected to display reasonable solubility in saturated hydrocarbons. We hoped that the pronounced insolubility of lithium aryloxides in saturated hydrocarbons would provide the necessary driving force for the reaction of $(MeC_5H_4)_3Th(OAr)$ with t-BuLi. Ideally, a bulky aryloxide will result in a relatively weak thorium-aryloxide bond, favoring the metathesis reaction with t-butyllithium. A toluene solution of $(MeC_5H_4)_4Th$ did not react with 2,6-di-t-butyl-4-methylphenol over 17 h at room temperature. Apparently, the chosen phenol was too bulky to substitute a methylcyclopentadienyl group on thorium. Scaling back our ambitions, we investigated 2,6-dimethylphenol next. A toluene solution of $(MeC_5H_4)_4Th$ was stirred at room temperature in the presence of 2,6-dimethylphenol for 36 h. After workup, the presence of a new compound as well as unreacted $(MeC_5H_4)_4Th$ was detected by ^1H-NMR spectroscopy. Presumably, 2,6-dimethylphenol is so bulky as to just barely be able to substitute a methylcyclopentadienyl group on thorium by protonation because of a sterically crowded transition state. When the reaction of $(MeC_5H_4)_4Th$ with 2,6-dimethylphenol was carried out at 70 °C for 48 h, the desired $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ was obtained in high yield (eq 11). The compound is indeed quite soluble in hexane. However, when t-butyllithium was added to a hexane solution of $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$, no immediate reaction was observed. After stirring at room temperature for 24 h, the only organometallic product recovered from the reaction mixture was $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ in 53% yield. Hence, once again a thorium-tertiary alkyl bond proved elusive.

(11)

Another attempt at reaction of t-butyllithium with $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ was made. After one equiv of t-BuLi and $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ were mixed in toluene solution, one equiv of tmeda was added to the reaction mixture. Because t-butyllithium exists as a tetramer in saturated hydrocarbon solution,[10] it was hoped that tmeda would break up the aggregates and thus provide a source of "more reactive" t-butyllithium. Upon addition of tmeda to the reaction mixture an immediate reaction indeed occurred. After workup, however, only $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ was recovered from the reaction. Thus, it appears that the presence of tmeda only resulted in an accelerated reaction of t-butyllithium with the methylcyclopentadienyl rings.

Sulfonates are good leaving groups. We attempted to prepare the *p*-toluenesulfonate of tris(methylcyclopentadienyl)thorium by reaction of *p*-toluenesulfonic acid with $(MeC_5H_4)_3ThMe$, hoping to eliminate methane. Although this approach does work, it seems that protonation of the methylcyclopentadienyl ligand is competitive with protonation of the methyl group, resulting in a low yield of the sulfonate. A better preparation of $(MeC_5H_4)_3Th(OTs)$ was achieved by reaction of *p*-toluenesulfonic acid with $(MeC_5H_4)_4Th$ in toluene solution (eq 12). Since now the methylcyclopentadienyl ligand is the only candidate for protonation, no competing side reactions are possible and the desired product is obtained in high yield.

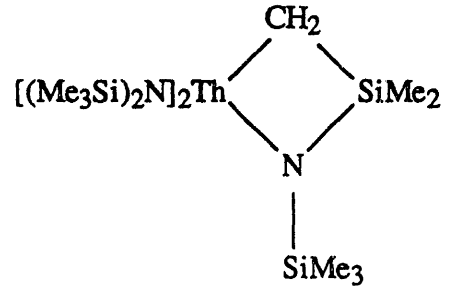
$$(MeC_5H_4)_4Th + HOTs \longrightarrow (MeC_5H_4)_3Th(OTs) + MeC_5H_5 \qquad (12)$$

As would be expected, $(MeC_5H_4)_3Th(OTs)$ reacts instantaneously with methyllithium to give $(MeC_5H_4)_3ThMe$ (eq 13).

$$(MeC_5H_4)_3Th(OTs) + MeLi \longrightarrow (MeC_5H_4)_3ThMe \qquad (13)$$

When t-butyllithium was added to a toluene solution of $(MeC_5H_4)_3Th(OTs)$ an immediate reaction occurred. From this reaction a small amount of white powder was isolated. The material is fairly insoluble in aromatic hydrocarbons and thus only a marginal ^1H-NMR spectrum of it could be obtained. The spectrum displayed only one set of resonances corresponding to a methylcyclopentadienyl ligand (5.94 AA'BB', 2H; 5.80 AA'BB', 2H and 2.26 s, 3H). No resonance attributable to a t-butyl group was observed. Furthermore, when the solid material was left exposed to ambient light for a prolonged period of time, it slowly turns dark-green. No such change took place when the material is protected from light. The solubility behavior and the ^1H-NMR spectrum are inconsistent with the formulation of a $(MeC_5H_4)_3Th(t\text{-}Bu)$ compound. Rather, the behavior is reminiscent of the green Cp_3Th compound, reported by Marks as the product of the photodecomposition of Cp_3ThR compounds.[6,11] While the trivalent thorium compound was incompletely characterized, it was reported to react with hydrogen to yield Cp_3ThH. This uncharacterized hydride species was reported to be poorly soluble and to revert back to green Cp_3Th upon photolysis or prolonged exposure to room light. The low solubility of the reaction product of $(MeC_5H_4)_3Th(OTs)$ with t-BuLi allows for the possibility of missing a hydride resonance in the ^{1}H-NMR spectrum. Since actinide-hydride infrared stretching frequencies do not fall in a characteristic region, characterization of the white material is difficult. The green material obtained after prolonged exposure of the white material to light did not give an EPR-signal as a powder sample at 4K. Given that the former investigators of the apparently related compounds Cp_3Th and Cp_3ThH never reported a more complete characterization of their materials, the subject was not pursued further. Finally, it should be noted that the isolated and well-characterized thorium hydride $[(Me_3Si)_2N]_3ThH$ does not display any marked photosensitivity.[12] Under thermal conditions, it decomposes to the tetravalent thorium metallacycle shown in Figure 2.[13] The dimeric compound $(Cp^*{}_2ThH_2)_2$ also does not seem to be photochemically labile.[14]

Figure 2: Thorium(IV) Metallacycle obtained by Thermolysis of $[(Me_3Si)_2N]_3ThH$



The ultimate leaving group is no leaving group at all, just an open coordination site. The best approximation to this situation is represented by the known cationic species $[(MeC_5H_4)_3Th][BPh_4]$. The preparation of this thorium cation with a non-coordinating anion is straightforward, using a trialkylammonium salt to eliminate methane from $(MeC_5H_4)_3ThMe$.[15] When trimethylammonium tetraphenylborate is used, the resulting trimethylamine coordinates to the thorium cation (eq 14). The trialkylammonium salt does not react with $(MeC_5H_4)_4Th$, no reaction is observed. Unfortunately, these cationic species are insoluble in hydrocarbon solvents. However, we reacted $[(MeC_5H_4)_3Th(NMe_3)][BPh_4]$ as a suspension in hexane with one equiv of t-butyllithium. Since the reaction was done as a suspension, we were unable to ascertain whether an immediate reaction occurred or not. After stirring at room temperature for 18 h, the only product that could be isolated from the reaction mixture was $(MeC_5H_4)_4Th$ in low yield. Thus, t-BuLi caused cyclopentadienyl ligand redistribution.

$$(MeC_5H_4)_3ThMe + (Me_3NH)(BPh_4) \longrightarrow [(MeC_5H_4)_3Th(NMe_3)][BPh_4] \qquad (14)$$

Not willing to stop yet, we adopted a different strategy. Instead of first attaching the cyclopentadienyl ligands to the thorium center, we decided to first form a thorium-tertiary butyl bond and then to create the thorium-cyclopentadienyl bonds. We therefore treated $ThCl_4(tmeda)_2$, a soluble source of $ThCl_4$, at -78 °C with one equiv of t-BuLi in toluene solution for 6 h. Then, 3 equiv of $Na(MeC_5H_4)_3$ were added at -78 °C as a solution in thf. After workup, the isolated product was identified as $(MeC_5H_4)_3Th(CH_2Ph)$. Apparently, some tmeda, liberated from the thorium starting material, activated the t-butyllithium. This resulted in rapid formation of benzyllithium, which then reacted with the thorium compound to yield the final product.

3.2 Tris(Trimethylsilylcyclopentadienyl)- and Tris(t-Butylcyclopentadienyl)Thorium Compounds

In order to pursue the reactions of tris(cyclopentadienyl)thorium cations with t-butyllithium, we turned our attention to the bulkier trimethylsilyl- and t-butylcyclopentadienyl systems. The base-free cation $[(Me_3SiC_5H_4)_3Th][BPh_4]$ is reported to be soluble in aromatic hydrocarbons. [15] Thus it would be an ideal substrate for investigation of its reactivity with t-BuLi. Even though the bulkier substituents on the cyclopentadienyl ligands would destabilize a hypothetical $(RC_5H_4)_3Th(t\text{-}Bu)$ compound, only an extremely weak interaction between the $(RC_5H_4)_3Th$ moiety and the tetraphenylborate anion would have to be broken.

Addition of an alkali metal salt of the appropriate cyclopentadienyl ligand to $ThCl_4$ in thf results in the formation of $(RC_5H_4)_3ThCl$ in moderate yield (eq 15). Attempts to increase the yield of these reactions by starting with $ThCl_4(tmeda)_2$, a soluble source of $ThCl_4$, rather than $ThCl_4$ were unsuccessful in the trimethylsilyl- and t-butylcyclopentadienyl systems. This contrast to the methylcyclopentadienyl system can be rationalized by postulating that the presence of tmeda in the reaction mixture results in stabilization of a species with two cyclopentadienyl rings coordinated to thorium, relative to a tris(cyclopentadienyl)thorium species. Even for R = H or Me, the compounds $(RC_5H_4)_2ThCl_2(dmpe)$ can be isolated (dmpe = 1,2-bis(dimethylphosphino)ethane).[16]

$$ThCl_4 + 3\ M(RC_5H_4) \xrightarrow{thf} (RC_5H_4)_3ThCl \qquad (15)$$

$R = SiMe_3$, t-Bu   M = Na, K

These $(RC_5H_4)_3ThCl$ compounds can then be treated with MeLi to yield the corresponding methyl compounds (eq 16).

$$(RC_5H_4)_3ThCl + MeLi \longrightarrow (RC_5H_4)_3ThMe \qquad (16)$$

$$R = SiMe_3, \text{t-Bu}$$

Unfortunately, $(Me_3SiC_5H_4)_3ThMe$ seems to be a liquid at room temperature and is thus difficult to handle and purify. To avoid this problem, we attempted to prepare the analogous $(Me_3SiC_5H_4)_3Th(CH_2Ph)$ compound, hoping that it would be a solid. Reaction of $(Me_3SiC_5H_4)_3ThCl$ with benzylpotassium does lead to formation of the desired $(Me_3SiC_5H_4)_3Th(CH_2Ph)$ (eq 17). However, because this compound is a waxy solid that is even more difficult to handle than $(Me_3SiC_5H_4)_3ThMe$, further characterization of the benzyl compound was not pursued.

$$(Me_3SiC_5H_4)_3ThCl + KCH_2Ph \longrightarrow (Me_3SiC_5H_4)_3Th(CH_2Ph) \qquad (17)$$

We now had a series of $(RC_5H_4)_3ThMe$ compounds with R = Me, Me_3Si, t-Bu in hand. It was of interest to determine what, if any, influence the change in substituent on the cyclopentadienyl group would have on the properties of the metal-alkyl bond. We recorded the ^{13}C-NMR spectra of these compounds in order to see if any trends would emerge as a function of the cyclopentadienyl substituent. The results are summarized in Table 3.1. As can be seen, no dramatic effects on the chemical shifts or the carbon-hydrogen coupling constant of the methyl group are apparent. The ^{1}H-NMR chemical shift for the thorium-bound methyl group seems to shift downfield with increasing bulk of the cyclopentadienyl substituent. The ^{13}C-NMR chemical shift for the thorium-bound methyl group on the other hand seems to shift downfield with increasing electron-donor ability of the substituent on the cyclopentadienyl ring. The C-H coupling stays constant, indicating no change in s-character in the bonding. The small magnitude of these effects does not allow any definite conclusions.

Table 3.1: NMR-Spectroscopic Properties of the Thorium-Bound Methyl Group in $(RC_5H_4)_3ThMe$

$(RC_5H_4)_3ThMe$	^1H δ(Me) ppm	^{13}C δ(Me) ppm	$^1J_{C\text{-}H}$(Me) Hz
R = Me	0.57	42.5	114
R = Me_3Si	0.74	37.3	115
R = t-Bu	0.85	42.2	114

An interesting feature of the ^{13}C-NMR spectrum of $(t\text{-}BuC_5H_4)_3ThMe$ is illustrated in Figure 3 and in more detail in Figure 4. In addition to the large one-bond C-H coupling, the t-butyl group of t-butylcyclopentadienyl in $(t\text{-}BuC_5H_4)_3ThMe$, observed at $\delta = 32.3$, also shows a smaller coupling to a set of either four or six equivalent hydrogens. The coupling to four hydrogens can be rationalized by virtual coupling to the four ring protons on the cyclopentadienyl ligand. Coupling to six equivalent hydrogens can be rationalized by coupling of one methyl carbon on the t-butyl substituent to the six protons on the other two methyl groups of the t-butyl substituents. No attempts were made to distinguish between those possibilities. It should be noted, however, that the ^{13}C Me_3Si-group resonance in $(Me_3SiC_5H_4)_3ThMe$ does not show any long range coupling.

The next step towards preparation of the desired $[(RC_5H_4)_3Th][BPh_4]$ cations then was to react the alkyl compounds $(RC_5H_4)_3ThMe$ with a trialkylammonium tetra-

