**Reaction of Tris(cyclopentadienyl)uranium Compounds
with Amines, Azides, and Related Ligands**

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Abstract

The trivalent uranium compound, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, serves as a one- or two-electron reducing agent towards azides, RN_3 . These reactions produce either the uranium(IV) azide, $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, or uranium(V) imides, $(\text{MeC}_5\text{H}_4)_3\text{UNR}$. The role of steric and electronic effects upon this reaction has been investigated using several series of azides. For Me_3XN_3 , the imides are produced when $\text{X} = \text{C}$ or Si , both products are formed when $\text{X} = \text{Ge}$, and the azide is produced when $\text{X} = \text{Sn}$. For Ph_3XN_3 , the azide is produced when $\text{X} = \text{C}$ or Sn . For $\text{Ph}_{3-x}\text{CH}_x\text{N}_3$, the imide is produced when $x = 2$ and both compounds are produced when $x = 1$. For substituted phenylazides, $\text{RC}_6\text{H}_4\text{N}_3$, only the imides are produced.

$(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ forms an adduct with the Lewis acid AlMe_3 . $(\text{RC}_5\text{H}_4)_3\text{UN}_3$ also forms an adduct with $(\text{RC}_5\text{H}_4)_3\text{U}$ ($\text{R} = \text{Me}$ or SiMe_3). The azide ligand is displaced upon reaction with $\text{Co}_2(\text{CO})_8$ to form $(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}[\text{Co}_3(\text{CO})_9]$.

The magnetic moments of the imides were measured to be $\mu_{\text{eff}} = 1.2 - 1.6$ B.M. (5-40 K), and $\mu_{\text{eff}} = 1.8 - 2.3$ B.M. (ca. 140 -280 K). $(\text{MeC}_5\text{H}_4)_3\text{UNAr}$ ($\text{Ar} = p\text{-tolyl}$) acts as an oxidizing agent; a mixture of this imide and the uranium(III) amine $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{Ar})$ yields the uranium(IV) amide, $(\text{MeC}_5\text{H}_4)_3\text{UNHAr}$. $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ inserts CO to give the bridged phenylisocyanate compound $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2-\mu\text{-PhNCO}$. The imides also are

reduced by azides to give $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, by $\text{Co}_2(\text{CO})_8$ to give $(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}[\text{Co}_3(\text{CO})_9]$, and by alcohols to give $(\text{MeC}_5\text{H}_4)_3\text{UOR}$.

The magnetic properties of uranium diimides, $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-NRN})$, were investigated. When $\text{NRN} = 1,4\text{-N}_2\text{C}_6\text{H}_4$, the compound is antiferromagnetic ($T_N = \text{ca. } 18 \text{ K}$; $J = \text{ca. } -19 \text{ cm}^{-1}$). For $1,3\text{-N}_2\text{C}_6\text{H}_4$, as well as stilbene and naphthalene diimides, no magnetic exchange is observed.

Several uranium(III) amines, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{R})$, were produced from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and RNH_2 , and NH_3 was found to be a better ligand towards $(\text{MeC}_5\text{H}_4)_3\text{U}$ than is PMe_3 . $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-1,4-(NH}_2)_2\text{C}_6\text{H}_4)$ was prepared and does not exhibit electronic exchange between the metal centers. The amines may be oxidized to $(\text{MeC}_5\text{H}_4)_3\text{UNHR}$ thermally or chemically; the rate of thermolysis was found to be first-order in $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{R})$.

$(\text{MeC}_5\text{H}_4)_3\text{UMe}$ is formed from $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ and AlMe_3 .

$(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$ is produced from either $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$,

$(\text{MeC}_5\text{H}_4)_3\text{UR}$ ($\text{R} = \text{Me, } ^i\text{Bu}$), or $(\text{MeC}_5\text{H}_4)_4\text{U}$ and phenylhydrazine; this phenylhydrazido(1-) complex may be thermolyzed to the amide, $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$.

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In the spring of 1984, I visited Berkeley on a rainy day. While walking from Latimer to the Faculty Club for lunch, Dick Andersen told me that he had become hooked on synthetic organometallic chemistry the first time he made an emerald green compound. Dick, I truly believe you about that, and never has a single comment and the way in which it was spoken had such an influence on my life. Right there, I decided on Berkeley, on working with you, and on organometallics, and it is a decision I will never regret for a moment. I don't expect to ever meet anyone with such a passion for chemistry. I have learned to think about molecules, to stand up for my ideas... the list of what you have taught is endless. I hope I've made you a tiny bit more famous in my time in the center of the universe; at the very least I hope you're pleased with what you got, because I certainly got so much from you. I will deeply miss talking science, baseball, and life with you, and hope we'll still get the chance. Every once in awhile you'll want to revoke this thing; do me a favor and resist the temptation.

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**to my parents
for supporting and loving me**

and

**to Dick
for teaching me**

Introduction

The field of organoactinide chemistry was established with the synthesis of Cp_3UCl and Cp_3ThCl by Reynolds and Wilkinson in 1956.¹ However, it was the proposal by R. D. Fischer that *f*-orbitals could properly overlap with the cyclooctatetraene dianion² and the subsequent synthesis of uranocene, $(\text{C}_8\text{H}_8)_2\text{U}$, by Streitwieser and Müller-Westerhoff in 1968³ that sparked the interest in the organometallic chemistry of the *f*-metals.

There are a number of reasons for choosing an actinide rather than a lanthanide to study the synthesis and reactivity of *f*-metal complexes. In the lanthanide series, the 4*f* electrons are, due to inefficient nuclear shielding, essentially core electrons; their energies are below those of the 5*s* and 5*p* electrons. Thus, these 4*f*-orbitals do not possess the spatial extent necessary for interaction with the ligand orbitals, and the bonding in lanthanide complexes is considered to be essentially ionic.⁴ Additionally, the oxidation states of the lanthanides are rather limited. All of the ions exhibit stable +3 states, Yb, Sm, Tm, and Eu have stable +2 oxidation states, and Ce, Tb, Nd, and Pr have stable +4 states.⁴ This, of course, limits the potential redox chemistry of these metals.

These factors, however, are different in the 5*f* series. In the early actinides, the 5*f*-orbitals are of similar energy to the 6*s*- and 6*p*-orbitals. This results in a greater radial extension of these *f*-orbitals, and allows the 5*f* and 6*d* electrons to participate in more covalent bonding interactions.⁴ Recent results by Stults and Brennan have dramatically shown this by demonstrating the effect of π -backbonding interactions in uranium(III) complexes.⁵ Although only uranium and thorium are available for the study of large scale

synthetic chemistry of the actinides, the wide variety of oxidation states available for uranium makes it an attractive element. While thorium has only a stable +4 oxidation state (and a much less stable +3), oxidation states in uranium range from +3 to +6.⁴ The bulk of the organometallic chemistry of uranium to date has utilized the tetravalent oxidation state, although in recent years study of the trivalent compounds has been undertaken in more detail.⁶

In 1985, Brennan and Andersen initiated the study of pentavalent organouranium compounds with the syntheses of the cyclopentadienyl uranium imide complexes $(\text{RC}_5\text{H}_4)_3\text{UNR}'$.⁷ Because no other organometallic compounds of uranium in the +5 state exist, we set out in work described in this thesis to study the syntheses of these materials and to elucidate their physical and chemical properties in more detail. Chapter 1 concentrates on these investigations. Transition metal imido complexes have been extensively investigated over the last 20-30 years,⁸ and comparisons of the properties and reactivity of our f-metal imide compounds with the d-metal materials will be discussed. As a consequence of the synthetic route into these uranium(V) imides, we synthesized tetravalent uranium azides, $(\text{RC}_5\text{H}_4)_3\text{UN}_3$. Although Cp_3UN_3 has been reported previously,^{6a} little information concerning this compound is available, and thus we felt it would be interesting to study the properties and the chemical reactions of the uranium azides. Azide compounds of main group and transition metals have been the subject of a great deal of study,⁹ and once again we would like to compare the differences and similarities between these compounds and our f-metal species. These azides are also discussed in Chapter 1.

Because of the core-like behavior of the 4f electrons, magnetic susceptibility measurements on compounds of the lanthanide series generally

yield magnetic moments close to that calculated for the free ion.⁴ Conversely, the magnetic moments of the actinide ions are complicated by spin-orbit coupling. The $5f^1$ system found in the pentavalent uranium complexes should be somewhat easier to interpret, and we therefore have investigated the magnetic behavior of several of the uranium imides, and these data are presented in Chapter 1.

One of the consequences of working with these $5f^1$ systems is the possibility of observing magnetic interactions between two pentavalent uranium atoms. This would require the synthesis of a compound containing an appropriate bridging ligand between the metal centers. This possibility is of particular interest in these systems because it has been proposed that $5f^n$ systems with half-integer values of J are most likely to exhibit magnetic ordering,¹⁰ and for $5f^1$, $J = 5/2$. Only in the extended lattice systems in the halides of uranium(III) and plutonium(III) (UCl_3 , UBr_3 , UI_3 , $PuCl_3$) has antiferromagnetic coupling been observed;¹¹ no discrete, molecular compound of the actinides has ever been found to exhibit this phenomenon. Very few compounds in the 4f series have been found in which the lanthanide atoms show evidence of magnetic exchange; the only published example is $Cp_4Dy_2(\mu-Br)_2$,¹¹ although several ytterbium compounds prepared by J. Boncella and D. Berg also exhibit this behavior.¹² Chapter 2 discusses the synthesis and properties of several dinuclear uranium diimide complexes, with a particular focus upon the magnetic behavior of these materials. Included among these compounds is one which exhibits the first example of antiferromagnetic coupling seen in a molecular actinide system.

The results we obtained using the imido ligand led us to study other nitrogen-containing materials. Nitrogen ligands are often reasonably good Lewis bases and thus should be reactive towards the actinide metal center; in

addition the presence of the lone pair on the nitrogen could give rise to further interesting reactivity and the formation of other novel uranium compounds. Many interesting types of nitrogen compounds exist, such as azides (used in the synthesis of the uranium imide and azide compounds), amines, and hydrazines, and these are known to be quite reactive. In particular, we were interested in synthesizing and studying families of related uranium compounds with the metal in different oxidation states, such as the series shown below:

Chapter 3 discusses the synthesis of uranium(III) primary amine complexes, as well as the oxidation of these materials to the corresponding uranium(IV) amides. No compounds of this type had been previously prepared in the f-metal series. A dinuclear diamine complex of uranium was also prepared, and the magnetism investigated in search of interactions such as those seen in the uranium(V) compounds discussed in Chapter 2. In addition, Chapter 3 will also report several reactions forming uranium(IV) hydrazide compounds, and the unusual thermolysis reaction of these materials resulting in the cleavage of the N-N bond.

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Chapter 1

Preparation and Reactions of Tris(cyclopentadienyl)uranium Azide and Imide Compounds

While a great deal of attention has been paid in recent years to organouranium chemistry in the +3 and +4 oxidation states, pentavalent uranium compounds have remained relatively rare. Indeed, the only compounds known of U(V) as of the mid-1980's were the pentavalent halides, UX_5 (and related compounds such as UF_6 and Na_3UF_6), the cationic oxide, UO_2^+ , and the oxychloride, $UOCl_3$.¹ In 1984, Brennan and Andersen reported the two-electron oxidation of $(MeC_5H_4)_3U(thf)$ by phenylazide to give the stable pentavalent imido complex $(MeC_5H_4)_3UNPh$ and dinitrogen (Scheme 1-1).²

Scheme 1-1: Preparation of a pentavalent uranium imide.

This was the first organometallic derivative of uranium(V). In addition to the crystal structure, the evidence for the presence of the unusual oxidation state of the metal center is supported by the relatively broad linewidths in the 1H NMR spectrum, giving MeC_5H_4 ring resonances with widths of $\nu_{1/2} = 40 - 60$ Hz. It has been noted that uranium(III) and uranium(V) compounds

generally exhibit linewidths an order of magnitude greater than similar uranium(IV) compounds.³ In addition, Berg obtained magnetic susceptibility data on the related compound, $\text{Cp}_3\text{UNSiMe}_3$, which indicated that the uranium is pentavalent.⁴

Due to an interest in further examining the properties and reactivity of these pentavalent uranium complexes, we undertook the study of the reactions of trivalent uranium with a wide variety of azides. Early in this work, we came upon a reaction which demonstrated a second possible pathway by which these reactions could proceed. When a solution of trityl azide (Ph_3CN_3) in diethylether was added to $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, a light green precipitate was obtained immediately. This is in marked contrast with the products that had previously been isolated from analogous reactions: there was no noticeable evolution of gas, and the pentavalent complexes $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ are quite soluble in ether as well as being very intensely colored. The pale green material could be recrystallized from either toluene or dichloromethane to yield green microcrystals. The ^1H NMR spectrum of this material showed narrow line widths for the ring protons on the cyclopentadiene ($\nu_{1/2} = <10$ Hz), and the infrared spectrum exhibited a strong, broad stretch at 2115 cm^{-1} .

This evidence suggested that the trivalent uranium had simply undergone a one-electron oxidation, with transfer of the azide group from the trityl group to the uranium, as shown below (Scheme 1-2).

Scheme 1-2: Formation of a uranium(IV) azide from trivalent uranium and tritylazide

It would then follow that the by-product from the reaction would be the relatively stable trityl radical, which would presumably then dimerize to form the well studied (and well debated) trityl dimer, or "hexaphenylethane."⁵ This was confirmed by performing the reaction of $(\text{MeC}_6\text{H}_4)_3\text{U}(\text{thf})$ with tritylazide in an NMR tube in deuterated benzene, and observing the ^1H NMR spectrum of the products. Several distinctive peaks can be easily seen in this spectrum, as shown in Figure 1-1. These include:

1. The three peaks from the tetravalent uranium complex $(\text{MeC}_6\text{H}_4)_3\text{UN}_3$, located at $\delta = 11.3$ ppm, -3.2 ppm, and -17.8 ppm.
2. The peaks resulting from tetrahydrofuran, seen as multiplets at $\delta = 3.55$ ppm and 1.40 ppm.
3. The peaks from the trityl dimer.^{5d,5e} These are located at $\delta = 4.9$ ppm (H_A , singlet), 5.95 ppm (H_b , doublet of doublets), and 6.45 ppm (H_c , doublet). There are also several resonances from the phenyl ring protons seen between $\delta = 7.0$ and 7.3 ppm.

The diagram below (Figure 1-2) of the currently accepted structure for this dimer^{5c} shows the designations of the protons:

Figure 1-2: The structure of the trityl dimer.

Reactions in which an organoazide functions as an azide transfer reagent are not without precedent, either in organic, inorganic, or transition metal chemistry,⁶ although these reactions generally involve replacement of

Figure 1-1: ^1H NMR spectrum from the NMR tube reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_3CN_3 . The symbols represent the following: N: $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$; t: thf; td: trityl dimer; g: stopcock grease.

some other group with the azide rather than a simple addition as described here. Perhaps the best azide for this purpose is trimethylsilylazide, which is used extensively in organic chemistry to put azide groups on organic molecules.^{6c} Azide transfer reactions are also known for transition metal complexes, although our use of trityl azide for this purpose seems to be rather unusual. One other example has been reported in the literature; this is the oxidation of Cp_2^*V with Ph_3CN_3 to produce a vanadium(III) azide^{6d} (Scheme 1-3).

Scheme 1-3: Oxidation of vanadocene by tritylazide.

In fact, we have found that a variety of Ph_3CX compounds may be used as one-electron oxidizing agents towards trivalent uranium. Examples of this are shown below (Scheme 1-4):

Scheme 1-4: Reaction of trivalent uranium with trityl compounds.
Note that when $\text{R} = \text{Me}$, $\text{L} = \text{thf}$, and when $\text{R} = \text{SiMe}_3$, the compound is base-free.

Each of the products shown below has been previously characterized, with the exception of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UNCS}$. $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UCl}$ was originally reported by Dormond and Duval,⁷ $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UF}$ has been prepared by Stults,⁸ and $[(\text{RC}_5\text{H}_4)_3\text{U}]_2-\mu\text{-S}$ by Brennan.⁹ It should be noted that Ph_3CNH_2 and Ph_3CH did not react with $(\text{RC}_5\text{H}_4)_3\text{U}$, and Ph_3COH gave a complex mixture of products.

The compound $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ is not the first reported uranium(IV) azide; Cp_3UN_3 was reported as unpublished results by Kanellakopulos *et. al.* in a review article published in 1979.¹⁰ The properties of this material appear to resemble that of the methylcyclopentadienyl compound: both are formed in high yield and both are green.

$(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was also prepared by an independent method in order to completely confirm its synthesis in the tritylazide reaction. Although the detailed synthesis for Cp_3UN_3 has not appeared in the literature, reactions

producing similar Cp_3UX materials are available. These syntheses frequently utilize a reaction first discovered by Reynolds and Wilkinson in 1956,¹¹ proceeding *via* formation of the aquated cation Cp_3U^+ from Cp_3UCl in thoroughly deoxygenated water solution. The cation may then be reacted with a variety of Na-X or K-X salts to yield Cp_3UX complexes in very good yield¹² (Scheme 1-5):

Scheme 1-5: Preparation of uranium cyclopentadienyls in aqueous solution.

This reaction scheme proved quite successful for the synthesis of the uranium azide. When $(\text{MeC}_5\text{H}_4)_3\text{UCl}$ was suspended in deoxygenated water, a light green color indicative of the uranium cation developed in the solution, with a great deal of the uranium chloride remaining as a brown solid. Addition of a solution of sodium azide in water resulted in an instant light green precipitate. The $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was recovered by filtering off the water, thoroughly drying the solid under reduced pressure, and recrystallizing the material from dichloromethane. This procedure typically provides greater than 80% yield of the uranium azide.

It is interesting to note that this procedure was unsuccessful in the attempted preparation of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$. When $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UCl}$ was suspended in deoxygenated H_2O , there was no noticeable coloring of the solution to the distinctive pale green of the aquated cation. Addition of a solution of sodium azide in water gave no immediate precipitate, however after several days a green precipitate was slowly formed. After a week of stirring, there seemed to be a great deal of this green solid, but after removing

the water and drying the exceedingly air-sensitive material, it could not be redissolved in hexane, ether, or toluene. This is in direct contrast with the solubility of a pure sample of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ obtained by oxidation of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ by trimethyltinazide, which is quite hexane soluble (Scheme 1-6).

Scheme 1-6: Preparation of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$.

A detailed discussion concerning reactions such as the one above as well as of the properties and reactivity of the uranium azide complexes will appear later in this chapter.

The discovery that organic azides could function either as one- or two-electron oxidizing agents towards uranium(III) led us to undertake a study of a larger group of azides. The goal of this study was to see how variations in the steric and electronic environment of the azide could change the reactivity towards uranium. Of particular interest was seeing whether electronic effects alone could play a significant role. The reason for this was that, as noted above, the one example we had found of an azide acting as an azide transfer reagent involved the very bulky triphenylmethyl group. Could we keep size relatively constant and still see changes in the reactivity? The azides chosen for study can be subdivided into several groups:

1. **Trimethyl Group IVA Azides.** These include t-butylazide, trimethylsilylazide, trimethylgermylazide, and trimethyltinazide. This

group should keep steric effects relatively minimal while greatly altering the electronic environment of the azide.

2. Triphenyl Group IVA Azides. These included tritylazide and triphenyltinazide.

3. Phenylmethylazides. These included tritylazide, diphenylmethylazide (benzhydrylazide), and phenylmethylazide (benzylazide). The behavior of this group should greatly reflect steric differences.

4. Substituted Phenylazides. This group allowed us to change electronic effects using para substituents, and steric effects using ortho substituents.

A brief mention should be made here on the synthesis and handling of these azides. It should be noted that azides are often unstable, exothermically decomposing with evolution of N_2 .¹³ This is particularly true in the presence of heavy metals or at high temperatures. All azide syntheses were carried out with care on relatively small scales (ca. 10-20 mMol) at room temperatures or below, unless it was quite certain that the azide was stable to elevated temperatures.

There were two primary synthetic methods used for the preparation of the azides. The first method involves replacement of a halide using sodium azide (Scheme 1-7). Solvent and reaction conditions vary depending on the particular azide involved.

Scheme 1-7: Formation of azides from halides.

This method is successful for the preparation of RN_3 when $R = t\text{-Bu}$,^{14a} GeMe_3 ,^{14b} SnMe_3 ,^{14b} Ph_2CH ,^{14c} and Ph_3Sn .^{14d}

The second technique for producing azides, used for all the substituted phenyl azides, is by diazotization reactions starting from substituted anilines.¹⁵ These reactions are typically done at between 0°C and -10°C to stabilize the diazonium salt. Once the diazonium salt has been made, it is allowed to react with NaN_3 , resulting in loss of N_2 and production of the azide (Scheme 1-8).

Scheme 1-8: Formation of azides by diazotization of amines.

These azides are isolated by ether extraction, and purified by vacuum distillation or recrystallization. When the azides were liquids, we found that reduced pressure, low temperature distillations greatly reduced decomposition and increased product yield (as well as improving the safety factor).

Table 1-1 shows a summary of the products of the reactions of trivalent uranium, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, with these azides. Further detail on these reactions is discussed below.

R	Product Percentages		Byproduct
	$\text{Cp}_3\text{U=NR}$	$\text{Cp}_3\text{U-N}_3$	
Me ₃ C	100	0	N ₂
Me ₃ Si	100	0	N ₂
Me ₃ Ge	70 - 80	30 - 20	N ₂ + (Me ₃ Ge) ₂
Me ₃ Sn	0	100	(Me ₃ Sn) ₂
Ph ₃ C	0	100	(Ph ₃ C) ₂
Ph ₃ Sn	0	100	(Ph ₃ Sn) ₂
Ph ₂ CH	85 - 90	15 - 10	N ₂ + (Ph ₂ CH) ₂
PhCH ₂	100	0	N ₂
Ph	100	0	N ₂
p-MeC ₆ H ₄	100	0	N ₂
p-MeOC ₆ H ₄	100	0	N ₂
p-Me ₂ NC ₆ H ₄	100	0	N ₂
o-MeC ₆ H ₄	100	0	N ₂
o- ⁱ PrC ₆ H ₄	100	0	N ₂
2,6-Me ₂ C ₆ H ₃	100	0	N ₂

Table 1-1: Summary of product distribution in reactions of (MeC₅H₄)₃U(thf) with azides.

Section 1.1: Results of Reactions of Trivalent Uranium Metallocenes with Azides

1.1.A: Results of Reactions Using Trimethyl Group IVA Azides

t-Butyl- and trimethylsilylazides reacted instantly with trivalent uranium metallocenes in diethyl ether, with evolution of gas. The products were extracted with hexane to give deep red solutions, and crystallization from hexane yielded brown/black needles. The ^1H NMR spectra of these materials showed very broad resonances, particularly for the cyclopentadienyl ring protons ($\nu_{1/2}$ = 130 - 150 Hz in the *t*-butyl and $\nu_{1/2}$ = 50 - 55 Hz in the trimethylsilyl). The spectra strongly suggest the presence of pentavalent uranium, and integration is consistent with the uranium(V) imides, $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ (R = *t*Bu, SiMe₃). The identity of these materials is confirmed by the parent ion in the electron impact mass spectrum.

When trimethylgermylazide (Me_3GeN_3) was added to an ether solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, there was no immediate gas evolution nor an obvious darkening of the solution color. The reaction mixture was stirred for three days, and the ether removed to give a red/brown residue. Some of this residue was found to be hexane soluble, and brown crystals could be obtained from this solution. This material appeared to be the uranium imide, $(\text{MeC}_5\text{H}_4)_3\text{UNGeMe}_3$, by ^1H NMR spectroscopy. The hexane-insoluble solid dissolved in dichloromethane, and subsequent analysis by ^1H NMR spectroscopy showed it to be identical with $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ obtained from the tritylazide or $\text{NaN}_3/\text{H}_2\text{O}$ preparations.

Thus, we had found the first example in which one azide, Me_3GeN_3 , could function as either a one-electron azide transfer reagent or a two-electron imide transfer reagent, although the reaction strongly favored the

production of the imide(>70% imide and <30% azide). Interestingly, even though a great deal of imide was formed, there was no instantaneous bubbling of the ether solution as is normally observed when imides were formed and N_2 produced. Perhaps this reaction proceeds far more slowly, with either a slow coordination step of the germanium azide or a slow step in which electron transfer occurs with loss of either N_2 or (presumably) the trimethylgermyl radical.

It seemed likely that as we proceeded down group IVA in the periodic table, the reaction may proceed further towards the uranium(IV) azide complex. Indeed, when trimethyltinazide was allowed to react with $(MeC_5H_4)_3U(thf)$, the only product isolated was $(MeC_5H_4)_3UN_3$.

Trimethyltinazide was also used to prepare the more soluble uranium azide complex, $(Me_3SiC_5H_4)_3UN_3$. Reaction of Me_3SnN_3 with the trivalent uranium species $(Me_3SiC_5H_4)_3U$ gave the azide in good yield.

1.1.B: Results of Reactions Using Triphenyl Group IVA Azides

Other than trityl azide, the only additional azide from this category that was utilized was triphenyltinazide, Ph_3SnN_3 . When ether was added to a mixture of $(MeC_5H_4)_3U(thf)$ and Ph_3SnN_3 , an immediate green precipitate was obtained. The ether was removed after stirring for one day, and 1H NMR spectroscopy indicated that the product was $(MeC_5H_4)_3UN_3$. Peaks were also seen in the phenyl region of the spectrum. Heating the material in a Schlenk tube to approximately 100°C under vacuum resulted in the sublimation of a white solid, which was removed from the tube and analyzed by mass spectroscopy. The spectrum showed a cluster at the correct masses for Ph_3Sn , indicating that the byproduct in this reaction was probably $Ph_3SnSnPh_3$. Presumably, the tin-tin bond is extremely weak, and the material dissociates

into the "monomeric" form in the mass spectrometer. Simulation of the isotopic cluster for $C_{18}H_{15}Sn$ showed excellent good agreement with the obtained spectrum, and both the actual and simulated spectra are shown in Figure 1-3.