Figure 3: ^{13}C-NMR Spectrum of (t-BuC$_5$H$_4$)$_3$ThMe

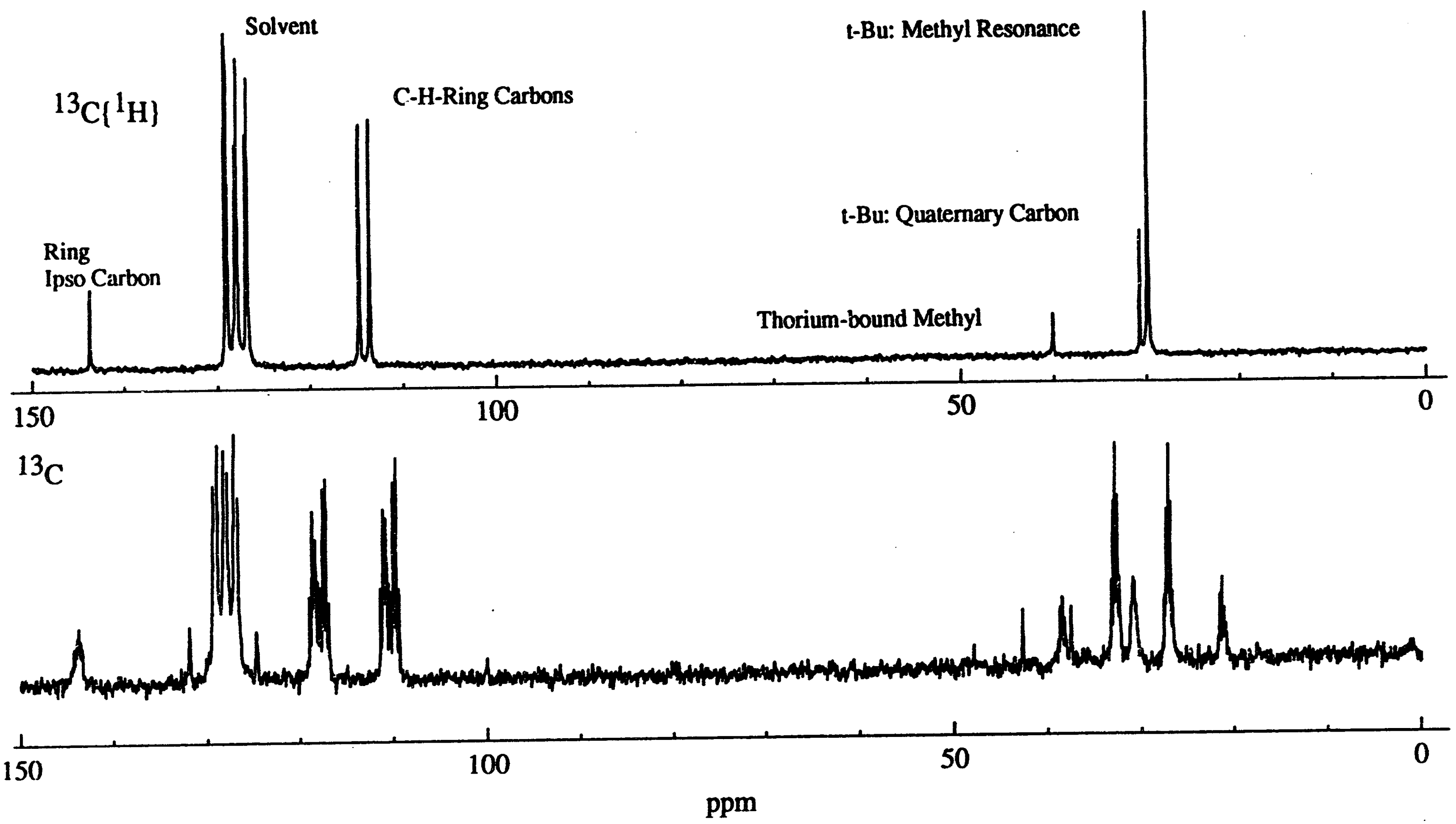
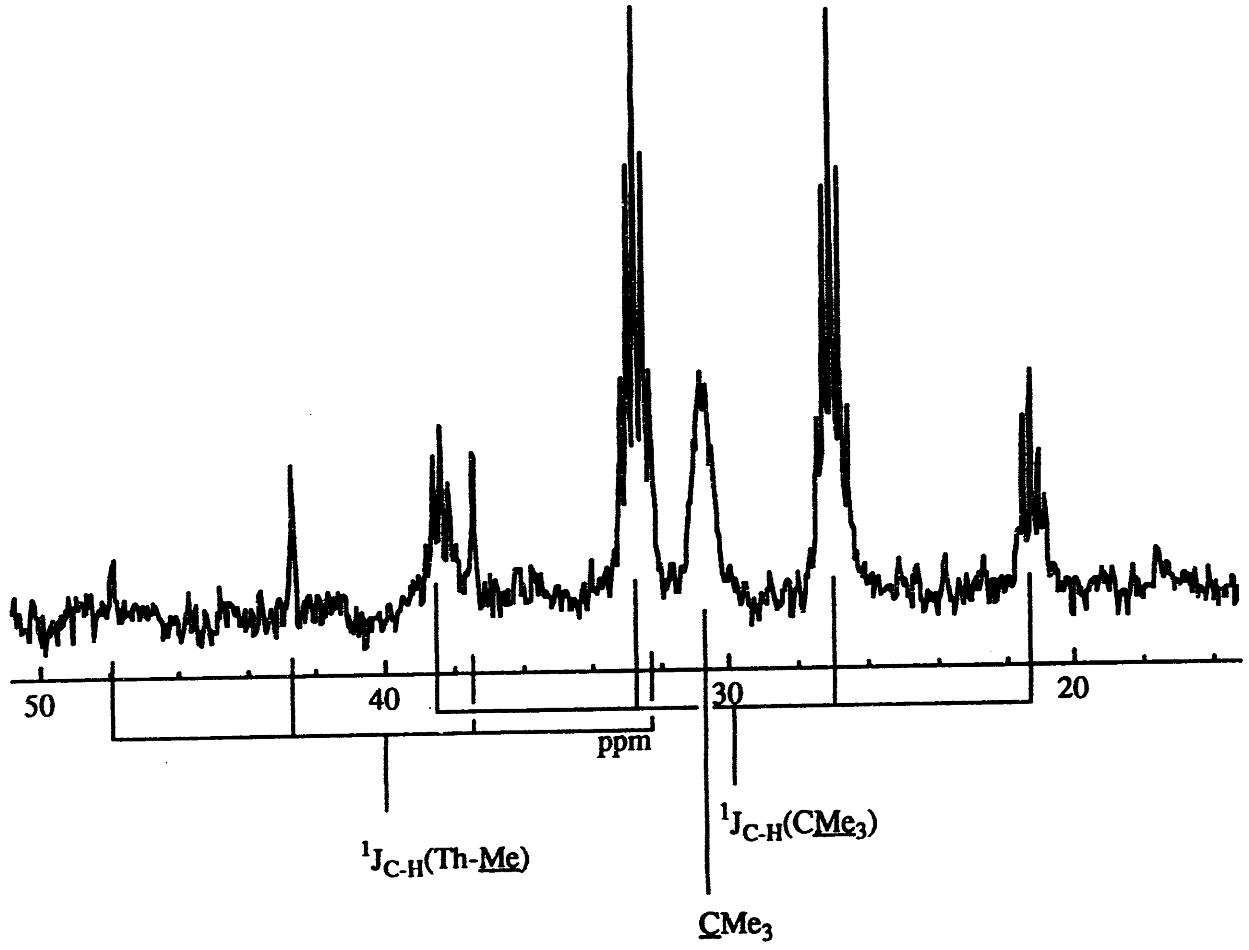


Figure 4: ^{13}C-NMR Spectrum of (t-BuC$_5$H$_4$)$_3$ThMe: t-Butyl Region



phenylborate salt (eq 18). The cationic species obtained showed marginal solubility in aromatic hydrocarbons.

$$(RC_5H_4)_3ThMe + (R'_3NH)(BPh_4) \longrightarrow [(RC_5H_4)_3Th][BPh_4] \qquad (18)$$

$R = SiMe_3$, t-Bu ; R' = Me, Et, n-Bu

Since for $R = SiMe_3$ and t-Bu both $(RC_5H_4)_3ThCl$ species are quite soluble in hexane, their reactivity towards t-BuLi in hexane solution was investigated. Again, no immediate reaction was observed when one equiv of t-butyllithium was added to hexane solutions of $(RC_5H_4)_3ThCl$. After ca. 1 h the formation of a precipitate was observed. The mixtures were allowed to react for ca. 30 h, filtered and then the solvent was removed under reduced pressure. The resulting solid was investigated by ^{1}H-NMR spectroscopy. In both cases two compounds were present, $(RC_5H_4)_3ThCl$ and a new compound. The new compounds displayed a pattern corresponding to one type of RC_5H_4-ligand and an additional distinctive resonance at 12.81 ppm ($R = SiMe_3$) and 13.98 ppm (R = t-Bu), respectively. These distinctive resonances, indicative of metal hydrides, integrated as one proton relative to 3 RC_5H_4-rings in each case. These compounds were assigned the formula $(RC_5H_4)_3ThH$. Their identity was later confirmed (vide infra). For the trimethylsilylcyclopentadienyl system, the ratio of $(RC_5H_4)_3ThCl$ to $(RC_5H_4)_3ThH$ obtained was about 1:1. In the t-butylcyclopentadienyl system, the ratio was about 2:1. When these reactions were carried out in an NMR-tube in benzene-d_6 solution and monitored by ^{1}H-NMR spectroscopy, integration showed that all the thorium containing material was not conserved. In both cases, the thorium-bound hydride was a hydride, not a deuteride. Within the accuracy of the integration, no deuterium incorporation in the hydride position was detected. The organic products of the reactions are isobutene and isobutane. No substantial deuterium incorporation into the isobutane was detected. Hence, we conclude that the isobutane is formed by deprotonation of the cyclopentadienyl ligand or the tetraphenylborate counterion by t-butyllithium. Such a species would be expected to be fairly reactive and lead to subsequent reactions with the starting $(RC_5H_4)_3ThCl$ compounds. This explains the loss of thorium-containing material observed during the reactions. The amount of isobutene is equivalent to the amount of $(RC_5H_4)_3ThH$ formed. It is therefore tempting to assign the formation of $(RC_5H_4)_3ThH$ to rapid β-hydrogen elimination from an intermediate $(RC_5H_4)_3Th(t\text{-}Bu)$ species. The analogous zirconium compound, $(Me_3SiC_5H_4)_3ZrCl$, reacts rapidly with t-BuLi to give $(Me_3SiC_5H_4)_3ZrH$ in good yield.[17]

Reaction of the cationic species $[(RC_5H_4)_3Th][BPh_4]$ with t-BuLi in toluene or hexane solution resulted in clean formation of $(RC_5H_4)_3ThH$ in good yield (eq 19).

$$[(RC_5H_4)_3Th][BPh_4] + t\text{-}BuLi \longrightarrow (RC_5H_4)_3ThH \qquad (19)$$

$$R = SiMe_3,\ t\text{-}Bu$$

The infrared spectra of the resulting $(RC_5H_4)_3ThH$ species did not allow unambiguous assignment of the metal-hydride stretching frequencies. Presumably, the metal-hydride stretching frequencies appear at such low frequency that they are not in a distinctive region of the infrared spectrum. In accord with this hypothesis, the infrared stretching frequencies of the analoguous uranium compounds have been assigned by preparation of the corresponding deuterides $(RC_5H_4)_3UD$. The reported values for υ(U-H) are 1395 and 1410 cm^{-1} for $(Me_3SiC_5H_4)_3UH$ and $(t\text{-}BuC_5H_4)_3UH$, respectively.[18] $(Me_3SiC_5H_4)_3ThH$ could also be prepared from $(Me_3SiC_5H_4)_3ThCl$ with 1 equiv of lithium triethylborohydride. However, the attempted hydrogenation of $(t\text{-}BuC_5H_4)_3ThMe$ gave no reaction over ca. 8 h at 220 psi of hydrogen.

While we have not established that these hydrides are formed by β-hydrogen elimination from an intermediate $(RC_5H_4)_3Th(t\text{-}Bu)$ species, this is nevertheless the most straightforward explanation. The analogous uranium-tertiary alkyl compounds apparently decompose by uranium-carbon bond homolysis (see Chapter 1). This pathway would not be available to the thorium compounds on the grounds of a prohibitive Th(IV)/Th(III) reduction potential. Because for $(Me_3SiC_5H_4)_3UCl$ and $(t\text{-}BuC_5H_4)_3UCl$ some degree of hydride formation, presumably by β-hydrogen elimination, competes with reduction to trivalent uranium it is not unreasonable to postulate that in thorium β-hydrogen elimination becomes the dominant decomposition pathway for an intermediate $(RC_5H_4)_3Th(t\text{-}Bu)$ species.

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8. For corresponding Th/U pairs, D(Th-R)-D(U-R) ≈ 10 kcal/mol, from ref. 2.
9. This point is questionable, since the difference in the Cl_3Th-Cl vs. Cl_3U-Cl bond strengths may be as large 33 kcal/mol, based on gas phase ΔH_f° values for $AnCl_4$ and $AnCl_3$ from ref. 1. It is difficult to predict, however, what effect a change in ancillary ligands will have on these relative bond strengths.
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Chapter Four

Homoleptic Cyclopentadienyl Compounds of Tetravalent Uranium

The tetrakis(cyclopentadienyl)actinides, UCp_4 and $ThCp_4$, were first prepared by Fischer in 1962.[1] The protactinium and neptunium compounds have been prepared as well.[2] The X-ray crystal structure of UCp_4 was reported by Burns in 1974.[3] It confirmed the nearly tetrahedral arrangement of four pentahapto-cyclopentadienyl ligands around the metal center, resulting in a molecule with idealized S_4-symmetry. The average U-C distance is somewhat longer than typically observed in other tetravalent uranium-cyclopentadienyl complexes and apparently reflects the pronounced crowding of the ligands about the metal center. The high symmetry has attracted the interest of spectroscopists, and the optical spectrum,[4] the photoelectron spectrum [5] as well as the magnetic properties [6] have been analyzed in detail. Because the NMR dipolar shift should be zero in a complex of cubic symmetry,[7] the room temperature proton signal at δ = -13.1 in UCp_4 has been interpreted as an unambiguous measure of the pure contact shift, and hence of the distribution of unpaired 5f-electron spin density.[8]

Our initial interest in tetrakis(cyclopentadienyl)uranium compounds was sparked by their potential use as starting materials. In contrast to the great number of physical and spectroscopic papers dealing with UCp_4, few attempts have been made to use these compounds as starting materials in organometallic chemistry.[9] No doubt, the poor solubility of UCp_4 deterred further investigation of its reaction chemistry.

4.1 Preparation and Reactions of Tetrakis(Methylcyclopentadienyl)-Uranium

The title compound is easily prepared according to eq 1. It can be isolated in high yield by crystallization from toluene. It can also be prepared starting from $UCl_4(tmeda)_2$, although in contrast to the analogous thorium system (see Chapter 3) the method offers no synthetic advantage in uranium.

$$UCl_4 + 4\ Na(MeC_5H_4) \longrightarrow (MeC_5H_4)_4U \qquad (1)$$

This synthetic approach gives UCp_4 in low yield, probably due to its poor solubility. Since $(MeC_5H_4)_4Th$ has been used successfully as a starting material for the preparation of various $(MeC_5H_4)_3ThX$ compounds (see Chapter 3), it seems likely that the analogous reactions with $(MeC_5H_4)_4U$ would prove equally successful. $(MeC_5H_4)_4U$ does react with alkyllithiums to give the corresponding alkyls $(MeC_5H_4)_4UR$ in good yield (eq 2). Thus methylcyclopentadienyl lithium does represent a viable leaving group for substitution reactions. Since $(MeC_5H_4)_4U$ also reacts with KCH_2Ph to yield $(MeC_5H_4)_3U(CH_2Ph)$ as discussed in Chapter 2, other alkali methylcyclopentadienyl salts are viable leaving groups as well.

$$(MeC_5H_4)_4U + RLi \longrightarrow (MeC_5H_4)_3UR \qquad (2)$$

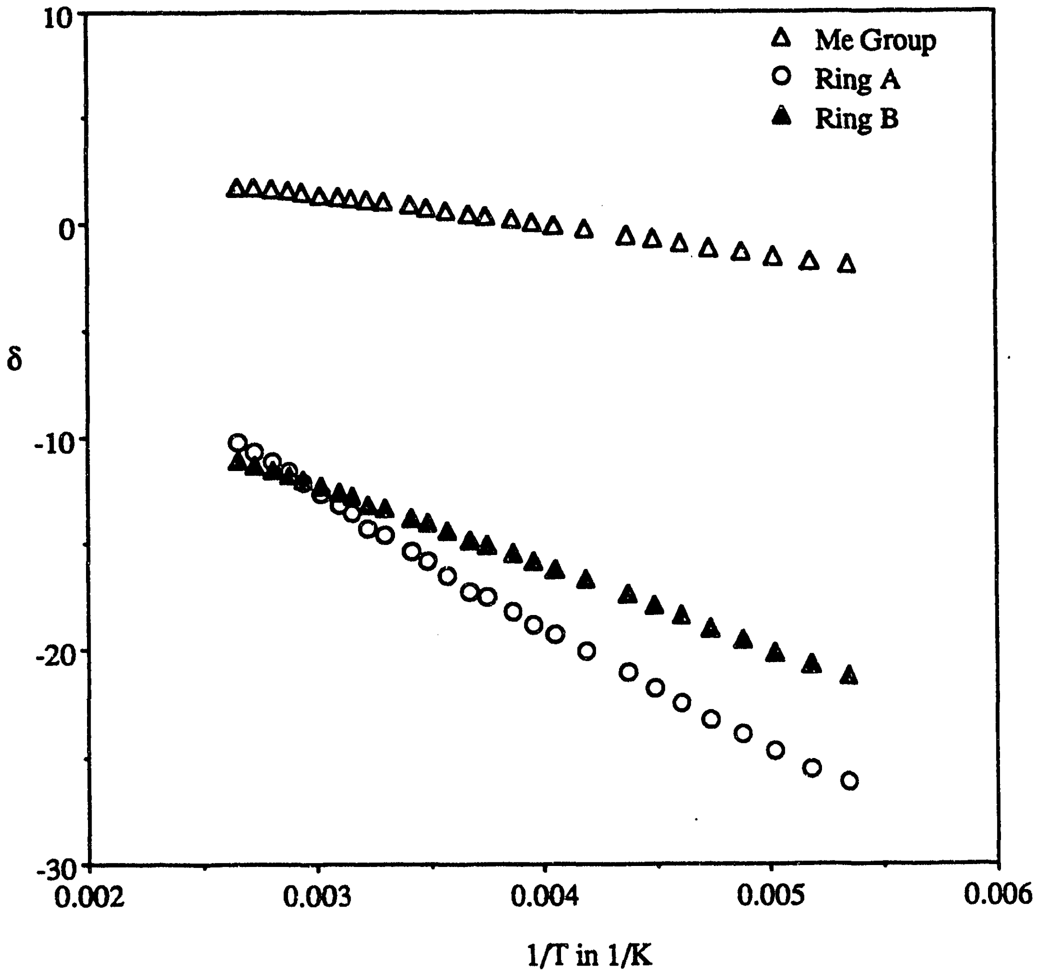
$$R = Me, t\text{-}Bu$$

Although we did not carry out any reactions of $(MeC_5H_4)_4U$ with acidic substrates HX to yield $(MeC_5H_4)_3UX$ and cyclopentadiene, it seems quite likely that these reactions, in analogy to the thorium system, will be successful. Interestingly, Rosen reacted $(MeC_5H_4)_4U$ with phenylhydrazine and obtained the uranium phenylhydrazide complex.[10] Relative acidities are generally a good indicator of whether a protonation reaction at uranium is favored or not, even though ΔG is determined by the relative bond energies and not the acidities. The relative acidities of methylcyclopentadiene and phenylhydrazine do not favor this reaction. It nevertheless represents the best synthetic method for the preparation of the uranium phenylhydrazide complex. Thus, the relief of steric congestion achieved in this reaction is sufficient to overcome a significant, unfavorable disparity in relative acidities.

In an attempt to see whether an η^1-η^5-equilibrium for the methylcyclopentadienyl ligands is established in solution, $(MeC_5H_4)_4U$ was treated with one equiv of t-butylisocyanide. Since t-butylisocyanide is able to insert into tris(cyclopentadienyl)-uranium-primary alkyl bonds,[11] it was hoped that a similar insertion into the suspected uranium-η^1-methylcyclopentadienyl bond would occur. However, no reaction was observed. To further explore the extent of steric congestion in $(MeC_5H_4)_4U$, a variable temperature ^{1}H-NMR spectrum in toluene solution was acquired (Figure 1). All three resonances of the compound obey the Curie Law in the temperature range investigated. Hence, the variable temperature ^{1}H-NMR spectrum provides no evidence of unusual temperature dependent behavior.

When equimolar amounts of $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(thf)$ are mixed in toluene-d_8 solution, only one set of broad resonances for the methylcyclopentadienyl ligand is observed at room temperature in the ^{1}H-NMR spectrum. At low temperatures (< -60 °C), the individual resonances for $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(thf)$ are visible. At high temperatures, only one set of averaged, sharp methylcyclopentadienyl ligand resonances is observed. Coalescence occurs at ca. 0 °C. Hence, a process occurring rapidly in solution renders all methylcyclopentadienyl ligands equivalent on this time scale. This could be either fast ligand-exchange between the tetravalent and the trivalent

Figure 1: Variable Temperature ^{1}H-NMR Spectrum of $(MeC_5H_4)_4U$ (+104 °C to -86 °C)



uranium species, or fast electron-transfer between the trivalent and tetravalent uranium species via transfer of a methylcyclopentadienyl radical (Scheme 1).

Scheme 1: Proposed Electron-Transfer Pathway between $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(thf)$

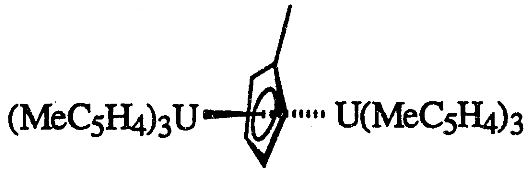
$$(MeC_5H_4)_3U(thf) \rightleftharpoons (MeC_5H_4)_3U + thf$$

$$(MeC_5H_4)_4U^* + (MeC_5H_4)_3U \rightleftharpoons (MeC_5H_4)_3U^* + (MeC_5H_4)_4U$$

In order to distinguish between these possibilities, equimolar amounts of $(MeC_5H_4)_4Th$ and $(MeC_5H_4)_3U(thf)$ were mixed in toluene-d_8 solution. Substituting the tetravalent thorium species for the tetravalent uranium species should not influence the rate of ligand exchange a great deal, since tetravalent thorium and uranium have similar ionic radii. However, any process involving electron transfer between the trivalent and the tetravalent species should be greatly perturbed due to the inaccessibility of trivalent thorium. No interaction was detected by ^1H-NMR spectroscopy between $(MeC_5H_4)_4Th$ and $(MeC_5H_4)_3U(thf)$ from +100 to -80 °C. Hence, it seems likely that the reaction does indeed involve electron-transfer, although the negative evidence does not establish it. The definitive experiment, reaction of $(MeC_5H_4)_4Np$ and $(MeC_5H_4)_3U(thf)$ to yield irreversibly $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3Np(thf)$, could not be done due to Tiger Team interference.

Equimolar mixtures of $(MeC_5H_4)_3UMe$ and $(MeC_5H_4)_3U(thf)$ show similar behavior. Only a single averaged set of methylcyclopentadienyl resonances is observed at high temperatures, whereas the individual species are observed at low temperatures. Again, when $(MeC_5H_4)_3ThMe$ and $(MeC_5H_4)_3U(thf)$ are mixed, no interaction is detected by ^{1}H-NMR spectroscopy up to 100 °C. However, no indication of electron-transfer is observed by ^{1}H-NMR spectroscopy between $(MeC_5H_4)_3U(t\text{-}Bu)$ and $(MeC_5H_4)_3U(thf)$ at room temperature. The transition state for electron-exchange between $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(thf)$ presumably involves a species with a doubly-η^5-bridging methylcyclopentadienyl ligand (Figure 2). For electron-exchange between $(MeC_5H_4)_3UMe$ and $(MeC_5H_4)_3U(thf)$, the transition state presumably involves a methyl group bridging both uranium centers. A similar molecule featuring a methyl group bridging two trivalent uranium centers, $(MeC_5H_4)_3U(\mu\text{-}Me)U(MeC_5H_4)_3$-anion, has been isolated and crystallographically characterized.[13]

Figure 2: Proposed Transition State for Electron-Exchange between $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(thf)$



Similar ^{1}H-NMR spectroscopic behavior has been reported for the analogous systems $Cp_3UX/Cp_3U(thf)$ (X = Cl, BH_4, Me).[12] Although the authors claim that the observed processes (time-averaged ^{1}H-NMR resonances) are due to fast electron-exchange, they did not offer irrefutable evidence of this. Exchange between penta- and tetravalent uranium does not occur since no interaction was detected by ^{1}H-NMR spectroscopy from +30 to +100 °C between $(MeC_5H_4)_4U$ and $(MeC_5H_4)_3U(NPh)$ and between $(MeC_5H_4)_3U(NHPh)$ and $(MeC_5H_4)_3U(NPh)$. Systems involving a trivalent and a pentavalent uranium species were not investigated, as these usually result in rapid irreversible formation of two tetravalent uranium species.[10]

Brennan prepared $(Me_3SiC_5H_4)_4U$ in low yield by exposing a toluene solution of $(Me_3SiC_5H_4)_3U$ to 0.5 equiv of oxygen.[14] The compound was also obtained as a minor side product in a number of oxidation reactions of $(Me_3SiC_5H_4)_3U$. However, Brennan reported that $(Me_3SiC_5H_4)_4U$ cannot be obtained by a metathesis reaction of $(Me_3SiC_5H_4)_3UCl$ with $K(Me_3SiC_5H_4)$ in either refluxing toluene or thf. Only unreacted starting materials were quantitatively recovered.

We attempted to prepare $(Me_3SiC_5H_4)_4U$ by reaction of $(Me_3SiC_5H_4)_3UCl$ with either $Na(Me_3SiC_5H_4)$ or $Mg(Me_3SiC_5H_4)_2$ in either thf or toluene. However, once again, these metathesis reactions did not proceed and only starting materials were recovered. Therefore, we set out to explore radical routes for introducing a cyclopentadienyl ligand to the trivalent $(Me_3SiC_5H_4)_3U$ fragment. The larger ionic radius of trivalent vs. tetravalent uranium as well as the lower charge density should result in a more substitutionally labile uranium center. This as well as the favorable redox couple for trivalent vs. tetravalent uranium suggests that this synthetic approach might be a general process, provided a good source of cyclopentadienyl radical can be found. We first investigated bis(cyclopentadienyl)mercury compounds as potential sources of a cyclopentadienyl radical, since these compounds have been useful in the generation of cyclopentadienyl radicals for EPR studies.[24]

4.2 Bis(Cyclopentadienyl)Mercury Reagents

Since the first preparation of Cp_2Hg by Wilkinson,[15] a σ-bonded structure has repeatedly been proposed on the basis of spectral properties and chemical behavior.[16] This structure has been questioned by others, who have suggested a π-bonded sandwich structure.[17] The recent X-ray crystal structure of Cp_2Hg established that the molecule is monomeric with σ-bonded η^1-cyclopentadienyl rings in the solid state.[18] The ^{1}H-NMR spectrum for Cp_2Hg, however, shows only a single resonance at all temperatures. Elegant NMR-studies on substituted bis(cyclopentadienyl)mercury compounds established the presence in solution of rapidly exchanging fluxional σ-bonded systems rather than of a π-bonded system.[19]

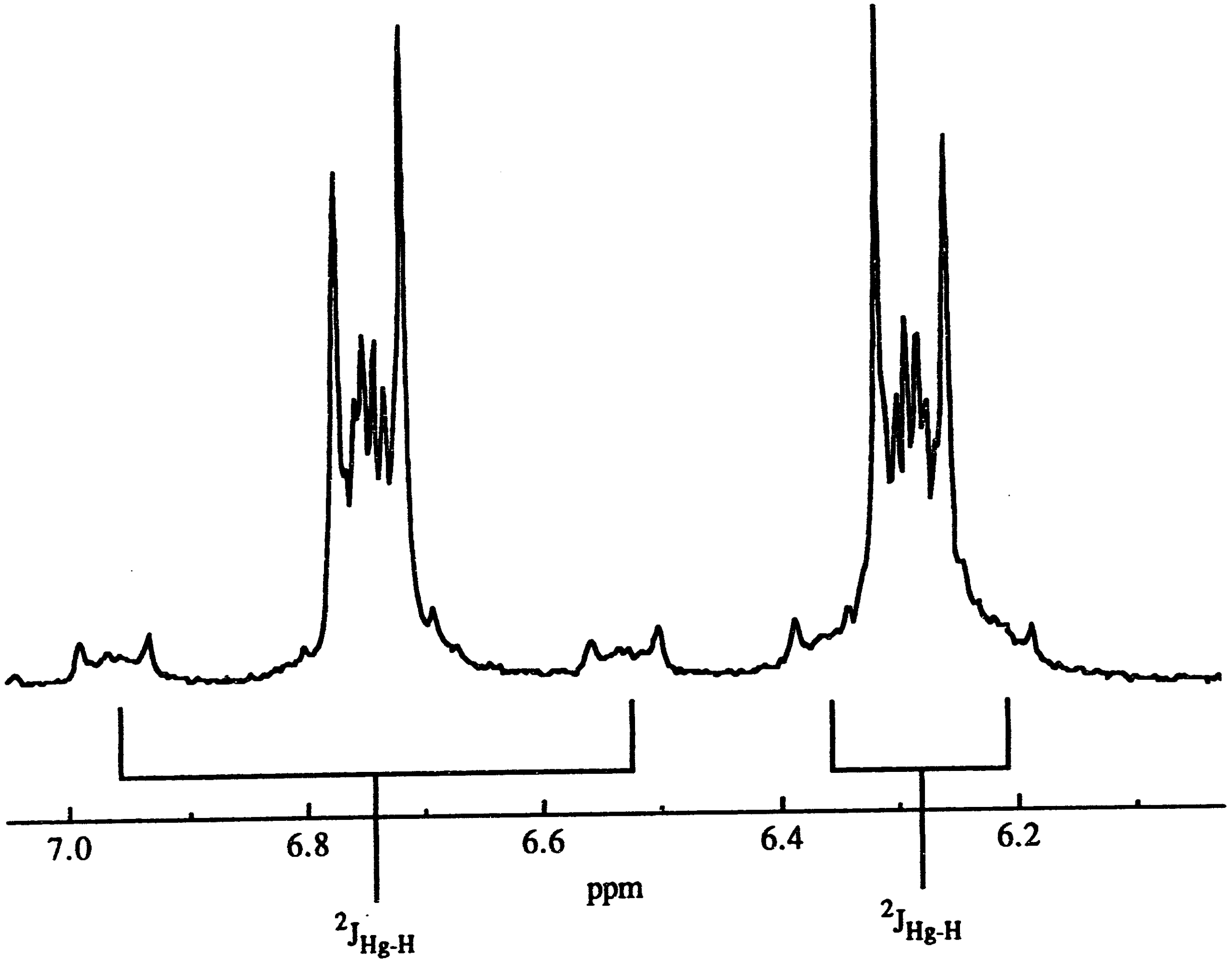
Bis(trimethylsilylcyclopentadienyl)mercury is easily prepared as shown in eq 3. The compound is not moisture sensitive, nor noticeably air sensitive. However, it is light sensitive and when to exposed to room light, noticeable decomposition occurs in the solid state over ca. 15 min. In toluene solution, when kept in the dark, the compound is thermally stable at room temperature for at least several weeks. Figure 3 shows the cyclopentadienyl ring proton resonance region of the ^{1}H-NMR spectrum at room temperature in benzene-d_6 solution. The ^{199}Hg-satellites ($I = 1/2$, 16.9%) are clearly visible.

$$HgCl_2 + 2\,Na(Me_3SiC_5H_4) \longrightarrow (Me_3SiC_5H_4)_2Hg \qquad (3)$$

The analogous bis(bis(trimethylsilyl)cyclopentadienyl)mercury compound can be prepared in a similar manner as shown in eq 4. The handling of this compound is somewhat complicated by its low melting point, which causes it to melt on touch.

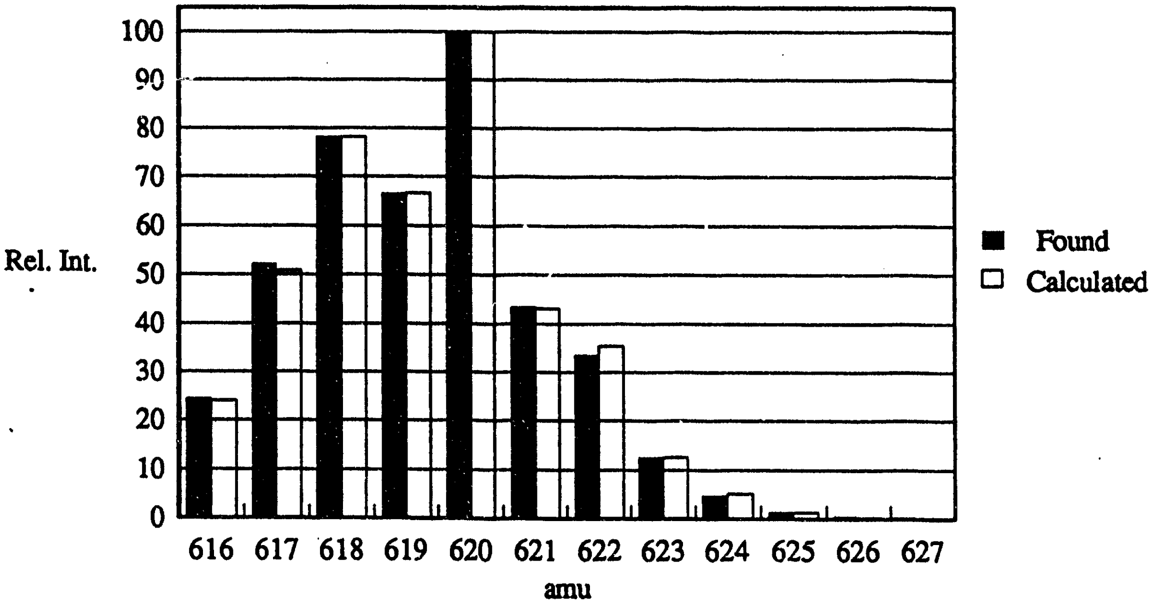
$$HgCl_2 + [(Me_3Si)_2C_5H_3]_2Mg \longrightarrow [(Me_3Si)_2C_5H_3]_2Hg \qquad (4)$$

Figure 3: ^{1}H-NMR Spectrum of $(Me_3SiC_5H_4)_2Hg$: Ring Proton Resonances



Both compounds show distinctive molecular ions in the E.I. mass spectrum, due to the presence of several mercury and silicon isotopes. This is illustrated in Figure 4. The observation of molecular ions in the mass spectrum further substantiates the significantly higher thermal stability of these substituted bis(cyclopentadienyl)mercury compounds relative to Cp_2Hg.

Figure 4: EIMS Molecular Ion for $[(Me_3Si)_2C_5H_3]_2Hg$



The fluxional processes that equilibrate the different η^1-bonded structures of bis(cyclopentadienyl)mercury compounds might be slowed down by the presence of bulky substituents on the cyclopentadienyl ligand. However, both $[(Me_3Si)_2C_5H_3]_2Hg$ and $(Me_3SiC_5H_4)_2Hg$ show only one symmetrical type of cyclopentadienyl ring environment in the ^{1}H-NMR spectrum at room temperature. We therefore investigated the variable temperature ^{1}H-NMR spectra of both compounds. The results are summarized in Tables 4.1 and 4.2. While no fluxional process could be frozen out at low temperature, several features in Tables 4.1 and 4.2 are worth noting. For both

Table 4.1: Variable Temperature ^{1}H-NMR Spectrum of $(Me_3SiC_5H_4)_2Hg$: Cyclopentadienyl Ring Proton (AA'BB'-Spin System) and Trimethylsilyl Group Resonances

T (°C)	δ(AA')	$^2J_{Hg-H}$(AA') (Hz)	δ(BB')	$^2J_{Hg-H}$(BB') (Hz)	δ(Me_3Si)
30	6.71	38.5	6.27	13.7	-0.02
15	6.73	38.1	6.26	13.6	-0.02
0	6.74	38.1	6.26	13.0	-0.02
-17	6.76	37.8	6.25	12.7	-0.01
-43	6.80	36.0	6.22	12.5	0.00
-72	6.83	---	6.18	---	0.02

Table 4.2: Variable Temperature ^{1}H-NMR Spectrum of $[(Me_3Si)_2C_5H_3]_2Hg$: Cyclopentadienyl Ring Proton (A_2B-Spin System) and Trimethylsilyl Group Resonances

T (°C)	δ(A_2)	$^2J_{Hg-H}$(A_2) (Hz)	δ(B)	$^2J_{Hg-H}$(B) (Hz)	δ(Me_3Si)
28	6.64	29.2	6.37	36.4	0.13
14	6.64	30.2	6.35	39.9	0.14
2	6.64	30.2	6.34	39.8	0.15
-19	6.65	30.9	6.30	43.1	0.16
-40	6.66	31.1	6.24	46.0	0.18
-54	6.67	32.6	6.18	50.8	0.20
-62	6.68	32.2	6.14	52.9	0.21
-75	6.70	---	6.06	---	0.22
-85	6.71	---	6.00	---	0.24

compounds, the chemical shifts for all three resonances are temperature dependent. Furthermore, the ^{199}Hg-H coupling constants for the cyclopentadienyl ring hydrogens are also temperature dependent. Similar behavior in bis(cyclopentadienyl)mercury compounds has been seen before.[19b] It has been interpreted in terms of rapidly exchanging fluxional σ-bonded systems and temperature dependent equilibria between the individual σ-bonded systems. Hence, $[(Me_3Si)_2C_5H_3]_2Hg$ and $(Me_3SiC_5H_4)_2Hg$ show no unusual behavior.