This latter reaction was also performed using the more soluble trivalent uranium metallocene $(Me_3SiC_5H_4)_3U$. This was done in order to attempt to better observe the byproduct of the reaction. After $(Me_3SiC_5H_4)_3U$ was allowed to react for a day with Ph_3SnN_3 and the ether removed, the solid material was washed with hexane to remove the soluble complex $(Me_3SiC_5H_4)_3UN_3$. This left an off-white solid, which was dissolved in deuterated benzene and examined by ^{119}Sn NMR spectroscopy at 33.34 MHz. The spectrum showed a single peak at approximately $\delta = -138$ ppm,¹⁶ and is shown in Figure 1-4. This strongly suggested that the tin-containing product is indeed hexaphenylditin, whose reported ^{119}Sn NMR shift is $\delta = ca. -144$ ppm.¹⁷ Please note that the ^{119}Sn NMR of Ph_3SnN_3 is also shown in Figure 1-4 to show that we did not simply observe excess azide in the spectrum rather than a true by-product.

1.1.C: Results of Reactions Using Phenylmethyl Azides

As mentioned earlier, the reason for sequentially removing phenyl groups from tritylazide was to observe what effect changing the steric environment of the azide had upon its reactivity towards trivalent uranium. Benzhydrylazide, Ph_2CHN_3 , is easily prepared from the corresponding chloride. When this azide was added to an ether solution of $(MeC_5H_4)_3U(thf)$, gas evolution was immediately observed, and the solution color darkened. Removal of the ether followed by extraction and crystallization from hexane

Figure 1-3: The mass spectrum of the sublimed white solid from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_3SnN_3 ; presumably this material is $\text{Ph}_3\text{SnSnPh}_3$. The highest observed mass is for Ph_3Sn , and the simulation of the isotopic cluster for this unit is shown on the right.

Figure 1-4: ^{119}Sn NMR spectra of Ph_3SnN_3 (bottom) and the white, hexane-insoluble solid from the reaction of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ with Ph_3SnN_3 (top; believed to be $\text{Ph}_3\text{SnSnPh}_3$).

gave brown crystals of the uranium(V) imide, $(\text{MeC}_5\text{H}_4)_3\text{UNCHPh}_2$, although ^1H NMR spectroscopy indicated that these crystals were slightly contaminated with $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The hexane insoluble material was extracted with dichloromethane, and this extract yielded a small amount of the uranium(IV) azide.

To try to gauge the product distribution in this reaction more accurately, the procedure was repeated in an NMR tube. Note that this involved a change of solvent from Et_2O to C_6D_6 , which may or may not affect the chemistry. When the reactants were mixed and the ^1H NMR spectrum obtained, it indicated that ca. 85 - 90% of the product was the pentavalent uranium imide, while only 10 - 15% was the tetravalent azide.

The reaction was also repeated on a preparative scale with ether as solvent. In this case, after one hour of stirring, the volatile materials were removed, and the residue directly analyzed by ^1H NMR spectroscopy (Figure 1-5). The spectrum once again indicated a predominance of the uranium(V) product, and the approximate percentages are 85 - 95% $(\text{MeC}_5\text{H}_4)_3\text{UNCHPh}_2$ and 5 - 15% $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$.

It should be noted that the broad peak widths obtained in the spectra of these uranium(V) imides makes accurate integration difficult. The numbers are meant to convey a fairly rough idea of whether one product or the other is the dominant product, but it would be incorrect to make conclusions based on small differences in product percentages obtained by these techniques. It is, however, comforting to see that the NMR experiments and the isolated products reflect roughly similar product distributions.

When a second phenyl ring was removed and benzylazide, PhCH_2N_3 , was used, the favored product was the uranium imide, $(\text{MeC}_5\text{H}_4)_3\text{UNCH}_2\text{Ph}$, and no evidence was seen for the formation of the uranium azide. The

Figure 1-5: The ^1H NMR spectrum from the NMR tube reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_2CHN_3 . The symbols represent the following: V: $(\text{MeC}_5\text{H}_4)_3\text{UNCHPh}_2$; IV: $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$; s: solvent; t: thf.

benzyl CH_2 group shows an highly unusual chemical shift in the ^1H NMR ($\delta = \text{ca. } +123 \text{ ppm}$); this is discussed in the later section on properties of the uranium imides.

The results obtained from these experiments suggest a strong steric effect in the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with phenylmethylazides. This will be discussed in further detail in Section 1.2.

1.1.D: Results of Reactions Using Substituted Phenylazides

In all cases in which $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ was allowed to react with a substituted phenyl azide, only the uranium(V) imides have been obtained. Substituents include the following: p-methyl, o-methyl, 2,6-dimethyl, p-methoxy, p-dimethylamino, o-isopropyl, and p-trifluoromethyl.

Section 1.2: Discussion of Reactions of Trivalent Uranium Metallocenes with Azides

The obvious question that must be addressed as a result of the data presented thus far is, "Why do some azides behave as one-electron oxidizing agents while some behave as two-electron oxidants?" It is important for this discussion to recognize the two accepted resonance structures by which azides may be represented (Figure 1-6):

Figure 1-6. Resonance structures of azides.

It seems reasonable to assume that resonance structure B is the one that is more likely to produce an imide upon reaction with a metal center. The reasons for this are twofold: firstly, the structure has an N-N triple bond, allowing easy loss of N₂ from the compound, and secondly, the concentration of electron density on the α-nitrogen would seem to allow for a very strong interaction with an electropositive metal center. On the other hand, structure A contains a considerably stronger bond between the α-nitrogen and the β-nitrogen, making it more difficult to break the N-N bond and form the uranium imide species.

Of course, the distribution of the products is certainly going to be dependent upon what form is taken by the reaction intermediate. Presumably, the reaction must go through a transition state in which either the α- or γ-nitrogen is coordinated to the uranium center. The β-nitrogen

can be eliminated as a possible coordination site due to the partial positive charge which all plausible resonance structures place upon this atom. It also seems most likely that the α -nitrogen must coordinate when the imide is formed, to keep the NR unit intact. A labelling study has been done to attempt to substantiate this, which will be presented shortly. The major question then becomes one of which possible intermediate leads to the formation of the uranium azide. The most reasonable possibilities would seem to be as follows (see Figure 1-7):

Possible mechanism #1: α -N coordination in all cases.

Possible mechanism #2: α -N coordination leads to uranium imide, γ -N coordination leads to uranium azide.

Figure 1-7: Possible mechanisms for reaction of uranium(III) with azides.

1. Coordination occurs at the α -nitrogen in all cases. Once the azide has coordinated, either electronic or steric effects could cause loss

of either N_2 or $R\cdot$. Electronic effects would involve the strength of the N-R bond as well as the stability of the resultant radical, while steric effects could dominate in how close the α -nitrogen could get to the metal center, resulting in either one or two electron transfer.

2. Coordination occurs at the α -nitrogen in the formation of the uranium imide, but at the γ -nitrogen in the formation of the uranium azide. In this case, the major electronic effect involves how much electron density is at the α - or γ -nitrogens to allow coordination with the uranium. Steric effects would suggest that the bulkier the R group of the azide, the more likely γ -coordination is to occur.

One way to gain partial understanding of the mechanism of this reaction is through labelling studies. α - ^{15}N labelled phenylazide is easily prepared from the labelled aniline, by diazotization and subsequent reaction with sodium azide.¹⁸ The percentage of ^{15}N in the azide was determined by mass spectroscopy, and was found to be >99% (see Figure 1-8). When this material was reacted with $(MeC_5H_4)_3U(thf)$, the resulting uranium imide showed essentially complete incorporation of the label. The mass spectra of both $(MeC_5H_4)_3UNPh$ and $(MeC_5H_4)_3U^{15}NPh$ are shown in Figure 1-8. Analysis of the spectra show >98% ^{15}N in the product from the labelling experiment.

The infrared spectra of the labelled and unlabelled imides are shown in Figure 1-9. Trogler *et. al.* have synthesized the compound Cp^*VNPh (by reaction of Cp^*V and PhN_3), and the infrared spectra of the labelled and unlabelled compounds have been analyzed in order to determine the positions of the C-N and V-N stretches.¹⁹ They report that the C-N stretch occurs at 1330 cm^{-1} in Cp^*VNPh and at 1307 cm^{-1} in $Cp^*V^{15}NPh$, while the V-N stretch is observed at 934 cm^{-1} in Cp^*VNPh and at 923 cm^{-1} in

Figure 1-8: Mass spectra of the labelled and unlabelled phenylazide and the labelled and unlabelled uranium(V) phenylimide.

Figure 1-9: Infrared spectra of (MeC₅H₄)₃UNPh (top) and (MeC₅H₄)₃U¹⁵NPh (bottom).

$\text{Cp}^*\text{V}^{15}\text{NPh}$. In the spectra of the uranium molecules, we observe a strong stretch at 1271 cm^{-1} for $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, which shifts to 1260 cm^{-1} in $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$. This is assigned as the C-N stretch. The only other absorption which is observed to shift significantly is a medium strength stretch which occurs at 909 cm^{-1} in $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and at 895 cm^{-1} in $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$. This is assigned as the U-N stretch.

The infrared data and the mass spectroscopy indicate that the ^{15}N from α -labelled phenylazide was completely incorporated in the final uranium imide product. What conclusions regarding the mechanism of azide reaction with trivalent uranium can we draw from this result? Certainly it shows that no unusual rearrangement of the azide occurs on coordination to the metal center. The nitrogen originally bonded to the aryl group remains bonded to it in the product. This strongly suggests an α -coordinated intermediate at the transition state of the reaction.

A more informative labelling study would be one in which a labelled azide was used to form the uranium(IV) azide compound, rather than the imide. In this case, we could examine where in the uranium product the ^{15}N is found, and possibly draw further conclusions concerning the mechanism (Scheme 1-9);

Scheme 1-9: Proposed reaction to produce an ^{15}N -labelled uranium azide.

^{15}N in the alpha position (directly bonded to the uranium) would suggest an intermediate in which the α -nitrogen on the organic azide coordinates to the

metal center. However, ^{15}N in the position gamma to the uranium would suggest an intermediate in which the γ -nitrogen on the organic azide coordinates to the metal center. Unfortunately, we have been unable to investigate these possibilities. The reason for this is that we are unable to generate a preferentially labelled azide starting material which forms the uranium(IV) product. Azides specifically labelled in the α -, β -, or γ -positions can be made by diazotization reactions of amines. Unfortunately, all azides made by diazotization form the uranium(V) imide. To make an azide which forms the uranium(IV) azide product, we must use the synthesis discussed earlier in which a halide is exchanged for the N_3^- unit. This reaction cannot be controlled to give pure products which are ^{15}N labelled in the α - or γ -positions (β -labelling is not useful in our mechanistic study).

Thus, to briefly summarize the results of our labelling attempts, the one labelling experiment we have been able to perform strongly hints at coordination of the α -nitrogen of the azide to the uranium center in a reaction which results in formation of the uranium(V) imide product. However, the more interesting question of whether α - or γ -coordination is responsible for the uranium(IV) azide formation remains unanswered.

Despite the problems with the labelling reactions, we can still at least advance some theories as to why the reactions of trivalent uranium with azides proceed by two different routes. I will discuss these ideas in the following sections, taking into account both the electronic and steric properties of the R group in RN_3 and how these properties might affect the reaction intermediate and therefore the final product.

1.2.A: Discussion of Reactions Using Trimethyl Group IVA Azides

This group of azides gives us perhaps the most interesting series in which we can look at electronic effects of the R group in RN_3 upon the reactivity towards trivalent uranium. The reactions showed that as we proceed down the periodic table in Me_3XN_3 (X = group IVA element), the products formed move from the uranium(V) imide (MeC_5H_4)₃UNR to the uranium(IV) azide (MeC_5H_4)₃UN₃, with Me_3GeN_3 forming both products. This trend should be explainable predominantly by electronic effects, since the steric bulk of the Me_3X groups are probably relatively similar.

We will assume for this discussion that the intermediate in the reaction of $(RC_5H_4)_3U$ with these group IVA azides involves α -coordination of the azide. Thus, at the transition state, cleavage of either the Me_3X-N bond (giving the uranium azide product), or the $\alpha N-\beta N$ bond (giving the uranium imide product) can occur (see Figure 1-7). Assuming we observe the thermodynamically preferred product in these reactions and not a kinetic product, we can predict the following:

1. When the N-N bond strength of the azide is greater than the N-XMe₃ bond strength, uranium(IV) azide formation is preferred.
2. When the N-XMe₃ strength of the azide is greater than the N-N bond strength, uranium(V) imide formation is preferred.
3. When the N-XMe₃ and N-N bond strengths are of the same order, both products will be formed.

We can therefore look at the trends in bond strengths for group IVA nitrogen compounds to attempt to rationalize our observations. The values reported for several dimethylamides of group IVA are shown in Table 1-2 below:

Compound	X-N Bond Strength (kcal mol ⁻¹)	Reference
H ₃ CNMe ₂	76	20
Me ₃ SiNMe ₂	79	21
Me ₃ GeNMe ₂	55	22
Me ₃ SnNMe ₂	41	22

Table 1-2: Group IVA X-N bond strength values.