We then proceeded to investigate the reactions of the bis(cyclopentadienyl)-mercury compounds with organouranium compounds.

4.3 Preparation and Solution Properties of a Bulky Tetrakis(Cyclopentadienyl)Uranium Compound

When $(Me_3SiC_5H_4)_3U$ is treated with half an equiv of $(Me_3SiC_5H_4)_2Hg$ in hexane solution, the deep-green uranium solution turns red-brown within one minute and small droplets of metallic mercury become visible. The product isolated in good yield from the reaction mixture is $(Me_3SiC_5H_4)_4U$ (eq 5). Since we know that $(Me_3SiC_5H_4)_2Hg$ is stable in toluene solution at room temperature in the dark, the rapid decomposition to metallic mercury in the presence of $(Me_3SiC_5H_4)_3U$ must be the result of a bimolecular reaction between $(Me_3SiC_5H_4)_3U$ and $(Me_3SiC_5H_4)_2Hg$. Presumably, the organomercury compound coordinates to the uranium center first, and subsequent electron transfer occurs through a bridging cyclopentadienyl ligand.

$$(Me_3SiC_5H_4)_3U + 1/2\ (Me_3SiC_5H_4)_2Hg \longrightarrow (Me_3SiC_5H_4)_4U + 1/2\ Hg \qquad (5)$$

As mentioned earlier, the X-ray crystal structure of $(Me_3SiC_5H_4)_4U$ was obtained by Brennan.[14] In the structure, all four cyclopentadienyl rings are η^5-bound to the uranium center. The trimethylsilyl groups are bent 20° out of the plane defined by the cyclopentadienyl rings, indicative of substantial steric congestion. In an attempt to see whether an η^1-η^5-equilibrium for the trimethylsilylcyclopentadienyl ligands is established in solution, a hexane solution of $(Me_3SiC_5H_4)_4U$ was exposed to 100 psi of carbon monoxide. Since carbon monoxide is able to insert into tris(cyclopentadienyl)uranium-alkyl bonds,[20] it was hoped that a similar insertion into the suspected uranium-η^1-trimethylsilylcyclopentadienyl bond would occur. However, no reaction was observed. To further explore the extent of steric congestion in $(Me_3SiC_5H_4)_4U$, a variable temperature ^{1}H-NMR spectrum in toluene-d_8 solution was acquired. The results are shown in Figure 5 and in more detail in Figure 6. No fluxional process can be frozen out.

Figure 5: Variable Temperature ^{1}H-NMR Spectrum of $(Me_3SiC_5H_4)_4U$ in toluene-d_8 (+110 to -78 °C)

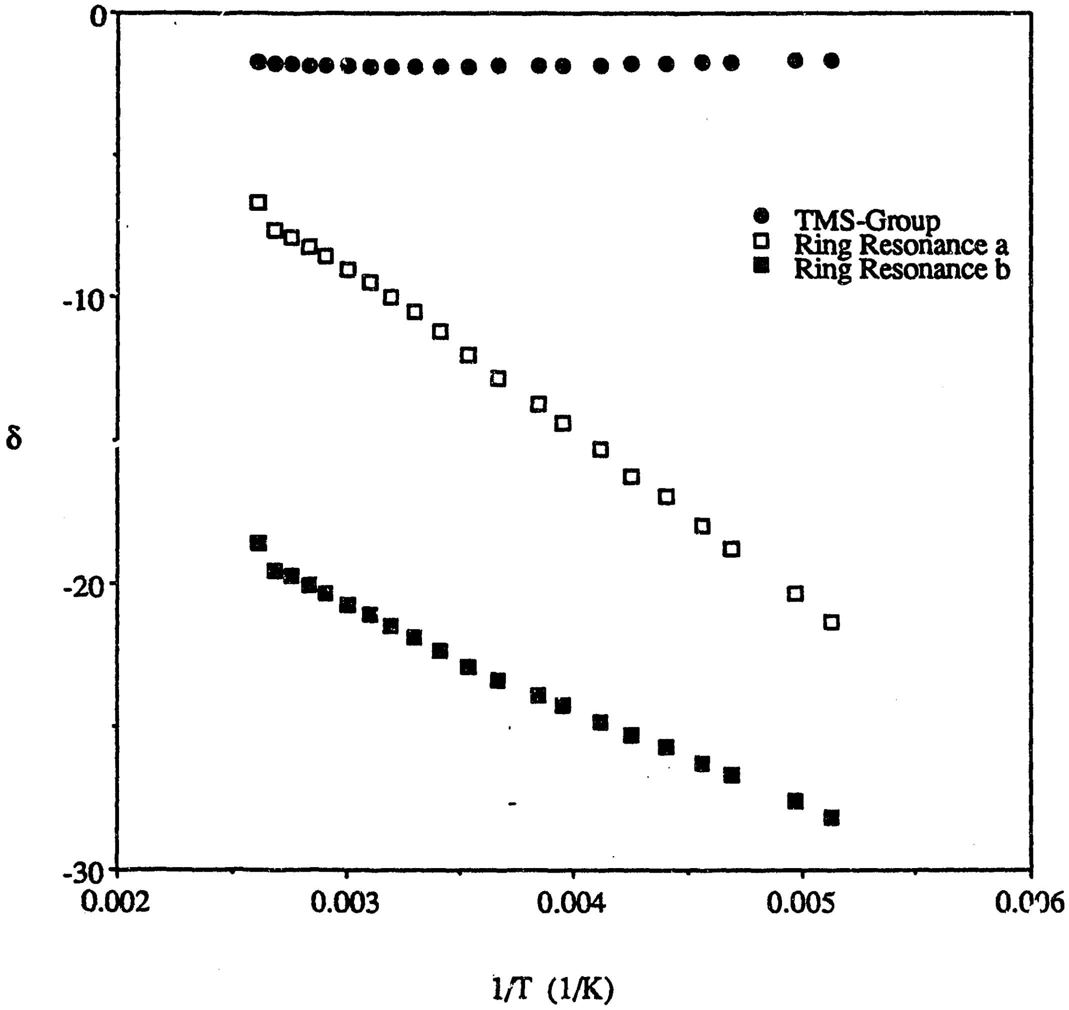


Figure 6: Variable Temperature ^{1}H-NMR Spectrum of $(Me_3SiC_5H_4)_4U$ in toluene-d_8 (+110 to -78 °C)

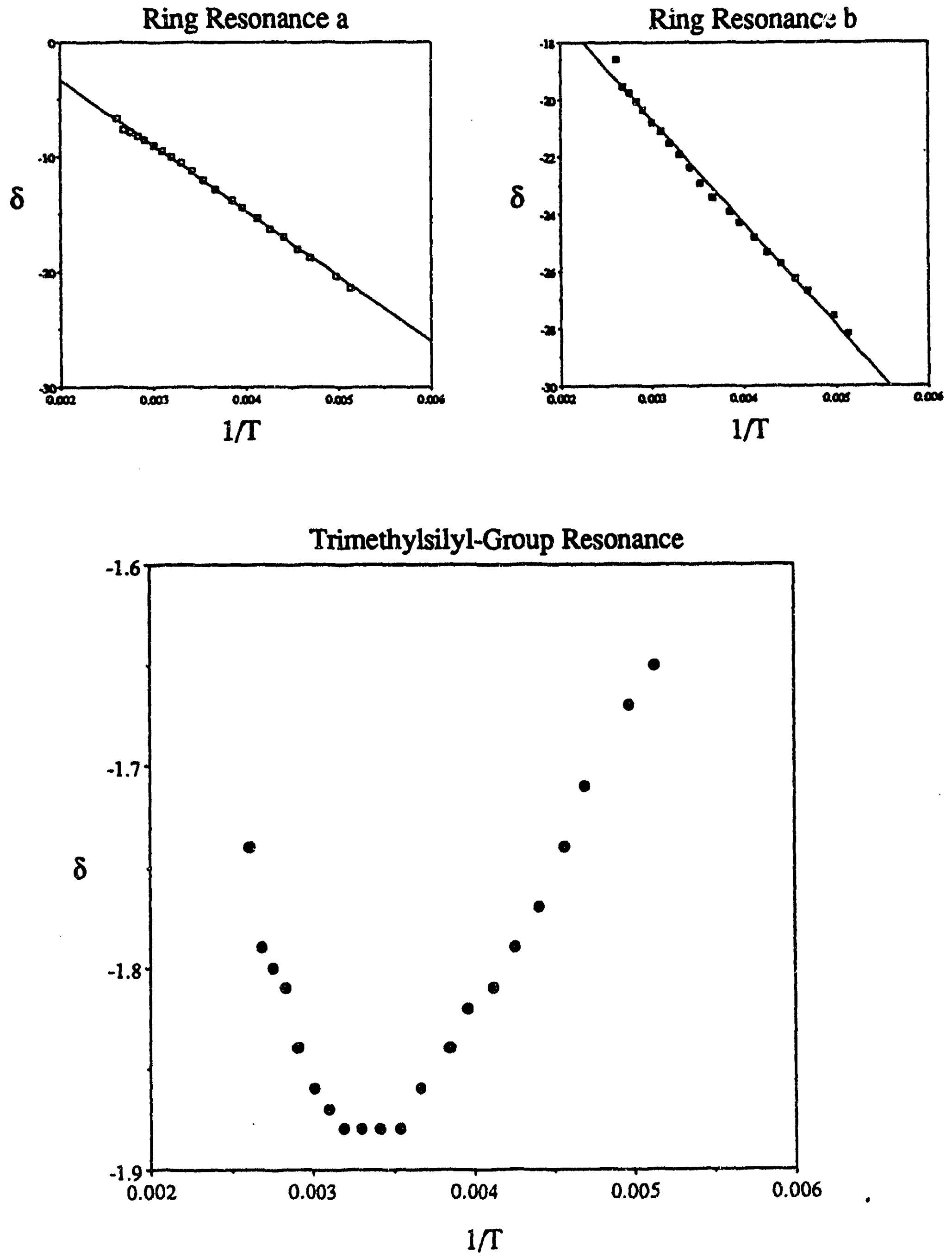


Figure 5 illustrates that the observed deviations from Curie Law are small in magnitude. However, as can be seen in Figure 6, the trimethylsilyl group resonance clearly exhibits non-linear behavior. Since the crystal structure shows the trimethylsilyl substituents to be significantly bent out of the cyclopentadienyl ring plane, it is tempting to ascribe this non-linear behavior to increasing temperature dependent bending of the substituent upon lowering of the temperature. Once again though, a temperature dependent conformational equilibrium is the most likely explanation for the observed behavior.

We attempted to extend this synthetic strategy to the bis(trimethylsilyl)cyclopentadienyl system. When a hexane solution of $[(Me_3Si)_2C_5H_3]_3U$ [21] was treated with half an equiv of $[(Me_3Si)_2C_5H_3]_2Hg$, no immediate reaction occurred. The reaction mixture was stirred at room temperature for several hours in the dark. Since no evidence of a reaction was visible, the reaction mixture was exposed to room light. It was hoped that the light-induced decomposition of $[(Me_3Si)_2C_5H_3]_2Hg$ would generate bis(trimethylsilyl)cyclopentadienyl radicals, which in turn would react with the trivalent uranium species. However, this was not the case. The light-induced decomposition of $[(Me_3Si)_2C_5H_3]_2Hg$ did not result in formation of a new uranium-containing species. Apparently, precoordination of the bis(cyclopentadienyl)mercury species to the uranium center is a necessary requirement for the oxidation of the trivalent uranium species. Since it has been established that $[(Me_3Si)_2C_5H_3]_3U$ is sterically encumbered and coordinates only to the most sterically undemanding rod-like ligands (RNC, RCN, Me_3PO),[22] it seems reasonable to postulate that $[(Me_3Si)_2C_5H_3]_2Hg$ will not be able to interact with $[(Me_3Si)_2C_5H_3]_3U$, and hence, no reaction occurs.

To further investigate conformational equilibria in congested uranium compounds, we measured the variable temperature ^1H-NMR spectra of $(Me_3SiC_5H_4)_3UCl$ and $(t\text{-}BuC_5H_4)_3UCl$. The results are shown in Figures 7 and 8. Once again, no fluxional

Figure 7: Variable Temperature ^{1}H-NMR Spectrum of $(Me_3SiC_5H_4)_3UCl$ in Toluene-d_8 (+91 to -92 °C)

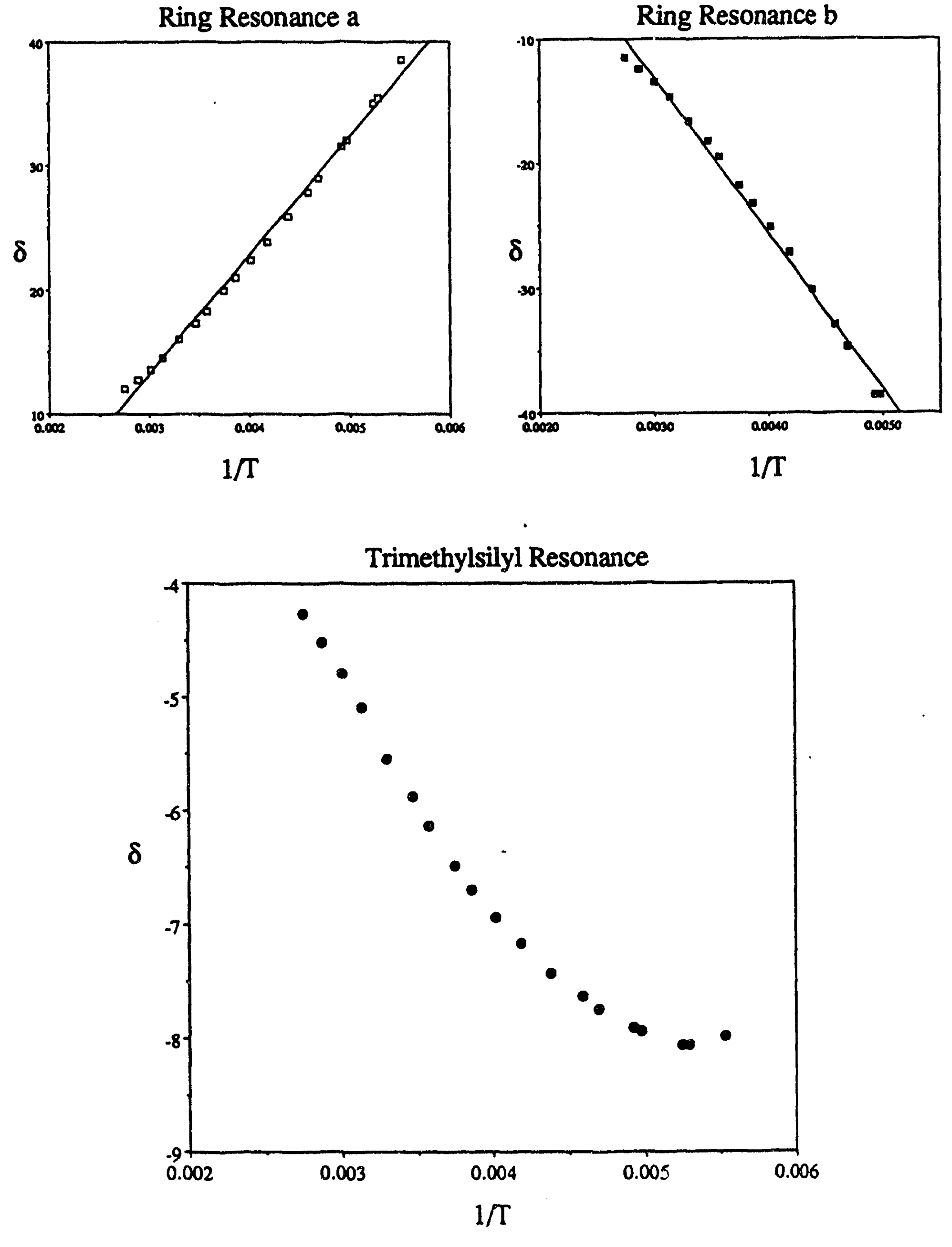
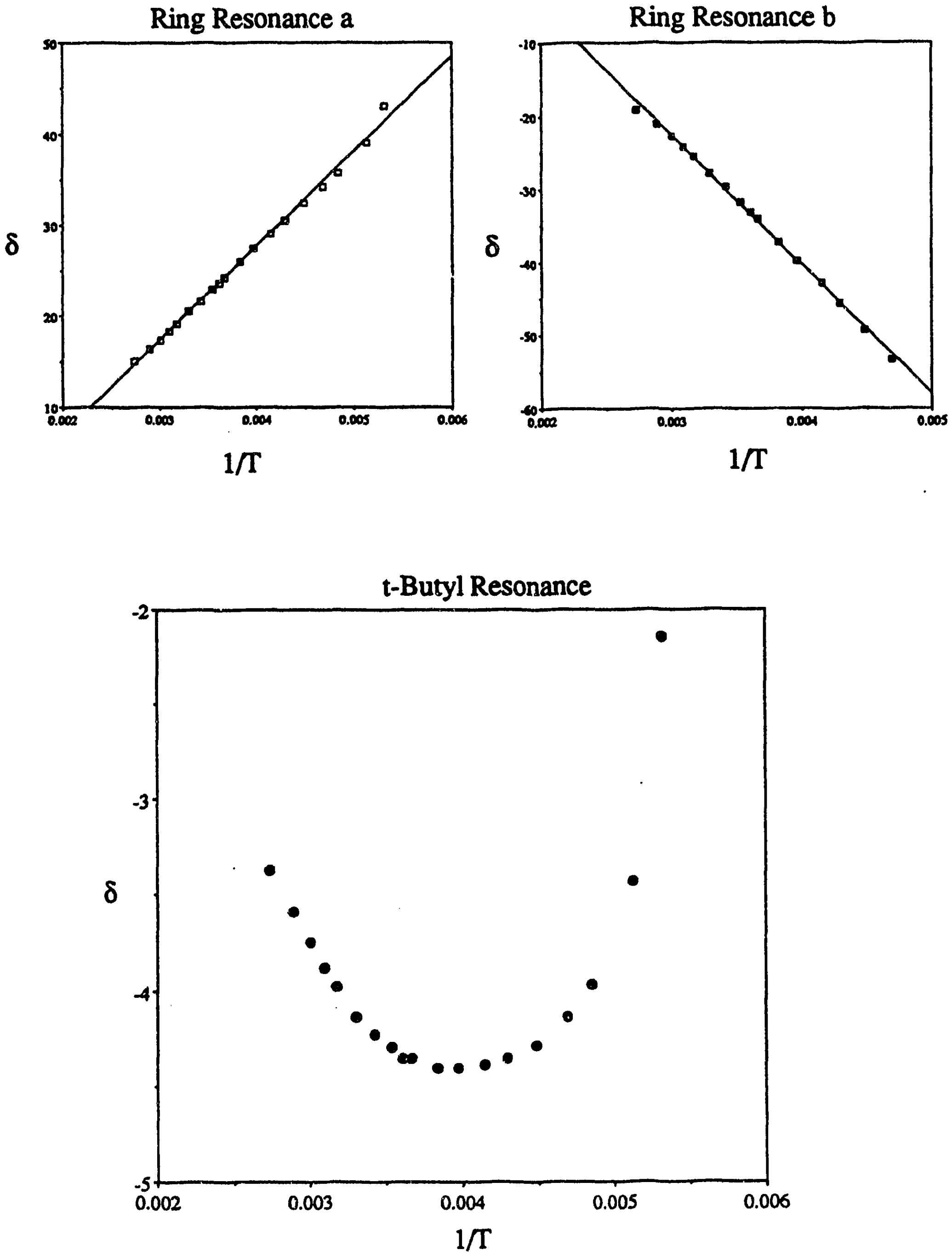


Figure 8: Variable Temperature ^{1}H-NMR Spectrum of $(t\text{-BuC}_5\text{H}_4)_3\text{UCl}$ in Toluene-d_8 (+92 to -85 °C)



processes could be frozen out. The resonances for both compounds, however, do show significant broadening at low temperature. Presumably, the rate of an exchange process is now close to the NMR time scale. For both compounds, some resonances clearly display non-linear behavior and hence the compounds do not obey the Curie law. The same observation has been made in the preceeding chapters for other $(RC_5H_4)_3UX$ compounds. The effect seems to correlate with steric bulk, i.e. the more sterically demanding the R- and X-groups are, the more likely it is that the effect is observed. Until a molecule is found in which the process responsible for this behavior can be frozen out, no definite conclusions can be drawn regarding the nature of the process. However, given the straightforward correlation with steric bulk, a temperature dependent conformational equilibrium seems the most likely explanation. Finally, caution should be exercised when comparing the variable temperature ^1H-NMR behavior of $(RC_5H_4)_4U$ compounds to the behavior of $(RC_5H_4)_3UX$ compounds. Whereas the former have approximately tetrahedral symmetry in solution, the latter have axial symmetry. The resulting magnetic susceptibility tensors, which are largely responsible for the observed isotropic shifts, will thus be different. Therefore, it is more prudent to treat the two systems separately.

We also investigated cyclopentadienyl ligand exchange in $(RC_5H_4)_3UCl$ systems. When equimolar amounts of $(t\text{-}BuC_5H_4)_3UCl$ and $(Me_3SiC_5H_4)_3UCl$ were mixed in benzene-d_6 solution, only the individual species were observed by ^1H-NMR spectroscopy. Heating the sample to 60 °C for 14 days did not result in any detectable exchange of cyclopentadienyl ligands. Therefore, in order to reduce steric barriers to ligand exchange, we investigated equimolar mixtures of $(t\text{-}BuC_5H_4)_3UCl$ and $(MeC_5H_4)_3UCl$, $(Me_3SiC_5H_4)_3UCl$ and $(MeC_5H_4)_3UCl$, Cp_3UCl and $(MeC_5H_4)_3UCl$. In all these samples, no evidence of cyclopentadienyl ligand exchange was detected by ^1H-NMR spectroscopy after heating the samples to 60 °C for 14 days. Also, addition of a trace amount of $(MeC_5H_4)_3U(thf)$ to a mixture of $(MeC_5H_4)_3UCl$ and Cp_3UCl did not result in cyclopentadienyl ligand exchange. Since $(MeC_5H_4)_3U(thf)$ is known to undergo fast-electron exchange with $(MeC_5H_4)_3UCl$ on the NMR time scale,[14] this process most likely occurs by chlorine atom exchange between the metal centers, rather than cyclopentadienyl ligand exchange. This observed lack of ligand exchange in tris(cyclopentadienyl)uranium chlorides contrasts with a literature report of cyclopentadienyl ligand exchange between $(t\text{-}BuC_5H_4)_3UCl$ and Cp_3UCl.[23] Since the presence of trace amounts of a trivalent uranium species does not seem to catalyze cyclopentadienyl ligand exchange, chloride being a better bridging ligand than cyclopentadienyl, we are not able to account for this discrepancy with the reported observation.

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Chapter Five

Experimental Section

5.1 General: Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Toluene, tetrahydrofuran, diethyl ether and hexane were distilled under nitrogen from potassium, sodium, or sodium/benzophenone immediately prior to use. Benzotrifluoride, hexafluorobenzene, perfluoromethylcyclohexane, methylcyclohexane-d_{14}, thf-d_8 and deuterated aromatic solvents were heated at reflux over sodium and subsequently distilled from sodium under nitrogen. Perfluorocyclohexane was sublimed under nitrogen through a P_2O_5 plug. Diphenylacetylene and 9,10-Dihydroanthracene were recrystallized from toluene. *p*-Toluenesulfonic acid was obtained dry by azeotropic removal of water in benzene solution. 2,6-Dimethylphenol was sublimed prior to use. The uranium and thorium tetrachlorides were treated as described previously.[3] Mercuric chloride was sublimed in vacuo prior to use. Cyclopentadienyl anion was prepared from freshly cracked cyclopentadiene as the sodium salt in tetrahydrofuran. Methylcyclopentadienyl sodium was prepared as reported by Wilkinson.[1] Ethylcyclopentadiene [2], trimethylsilylcyclopentadiene [3] and t-butylcyclopentadiene [11] were prepared according to literature procedures and were used as either the potassium salt in diethyl ether or the sodium salt in thf. $(Me_3SiC_5H_4)_3UCl$ [3] and $(t\text{-}BuC_5H_4)_3UCl$ [4] were prepared as reported previously. Benzylpotassium [12], t-butyl- and ethylisocyanide [5] were prepared according to literature procedures. The trialkylammonium tetraphenylborate salts were prepared according to literature procedures.[13] All compounds were handled using standard Schlenk techniques under a nitrogen or argon atmosphere or in an inert atmosphere dry box under argon.

Melting points were determined in sealed capillaries under argon using a Buchi melting point apparatus and are uncorrected. Infrared spectra were recorded as Nujol mulls between CsI or KBr plates on a Perkin-Elmer 580 or Mattson Sirius 100 instrument. ^{1}H-NMR spectra were measured at 89.56 MHz on a JEOL-FX90Q instrument equipped with Tecmag Libra software and are reported in δ values relative to tetramethylsilane with positive values to high frequency. ^{19}F-NMR spectra were measured at 84.26 MHz on the same instrument and are reported in δ values relative to $CFCl_3$ with positive values to high frequency. ^{13}C-NMR spectra were measured at 22.50 MHz on the same instrument and are reported in δ values relative to tetramethylsilane with positive values to high frequency. Samples for routine NMR spectroscopy were prepared in serum capped NMR tubes in the drybox. Samples for variable temperature, kinetic and quantitative NMR experiments were prepared in NMR tubes equipped with a J. Young Teflon valve in the drybox. Electron impact mass spectra were obtained with an Atlas MS-12 spectrometer operated by the Mass Spectrometry Laboratory operated by the College of Chemistry, University of California, Berkeley. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley. Analytical gas chromatography traces were obtained on a Hewlett-Packard HP-5790 instrument equipped with a HP-3390A integrator and a HP-19091B Option112 ultra high performance capillary column (crosslinked 5% phenylmethylsilicone, length 25 m, int. diameter 0.31 mm), or a HP-5890 chromatograph equipped with a HP-3396A integrator and a JNW-Scientifics capillary column (stationary phase: DB-5, length 30 m, int. dia. 0.25 mm). GC-MS was performed with a Hewlett-Packard 5890 GC equipped with a HP 5970 series mass selective detector (70 eV) and JNW-Scientifics column as above. Preparative gas chromatography was performed on a Varian Aerograph Model 920 chromatograph equipped with a 5' stainless steel column (1/4" O.D.) packed with 10% OV-101 on 100/120 Chromsorb W (Alltech).

5.2 Experimental Details: Chapter 1

$(C_5H_5)_3UCl$: To a solution of UCl_4 (4.21 g, 11.1 mmol) in 50 mL of thf was added by syringe 23.5 mL (33.4 mmol, 1.42M in thf) of $Na(C_5H_5)$. Upon addition the green solution turned dark red-brown instantly. After stirring for 12 h the solvent was removed under reduced pressure. The resulting solid was stirred with 200 mL of toluene at 70 °C for 3 h. After allowing the solid to settle, the dark red-brown toluene solution was filtered at 70 °C. The filtrate was concentrated to ca. 80 mL under reduced pressure. Cooling to -80 °C yielded red-brown crystals of $(C_5H_5)_3UCl$ (4.44 g; 85.5%). ^{1}H-NMR (C_6D_6; 30 °C): δ = -3.24 ppm. The spectrum agrees very closely with the previously reported value.[4]

$(MeC_5H_4)_3UCl$: To a solution of UCl_4 (4.44 g, 11.7 mmol) in 45 mL of thf was added by syringe 23.6 mL (35.2 mmol, 1.49M in thf) of $Na(MeC_5H_4)$. Upon addition the green solution turned dark red-brown instantly. After stirring for 3 h the solvent was removed under reduced pressure. The resulting solid was stirred with 150 mL of toluene at 65 °C for 1 h. After allowing the solid to settle, the dark red-brown toluene solution was filtered at 65 °C. The filtrate was concentrated to ca. 60 mL under reduced pressure. Cooling to -80 °C yielded red-brown crystals of $(MeC_5H_4)_3UCl$ (4.72 g; 79.0%), m.p. 207-210 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 11.84 (s, 6H); -0.41 (s, 9H); -19.55 (s, 6H) ppm. IR (CsI): 1490(w), 1345(w), 1260(w), 1070(w), 1047(w), 1028(s), 932(m), 840(m), 785(s), 720(w), 696(w), 609(m), 345(m), 240(s) cm^{-1}. EIMS: M^+ = 468 amu. The data agree very closely with previously reported values.[3]

$(EtC_5H_4)_3UCl$: To a solution of UCl_4 (2.04 g, 5.37 mmol) in 30 mL of thf was added by syringe 14.0 mL (16.1 mmol, 1.15M in diethyl ether) of $K(EtC_5H_4)$. Upon addition the green solution immediately turned dark red-brown. After stirring the reaction mixture for 4 h the solvent was removed under reduced pressure. The remaining light yellow solid was extracted with 90 mL of toluene at 60 °C. After allowing the solid to settle, the dark red-brown toluene solution was filtered at 60 °C. The filtrate was concentrated to ca. 25 mL under reduced pressure. Cooling to -80 °C yielded dark brown crystals of $(EtC_5H_4)_3UCl$ (2.30 g; 77.5%), m.p. 98-101 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 13.51 (s, 6H); 0.50 (t, J = 7.8 Hz, 9H); -3.92 (q, J = 7.8 Hz, 6H); -20.55 (s, 6H) ppm. IR (CsI): 1485(m), 1410(m), 1315(m), 1260(m), 1235(m), 1215(w), 1205(w), 1095(w), 1070(w), 1055(w), 1050(w), 1025(s), 985(w), 910(s), 900(w), 855(w), 845(w), 840(s), 810(w), 785(s), 665(w), 625(m), 600(w), 430(m), 340(m), 245(s) cm^{-1}. Anal. Calcd for $C_{21}H_{27}ClU$: C 45.6, H 4.93. Found: C 45.3, H 4.92. EIMS: M$^+$ = 552 amu.

$(C_5H_5)_3U(t\text{-}Bu)$: A solution of $(C_5H_5)_3UCl$ (0.82 g, 1.7 mmol) was prepared in 50 mL of toluene. Upon addition of t-BuLi (1.76 mmol, 0.95 mL 1.85M in hexane) the dark red-brown solution turned dark green within 1 min. After stirring the reaction mixture for 40 min the solvent was removed under reduced pressure. Proceeding under exclusion of light, the resulting solid was extracted with 50 mL of diethyl ether for 1 h. The diethyl ether solution was filtered and the volume of the filtrate was reduced to ca. 30 mL. Cooling to -80 °C yielded dark green microcrystals of $(C_5H_5)_3U(t\text{-}Bu)$ (0.39 g, 45%), m.p. 195-200 °C dec.. ^{1}H-NMR (C_6D_6; 30 °C): δ = -4.20 (s, 15H); -15.28 (s, 9H) ppm. IR (KBr): 1455(m), 1352(w), 1093(w), 1067(w), 1013(m), 812(m), 785(s) cm^{-1}. Anal. Calcd for $C_{19}H_{24}U$: C 46.5, H 4.94. Found: C 46.6, H 5.07. The ^{1}H-NMR spectrum agrees very closely with previously reported values.[6]

$(MeC_5H_4)_3U(t\text{-}Bu)$: a) A solution of $(MeC_5H_4)_3UCl$ (1.60 g, 3.13 mmol) was prepared in 60 mL of toluene. Upon addition of t-BuLi (3.14 mmol, 1.65 mL 1.90M in hexane) the dark red-brown solution turned dark green within 1 min. After stirring the reaction mixture for 30 min the solvent was removed under reduced pressure. Proceeding under exclusion of light, the resulting solid was extracted with 65 mL of diethyl ether for 1 h. The diethyl ether solution was filtered and the volume of the filtrate was reduced to ca. 20 mL. Cooling to -80 °C yielded dark green needles of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.92 g, 58%), m.p. 224-228 °C dec.. ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 9.96$ (s, 6H); -6.25 (s, 6H); -8.98 (s, 9H); -18.96 (s, 9H) ppm. Anal. Calcd for $C_{22}H_{30}U$: C 49.6, H 5.68. Found: C 49.9 , H 5.29. The data agree very closely with previously reported values.[3]

b) To a solution of $(MeC_5H_4)_4U$ (2.00 g, 3.61 mmol) in 50 mL of toluene was added by syringe t-BuLi (3.70 mmol, 1.65 mL 2.24 M in hexane). The red brown solution rapidly turned dark green. The mixture was stirred for 45 min and then the solvent was removed under reduced pressure. Proceeding under exclusion of light, the resulting solid was extracted with 100 mL of diethyl ether for 1 h. The diethyl ether solution was filtered and the volume of the filtrate was reduced to ca. 40 mL. Cooling to -80 °C yielded dark green needles of $(MeC_5H_4)_3U(t\text{-}Bu)$ (1.01 g , 52.6%). The materials obtained using methods a) and b) exhibited identical physical and spectroscopic properties.