These values may be contrasted with the energy required to break the α N- β N bond. Some values of bond strengths of N-N single bonds can be obtained from hydrazines; in H₂NNH₂, 66 kcal mol⁻¹, and in Me₂NNH₂, 59 kcal mol⁻¹.²⁰ Thus, we see that C-N and Si-N bonds are considerably stronger than the N-N bond, and only the uranium(V) product is observed from the silicon and carbon azides of this group. The Ge-N bond strength, on the other hand, is of the same order as an N-N single bond, and indeed we observe both the uranium(IV) and uranium(V) products in the reaction of Me₃GeN₃ with (MeC₅H₄)₃U(thf). The much weaker Sn-N bond allows formation of only the uranium(IV) product.

1.2.B: Discussion of Reactions Using Triphenyl Group IVA Azides

As discussed earlier, both Ph₃CN₃ and Ph₃SnN₃ yield only (MeC₅H₄)₃UN₃ as the uranium containing product when allowed to react with (MeC₅H₄)₃U(thf). It is presumed that this product comes about primarily for steric reasons; the three phenyl rings would create an enormously bulky transition state if the azide coordinated at the α -nitrogen, and the uranium imide product would therefore be sterically disfavored. Because of this, it seems that initial coordination of the azide through the γ -nitrogen is the most

likely possibility for the intermediate in this reaction. Experimental evidence for this is desirable, but as noted previously, a meaningful labelling study on systems of these sorts has, thus far, proven impossible.

As noted earlier in this chapter, results similar to those obtained for $(\text{MeC}_5\text{H}_4)_3\text{U}$ were obtained in reactions of vanadium metallocenes with bulky azides.^{6d} Both Ph_3CN_3 and Ph_3SiN_3 react with Cp_2^*V to yield the azide, Cp_2^*VN_3 . The authors also propose a γ -nitrogen coordination. Interestingly, Me_3SiN_3 also reacts with Cp_2^*V to give Cp_2^*VN_3 , rather than the imide. This is again attributed to steric interactions, although this seems odd in light of our observations with uranium.

1.2.C: Discussion of Reactions Using Phenylmethyl Azides

This series of azides, utilizing Ph_3CN_3 , Ph_2CHN_3 , and PhCH_2N_3 , demonstrates primarily the results of changing the steric effects of the azides. The product of the reaction of these azides with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ proceeds from only the uranium azide, $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, in the case of the bulky trityl azide, to a mixture of azide and imide for benzhydryl azide (Ph_2CHN_3), to only the imide, $(\text{MeC}_5\text{H}_4)_3\text{UNCH}_2\text{Ph}$, for benzyl azide.

We can see that these changes in product distribution are caused only by steric effects if we look briefly at the electronic nature of this series of azides. Replacing the hydrogens on methylazide (H_3CN_3) with electron withdrawing phenyl rings should make the central carbon more electronegative. This will cause the C-N bond in the azide to become less polarized, and therefore would tend to stabilize the B resonance structure of the azide. Following this argument, the B resonance structure would be more favored in Ph_3CN_3 than in PhCH_2N_3 . However, if the the B structure is indeed, as we have assumed, the one that is more likely to produce a

uranium(V) imide, then some other effect must be dominating the electronic changes. This is, presumably, the steric effect.

We can then ask why the product distribution changes so dramatically in moving from trityl azide to benzhydryl azide. The reaction of trityl azide with trivalent uranium gives 100% uranium(IV) azide product; the reaction of benzhydryl azide with trivalent uranium gives *ca.* 85% uranium(V) imide and 15% uranium(IV) azide. The steric interactions at the proposed transition states help explain this observation. Let's once again assume, as previously proposed, that coordination at the α -nitrogen of the azide is required for production of the uranium(V) imide product. Trityl azide, with the three large aryl rings on the carbon bound to this α -nitrogen, should have enormous steric problems getting this nitrogen close enough to the metal center for reaction to occur. Presumably, the azide then coordinates through the γ -nitrogen, producing the uranium(IV) azide. However, if we replace just one aryl ring with a hydrogen, we can easily picture a much less bulky transition state in which α -coordination would be somewhat more favorable. Two of the phenyl rings could point away from the metal, minimizing their steric interactions with the methylcyclopentadienyl rings, while the single hydrogen would point inward. Removing a second aryl ring should further reduce the crowding in the transition state, and indeed we see no uranium(IV) azide when benzylazide is used.

The bond strength arguments used in section 1.2.A can also be applied to these azides. The C-N bond in $\text{PhCH}_2\text{NMe}_2$ has a bond strength of 62 kcal mol⁻¹.²⁰ Although a value for the C-N bond in $\text{Ph}_2\text{CHNMe}_2$ has not been reported, we can estimate that it is on the order of 4 kcal mol⁻¹ less. We make this estimate by comparison of the C-H bond strengths in PhCH_3 and Ph_2CH_2 ; these are -4 kcal mol⁻¹ different.²⁰ The important point is that these values

are very close to the value for an N-N single bond, and we thus observe both the uranium(V) and uranium(IV) products in the case of Ph_2CHN_3 , although the uranium(V) product is strongly favored. The small gain in C-N bond energy in going from Ph_2CHN_3 to PhCH_2N_3 may be sufficient to cause only production of the uranium(V) imide product.

1.2.D: Discussion of Reactions Using Substituted Phenylazides

Unfortunately, attempts to utilize substituents on phenyl rings to electronically "tune" the azides were unsuccessful. The reactions of all of the substituted phenylazides we tried yielded only the uranium(V) imide products, with certain special exceptions that will be mentioned at the end of this section.

The basis for these attempts was relatively simple. Electron donating substituents on the phenyl ring should make the carbon bonded to the N_3^- ligand less electronegative. This increases the polarity of the C-N bond, destabilizing the B resonance structure which we believe produces the uranium(V) product. Donating groups were tried at the para- and ortho-positions, and included p-methyl, o-methyl, p-methoxy, p-dimethylamino, o-isopropyl, and 2,6-dimethyl. It is interesting to note that the ortho substitution should have a significant steric effect in addition to the electronic changes, but even a bulky group such as isopropyl did not apparently destabilize the α -coordinated intermediate significantly to cause production of any $(\text{MeC}_3\text{H}_7)_3\text{UN}_3$.

Why did attempts at tuning the electronics of aryl azides fail so greatly, especially since para-substitution of this nature has been studied extensively in organic chemistry and found to have a strong influence on reaction rates?²³ The reason is probably related to results summarized by Kaftory

involving X-ray diffraction data on azides.²⁴ He found that sp^2 hybridized carbon azides show a slightly greater difference in their N-N bond lengths when compared to sp^3 azides, demonstrating a favoritism for the B resonance structure over the A isomer. This is explained by the greater electronegativity of the sp^2 carbon, which causes a less polar C-N bond and therefore stabilization of electron density and negative charge on the α -nitrogen. In addition, there is a second important electronic situation in these azides, the possible π -bonding interaction between the N_3^- and the aryl π -system. This interaction would tend to strengthen the C-N bond, and would again favor the B resonance structure by delocalization of electron density from the α -nitrogen into the aryl π -orbitals.

Apparently, these two effects so strongly favor the B resonance form, and, concurrently, the production of uranium(V) imides, that they cannot be reversed by simple substitution on the ring. Although it seems intuitive that electron-donating groups will change the electronic properties of the azide in the direction we desire, it seems that we simply cannot put enough e^- density into the aryl ring to reverse the trend in reactivity. Altering the steric properties of these compounds is more likely to produce the uranium(IV) azide (perhaps 2,6-diisopropyl, although this is not a known compound), but this is far less interesting to us, as this type of "steric tuning" was already easily accomplished in the phenylmethyl azide series.

I mentioned earlier that there were several special cases in these aryl substitution reactions; this involved azides in which e^- -withdrawing groups were used on the ring. When para-nitrophenylazide, $p-O_2NC_6H_4N_3$, was allowed to react with $(MeC_3H_7)_3U(thf)$, only a dark, insoluble precipitate was obtained. It seems quite likely that the uranium coordinated to the nitro-

oxygen rather than the azido ligand; this is consistent with the insoluble materials formed by accidental air oxidation of these types of compounds.

Reaction of para-trifluoromethylphenylazide, $p\text{-F}_3\text{CC}_6\text{H}_4\text{N}_3$, with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, produced a crystalline product whose ^1H NMR is certainly consistent with the formulation $(\text{MeC}_5\text{H}_4)_3\text{UN}(p\text{-F}_3\text{CC}_6\text{H}_4)$. However, this compound was impure, the impurity being the tetravalent uranium fluoride, $(\text{MeC}_5\text{H}_4)_3\text{UF}$. Recrystallization failed to separate these two materials despite what appears to be a large solubility difference (the fluoride is quite insoluble in hexane), and it is possible that the imide slowly decomposes to the fluoride. When the ortho-substituted trifluoromethylphenylazide was used, the dominant product was $(\text{MeC}_5\text{H}_4)_3\text{UF}$. Very small resonances that are probably due to $(\text{MeC}_5\text{H}_4)_3\text{UN}(o\text{-F}_3\text{CC}_6\text{H}_4)$ are also observed in the spectrum (by comparison with spectra of other ortho-substituted imides). These reactions were not pursued further.

Section 1.3: Properties and Reactions of $(\text{RC}_5\text{H}_4)_3\text{UN}_3$ (R = Me or SiMe₃)

1.3.A: Properties of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$

As reported earlier in this chapter, these compounds are synthesized by several different methods. For the MeC_5H_4 compound, two techniques were commonly used to produce clean material in high yield: replacement of the chloride of $(\text{MeC}_5\text{H}_4)_3\text{UCl}$ in aqueous solution or oxidation of the trivalent compound $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with trityl azide. Either reaction can be performed on relatively large scales (ca. 3 g). The aqueous process typically gives an 80-90% yield of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, while the trityl azide preparation gives yields of ca. 50%. The trityl azide reaction is, though, easier to perform; $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and Ph_3CN_3 are simply mixed as solids in a 1:1 molar ratio, diethyl ether added to give an immediate green precipitate, and, after stirring for one hour, the ether is filtered off to give a very pure green powder of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The compound instantly turns brown/black in the presence of oxygen, and in fact will smoke and spark on exposure as a finely divided powder to O_2 .

One other reaction in which $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was produced was carried out. This is the oxidation of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ to the azide using hydrazoic acid, HN_3 (Figure 1-10):

Figure 1-10: Oxidation of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ by hydrazoic acid.

An ethereal solution of HN_3 is easily prepared by combining NaN_3 and H_2SO_4 in an ether/water mixture, followed by careful distillation of the ether layer.²⁵ Because hydrazoic acid is explosive, all manipulations were carried out behind a shield. The HN_3 /ether solution was then titrated and used. Adding one molar equivalent of HN_3 to a solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ in ether yielded a green precipitate and pale solution. After removal of the volatile materials, the green solid was sublimed at 120-130°C to give pure $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ in fairly low yield. Some of the residue from the sublimation dissolved in dichloromethane and a small additional amount of the uranium azide was crystallized. It appears that HN_3 simply acts like the other ionic azides in its reactivity towards trivalent uranium, not a very surprising result. The low yields obtained from this reaction are probably due to protonation of the MeC_5H_4 rings by the acid, resulting in decomposition of the uranium species. This is not unexpected due to the highly acidic nature of HN_3 [$\text{pK}_a(\text{H}_2\text{O}) = 4.8$]²⁶.

The compound $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$, as described earlier, cannot be prepared by the aqueous technique mentioned above. Instead, it must be made by oxidation of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ using Me_3SnN_3 . The compound is isolated as brown crystals from either hexane or hexamethyldisiloxane [$(\text{Me}_3\text{Si})_2\text{O}$] in yields of ca. 40%. This compound is also exceedingly oxygen sensitive.

There are marked differences in the solubilities of the methylcyclopentadienyl and trimethylsilylcyclopentadienyl uranium azides. $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ is extremely soluble in common organic solvents such as hexane, ether, thf, and toluene, giving brown solutions with a green tint. This certainly suggests that the compound is monomeric, not a very surprising result considering the bulk of the Me_3Si groups. $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$,

on the other hand, is far less soluble. The compound is completely insoluble in hexane, very slightly soluble in ether, and somewhat more soluble in toluene, thf, and CH_2Cl_2 .

There are two primary reasons for the extreme solubility difference between these two compounds. First, the size of the Me_3Si group compared with a Me group decreases the ability of the molecule to pack tightly in the crystal. This makes it easier for a less polar solvent to break up the lattice. Secondly, the rather narrow azide unit may be capable of interacting with a second metal center in $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, yielding an oligomeric material such as shown below (Figure 1-11):

Figure 1-11: Possible oligomeric structure of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$.

This type of structure is not unknown; $\text{Cp}_3\text{UCN}^{27}$, $\text{Cp}_3\text{UC}(\text{CN})_3^{28}$, and $[\text{Cp}_3\text{U}]_2[\text{Pt}(\text{CN})_4]^{29}$ are examples of compounds believed to be oligomeric. In addition, the trigonal bipyramidal structure such an oligomer would require has been observed previously in triscyclopentadienyl uranium compounds, such as $\text{Cp}_3\text{U}(\text{NCS})(\text{MeCN})$.³⁰ It is also interesting to note that a similarly insoluble azide was produced recently using ytterbium.³¹ This azide, $(\text{Me}_5\text{C}_5)_2\text{YbN}_3$, appears to be oligomeric, and, in fact, the azide stretches in the infrared spectra of these materials are alike both in position and shape. Presumably, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ cannot have intermolecular interactions of this sort due to the steric requirements of the cyclopentadienyl ligands.