$(EtC_5H_4)_3U(t\text{-}Bu)$: A solution of $(EtC_5H_4)_3UCl$ (1.99 g, 3.60 mmol) was prepared in 35 mL of toluene. Upon addition of t-BuLi (3.61 mmol, 1.90 mL 1.90M in hexane) the dark red-brown solution turned dark green within 1 min. After stirring the reaction mixture for 30 min the solvent was removed under reduced pressure. Proceeding under exclusion of light, the resulting solid was extracted with 50 mL of diethyl ether for 1 h. The diethyl ether solution was filtered and the volume of the filtrate was reduced to ca. 20 mL. Cooling to -80 °C yielded dark green crystals of $(EtC_5H_4)_3U(t\text{-}Bu)$ (0.68 g, 35%), m.p. 195-200 °C dec.. ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 9.90$ (s, 6H); -1.79 (t, J = 7 Hz, 9H); -6.39 (s, 6H); -12.15 (q, J = 7 Hz, 6H); -19.20 (s, 9H) ppm. IR (CsI): 1315(w), 1255(w), 1045(w), 1025(m), 905(w), 855(w), 845(w), 770(s), 740(s), 650(w), 600(w), 420(w), 330(w) cm^{-1}. Anal. Calcd for $C_{25}H_{36}U$: C 52.3, H 6.32. Found: C 49.0, H 5.98.

Decomposition kinetics: For a typical experiment, in the drybox a small amount of Cp_3U(t-Bu) was dissolved in the appropriate deuterated aromatic solvent. The solution was filtered. To the filtrate was added, by microsyringe, a known amount of cyclohexane (internal standard). The volume of the solution was adjusted to an exact volume (typically 0.3-0.5 mL) in a graduated cone. Then the solution was transferred to an NMR tube equipped with a J. Young Teflon valve. A ^{1}H-NMR spectrum was acquired at 30 °C and the concentration of Cp_3U(t-Bu) was determined by integration of the cyclopentadienyl resonance relative to the cyclohexane resonance.

a) Kinetics at T > 50 °C: The sample tube was placed in a constant temperature bath at the desired reaction temperature for an exactly determined, appropriate time interval. Then the sample was quenched in a water bath at 20 °C and a ^{1}H-NMR spectrum was acquired at 30 °C. The procedure was repeated for at least three half-lives for the decay of Cp_3U(t-Bu).

b) Kinetics at T ≤ 50 °C: The sample tube was placed in the NMR probe which was preequilibrated at the desired reaction temperature. A ^{1}H-NMR spectrum was acquired after an exactly determined, appropriate time interval. The procedure was repeated for at least three half-lives for the decay of Cp_3U(t-Bu). The resulting data were analysed using the Passage II data analysis program (©1988 Passage Software Inc., Fort Collins, CO) on a Macintosh II computer.

5.2 Experimental Details: Chapter 2

$(MeC_5H_4)_3U(thf)$: To a solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.31 g, 0.58 mmol) in 25 mL of toluene was added 47 µL (0.58 mmol) of thf. After stirring the reaction mixture for 28 h the solvent was removed under reduced pressure. The remaining solid was extracted with 50 mL of diethyl ether. The ether solution was filtered and the volume of the filtrate was reduced to ca. 10 mL. Cooling to -80 °C yielded 0.12 g (36%) of $(MeC_5H_4)_3U(thf)$, m.p. 136-140 °C. ^1H-NMR (C_6D_6; 30 °C): $\delta = -11.55$ (s, 6H); -13.78 (s, 4H); -14.32 (s, 6H); -15.52 (s, 9H); -30.49 (s, 4H) ppm. IR (CsI): 1650(w), 1590(w), 1505(w), 1485(w), 1335(w), 1260(w), 1235(w), 1210(w), 1170(w), 1045(w), 1030(s), 1010(s), 970(w), 945(w), 925(m), 850(s), 820(s), 770(w), 765(s), 755(s), 660(w), 630(w), 610(m), 530(w), 390(w), 325(m) cm^{-1}. The values agree very closely with previously reported values.[7]

$(MeC_5H_4)_3U(NC\text{-}t\text{-}Bu)$: To a solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.83 g, 1.6 mmol) in 20 mL of toluene was added 180 µL (1.64 mmol) of t-BuCN. The dark green solution turned red-brown over ca. 2 min and precipitate formed. The reaction mixture was stirred for 1 h and then the solvent was removed under reduced pressure. The residual solid was extracted with 25 mL of diethyl ether. After filtration the volume of the ether extract was reduced in vacuo to ca. 10 mL. Cooling to -80 °C yielded dark brown crystals of $(MeC_5H_4)_3U(NC\text{-}t\text{-}Bu)$ (0.25 g, 29%), m.p. 129-132 °C dec.. ^1H-NMR (C_6D_6; 30 °C): $\delta = -5.49$ (s, 6H); -11.03 (s, 9H); -12.28 (s, 9H); -21.80 (s, 6H) ppm. IR (CsI): 2220(w), 1235(m), 1205(w), 1155(w), 1055(w), 1040(w), 1025(m), 925(w), 865(w), 845(w), 810(m), 760(s), 740(s), 610(m), 325(m) cm^{-1}. Anal. Calcd for $C_{23}H_{30}NU$: C 49.5, H 5.42, N 2.51. Found: C 49.2 , H 5.47, N 2.64.

$(MeC_5H_4)_3U(CN\text{-}t\text{-}Bu)$: A solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.96 g, 1.8 mmol) was prepared in 40 mL of toluene. Upon addition of t-BuNC (0.20 mL, 1.8 mmol) the dark green solution instantly turned dark purple. The reaction mixture was stirred for 40 min and then the solvent was removed under reduced pressure. The residual solid was extracted with 30 mL of hexane. After filtration the volume of the hexane extract was reduced in vacuo to ca. 20 mL. Cooling to -20 °C yielded dark red needles of $(MeC_5H_4)_3U(NC\text{-}t\text{-}Bu)$ (0.33 g, 33%), m.p. 100-102 °C dec.. ^1H-NMR (C_6D_6; 30 °C): δ = -8.22 (s, 6H); -10.20 (s, 9H); -15.56 (s, 9H); -19.20 (s, 6H) ppm. IR (CsI): 3080(w), 2720(w), 2280(w), 2140(s), 1235(m), 1195(s), 1060(w), 1040(s), 1025(s), 970(w), 925(s), 845(w), 820(s), 755(s), 700(w), 610(m), 520(m), 325(s), 220(m) cm^{-1}. Anal. Calcd for $C_{23}H_{30}NU$: C 49.5, H 5.42, N 2.51. Found: C 49.7 , H 5.49, N 2.50.

$(MeC_5H_4)_3U(CNEt)$: A solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.44 g, 0.83 mmol) in 50 mL of toluene was cooled to -78 °C in a dry ice/acetone bath. By syringe EtNC (0.06 mL, 0.82 mmol) was added. The mixture was stirred for 5 h at -78 °C, during which the dark green solution gradually turned red. Then the solution was allowed to warm to room temperature while simultaneously the solvent was removed under reduced pressure. The resulting solid was extracted with 25 mL of hexane. After filtration the volume of the hexane extract was reduced in vacuo to ca. 20 mL. Cooling to -20 °C yielded dark red needles of $(MeC_5H_4)_3U(CNEt)$ (0.14 g, 31.3%), m.p. 59-60 °C. ^1H-NMR (C_6D_6; 30 °C): δ = -8.46 (s, 6H); -8.94 (s, 3H); -16.04 (s, 9H); -18.96 (s, 6H); -60.51 (s, 2H) ppm. The values agree very closely with previously reported values.[3]

Kinetic Experiments: For a typical experiment, in the drybox a small amount of $Cp_3U(t\text{-}Bu)$ was dissolved in the appropriate deuterated aromatic solvent. The solution was filtered. To the filtrate was added, by microsyringe, a known amount of cyclohexane (internal standard). The volume of the solution was adjusted to an exact volume (typically

0.25-0.35 mL) in a graduated cone. To this solution was added, by microsyringe, an exact amount of thf-d_8. The total volume of the solution was checked and the solution was transferred to an NMR tube equipped with a J. Young Teflon valve. As quickly as possible, the sample was removed from the drybox and placed in the preequilibrated NMR probe at 30 °C and an initial ^{1}H-NMR spectrum was acquired (typical time lapse from mixing the thf and organometallic solution to first acquisition: ca. 2 min). The next ^{1}H-NMR spectrum was acquired after an exactly determined, appropriate time interval. The procedure was repeated for at least three half-lives for the decay of Cp_3U(t-Bu). The resulting data were analysed using the Passage II data analysis program (©1988 Passage Software Inc., Fort Collins, CO) on a Macintosh II computer.

$(MeC_5H_4)_3U$(C(O)-t-Bu): A solution of $(MeC_5H_4)_3U$(t-Bu) (0.89 g, 1.7 mmol) in 30 mL of toluene was transferred by cannula into a Fischer-Porter pressure bottle under an atmosphere of nitrogen. Carbon monoxide (20 psi) was introduced into the pressure bottle. The deep-green solution was stirred for 4 h during which it gradually turned red. Then the pressure was released and the solution was transferred by cannula to a Schlenk tube. The solvent was removed under reduced pressure and the resulting solid was extracted with 35 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 25 mL. Cooling to -80 °C yielded red needles of $(MeC_5H_4)_3U$(C(O)-t-Bu) (0.33 g). The volume of the mother liquor was reduced to ca. 5 mL. Cooling to -80 °C yielded a second crop of $(MeC_5H_4)_3U$(C(O)-t-Bu) (0.11 g) (combined yield: 47%). ^{1}H-NMR (C_7D_8; 31 °C): $\delta =$ 4.74 (s, 9H); -6.65 (s, 6H); -6.83 (s, 9H); -13.75 (s, 6H) ppm. The values agree very closely with previously reported values.[3]

$(MeC_5H_4)_3U(CH_2CH_2$-t-Bu): In a Fischer-Porter pressure bottle a solution of $(MeC_5H_4)_3U$(t-Bu) (0.76 g, 1.4 mmol) in 25 mL of toluene was stirred under an atmosphere of ethylene at 210 psi. The dark green solution gradually turned red. After 5 h the pressure was released and the solution was transferred by cannula to a Schlenk flask. The solvent was removed under reduced pressure. The resulting solid was extracted with 50 mL of hexane. After filtration the volume of the hexane extract was reduced in vacuo to ca. 20 mL. Cooling to -80 °C yielded red blocks of $(MeC_5H_4)_3U(CH_2CH_2\text{-t-Bu})$ (0.19 g, 24%), m.p. 78-81 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 1.00 (s, 6H); -2.35 (s, 6H); -7.19 (s, 9H); -13.27 (s, 9H); -27.66 (m br., 2H); -190.45 (s br., 2H) ppm. IR (CsI): 1360(w), 1260(m), 1080(m), 1030(s), 905(m), 845(m), 790(m), 770(s), 720(w), 670(w), 610(w), 395(w), 325(w), 235(w) cm^{-1}. Anal. Calcd for $C_{24}H_{34}U$: C 51.4, H 6.11. Found: C 51.1, H 6.05.

$(MeC_5H_4)_3UF$: To a solution of $(MeC_5H_4)_3U(\text{t-Bu})$ (0.63 g, 1.2 mmol) in 20 mL of toluene was added by syringe 143μL (1.24 mmol) of hexafluorobenzene. The reaction mixture was heated to 65 °C for 8 h and then the solvent was removed under reduced pressure. The remaining solid was extracted with 25 mL of toluene. After filtration the volume of of the toluene extract was reduced in vacuo to ca. 15 mL. Cooling to -80 °C yielded green microcrystals of $(MeC_5H_4)_3UF$ (0.14 g, 24%), m.p. 198-202 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 5.54 (s, 6H); -2.09 (s, 9H); -19.18 (s, 6H) ppm. The values agree very closely with previously reported values.[8]

C_6F_5-t-Bu: To a solution of hexafluorobenzene (0.20 mL, 1.73 mmol) in 4 mL of hexane was added by syringe 0.72 mL (1.73 mmol, 2.4M in hexane) of t-BuLi. The mixture was stirred for 9 h, during which time the solution turned yellow and cloudy. Then the mixture was opened up to air and filtered through Celite. Most of the hexane was removed from the filtrate by distillation at 69 °C. A gas chromatogram of the remaining reaction mixture revealed the presence of hexane, C_6F_5-t-Bu and two higher boiling fractions. The desired product was then further purified by preparative gas chromatography, after which a colorless liquid was obtained (85 mg, 22%). ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 1.22$ (t, $^5J_{H\text{-}F} = 2.3$ Hz) ppm. ^{19}F-NMR (C_6D_6; 30 °C): $\delta = -139.04$ (m, 2F); -159.32 (m, 1F); -163.75 (m, 2F) ppm. HR-MS: $M^+ = 224.0627$ amu. Calcd for $C_{10}H_9F_5$: 224.0624 amu.

Reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with $PhCF_3$: a) *Neat $PhCF_3$:* In the drybox, a small amount (ca. 20 mg) of $(MeC_5H_4)_3U(t\text{-}Bu)$ was dissolved in ca. 0.5 mL of $PhCF_3$. The dark green solution was placed in an NMR-tube equipped with a J. Young Teflon valve. The sample was then heated to 65 °C in a constant temperature bath for ca. 20 min, after which the solution was light green in color. The volatile materials were removed under reduced pressure and collected in a liquid nitrogen-cooled trap. The remaining solid was completely redissolved in ca. 0.5 mL of toluene-d_8. A ^{1}H-NMR spectrum revealed $(MeC_5H_4)_3UF$ as the only compound present. Among the volatile organic products, isobutane and isobutene were identified by comparison to known standards by GC. By GC-MS, Ph-CF_2-t-Bu could be identified:

m/e (>50 amu)	Intensity	Assignment
184	24	Ph-CF_2-t-Bu
169	4	Ph-CF_2-CMe_2
133	3	
127	37	Ph-CF_2
109	4	
91	6	
77	16	Ph
65	3	
57	100	t-Bu
51	10	

b) *Xylene Solution*: A small amount of $(MeC_5H_4)_3U(t\text{-}Bu)$ (10 mg, 19 μmol) was dissolved in ca. 0.5 mL of *p*-xylene-d_{10}. By microsyringe, 5 μL (41 μmol) $PhCF_3$ was added. The deep green solution was transferred to an NMR-tube equipped with a J. Young Teflon valve. A ^1H-NMR spectrum of the reaction mixture was acquired. The reaction mixture was allowed to react at 35 °C for 72 h, during which the reaction mixture gradually turned light green. No precipitate formed. A ^1H-NMR spectrum revealed $(MeC_5H_4)_3UF$ as the only organometallic product present in solution. In addition, isobutane and isobutene (ratio 1:1) were present accounting for all the initial t-butyl group intensity within experimental error. The volatile materials were then removed from the reaction mixture under reduced pressure and collected in a liquid nitrogen-cooled trap. By GC-MS of the volatile materials, no organic products other than isobutane, isobutene and unreacted $PhCF_3$ could be identified unambiguously.

Reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with C_7F_{14}: In the drybox, a small amount of $(MeC_5H_4)_3U(t\text{-}Bu)$ (15 mg, 29 μmol) was suspended in ca. 0.5 mL of C_7F_{14} in an NMR tube equipped with a J. Young Teflon valve. The mixture was heated to 65 °C for 6 h and then the volatile materials were removed in vacuo. Benzene-d_6 (ca. 0.8 mL) was added to the dry residue. A ^1H-NMR spectrum revealed $(MeC_5H_4)_3UF$ as the only organometallic species in solution. Some solid residue that would not redissolve in benzene-d_6 was removed by filtration. The benzene filtrate was taken to dryness, yielding 10 mg (70%) of $(MeC_5H_4)_3UF$.

Reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with C_6F_{12}: a) In the drybox, a small amount of $(MeC_5H_4)_3U(t\text{-}Bu)$ (8 mg, 15 μmol) was dissolved in ca. 0.5 mL of *o*-xylene-d_{10}. The solution was transferred to an NMR-tube equipped with a J. Young Teflon valve. A solid sample of C_6F_{12} (10 mg, 33 μmol) was dissolved in the solution. The sample was sealed and kept at room temperature in the dark for 12 h. The color of the solution gradually changed from deep-green to light-green. No precipitate had formed. A ^{1}H-NMR spectrum revealed $(MeC_5H_4)_3UF$ as the only organometallic species present. Isobutane and isobutene were present as well (approximate ratio 1:1). The volatile materials were removed under reduced pressure and collected in a liquid nitrogen-cooled trap. The presence of isobutane and isobutene among the volatile materials was confirmed by GC.

b) A solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.12 g, 0.22 mmol) and C_6F_{12} (0.33 g, 1.1 mmol) in 20 mL of toluene was stirred at room temperature in the dark for 24 h. Then the volatile materials were removed under reduced pressure and collected in a liquid nitrogen-cooled trap. A ^{1}H-NMR spectrum of the solid residue revealed the presence of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$ in a 1:1 ratio. Among the volatile materials, isobutane, isobutene and $C_6F_{11}H$ were detected by GC and GC-MS.

Reaction of $(MeC_5H_4)_3U(t\text{-}Bu)$ with C_6F_{12} and 9,10-Dihydroanthracene: A solution of $(MeC_5H_4)_3U(t\text{-}Bu)$ (0.12 g, 0.22 mmol), 9,10-dihydroanthracene (0.12 g, 0.66 mmol) and C_6F_{12} (0.33 g, 1.1 mmol) in 30 mL of toluene was stirred at room temperature in the dark for 12 h. Then the volatile materials were removed under reduced pressure and collected in a liquid nitrogen-cooled trap. A ^{1}H-NMR spectrum of the solid residue revealed the presence of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$ in a 20:1 ratio. Among the volatile materials, isobutane and anthracene were identified by comparison to known standards by GC. By GC-MS, $C_6F_{11}H$ could be identified:

m/e (>50 amu)	Intensity	Assignment
282	0.7	$C_6F_{11}H$
281	2	C_6F_{11}
231	14	C_5F_9
193	3	C_5F_7
181	20	C_4F_7
162	3	C_4F_6
131	100	C_3F_5
119	5	C_2F_5
100	31	C_2F_4
93	18	C_3F_3
74	4	C_3F_2
69	75	CF_3

$(MeC_5H_4)_3U(CH_2Ph)$: a) To a suspension of KCH_2Ph (0.22 g, 1.7 mmol) in 20 mL of toluene was added by cannula a solution of $(MeC_5H_4)_4U$ (0.89 g, 1.6 mmol) in 30 mL of toluene. After stirring the reaction mixture for 28 h, the solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of hexane. The hexane solution was filtered and the volume of the filtrate was reduced in vacuo to ca. 80 mL. Cooling to -20 °C yielded red-brown crystals of $(MeC_5H_4)_3U(CH_2Ph)$ (0.35 g). The volume of the mother liquor was reduced to ca. 25 mL. Cooling to -80 °C yielded a second crop of $(MeC_5H_4)_3U(CH_2Ph)$ (0.15 g) (combined yield: 55%), m.p. 95-97 °C dec.. ^1H-NMR (C_6D_6; 30 °C): $\delta = 1.40$ (t, 2H); 1.24 (s, 6H); 0.78 (s, 6H); -3.18 (t, 1H); -9.27 (s, 9H); -21.62 (d, 2H); -204.00 (s br., 2H) ppm. IR (KBr): 1590(m), 1490(m), 1380(s), 1210(m), 1040(w), 920(m), 910(m), 875(w), 860(w), 815(w), 800(s), 780(s), 745(m), 700(w) cm^{-1}. Anal. Calcd for $C_{24}H_{34}U$: C 53.0, H 4.99. Found: C 52.7, H 5.07.

b) To a suspension of KCH_2Ph (0.28 g, 2.2 mmol) in 25 mL of toluene was added by cannula a solution of $(MeC_5H_4)_3UCl$ (1.07 g, 2.09 mmol) in 50 mL of toluene. After stirring the reaction mixture for 4 h at room temperature, the solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of hexane. The hexane solution was filtered and the volume of the filtrate was reduced in vacuo to ca. 60 mL. Cooling to -80 °C yielded red-brown crystals of $(MeC_5H_4)_3U(CH_2Ph)$ (0.66 g, 56%). The materials obtained using methods a) and b) exhibited identical physical and spectroscopic properties.

5.4 Experimental Details: Chapter 3

$ThCl_4(tmeda)_2$: To a suspension of $ThCl_4$ (2.82 g, 7.54 mmol) in 60 mL of toluene was added by syringe tetramethylethylenediamine (tmeda) (3.66 mL, 24.75 mmol). After stirring for 3 d at room temperature the solution was filtered and concentrated to ca. 40 mL. Cooling the solution to -80 °C yielded white microcrystals of $ThCl_4(tmeda)_2$ (3.88 g, 84.9%). ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 2.78$ (s, 12H); 2.28 (s br., 4H) ppm. The values agree very closely with previously reported values.[9]

$(MeC_5H_4)_3ThCl$: a) To a solution of $ThCl_4$ (3.90 g, 10.4 mmol) in 100 mL of thf was added by syringe 21.0 mL (31.3 mmol, 1.49M in thf) of $Na(MeC_5H_4)$. The mixture was then heated at reflux for 30 h. Subsequently the solvent was removed under reduced pressure. The residue was extracted with toluene (2X 100 mL) at 80 °C. The volume of the combined extracts was reduced in vacuo to ca. 80 mL. Cooling to -80 °C yielded white microcrystals of $(MeC_5H_4)_3ThCl$ (1.72 g, 32.7%), m.p. 199-202 °C. ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 5.99$ (AA'BB', 6H); 5.84 (AA'BB', 6H); 2.23 (s, 9H) ppm. IR (CsI): 1485(m), 1350(w), 1260(w), 1240(w), 1065(w), 1045(w), 1025(s), 930(m), 885(w), 835(s), 780(s), 645(w), 610(w), 330(m), 245(s) cm^{-1}. EIMS: $M^+ = 504$ amu. Anal. Calcd for $C_{18}H_{21}ClTh$: C 42.8, H 4.20. Found: C 43.2, H 4.35.

b) To a solution of $ThCl_4(tmeda)_2$ (2.96 g, 4.88 mmol) in 50 mL of thf was added by syringe 16.3 mL of $Na(MeC_5H_4)$ (14.7 mmol, 0.90M in thf). After stirring for 9 h the solvent was removed under reduced pressure. The resulting solid was extracted with 150 mL of toluene at 70 °C. The volume of the toluene extract was reduced in vacuo to ca. 80 mL and cooling to -80 °C yielded white microcrystals of $(MeC_5H_4)_3ThCl$ (1.50 g, 60.9%). The materials obtained using methods a) and b) exhibited identical physical and spectroscopic properties.

$(MeC_5H_4)_3ThI$: To a solution of $(MeC_5H_4)_3ThCl$ (1.20 g, 2.38 mmol) in 140 mL of toluene was added by syringe trimethylsilyliodide (0.80 mL, 5.6 mmol) freshly vacuum-transferred from copper. The reaction mixture was kept in the dark and heated to 100 °C under a slow stream of dinitrogen for 41 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting solid was extracted with 50 mL of toluene at 100 °C. Following filtration, cooling of the toluene extract to -80 °C yielded a white powder of $(MeC_5H_4)_3ThI$ (0.33 g, 23%). The compound does not appear to melt up to 260 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 5.96 (s, 4H); 2.21 (s, 3H) ppm. EIMS: M^+ = 596 amu. Further characterization was not pursued.

$(MeC_5H_4)_3ThMe$: a) To a suspension of $(MeC_5H_4)_3ThCl$ (0.64 g, 1.3 mmol) in 100 mL of toluene was added by syringe 1.3 mL of MeLi (1.0M in diethyl ether, 1.3 mmol). The resulting mixture was stirred at room temperature for 5 h and then the solvent was removed under reduced pressure. The remaining solid was extracted with 90 mL of diethyl ether. After filtration the volume of the ether extract was reduced in vacuo to ca. 50 mL. Cooling to -80 °C yielded white shiny plates of $(MeC_5H_4)_3ThMe$ (0.32 g, 52%), m.p. 225-230 °C dec.. ^{1}H-NMR (C_6D_6; 30 °C): δ = 5.86 (AA'BB', 6H); 5.65 (AA'BB', 6H); 2.08 (s, 9H); 0.57 (s, 3H) ppm. ^{13}C-NMR (C_6D_6; 30 °C): δ = 116.99 (d of m, $^1J_{C\text{-}H}$ = 174 Hz); 115.00 (d of m, $^1J_{C\text{-}H}$ = 162 Hz); 42.54 (q, $^1J_{C\text{-}H}$ = 114 Hz); 15.06 (q, $^1J_{C\text{-}H}$ = 127 Hz) ppm. IR (KBr): 1491(w), 1400(w), 1350(w), 1242(w), 1091(w), 1064(w), 1048(w), 1031(m), 864(m), 846(s), 834(s), 797(s), 774(s), 617(w) cm^{-1}. Anal. Calcd for $C_{19}H_{24}Th$: C 47.1, H 5.00. Found: C 47.1, H 5.18. EIMS: M^+-H = 483 amu.

b) To a solution of $(MeC_5H_4)_4Th$ (0.13 g, 0.24 mmol) in 30 mL of diethyl ether was added by syringe 0.46 mL of MeLi (0.24 mmol, 0.52M in diethyl ether). The reaction mixture was stirred for 5 h at room temperature. The solution was filtered and the volume of the filtrate was reduced in vacuo to ca. 10 mL. Cooling to -80 °C yielded white shiny plates, which were filtered while the lab was thoroughly shaken for ca. 15 s in a magnitude 7.1 earthquake. Yield: 50 mg, 43.0%. The materials obtained under a) and b) exhibited identical physical and spectroscopic properties, and it was concluded that shaking has no effect on the physical properties.

$(MeC_5H_4)_4Th$: To a solution of $ThCl_4(tmeda)_2$ (3.47 g, 5.72 mmol) in 100 mL of thf was added by syringe $Na(MeC_5H_4)$ (22.5 mL 1.02M in thf, 23.0 mmol). After stirring the resulting mixture for 4 h the solvent was removed under reduced pressure. The white solid was extracted with 120 mL of toluene. After filtration of the toluene extract, toluene was removed under reduced pressure yielding a white powder of $(MeC_5H_4)_4Th$ (2.67 g, 85.2%). The compound does not appear to melt up to 260 °C. ^1H-NMR (C_6D_6; 30 °C): $\delta = 6.31$ (AA'BB', 2H); 5.91 (AA'BB', 2H); 2.17 (s, 3H) ppm. IR (KBr): 1494(m), 1244(m), 1042(s), 932(w), 894(w), 865(s), 852(s), 783(s), 760(s), 657(w), 602(s) cm^{-1}. Anal. Calcd for $C_{24}H_{28}Th$: C 52.5, H 5.15. Found: C 52.6, H 5.22. EIMS: $M^+ = 548$ amu.

$(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$: A solution of $(MeC_5H_4)_4Th$ (0.81 g, 1.5 mmol) in 35 mL of toluene was prepared. A solution of 2,6-Dimethylphenol (0.18 g, 1.5 mmol) in 20 mL of toluene was added by cannula. The mixture was heated to 70 °C for 48 h. After the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of hexane at 55 °C. After filtration the volume of the hexane extract was reduced in vacuo to ca. 80 mL. Cooling first to -20 °C then to -80 °C yielded thin white needles of $(MeC_5H_4)_3Th(O\text{-}2,6\text{-}Me_2C_6H_3)$ (0.61 g, 70%), m.p. 150-152 °C. ^1H-NMR (C_6D_6; 30 °C): $\delta = 7.06$ (m, 2H); 6.79 (m, 1H); 6.10 (s, 12H); 2.45 (s, 6H); 2.06 (s, 9H) ppm. IR

(KBr): 1592(w), 1493(w), 1424(w), 1413(w), 1295(w), 1271(s), 1243(w), 1227(s), 1094(m), 1070(w), 1048(w), 1032(w), 931(w), 860(m), 833(w), 798(w), 795(w), 781(w), 767(s), 741(w), 710(m), 614(w), 539(m) cm^{-1}. Anal. Calcd for $C_{26}H_{30}OTh$: C 52.9, H 5.12. Found: C 53.2, H 5.07. EIMS: $M^+ = 590$ amu.

$(MeC_5H_4)_3Th(O_3SC_6H_4Me)$: A solution of $(MeC_5H_4)_4Th$ (1.36 g, 2.48 mmol) in 65 mL of toluene was prepared. A solution of *p*-toluenesulfonic acid (0.43 g, 2.5 mmol) in 20 mL of toluene was added by cannula. Upon addition the colorless thorium solution turned bright yellow. The bright yellow color then gradually receded over ca. 20 min. The mixture was stirred at room temperature for an additional 20 h. The solution was filtered and the volume of the filtrate was reduced in vacuo to ca. 20 mL. Cooling to -80 °C yielded a white powder of $(MeC_5H_4)_3Th(O_3SC_6H_4Me)$ (0.87 g, 55%), m.p. 124-129 °C dec.. ^1H-NMR (C_6D_6; 30 °C): $\delta = 8.13$ (AA'BB', 2H); 6.91 (AA'BB', 2H); 6.05 (s, 12H); 2.13 (s, 9H); 1.94 (s, 3H) ppm. IR (KBr): 1599(m), 1495(m), 1396(w), 1259(s), 1215(m), 1162(s), 1107(s, br.), 1035(s), 1009(s), 979(w), 936(w), 890(w), 850(s), 817(s), 777(s), 731(m), 710(w), 695(w), 680(s), 636(w), 611(w), 598(w), 565(s), 551(s) cm^{-1}. Anal. Calcd for $C_{25}H_{28}O_3STh$: C 46.9, H 4.41. Found: C 47.0, H 4.40. EIMS: $M^+-H = 639$ amu.

$[(MeC_5H_4)_3Th(NMe_3)][BPh_4]$: A solution of $(MeC_5H_4)_3ThMe$ (0.66 g, 1.4 mmol) in 50 mL of toluene was added to $(Me_3NH)(BPh_4)$ (0.51 g, 1.3 mmol). The resulting suspension was stirred at room temperature for 72 h. The solvent was removed under reduced pressure. The resulting solid was washed with 10 mL of hexane and dried under reduced pressure. Yield: 1.07 g, 94.2%. ^1H-NMR (thf-d_8; 30 °C): $\delta = 7.29$ (m br., 8H); 6.87 (m, 12H); 6.51 (AA'BB', 6H); 6.31 (AA'BB', 6H); 2.39 (s, 9H); 2.15 (s, 9H) ppm. The resonance at $\delta = 2.15$ ppm corresponds to free trimethylamine. The other chemical shift values agree very closely with previously reported values.[10]

$(MeC_5H_4)_3Th(CH_2Ph)$: A solution of $ThCl_4(tmeda)_2$ (0.61 g, 1.0 mmol) in 100 mL of toluene was cooled to -78 °C. By syringe, 0.45 mL of t-BuLi (2.24M in hexane, 1.01 mmol) was added, and the reaction mixture was stirred at -78 °C for 6 h. $Na(MeC_5H_4)$ (3.0 mL 1.02M in thf, 3.1 mmol) was added by syringe, the solution turning bright yellow upon addition. The reaction mixture was stirred at -78 °C for 30 min and then allowed to warm gradually to 0 °C. The solvent was removed under reduced pressure and the resulting solid was extracted with 120 mL of hexane. After filtration, the hexane filtrate was taken to dryness under reduced pressure. The resulting solid was washed with 10 mL of hexane at -20 °C and dried under reduced pressure, leaving a white powder of $(MeC_5H_4)_3Th(CH_2Ph)$ (0.56 g, 99%). ^1H-NMR (C_6D_6; 30 °C): $\delta = 7.36$ (d br., 1H); 7.28 (m, 2H); 7.26 (s br., 2H); 5.79 (s, 12H); 2.40 (s, 2H); 2.00 (s, 9H) ppm. Further characterization was not pursued.

$(Me_3SiC_5H_4)_3ThCl$: To a suspension of $ThCl_4$ (2.63 g, 7.04 mmol) in 50 mL of thf was added by syringe $K(Me_3SiC_5H_4)$ (23.0 ml 0.92M in diethyl ether; 21.2 mmol). The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the resulting white solid was extracted with 150 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 80 mL. Cooling to -80 °C yielded white crystals of $(Me_3SiC_5H_4)_3ThCl$ (1.28 g, 26.8%). ^1H-NMR (C_6D_6; 30 °C): $\delta = 6.40$ (s, 4H); 0.36 (s, 9H) ppm. The values agree very closely with previously reported values.[3]

$(Me_3SiC_5H_4)_3ThMe$: To a solution of $(Me_3SiC_5H_4)_3ThCl$ (1.09 g; 1.60 mmol) in 50 mL of diethyl ether was added by syringe MeLi (2.60 mL 0.66M in diethyl ether; 1.7 mmol). A white precipitate formed within seconds. The reaction mixture was stirred at room temperature for 24 h and then the solvent was removed under reduced pressure.