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ exhibits a relatively low melting point of 103-105°C. This value can be compared with similar $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UX}$ compounds; for $\text{X} = \text{Cl}$, the m.p. is 101-102°C, and for $\text{X} = \text{F}$, the m.p. is 73-75°C. The compound appears to melt without a color change or any other evidence of decomposition. Conversely, $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ melts from 152-160°C with apparent decomposition; the material changes from a bright green to deep brown while slowly melting over this temperature range. More about the thermolysis behavior of these compounds will be discussed in the following section.

The ^1H NMR spectra of these two compounds are shown in Figure 1-12. Neither of these spectra is remarkable; both show the typical patterns and linewidths of tetravalent $(\text{RC}_5\text{H}_4)_3\text{UX}$ compounds. The dominant feature of the infrared spectra of these materials is the extremely strong asymmetric azide stretch above 2000 cm^{-1} (Figure 1-13). In $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$, this stretch is observed at 2082 cm^{-1} , and is relatively sharp. The stretch is considerably broader and at higher energy in $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, occurring at 2115 cm^{-1} . The broadness of this stretch may be indicative of the type of structure depicted earlier in Figure 1-11, and, as mentioned above, the shape of this stretch is very similar to that of bis(pentamethylcyclopentadienyl)ytterbium azide. The higher energy of the stretch in $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ may be best explained by considering this oligomeric arrangement as a Lewis acid coordination adduct of the azide, with each $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ unit acting both as the acid and the donor base. Adducts of this sort have been shown to exhibit asymmetric azide stretches at higher frequencies than that of the uncoordinated azide, as Thayer and others found for nitrogen-bound Lewis acid adducts of inorganic azides.³²

Figure 1-12: ^1H NMR spectra of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (top) and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ (bottom) [s: solvent].

Figure 1-13: Infrared spectra (Nujol mulls) of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ (top) and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (bottom).

Both compounds exhibit molecular ions in the electron impact mass spectrum, and the simulated spectra agree well with those determined experimentally.

1.3.B: Reactions of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$

Our earliest attempts at exploring the chemistry of these azides involved pyrolysis reactions. The goal of these experiments was to eliminate dinitrogen from the azide to produce a uranium nitride, $(\text{RC}_5\text{H}_4)_3\text{UN}$, formally a uranium(VI) species.³³ When $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was heated to *ca.* 200°C under one atmosphere of nitrogen or argon, the green solid slowly turned black. There was no obvious evidence of gas evolution, and the black solid was completely insoluble in organic solvents. Similar results were obtained when the material was thermolyzed in refluxing decane (b.p. 174°C). A black precipitate formed which would not redissolve. When this azide was heated under vacuum (*ca.* 10^{-4} torr), the bright green solid was found to sublime unchanged at 90-100°C.

It appears from these results that the N-N bonds in this azide are relatively strong, and that the two-electron oxidation to the uranium nitride is not favorable. If the nitride is being formed in the solid phase pyrolysis or in the solution reaction, it is a polymeric material that we cannot characterize. It is quite possible, however, that at these temperatures reactions involving the cyclopentadienyl rings may also occur, and the material may simply decompose completely.

Several attempts were made to thermolyze $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ in the solid phase. These reactions were done under an argon atmosphere in sealed ampoules. When the material was heated for two hours at 200°C, only unreacted starting material was recovered. This indicates a considerably

greater thermal stability for this azide relative to $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. However, when the azide was heated to 250°C for $1\frac{1}{4}$ hours, a yellow material sublimed up the sides of the tube, and a brown residue remained at the bottom. The ^1H NMR spectra of both materials were uninterpretable. The material at the base of the tube was quite insoluble and showed very few peaks in the NMR, while the sublimed material gave a complex spectrum. When the azide was heated to higher temperatures, even more complex spectra resulted. It is quite obvious that this reaction is not clean or straightforward, and it seems likely that a large number of products are formed. No further work on pyrolysis of the azides was performed.

A second attempt to explore the reactivity of this compound involved the use of a good Lewis acid, trimethylaluminum, to see whether the lone pairs on the azide were accessible for coordination. When a solution of AlMe_3 in hexane was added to $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ dissolved in toluene, no color change was observed. Subsequent work-up of the reaction mixture yielded only the unreacted uranium azide. However, when trimethylaluminum in hexane was added to $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ dissolved in dichloromethane, an instant color change from light green/brown to darker brown was observed. Removal of the volatile materials followed by extraction and crystallization from toluene yielded brown crystals. These crystals, when treated with diethyl ether, immediately turned bright green, and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ could once again be isolated from the solution. This result suggested that the compound formed is a weak coordination complex of the formula $(\text{MeC}_5\text{H}_4)_3\text{UN}_3 \cdot \text{AlMe}_3$. Further evidence for a relatively weak coordination was given by studying the ^1H NMR spectrum of the complex. The spectrum of a mixture of the trimethylaluminum adduct and additional $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ showed only one set of shifted resonances, with a greatly reduced resonance at

$\delta = -7.7$ ppm attributed to the AlMe_3 protons. Spectra of the pure materials and the mixture are shown in Figure 1-14.

Additional evidence of a weak coordination was seen in the fact that it proved difficult to isolate the 1:1 adduct in pure form. Even when $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was allowed to react with ca. 15 molar equivalents of AlMe_3 , the product showed an AlMe_3 resonance in the ^1H NMR spectrum with an intensity of approximately 50-80% of the expected value. It is possible that trimethylaluminum dissociates when the crystals are dried under vacuum or during crystallization from toluene. The adduct does not give a parent ion in the E.I.-M.S., instead showing only the uncoordinated uranium azide. The asymmetric N_3 stretch in the infrared spectrum of this complex occurs at 2110 cm^{-1} . This is not significantly shifted from the uncoordinated azide, consistent with the idea that the starting material may be oligomeric.

Another piece of evidence suggesting that $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ may be oligomeric comes from the fact that the AlMe_3 adduct was formed in dichloromethane but not in toluene solution. We would expect that the more polar solvent would be more effective at breaking up the interactions between the azide units, allowing coordination of the Lewis acid.

There are, of course, two possible sites for coordination of the trimethylaluminum to the azide: the α - or the γ -nitrogens. No definitive statement concerning which coordination exists in $(\text{MeC}_5\text{H}_4)_3\text{UN}_3 \cdot \text{AlMe}_3$ may be made, but it should be noted that α -coordination is proposed in the compounds $\text{Me}_3\text{SiN}_3 \cdot \text{BBr}_3^{34}$, $\text{Ph}_3\text{SiN}_3 \cdot \text{PPh}_3^{35}$, and $\text{MeN}_3 \cdot \text{SbCl}_5^{36}$, while γ -coordination has been suggested for $\text{Ph}_3\text{CN}_3 \cdot \text{PPh}_3^{37}$.

Several reactions that have been observed with organic and inorganic azides were also attempted with the uranium azides, $(\text{RC}_5\text{H}_4)_3\text{UN}_3$. For

Figure 1-14: ^1H NMR spectra of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3 \cdot \text{AlMe}_3$ (top), $(\text{MeC}_5\text{H}_4)_3\text{UN}_3 \cdot \text{AlMe}_3 + (\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (center), and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (bottom) [s: solvent; g: stopcock grease].

example, most organic azides react with tertiary phosphines, eliminating N_2 and forming phosphineimines as shown in Scheme 1-10 below:^{38,39}

Scheme 1-10: Reaction of azides with phosphines to produce a phosphineimine.

This reaction has also been found to proceed with some inorganic azides, such as R_3SiN_3 ($R = Ph, Me$).^{144,40} However, an attempt at a similar reaction of $(Me_3SiC_5H_4)_3UN_3$ with PMe_3 yielded only recovered starting material. It should be noted, however, that this reaction was attempted at room temperature, while many of the known cases require higher temperatures.

Another type of reaction known for organic azides is 1,3-dipolar cycloaddition.⁴¹ In the case of alkynes, such reactions have also been observed for silicon and tin azides (Scheme 1-11):⁴²

Scheme 1-11: Cycloaddition of azides with alkynes.

Another cycloaddition of this type is reaction of an azide with CS_2 . This reaction has been observed with a copper azide, $Cu(PPh_3)_2N_3$, eventually yielding $Cu(PPh_3)_2NCS$, but believed to proceed through an addition product like those shown in Figure 1-15 below:⁴³

Figure 1-15: Postulated addition product of a copper azide with CS_2 .

Unfortunately, mixing $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ with either diphenylacetylene or carbon disulfide afforded no reaction and only starting material was recovered. Again, these reactions were performed at room temperature and high temperature reactions were not pursued.

Because of an interest in our research group in reactions of transition metal carbonyls with uranium compounds, the azide $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was also reacted with $\text{Co}_2(\text{CO})_8$. Interestingly, when $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was stirred overnight with $\text{Co}_2(\text{CO})_8$ in dichloromethane, red crystals were obtained. The infrared spectrum of these crystals showed strong, broad stretches in the area of 2000 cm^{-1} . The ^1H NMR showed only one very simple 3:2:2 pattern for the MeC_5H_4 resonances and indicated uranium(IV) by the narrow linewidths. The IR and NMR spectra were identical to spectra obtained by Brennan of red crystals from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with $\text{Co}_2(\text{CO})_8$.^{9b} The compound was identified as $(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}[\text{Co}_2(\text{CO})_9]$. The identification was performed as follows: First, it was found that $(\text{MeC}_5\text{H}_4)_3\text{UNR}$, when allowed to react with $\text{Co}_2(\text{CO})_8$, produced an identical product (this reaction will be discussed in more detail later in this chapter). Then, Cp_3UNR was reacted with $\text{Co}_2(\text{CO})_8$ to produce the analogous unsubstituted cyclopentadienyl product. The compound obtained in this way was found to be identical in IR and NMR properties with those reported in the literature

for $\text{Cp}_3\text{U}-\mu\text{-OC}[\text{Co}_3(\text{CO})_9]$, made by Stutte and Schmid by the following reaction (Scheme 1-12):⁴⁴

Scheme 1-12: Stutte and Schmid preparation of the uranium-cobalt carbonyl complex.

It is interesting to note that, in the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ with $\text{Co}_2(\text{CO})_8$, a second product was obtained whose IR spectrum suggested that it contains both azide and carbonyl units. This compound gave no ^1H NMR spectrum, and was isolated in very low yield and its characterization was not pursued.

One final set of reactions will be discussed in this section. These were reactions to see whether the azide group could bridge between two uranium centers to form a mixed-valence uranium complex (Scheme 1-13):

Scheme 1-13: Preparation of a mixed-valence bridged uranium azide.

A large number of examples of complexes in which the azide group bridges two metal centers are known. These can involve 1,1-bridging, in which both metals are coordinated to the same nitrogen, or, more rarely, 1,3-bridging, in which the α - and γ -nitrogens are each coordinated to one metal, as shown below (Figure 1-16):

Figure 1-16: Modes of bonding in bridging azide complexes.

Examples of structure A include $[\text{Pd}_2(\text{N}_3)_6]^{2-45}$ and $[(\text{CO})_3\text{Mn}(\text{N}_3)_3\text{Mn}(\text{CO})_3]^{-46}$, while structure B is seen in $[\text{Cu}(\text{PPh}_3)_2\text{N}_3]_2^{47}$

Attempts at producing this type of compound were made in two ways: either on a preparative scale with attempted isolation of a crystalline product, or by mixing the two uranium species in an NMR tube and observing the resulting spectrum.

Two different NMR experiments were done (Scheme 1-14):

Scheme 1-14: NMR tube reactions of uranium(IV) azides with uranium(III) complexes.

In the case of the MeC_5H_4 compounds, the experiment was quite crude, since the azide is quite insoluble at low temperatures. At room temperature, there appeared to be four fairly broad peaks in the spectrum (in addition to the solvent). However, when the temperature was decreased to -30°C , the spectrum sharpened and there seemed to be a recognizable pattern, viz., the 3:2:2 pattern typical of $(\text{MeC}_5\text{H}_4)_3\text{U}$ compounds was observed at $\delta = -0.57$,

-27.42, and +16.07 ppm. In addition, two peaks in the diamagnetic region of the spectrum at $\delta = 3.47$ and 1.36 ppm are assigned to uncoordinated thf. This spectrum remained relatively unchanged (except for shifts in the paramagnetic peaks) at -74°C. Although this was certainly not definitive evidence of a bridged azide complex, the presence of the free thf was encouraging, and seemed to suggest that the Cp_3UN_3 unit is capable of interacting to some extent with a second metal center.

When the $\text{Me}_3\text{SiC}_5\text{H}_4$ compounds were used, again only resonances due to one species were observed in solution. At room temperature, the typical 9:2:2 pattern of these compounds was seen, although one of the ring resonances was quite broad ($\nu_{1/2} = 39$ Hz; see Figure 1-17). This mixture was then examined by variable temperature NMR spectroscopy. At higher temperatures (up to 80°C), the spectrum shifted but remained essentially similar to the room temperature spectrum. The position of the resonances at various temperatures are given in Table 1-3 below:

Temperature (°C)	δ (Me_3Si) (ppm)	δ (Ring H_1) (ppm)	δ (Ring H_2) (ppm)
31	-8.75	+1.2	-16.68
59	-7.68	+2.45	-14.53
70	-7.44	+3.00	-13.79
80	-7.05	+4.5	-12.92

Table 1-3: ^1H NMR chemical shifts in NMR reaction of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$.

The broad ring resonance did not sharpen significantly as the temperature was raised, and the other resonances did not seem to change shape greatly,

Figure 1-17: The ^1H NMR spectrum from the NMR tube reaction of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ with $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$; only one species is observed in the solution [s: solvent; g: stopcock grease].

either. At higher temperatures, other small peaks were observed in the spectrum, but these are probably due to decomposition products from either small amounts of air oxidation or thermal decomposition. The spectra at low temperatures were somewhat more complex; several unexplained peaks appeared to grow in. However, there remained only one Me_3Si resonance with little broadening throughout the experiment (down to -88°C). The important part of these experiments is that there is only one predominant species present in these solutions, a bridged azide that has equivalent $(\text{RC}_5\text{H}_4)_3\text{U}$ groups on the ^1H NMR time scale.

The most interesting of the experiments done on a preparative scale involved the trimethylsilylcyclopentadienyl derivatives. When $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ (pale green/brown) and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (dark green) were mixed in hexane, the solution immediately turned a very deep brown, and brown crystals could be obtained from hexane. The room temperature ^1H NMR of this material was clean, and showed the identical spectrum to the room temperature spectrum obtained in the NMR tube experiment described above. The material exhibited a sharp melting point of $83-86^\circ\text{C}$ [$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ melts at $76-77^\circ\text{C}$,^{9b} $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ melts at $103-105^\circ\text{C}$], but the most interesting feature was the infrared spectrum: two asymmetric azide stretches were observed, at 2122 and 2081 cm^{-1} [the stretch in $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ is at 2082 cm^{-1}].

The similar reaction was also done with the mixed cyclopentadienes as shown below (Scheme 1-15):

Scheme 1-15: Mixed cyclopentadienyl reaction of uranium(IV) azide with trivalent uranium.

This reaction was done in toluene, and again the solution turned deep brown. Brown crystals were obtained from hexane, and once again two azide stretches were observed in the infrared spectrum, at 2128 and 2079 cm^{-1} . The ^1H NMR spectrum of this material was quite complex, and looking at the mass spectrum helped explain why. While some higher masses that may contain two uraniums were seen, the interesting peaks are the monomeric compounds. These show mixing of the cyclopentadienyl groups; the species $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$, $(\text{Me}_3\text{SiC}_5\text{H}_4)_2(\text{MeC}_5\text{H}_4)\text{UN}_3$, $(\text{Me}_3\text{SiC}_5\text{H}_4)(\text{MeC}_5\text{H}_4)_2\text{UN}_3$, and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ were all observed in the spectrum. If this swapping of rings occurred in solution as well, it would make the NMR spectrum complex since resonances due to all of the individual species would be observed.

In summary, although unequivocal proof of formation of an azide bridged species was not obtained, it certainly appears likely that one was formed. Particularly in the case of the proposed $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2-\mu\text{-N}_3$, the evidence is reasonably compelling; the dramatic color change, the very simple and clean ^1H NMR, and the sharp melting point all lead towards the idea that some interaction has occurred. The presence of two stretches in the infrared spectrum may be explained by assuming that the bridged complex contains two different uranium centers on the infrared timescale. This can be drawn as shown below (Figure 1-18):

Figure 1-18: A uranium μ -azide complex with localized oxidation states.

In this case, we can observe two stretches: one stretch is the ν_{N_3} of $U(III)-N_3U(IV)$ and one is the ν_{N_3} stretch of $U(IV)-N_3U(III)$. On the much longer NMR timescale, however, we see averaged uranium centers, presumably due to some type of exchange mechanism.

Section 1.4: Properties and Reactions of $(\text{MeC}_5\text{H}_4)_3\text{UNR}$

1.4.A: Properties of $(\text{MeC}_5\text{H}_4)_3\text{UNR}$

As discussed earlier, a large number of pentavalent uranium imides have been synthesized. These are summarized in Table 1-4 below, showing the various R groups as well as melting points and colors:

	R	Color	M.P. (°C)
I	CMe ₃	red	232-237
II	SiMe ₃	red	132-140 ^{9b}
III	GeMe ₃	red	187-189
IV	Ph	red	109-112 ^{2,9b}
V	p-MeC ₆ H ₄	red	89-92
VI	p-Me ₂ NC ₆ H ₄	red	147-148
VII	p-MeOC ₆ H ₄	red	97-99
VIII	p-CF ₃ C ₆ H ₄	red	-
IX	o-MeC ₆ H ₄	red	118-120
X	o- ⁱ PrC ₆ H ₄	red	77-83
XI	2,6-Me ₂ C ₆ H ₃	red	154-156
XII	CH ₂ Ph	red	57-59
XIII	CHPh ₂	red	89-91

Table 1-4: Summary of $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ compounds.

Each of the imides was synthesized by reaction of the appropriate azide, RN_3 , with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ in ether. In cases where a mixture of the imide and the uranium(IV) azide was produced ($\text{R} = \text{GeMe}_3, \text{CHPh}_2$), the

compounds were separated by fractional recrystallization. While the azide is insoluble in hexane, all of the imides are readily hexane soluble. Some of the phenylimide complexes are slightly less soluble, presumably due to the ability of the phenyl rings to pack efficiently in the crystal.

The ^1H NMR spectra of the materials showed patterns and linewidths similar to those found by Brennan^{2,9b} in $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$, and which we have now found to be typical for these pentavalent uranium complexes. A collection of the linewidths of the cyclopentadienyl ligands are shown below (Table 1-5), to demonstrate the consistently broad lines that have been observed in these compounds.

	$\nu_{1/2}$ (Hz)		
	Ring Me	Ring H	Ring H
I	30	150	135
III	15	54	51
IV	20	60	49
V	20	50	50
VI	25	70	74
VII	18	75	60
VIII	16	43	37
IX	18	64	67
X	23	78	78
XI	25	76	87
XII	23	94	78
XIII	24	65	80

Table 1-5: ^1H NMR linewidths in uranium(V) imides.

The ^1H NMR chemical shifts for the compounds I - III are shown in Table 1-6 below:

	X	Chemical Shift (ppm)			
		Ring Me	Ring H	Ring H	XMe ₃
I	C	+4.2	-4.2	-9.9	+13.6
II	Si	+3.0	-2.0	-10.8	+6.9
III	Ge	+2.9	-1.5	-11.1	+6.5

Table 1-6: Chemical shifts in $(\text{MeC}_5\text{H}_4)_3\text{UNXMe}_3$ compounds.

The spectra are all quite similar and unremarkable. The linewidths of the resonances due to the XMe₃ groups are similar to that observed for the cyclopentadienyl ring methyl groups. Note that the resonance for the XMe₃ group (X = C, Si, or Ge) shifts upfield as we progress down the group IVA elements. This suggests that these methyl protons are becoming more shielded, a trend which follows the decreasing electronegativities as we move down the column (moving down the column, the bond between the methyl carbon and the central atom X becomes more polarized towards the methyl carbon due to the electronegativity difference, thus more negative charge on the methyl groups and an upfield shift).

The chemical shifts for the various uranium phenylimides, compounds IV - XI, are shown in Table 1-7. The spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, which is typical of these uranium(V) imides, is shown in Figure 1-19. The spectrum is presented at two different temperatures, because the resonance for the ortho protons on the phenyl ring overlaps with the

Table 1-7: ^1H NMR Chemical Shifts in Tris(methylcyclopentadienyl) Uranium Phenylimides, 30°C.

		MeC ₅ H ₄			Phenyl			
Imide		Me	Ring1	Ring2	ortho	meta	para	substituent
IV	C ₆ H ₅	+3.67	-3.32	-10.92	~+3.5	+18.67	-2.40	
V	p-MeC ₆ H ₄	+3.68	-3.48	-10.96	+3.37	+18.05		+19.01
VI	p-Me ₂ NC ₆ H ₄	+3.66	-4.01	-10.92	+2.60	+17.85		+10.20
VII	p-MeOC ₆ H ₄	+3.68	-3.66	-10.92	+2.94	+17.98		+7.04
VIII	p-CF ₃ C ₆ H ₄	+3.59	-3.12	-11.18	+3.16	+18.25		
IX	o-MeC ₆ H ₄	+4.73	-7.52	-8.67	+5.14	+19.95, +19.29	-3.15	+15.27
X	o- ⁱ PrC ₆ H ₄	+4.71	-8.18	-8.18	+5.04	+20.16, +19.27	-2.75	+1.81
XI	2,6-Me ₂ C ₆ H ₃	+5.67	-4.60	-14.23		+20.58	-5.49	+19.79

Figure 1-19: ^1H NMR spectra of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ at 30°C (top) and 60°C (bottom). The phenyl ring resonances are marked as follows: o: ortho; m: meta; p: para [s: solvent].

MeC_5H_4 methyl group resonance at room temperature. Note that all of the chemical shifts shown in the table are fairly similar; the spectra of these phenylimides are qualitatively the same in appearance. The assignments of the phenyl ring resonances were made both by the integration and by looking at which resonances remained when substituents on the ring were varied.

The ^1H NMR spectra of compounds XII and XIII, the phenylmethylimides, are also fairly similar to one another. For compound XII, $(\text{MeC}_5\text{H}_4)_3\text{UNCH}_2\text{Ph}$, the MeC_5H_4 resonances occur at $\delta = 3.42$ ppm (ring Me), $\delta = -2.81$ ppm (ring H), and $\delta = -11.33$ ppm (ring H), while the phenyl ring resonances occur at $\delta = +8.60$ ppm (ortho), $\delta = +12.73$ ppm (meta), and $\delta = +7.63$ ppm (para). Compound XIII shows resonances shifted only slightly from these values. The particularly interesting feature of the spectrum of the benzylimide $[(\text{MeC}_5\text{H}_4)_3\text{UNCH}_2\text{Ph}]$, however, is the resonance for the benzyl CH_2 protons. This resonance is seen at $\delta = \text{ca. } +123$ ppm, and has $\nu_{1/2} = \text{ca. } 450\text{--}500$ Hz. The reasons for the severe deshielding of these protons are not entirely clear. The best suggestion seems to be simply that this CH_2 group is surrounded by two electron withdrawing groups; the phenyl ring on one side and the $\text{N}=\text{U}$ unit on the other. If the nitrogen lone pairs are being pulled towards the uranium as expected, this nitrogen would become even more electronegative and therefore further remove electron density from the CH_2 group. Note that this resonance was not observed for the benzhydryl proton in compound XIII, $(\text{MeC}_5\text{H}_4)_3\text{UNCHPh}_2$; it may simply be too broad to observe at room temperature.

The electron impact mass spectra of these compounds all demonstrate parent molecular ions for the intact $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ species. The spectra all agree well with the simulated spectra (for more details, see Chapter 4). A typical spectrum, that of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, was presented earlier in this

chapter (Figure 1-8). Note in this sample that the first fragmentation of the molecule involves loss of a MeC_5H_4 ring, rather than dissociation of the NPh group. This is a trend observed in almost all of these imides, suggesting that the uranium-nitrogen interaction is stronger than the U-Cp interaction.

The infrared spectra of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$ were also shown earlier in this chapter (Figure 1-9). From comparison of these compounds, the C-N stretch was assigned at 1271 cm^{-1} , and the U-N stretch at 909 cm^{-1} . Similar stretches are observed in the other uranium(V) phenylimides, but it is very difficult to assign the U-N stretches in the other molecules without labelling studies. Presumably the nature of the R group bonded to the nitrogen will have a reasonably large effect on this U-N stretch.

Only two reports of the magnetic susceptibility of a pentavalent uranium complex have appeared, and both of these reports involved the halide $\text{UCl}_5(\text{tcac})$ (tcac = trichloroacetylchloride, $\text{Cl}_2\text{CCClCOCl}$). The first report, by Selbin *et. al.*, only gave a magnetic moment measured at 300 K.⁴⁸ This value was reported to be $\mu_{\text{eff}} = 1.54\text{ B.M.}$ The second report, by Fuji *et. al.*, showed a plot of χ_M vs. T, but gave no values for μ_{eff} .⁴⁹

The susceptibility of $\text{Cp}_3\text{UNSiMe}_3$, prepared by Brennan,^{9b} was measured previously by D. Berg.⁴ The plot of $1/\chi_M$ vs. T for this compound showed two linear regions, one at low temperatures (below ca. 30 K), and one at high temperatures (above ca. 100 K). From this plot, values of $\mu_{\text{eff}} = 1.19\text{ B.M.}$ for the low temperature data and $\mu_{\text{eff}} = 1.83\text{ B.M.}$ for the high temperature data were obtained.