The resulting thick oil was extracted with 40 mL of hexane. After filtration, the solvent was removed under reduced pressure from the hexane extract, leaving behind a yellow oil of $(Me_3SiC_5H_4)_3ThMe$ (0.76 g; 72%). ^1H-NMR (C_6D_6; 30 °C): δ = 6.24 (s, 12H); 0.74 (s, 3H), 0.32 (s, 27H) ppm. ^{13}C-NMR (C_6D_6; 30 °C): δ = 125.3 (m); 124.5 (d of m, $^1J_{C\text{-}H}$ = 167 Hz); 119.2 (d of m, $^1J_{C\text{-}H}$ = 167 Hz); 37.3 (q, $^1J_{C\text{-}H}$ = 115 Hz); 1.3 (q, $^1J_{C\text{-}H}$ = 118 Hz) ppm. The ^1H-NMR spectrum agrees very closely with previously reported values.[10]

$(Me_3SiC_5H_4)_3Th(CH_2Ph)$: A solution of $(Me_3SiC_5H_4)_3ThCl$ (1.00 g, 1.47 mmol) in 35 mL of toluene was added by cannula to a suspension of $K(CH_2Ph)$ (0.21 g, 1.6 mmol) in 30 mL of toluene. The reaction mixture was stirred at room temperature for 72 h. The solvent was removed under reduced pressure. The resulting sticky solid was extracted with 50 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 5 mL. Cooling to -80 °C yielded white crystalline material. The crystals were collected by filtration at -80 °C and dried under reduced pressure. Upon warming to room temperature, the crystals appeared to desolvate, leaving behind a waxy solid of $(Me_3SiC_5H_4)_3Th(CH_2Ph)$ (0.55 g, 51%). ^1H-NMR (C_6D_6; 30 °C): δ = 7.37-7.32 (complex pattern, 5H); 6.47 (AA'BB', 6H); 2.63 (s, 2H); 0.33 (s, 27H) ppm. Further characterization was not pursued.

$[(Me_3SiC_5H_4)_3Th][BPh_4]$: A solution of $(Me_3SiC_5H_4)_3ThMe$ (1.09 g, 1.65 mmol) in 40 mL of toluene was added by cannula to a suspension of $(Me_3NH)(BPh_4)$ (0.66 g, 1.7 mmol) in 20 mL of toluene. The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of toluene at 55 °C. After filtration, the volume of the toluene extract was reduced to ca. 50 mL. Cooling to -80 °C yielded 0.47 g (30%) of $[(Me_3SiC_5H_4)_3Th][BPh_4]$. ^1H-NMR (thf-d_8; 30 °C): δ = 7.30 (m, 8H); ; 7.00 (AA'BB', 6H); 6.86 (m, 12H); 6.66 (AA'BB', 6H), 0.38 (s, 27H) ppm. The ^{1}H-NMR spectrum agrees very closely with previously reported values.[10]

$(Me_3SiC_5H_4)_3ThH$: a) To a solution of $[(Me_3SiC_5H_4)_3Th][BPh_4]$ (0.36 g, 0.37 mmol) in 80 mL of toluene was added by syringe t-BuLi (0.17 mL 2.24M in hexane, 0.38 mmol). Within 1 min, the solution became cloudy. The reaction mixture was stirred at room temperature for 11 h and then the solvent was removed under reduced pressure. The resulting solid was extracted with 30 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 5 mL. Cooling to -80 °C yielded white crystals of $(Me_3SiC_5H_4)_3ThH$ (0.15 g, 62%), m.p. 87-89 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 12.81 (s, 1H); 6.31 (AA'BB', 6H); 5.68 (AA'BB', 6H); 0.41 (s, 27H) ppm. IR (KBr): 1444(s), 1415(m), 1403(m), 1366(m), 1311(w), 1249(s), 1191(w), 1176(s), 1093(m), 1062(m), 1041(s), 902(s), 885(m), 860(s), 834(s), 810(s), 796(s), 783(s), 774(s), 756(s), 688(m), 635(s), 629(s), 596(m), 523(m) cm^{-1}. Anal. Calcd for $C_{24}H_{40}Th$: C 44.7, H 6.26. Found: C 43.2, H 6.37. EIMS: M^+-H = 643 amu.

b) To a solution of $(Me_3SiC_5H_4)_3ThCl$ (1.28 g, 1.88 mmol) in 40 mL of thf was added by syringe $Li(BHEt_3)$ (2.0 mL 1.0M in thf, 2.0 mmol). The reaction mixture was stirred at room temperature for 3 h. Then the solvent was removed under reduced pressure. The resulting oily solid was extracted with 50 mL of hexane. After filtration, the volume of the hexane extract was reduced to ca. 10 mL. Cooling to -80 °C yielded white crystals of $(Me_3SiC_5H_4)_3ThH$ (0.32 g, 26%). The materials obtained using methods a) and b) exhibited identical physical and spectroscopic properties.

$(t\text{-}BuC_5H_4)_3ThCl$: To a suspension of $ThCl_4$ (2.76 g, 7.38 mmol) in 30 mL of thf was added by syringe $Na(t\text{-}BuC_5H_4)$ (105 mL 0.22M in thf, 23.1 mmol). The reaction mixture was stirred at room temperature for 48 h and then the solvent was removed under reduced pressure and the resulting solid was extracted with 150 mL of hexane. After filtration, the saturated hexane extract was cooled to -20 °C and after 3 h to -80 °C yielding colorless crystals of $(t\text{-}BuC_5H_4)_3ThCl$ (1.56 g). The crystals were isolated by filtration and dried under reduced pressure. The reaction mixture residue was reextracted with 100 mL of hexane. After filtration, the second hexane extract was combined with the mother liquor from the first hexane extraction. The volume of the combined extracts was reduced to ca. 100 mL. Cooling to -80 °C yielded an additional 0.80 g of $(t\text{-}BuC_5H_4)_3ThCl$. Combined yield: 2.36 g (50.7%), m.p. 160-163 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 6.21 (AA'BB', 2H); 5.98 (AA'BB', 2H); 1.37 (s, 9H) ppm. IR (KBr): 1482(m), 1436(w), 1397(m), 1384(m), 1365(s), 1361(s), 1356(s), 1274(s), 1199(m), 1190(m), 1154(s), 1047(m), 1037(m), 1027(m), 924(m), 913(m), 857(m), 849(m), 834(s), 834(s), 826(m), 816(m), 798(s), 786(s), 780(s), 767(s), 679(m), 667(m) cm^{-1}. Anal. Calcd for $C_{27}H_{39}ClTh$: C 51.4, H 6.24. Found: C 51.3, H 6.15. EIMS: M^+ = 630 amu.

$(t\text{-}BuC_5H_4)_3ThMe$: To a solution of $(t\text{-}BuC_5H_4)_3ThCl$ (1.41 g, 2.23 mmol) in 50 mL of diethyl ether was added by syringe methyllithium (5.8 mL 0.40M in diethyl ether, 2.3 mmol). A white precipitate formed upon addition of methyllithium. The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure. The resulting solid was extracted with 50 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 35 mL. Cooling to -80 °C yielded colorless blocks of $(t\text{-}BuC_5H_4)_3ThMe$ (0.90 g, 66%), m.p. 108-110 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 6.03 (AA'BB', 6H); 5.91 (AA'BB', 6H); 1.31 (s, 27H), 0.85 (s, 3H) ppm. ^{13}C-NMR (C_6D_6; 30 °C): δ = 143.3 (m); 115.0 (d of m, $^1J_{C\text{-}H}$ = 167 Hz); 114.0 (d of m, $^1J_{C\text{-}H}$ = 165 Hz); 42.2 (q, $^1J_{C\text{-}H}$ = 114 Hz); 33.1 (m); 32.3 (q of m, $^1J_{C\text{-}H}$ = 125 Hz) ppm. IR (KBr): 1480(m), 1410(w), 1395(m), 1365(s), 1355(s), 1275(s), 1195(w), 1190(w), 1155(s), 1095(m), 1050(m), 1035(m), 1020(w), 925(w), 910(w), 845(m), 825(s), 820(s), 815(m), 790(s), 780(s), 770(s), 760(s), 675(m), 670(m) cm^{-1}. Anal. Calcd for $C_{28}H_{42}Th$: C 55.1, H 6.95. Found: C 55.2, H 6.97. EIMS: M^{+}-Me = 595 amu.

[(t-BuC$_5$H$_4$)$_3$Th][BPh$_4$]: A solution of (t-$BuC_5H_4)_3ThMe$ (0.47 g, 0.77 mmol) in 20 mL of thf was cooled to -60 °C and then added by cannula to a solution of $(Et_3NH)(BPh_4)$ (0.32 g, 0.76 mmol) in 10 mL of thf, also cooled to -60 °C. The reaction mixture was allowed to warm to room temperature and then stirred at room temperature for 3 h. The solvent was removed under reduced pressure. The resulting solid was washed with 30 mL of hexane and dried under reduced pressure, yielding 0.64 g (92%) of [(t-$BuC_5H_4)_3Th][BPh_4]$, m.p. 149-155 °C. ^{1}H-NMR (thf-d_8; 30 °C): δ = 7.31 (m, 8H); 6.85 (m, 12 H); 6.69 (AA'BB', 6H); 6.41 (AA'BB', 6H), 1.39 (s, 27H) ppm. IR (KBr): 1591(w), 1580(w), 1478(s), 1430(m), 1363(s), 1342(w), 1277(m), 1240(m), 1155(m), 1066(w), 1042(m), 1033(m), 1022(w), 915(w), 844(m), 822(m), 815(m), 779(s, br.), 759(m), 744(m), 735(s), 705(s), 667(w), 612(m) cm^{-1}. Anal. Calcd for $C_{51}H_{59}BTh$: C 66.9, H 6.51. Found: C 67.3, H 6.71.

(t-BuC$_5$H$_4$)$_3$ThH: A suspension of [(t-$BuC_5H_4)_3Th][BPh_4]$ (0.50 g, 0.55 mmol) in 20 mL of hexane was cooled to -78 °C. Then t-BuLi (0.25 mL 2.24M in hexane, 0.56 mmol) was added by syringe. The reaction mixture was allowed to warm to room temperature and the mixture was stirred at room temperature for 24 h. The solid was allowed to settle and the solution was filtered. The volume of the filtrate was reduced in vacuo to ca. 10 mL. Cooling to -20 °C yielded colorless crystals of (t-$BuC_5H_4)_3ThH$ (0.20 g, 61%), m.p. 143-148 °C. ^{1}H-NMR (C_6D_6; 30 °C): δ = 13.98 (s, 1H); 6.06 (AA'BB', 6H); 5.47 (AA'BB', 6H); 1.43 (s, 27H) ppm. IR (KBr): 1485(s), 1437(s), 1420(s), 1393(s), 1383(s), 1363(s), 1359(s), 1278(s), 1202(m), 1190(m), 1155(s), 1049(s), 1043(s), 1023(s), 915(s), 842(s), 825(s), 818(s), 784(s), 773(s), 762(s), 676(s), 613(w), 578(m), 571(m) cm^{-1}. Anal. Calcd for $C_{27}H_{40}Th$: C 54.3, H 6.77. Found: C 54.5, H 6.94. EIMS: $M^+ = 596$ amu.

5.5 Experimental Details: Chapter 4

$(MeC_5H_4)_4U$: To a solution of UCl_4 (1.89 g, 4.98 mmol) in 60 mL of thf was added by cannula a solution of $Na(MeC_5H_4)$ (2.05 g, 20.1 mmol) in 60 mL of thf. Upon addition, the green uranium solution turned deep red. After stirring for 24 h the solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of toluene at 65 °C. After filtration of the toluene extract at 65 °C, the toluene was removed under reduced pressure, yielding a deep red powder of $(MeC_5H_4)_4U$ (2.08 g, 75.3%), m.p. 248-252 °C. ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 0.94$ (s, 3H); -13.44 (s, 2H); -14.84 (s, 2H) ppm. IR (KBr): 1496(w), 1255(m), 1075(w), 1042(s), 914(s), 874(s), 850(s), 799(s), 774(s), 612(m), 598(m) cm^{-1}. Anal. Calcd for $C_{24}H_{28}U$: C 52.0, H 5.10. Found: C 51.8, H 5.03. EIMS: $M^+ = 554$ amu.

$(C_5H_5)_4U$: To a solution of UCl_4 (0.21 g, 0.55 mmol) in 30 mL of thf was added by syringe $Na(C_5H_5)$ (1.6 mL 1.42M in thf, 2.3 mmol). Upon addition, the uranium solution turned raspberry-red. The reaction mixture was stirred at room temperature for 10 h and then the solvent was removed under reduced pressure. The resulting solid was extracted with 130 mL of toluene at 60 °C. After filtration at 60 °C, the toluene filtrate was allowed to cool to room temperature, resulting in formation of red microcrystals. The toluene filtrate was cooled further to -80 °C, yielding red microcrystals of $(C_5H_5)_4U$ (30 mg, 11%). ^{1}H-NMR (C_6D_6; 30 °C): $\delta = -12.85$ (s) ppm. The value agrees very closely with the previously reported value.[14]

$(Me_3SiC_5H_4)_2Hg$: In the dark, a solution of $Na(Me_3SiC_5H_4)$ (20.5 mL 0.47M in thf, 9.6 mmol) was added by syringe to a solution of $HgCl_2$ (1.29 g, 4.75 mmol) in 50 mL of diethyl ether at -50 °C. The solution instantly turned lemon-yellow. The reaction mixture was stirred at -50 °C for 15 min and then was allowed to warm to room temperature. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure. The resulting solid was extracted with 100 mL of diethyl ether. After filtration, the volume of the filtrate was reduced in vacuo to ca. 15 mL. Cooling to -80 °C yielded 1.30 g (57.7%) of lemon-yellow, light sensitive needles of $(Me_3SiC_5H_4)_2Hg$, m.p. 80-83 °C. ^{1}H-NMR (C_6D_6; 30 °C): $\delta = 6.75$ (m, $^2J_{Hg-H} = 38.5$ Hz, 2H); 6.29 (m, $^2J_{Hg-H} = 13.7$ Hz, 2H); -0.02 (s, 9H) ppm. IR (KBr): 1407(m), 1383(m), 1249(s), 1128(m), 1027(m), 993(m), 899(w), 862(s), 844(s), 834(s), 826(s), 802(s), 755(s), 748(s), 740(s), 730(s), 717(s), 711(s), 689(s), 625(m) cm^{-1}. Anal. Calcd for $C_{16}H_{26}HgSi_2$: C 40.4, H 5.53. Found: C 40.8, H 5.66. EIMS: M$^+$ = 476 amu, isotopic cluster.

$[(Me_3Si)_2C_5H_3]_2Hg$: In the dark, a solution of $[(Me_3Si)_2C_5H_3]_2Mg$ (0.77 g, 1.7 mmol) in 25 mL of diethyl ether was added by cannula to a solution of $HgCl_2$ (0.47 g, 1.7 mmol) in 60 mL of diethyl ether at -60 °C. The reaction mixture was stirred at -60 °C for 15 min and then was allowed to warm to room temperature. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure. The resulting solid was extracted with 50 mL of hexane. After filtration, the volume of the hexane extract was reduced in vacuo to ca. 5 mL. Cooling to -80 °C yielded pale-yellow, light sensitive crystals of $[(Me_3Si)_2C_5H_3]_2Hg$ (0.99 g, 92%), m.p. 30-31 °C. ^{1}H-NMR (C_7D_8; 28 °C): $\delta = 6.64$ (d, $^4J_{H-H} = 1.5$ Hz, $^2J_{Hg-H} = 29.2$ Hz, 2H); 6.37 (t, $^4J_{H-H} = 1.5$ Hz, $^2J_{Hg-H} = 13.7$ Hz, 1H); 0.13 (s, 18H) ppm. IR (KBr): 1502(m), 1442(m), 1412(s), 1339(m), 1313(m), 1278(m), 1260(s), 1248(s), 1159(m), 1128(m), 1068(m), 1051(m), 1020(s), 903(s), 879(s), 844(s), 835(s), 825(s), 814(vs), 751(s), 730(s), 718(s), 690(s), 624(s) cm^{-1}. Anal. Calcd for $C_{22}H_{42}HgSi_4$: C 42.6, H 6.85. Found: C 42.2, H 6.81. EIMS: M$^+$ = 620 amu, isotopic cluster.

$(Me_3SiC_5H_4)_4U$: To a solution of $(Me_3SiC_5H_4)_3U$ (0.55 g, 0.85 mmol) in 40 mL of toluene was added by cannula a solution of $(Me_3SiC_5H_4)_2Hg$ (0.21 g, 0.44 mmol) in 25 mL of toluene, that was kept in the dark. Upon addition, the deep-green uranium solution turned red-brown within 1 min and droplets of metallic mercury became visible. The reaction mixture was stirred at room temperature for 5 h. The solution was filtered and the volume of the filtrate was reduced in vacuo to ca. 20 mL. Cooling to -80 °C yielded red-brown crystals of $(Me_3SiC_5H_4)_4U$ (0.36 g, 54%). ^{1}H-NMR (C_6D_6; 30 °C): δ = -1.94 (s, 9H); -10.27 (s, 2H); -22.13 (s, 2H) ppm. The values agree very closely with previously reported values.[3]

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