J. Stewart has synthesized several pentavalent uranium imides and measured their moments.⁵⁰ She observed the same qualitative shape for the plots of inverse susceptibility versus temperature (two linear regions), as well as obtaining similar quantitative values. For the compound

$U[N(SiMe_3)_2]_3[N(p-MeC_6H_4)]$, linear least squares fitting of the data gave $\mu_{eff} = 1.49$ B.M. at low temperature (5-40 K) and $\mu_{eff} = 2.26$ B.M. at high temperature (140-240 K). For the compound $U[N(SiMe_3)_2]_3(NSiMe_3)$, the values were $\mu_{eff} = 1.61$ B.M. (5-40 K) and $\mu_{eff} = 2.04$ B.M. (140-280 K). As Stewart points out, the magnetic measurements on these compounds seems to provide useful oxidation state information, in contrast with uranium(III) and (IV) complexes, which often yield similar values of μ_{eff} . In fact, when one uses the Van Vleck equation³¹ to calculate the free ion moments for uranium(III), (IV), and (V), similar values are obtained for uranium(III) and (IV), while a much lower value is found for uranium(V) (Table 1-8):

Uranium Oxidation State	Electron Configuration	Calculated Free Ion Magnetic Moment
III	$[Rn]5f^3$	3.62 B.M.
IV	$[Rn]5f^2$	3.58 B.M.
V	$[Rn]5f^1$	2.54 B.M.

Table 1-8: Calculated free ion magnetic moments for various uranium oxidation states.

The magnetic susceptibility of two of the $(MeC_5H_4)_3UNR$ compounds discussed here has been measured. These were compounds IV and VI, $(MeC_5H_4)_3UNPh$ and $(MeC_5H_4)_3UN(p-Me_2NC_6H_4)$. The measurements were made over a temperature range of 5-300 K, and at magnetic fields of 5 kG and 40 kG. Both compounds exhibited susceptibility vs. temperature curves that had similar appearances to those measured by Berg and Stewart. For compound IV, the plots of χ_M vs. T and $1/\chi_M$ vs. T are shown in Figures 1-20 and 1-21. Linear regression performed on the $1/\chi_M$ plot yielded a value of $\mu_{eff} = 1.25$ B.M. in the low temperature region (7-40 K) and $\mu_{eff} = 1.96$ B.M. in the

Fig. 1-20: Chi vs T plot for $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$.

Fig. 1-21: $1/\chi_i$ vs T plot for $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$.

high temperature region (140-280 K). These values are quite similar to those obtained by Berg for the closely related $\text{Cp}_3\text{UNSiMe}_3$ system, and reasonably close to the values found by Stewart.

The data for compound VI is shown in Figure 1-22 (χ_M vs. T) and Figure 1-23 ($1/\chi_M$ vs. T). The linear regression yielded values of $\mu_{\text{eff}} = 1.40$ B.M. (5-40 K) and $\mu_{\text{eff}} = 2.21$ B.M. (120-220 K). The magnetic moments for all the uranium(V) imides that have been measured thus far are shown in Table 1-9 below:

Compound	μ_{eff} (B.M.) (Low Temp.)	μ_{eff} (B.M.) (High Temp.)	Ref.
$\text{Cp}_3\text{UNSiMe}_3$	1.19 (5-30 K)	1.83 (100-300 K)	4
$\text{U}[\text{N}(\text{SiMe}_3)_2]_3[\text{N}(\text{p-tolyl})]$	1.49 (5-40 K)	2.26 (140-240 K)	50
$\text{U}[\text{N}(\text{SiMe}_3)_2]_3(\text{NSiMe}_3)$	1.61 (5-40 K)	2.04 (140-280 K)	50
$(\text{MeC}_5\text{H}_4)_3\text{UNPh}$	1.25 (7-40 K)	1.96 (140-280 K)	
$(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{p-Me}_2\text{NC}_6\text{H}_4)$	1.40 (5-40 K)	2.21 (120-220 K)	

Table 1-9: Magnetic moments of uranium(V) imides.

1.4.B: Reactions of $(\text{MeC}_5\text{H}_4)_3\text{UNR}$

One of the questions we hoped to answer in studying the chemistry of these uranium imides was whether the lone pair on the nitrogen was accessible, and if so, would chemical reactions result? The crystal structure of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}^2$ seemed to suggest that this lone pair is not accessible to

Fig. 1-22: χ_m vs T plot for $(\text{MeC}_5\text{H}_4)_3\text{UNp-Me}_2\text{NC}_6\text{H}_4$

Fig. 1-23: $1/\chi_m$ vs T plot for $(\text{MeC}_5\text{H}_4)_3\text{UNp-Me}_2\text{NC}_6\text{H}_4$

acids. This was inferred from the U-N-C bond angle, which is nearly linear at 163° , suggesting that the nitrogen lone pair is interacting with the uranium to make a formal triple bond. The extremely short U-N distance of $2.06\text{\AA}$ seems to help support this argument.

Brennan attempted to see whether the lone pair was accessible by reaction of the imides with a good Lewis acid, AlMe_3 . He found that no adduct was formed using either $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ or $\text{Cp}_3\text{UNSiMe}_3$.^{9b} However, in the UNSiMe_3 case, it is possible that the electrons are involved in backbonding with a vacant silicon d-orbital, and in the UNPh case, the lone pair may be interacting with the phenyl π -system. Either of these effects could render these electrons inaccessible. For these reasons, the complex $(\text{MeC}_5\text{H}_4)_3\text{UNCMe}_3$ was reacted with AlMe_3 . Again, no adduct was isolated, and only unreacted starting material was recovered. We conclude from this that the nitrogen lone pair is probably interacting with the highly positively charged metal center, although we cannot discount the possibility of steric effects precluding the AlMe_3 from getting close enough to the nitrogen for interaction to occur.

Brennan made several attempts at reaction of $(\text{RC}_5\text{H}_4)_3\text{UNSiMe}_3$ with relatively small molecules.^{9b} The reactions shown below yielded only the unreacted silylimide complex (Scheme 1-16):

Scheme 1-16: Brennan's attempted reactions of the uranium silylimide complex.

Perhaps the most interesting reaction of this group was the failure of the material to reduce under several atmospheres of deuterium gas. The aqueous uranium(V)/uranium(IV) reduction potential is *ca.* +0.58 V,¹ and although there is no reported value for uranium(V) organometallic compounds, we still might expect the imide to reduce to the more favored +4 state.

A similar reduction was also attempted using the phenylimide, (MeC₅H₄)₃UNPh. When this compound was placed under 220 psi of H₂ for 2 days, only the unreacted starting material was recovered. The failure of any reduction to occur may reflect the fact that the hydrogen may be unable to coordinate to the sterically crowded and quite small uranium(V) metal center.

Interestingly, the compound may be reduced to uranium(IV) using a different technique. If the driving force of going from uranium(V) to uranium(IV) is not strong enough to cause reduction with hydrogen, perhaps combining this process with one that also causes a second uranium complex to be oxidized from uranium(III) to uranium(IV) will enable us to reduce the imide. This turns out to be the case. Uranium(III) complexes of the type (MeC₅H₄)₃U(NH₂R) are easily synthesized from (MeC₅H₄)₃U(thf) and primary amines. These syntheses and the properties of the complexes will be discussed in detail in Chapter 3. When the amine complex is allowed to react with a uranium(V) imide, two equivalents of the corresponding uranium(IV) amide are formed (Scheme 1-17):

Scheme 1-17: Reaction of a uranium(III) amine with a uranium(V) imide.

An attempt with was also made to see whether unsaturated hydrocarbons could insert into the U-N bond. This, as mentioned above, was tried unsuccessfully by Brennan utilizing the UNSiMe_3 complex and diphenylacetylene. We found that the phenylimide, $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, also did not react with either diphenylacetylene (1:1 molar ratio in toluene solution) or ethylene (200 p.s.i. for 24 hours in toluene solution).

One interesting set of reactions involving these compounds was performed using the series of molecules shown below (Figure 1-24):

Figure 1-24: Small σ -donating molecules used in reactions with uranium imides.

The common features of these materials is that they are all small, σ -donating molecules with partial negative charge on the donating atom. This should

enable them to coordinate very effectively with the highly positively charged metal center.

Brennan performed several of these reactions using both the silylimide, $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$, and the phenylimide, $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$.^{9b} When $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ was placed under an atmosphere of carbon monoxide, a light green precipitate was formed. This material was found to be insoluble in common organic solvents, including dichloromethane. This rules out the formulation of the product as $(\text{MeC}_5\text{H}_4)_3\text{UNCO}$, a compound I have prepared by an aqueous route analogous to that described earlier for the preparation of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (Scheme 1-18).

Scheme 1-18: Preparation of the uranium isocyanate in aqueous medium.

The isocyanate complex can be recrystallized from dichloromethane to give pale green microcrystals in high yield. The material shows a strong stretch in the infrared spectrum at 2180 cm^{-1} , in contrast with the material Brennan isolated, which exhibited a stretch at 2060 cm^{-1} . It is possible that one of these materials is a U-NCO complex, while the other is U-OCN, but these two compounds cannot be distinguished by their infrared spectra.³² No conclusive identification of the compound obtained from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with CO was ever obtained.

When the uranium phenylimide, $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, was placed under ca. 185 p.s.i. of CO in ether solution, an insertion product was obtained. A pale orange material formed, and this compound was found by ^1H NMR to be

identical to one obtained by Brennan from reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with PhNCO . The material is the phenylisocyanate dimer, $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2-\mu\text{-PhNCO}$, which has been structurally characterized² (Scheme 1-19).

Scheme 1-19: Preparations of $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2-\mu\text{-PhNCO}$.

Since Brennan had completely characterized this molecule, no characterization other than the ^1H NMR was carried out. A plausible mechanism for this insertion reaction is shown in Scheme 1-20.

Scheme 1-20: Possible mechanism for formation of an isocyanate complex from $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and CO.

Relatively few examples exist of similar insertions into metal-imido bonds to form isocyanates. This is despite the fact that this reaction is believed to be involved in catalytic carbonylation of organoazides and nitroaromatic compounds, proceeding through imide intermediates.⁵³ Recently, two examples of CO insertion into an N-Ar (Ar = Ph or p-MeC₆H₄) of a ruthenium trimer have appeared. In the first example, the isocyanate-metal complex is not isolated, but free isocyanate is formed (Scheme 1-21):⁵⁴

Scheme 1-21: Formation of phenylisocyanate from a ruthenium- μ_3 -NPh complex.

In the second example, a tautomeric mixture of $\text{Rh}_2(\mu\text{-NHR})(\text{CO})_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ and $\text{Rh}_2(\mu\text{-NR})(\text{CO})_2(\mu\text{-dppm})_2$ [$\text{R} = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$, $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$] was treated with one atmosphere of CO to yield a bridged isocyanate complex, $\text{Rh}_2(\mu\text{-}\eta^2\text{-RNCO})(\text{CO})_2(\text{m-dppm})_2$.⁵⁵ In addition, an insertion into an imidoiridium complex has been reported (Scheme 1-22):⁵⁶

Scheme 1-22: CO insertion into an imide-iridium bond.

Several other reports of isocyanate formation from imides have appeared.⁵⁷

Brennan also reacted $(\text{RC}_5\text{H}_4)_3\text{UNSiMe}_3$ ($\text{R} = \text{H, Me}$) with both ethylisocyanide (EtNC) and 2,6-xylylisocyanide.^{5b} From the EtNC reactions he obtained light green crystalline materials with an infrared stretch at 2080 cm^{-1} . From various data, he formulated the compounds as $(\text{RC}_5\text{H}_4)_3\text{UNCNEt}$, but firm characterization was not obtained. The reactions with ethylisocyanide gave a mixture of products and was not pursued.

When Brennan reacted $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with ethylisocyanide, a different product was obtained. This light red material was found to be the uranium amide, $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$. This compound has been synthesized by several other methods which will be discussed in Chapter 3. Because it was difficult to imagine a mechanism by which an $\text{H}\cdot$ could be transferred, this reaction was repeated in my work, and it was found to be correct. It is especially interesting that this reduction from uranium(V) to uranium(IV) occurs in this reaction, but not under *ca.* 15 atmospheres of H_2 or D_2 . Presumably, it is the ability of the isocyanide to coordinate to the metal center that facilitates the reaction, a coordination unlikely to occur with hydrogen. Using the idea that the isocyanide is able to coordinate, we can imagine a mechanism where an α -hydrogen on the isocyanide is transferred to the imido group (Scheme 1-23):

Scheme 1-23: Possible mechanism for reduction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with EtNC .

A labelling study of this reaction using PhCH_2NC and PhCD_2NC would help elucidate the mechanism. In addition, we did not search for the organic

byproducts of this reaction; identifying these could also help with an understanding of the process. This reaction formally involves the transfer of an H- from the isocyanide to the uranium, thus attempting to protonate the imide using an acid should not result in the same product. Indeed, we found that $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ does not undergo any reaction with p-toluenesulfonic acid.

Of course, if this postulate of the mechanism is correct, reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with an isocyanide containing no α -hydrogens should not give this product. This was found to be the case. Reaction of the phenylimide with either $^t\text{BuNC}$ or 2,6-xylylisocyanide yielded orange crystalline products. In both cases, the ^1H NMR of the materials was extremely complex. The xylylisocyanide reaction was not pursued any further.

Attempts at characterization of the $^t\text{BuNC}$ reaction product were unsuccessful. As stated above, the orange crystals gave an extremely complex ^1H NMR spectrum in C_6D_6 , and the spectrum was observed to change over several hours, along with a change in solution color from orange to pale yellow. This spectrum was complex. An attempt to obtain the spectrum in $\text{d}_8\text{-thf}$ also failed, as the color lightened and the spectrum changed even more quickly. The infrared spectrum of this material showed a sharp stretch at 2180 cm^{-1} , in the $\text{C}\equiv\text{N}$ region of the spectrum (free $^t\text{BuNC}$ has a stretch at $2135\text{--}2140\text{ cm}^{-1}$). This increase in the stretching frequency is consistent with a coordinated $^t\text{BuNC}$. Similar results have been observed with other cyclopentadienyl uranium isocyanide complexes.³⁰ The remainder of the spectrum was quite different from the phenylimide starting material. A mass spectrum of this material gave little useful information, and elemental analysis showed a high percentage of nitrogen.

A single crystal of this material was mounted in a quartz capillary and X-ray diffraction analysis performed. The crystal was found to be in a P-centered, orthorhombic space group ($P2_12_12_1$) with unit cell parameters $a = 15.24 \text{ \AA}$, $b = 18.21 \text{ \AA}$, and $c = 12.10 \text{ \AA}$. Unfortunately, the crystal structure could not be solved.

It seems likely that this material is an insertion product of some sort, although it is unfortunate that the material could not be characterized. It should be noted that a second product was obtained in this reaction, and this material was found to be $(\text{MeC}_5\text{H}_4)_4\text{U}$ by comparison of the ^1H NMR spectrum of this compound with the spectrum of an authentic sample provided by M. Weydert.³⁹ The presence of this product suggests a redistribution of ligands in the course of the reaction, perhaps explaining the apparent complexity of this reaction as well as the high nitrogen content found in the product.

The reactions of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and $(\text{MeC}_5\text{H}_4)_3\text{USiMe}_3$ with organoazides, $\text{R}'\text{N}_3$, proved particularly interesting. In cases where reaction occurred, the uranium(V) imide was reduced to the uranium(IV) azide, as shown below (Scheme 1-24):

Scheme 1-24: Reaction of uranium(V) imides with azides.

Several different azides were used in these reactions (Figure 1-25):

Figure 1-25: Azides used in reactions with uranium(V) imides.

To compare the effects of the R and R' groups in the reaction shown in Scheme 1-24, a series of eight reactions was carried out under similar conditions. The uranium(IV) imide was dissolved in toluene with ca. 1.6-1.7 molar equivalents of the appropriate azide, R'N₃. The mixture was then stirred for 24 hours at room temperature. At the end of this time, volatile materials were removed and the residues examined by ¹H NMR spectroscopy, to determine the relative amounts of (MeC₅H₄)₃UNR remaining and (MeC₅H₄)₃UN₃ produced. Table 1-10 below summarizes the results of these reactions:

R	R'	(MeC ₅ H ₄) ₃ UNR (%)	(MeC ₅ H ₄) ₃ UN ₃ (%)
Ph	p-MeC ₆ H ₄	100	0
Ph	CPh ₃	100	0
Ph	SiMe ₃	85	15
Ph	SnMe ₃	5	95
SiMe ₃	Ph	100	0
SiMe ₃	CPh ₃	98	2
SiMe ₃	SiMe ₃	92	8
SiMe ₃	SnMe ₃	7	93

Table 1-10: Summary of results of reaction of (MeC₅H₄)₃UNR with R'N₃.

The results shown above can be rationalized easily by once again looking at the resonance structures of azides (Figure 1-26):

Figure 1-26: Resonance structures of azides.

In this case, we would predict that resonance structure A is more likely to produce the uranium(IV) azide product from the uranium(V) imide. This is because the electron density and negatively charged γ -nitrogen will be more likely to coordinate to the highly positively charged metal center. Presumably, a γ -coordination of this type is necessary to avoid steric interactions at the transition state and enable the reaction to occur.

The reaction product distribution did indeed seem to follow the expected order based on the above prediction. Trimethyltinazide is certainly the most ionic azide of the group, therefore tending more towards structure A. It easily reacted the fastest, with the reaction going approximately 90% to the uranium(IV) azide after one day. Silyl azides are reported to tend more towards structure A than alkyl azides;⁶⁰ and we would thus expect Me_3SiN_3 to react somewhat faster than Ph_3CN_3 , and this is the observed result. Neither azide reacts quickly; Me_3SiN_3 , when reacted with the imide, yielded less than 10% of the azide after one day, while Ph_3CN_3 does not react appreciably at all with $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and only very slightly with $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ after one day. Finally, aryl azides tend quite strongly towards structure B, and are, as expected, the slowest to react. In fact, no uranium(IV) azide was observed

when ArN_3 ($\text{Ar} = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) was allowed to react with either of the uranium(V) imides.

In order to show that this reaction simply replaces the NR group with the N_3 group from $\text{R}'\text{N}_3$ and that no odd rearrangement occurs, a labelling reaction was carried out. $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$ [ca. 99% ^{15}N , prepared from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and Ph^{15}NNN] was allowed to react with Me_3SnN_3 for four days in toluene. At the end of this time, the volatile materials were removed and collected in a liquid nitrogen trap. The ^1H NMR spectrum of the green-brown residue indicated only uranium(IV) azide and no remaining imide. There were also several peaks in the diamagnetic region of the spectrum, presumably from the byproducts of the reaction. A mass spectrum of this material indicated that no ^{15}N remained in the product $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The spectrum and a simulation of the molecular ion are shown in Figure 1-27.

Interestingly, a second product was also seen in the mass spectrum. The spectrum is consistent with the formulation $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$, and this spectrum is shown with the simulation of the molecular ion in Figure 1-28. Further confirmation that this material was produced was found when the ^1H NMR spectrum was studied more closely. The spectrum of $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$ has been reported, at 31°C in CS_2 solvent.⁶¹ The report assigns the MeC_5H_4 ring resonances at $\delta = 5.66$ and 5.53 ppm, the MeC_5H_4 methyl group resonance at $\delta = 2.04$ ppm, and the trimethyltin methyl groups at $\delta = -0.01$ ppm. In order to look for these resonances and examine the by-products more closely, the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and Me_3SnN_3 was run once again. This time, the materials were allowed to react for nine days in toluene. The volatile materials were removed, and the mixture was extracted with hexane. When the hexane was removed, a pale brown oily solid was obtained, which was dissolved in C_6D_6 and transferred to a 10 mm NMR tube. The ^1H NMR

Figure 1-27: The mass spectrum of the product mixture from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$ with Me_3SnN_3 . The highest observed mass is for $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, and the simulation of the isotopic cluster for this unit is shown on the right. There is no ^{15}N in the product.

Figure 1-28: The mass spectrum of the product mixture from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NPh}$ with Me_3SnN_3 . The highest observed mass is for $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$, and the simulation of the isotopic cluster for this unit is shown on the right.

spectrum of this material indicated that $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$ is formed in the reaction. Two small peaks are seen in the spectrum at $\delta = 5.6 - 5.8$ ppm, and a larger peak is observed at $\delta = \text{ca. } 2.1$ ppm. These are consistent with the values described above for $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$. Between *ca.* 0 and 0.5 ppm the spectrum contains several peaks, and it is difficult to definitively identify any other byproduct.

However, additional information is obtained by taking the ^{119}Sn NMR of the material at 33.3 MHz. This was done using the conditions described in the experimental section (Chapter 4). After 3500 accumulations, a very clean spectrum was obtained, which contained the following peaks (referenced to Me_4Sn at $\delta = 0.0$ ppm): $\delta = +64.6$ ppm, $\delta = +48.9$ ppm, and $\delta = +26.3$ ppm. The spectrum is shown in Figure 1-29.

What do we learn from this spectrum? First of all, the ^{119}Sn spectrum of CpSnMe_3 is known. The tin resonance is reported to occur at either $\delta = -26$ ppm⁶² or $\delta = +32$ ppm.⁶³ We would expect the spectrum of $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$ to be almost identical, thus we conclude that the peak we observed at $\delta = +26.3$ ppm is from $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$.

What about the other two peaks in our tin spectrum? If the Me_3Sn group from the starting azide couples with the NPh group that dissociates from the uranium(V) imide in this reaction, we could easily envision two other products being formed: Me_3SnNHPH , from the coupled byproduct picking up a proton, or $[\text{Me}_3\text{SnNPh}]_2$, from dimerization to form the substituted hydrazine (see Scheme 1-25). The ^{119}Sn NMR spectrum of Me_3SnNHPH has been reported, with a tin resonance at $\delta = +46.4$ ppm.⁶⁴ This is very close to the peak we observed at $\delta = +48.9$ ppm. In addition, the ^1H NMR of our material showed a fairly distinct, broad resonance at $\delta = 2.65$ ppm. This is quite consistent with the reported value for the N-H resonance

Figure 1-29: The ^{119}Sn NMR spectrum of the residue from the hexane extract of the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with Me_3SnN_3 .

Scheme 1-25: Possible mechanism for the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with Me_3SnN_3 , attempting to show the formation of the observed and postulated by-products.

of Me_3SnNHPh , which is $\delta = 2.8$ ppm.⁶⁴ The Me_3Sn resonance in the ^1H NMR of this compound is reported to be found at $\delta = 0.21$ ppm; we see a large resonance at $\delta = 0.28$ ppm (although impurities such as grease make this resonance impossible to identify unambiguously).

Presumably, the remaining resonance in the ^{119}Sn NMR ($\delta = +64.6$ ppm) is due to the hydrazine, $(\text{Me}_3\text{Sn})(\text{Ph})\text{NN}(\text{Ph})(\text{Me}_3\text{Sn})$. Unfortunately, the ^{119}Sn NMR of this compound has not been reported. However, the Me_3Sn group in the ^1H NMR is reported at $\delta = 0.40$ ppm,⁶⁵ and we observe a fairly small resonance at this value. Also, since this Me_3Sn resonance shifts downfield in the ^1H NMR relative to that in the compound Me_3SnNHPh , we would expect the ^{119}Sn resonance to also move downfield, and this is consistent with what we observed in the ^{119}Sn NMR.

The finding that $(\text{MeC}_5\text{H}_4)\text{SnMe}_3$ is one of the by-products in the reaction suggests that once the azide has coordinated to the metal center, it may choose to react with either a cyclopentadienyl ring [leaving $(\text{MeC}_5\text{H}_4)_2\text{U}(\text{NR})(\text{N}_3)$, which presumably decomposes] or the imido ligand. This may mean that in some cases the azide coordinates opposite from the imido ligand in a trigonal bipyramidal type of arrangement (as discussed earlier in this chapter), while it sometimes coordinates adjacent to the imide.

A very similar reaction to the one described above has recently been reported using germanium compound.⁶⁶ When a germanium(II) silylamide is reacted with Me_3SiN_3 , a mixed amido/azido complex is obtained, as shown below (Scheme 1-26):

Scheme 1-26: Reaction of a germanium silylamide with Me_3SiN_3 .

Presumably, this reaction proceeds in a similar manner to the one we observed with uranium. A germanium silylimide is probably initially formed, followed by coordination of a second azide (Me_3SiN_3) and transfer of the Me_3Si group to the imido ligand. This then yields the stable germanium(IV) product. This mechanism is outlined below (Scheme 1-27):

Scheme 1-27: Possible mechanism for germanium amide/azide complex formation.

The first step of this, the formation of the germanium imide, is expected since $\text{R}'_3\text{SiN}_3$ ($\text{R}' = \text{Et}, \text{O}^t\text{Bu}$) react with the germanium(II) compound to give stable imides (Scheme 1-28):

Scheme 1-28: Preparation of a germanium(IV) imide.

These two imides appear to stop at this stage due to the steric requirements of the R' group.

It seems sensible that the germanium amide/azide complex is favored because it is a stable germanium(IV) compound. However, in the case of uranium, the compound $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{N}_3)(\text{NRR}')$ would presumably be extremely bulky and, since energy is gained by reduction to uranium(IV), the amido ligand is lost. Our observation that the imido R group couples with the R' group from the incoming azide appears to be supported by these germanium complexes in which an identical coupling is seen.

Two other reactions of the imides were done. The first is the reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with alcohols. When the silylimide was heated in toluene with one molar equivalent of methanol for several days, a mixture of the unreacted starting material and the uranium(IV) methoxide, $(\text{MeC}_5\text{H}_4)_3\text{UOMe}$, was produced. The methoxide was identified by its ^1H NMR spectrum, which was identical to material produced by the two reactions below (Scheme 1-29):

Scheme 1-29: Preparations of a uranium(IV) methoxide. The top reaction is from this work; the bottom reaction is from reference 67.

Similarly, a mixture of starting material and the uranium phenoxide $(\text{MeC}_5\text{H}_4)_3\text{UOPh}$ was obtained from the silylimide and phenol in diethylether. Again, the phenoxide was identified by its ^1H NMR, which was found to be identical to the NMR of the product obtained by Stults from the reaction of $(\text{MeC}_5\text{H}_4)_3\text{U(thf)}$ with phenol.⁶⁷ The apparently slow rate of these reactions may reflect the need for two molar equivalents of the alcohol to protonate off the imide as the amine.

These reactions are not particularly unusual; in 1961 Thomas found that a tantalum imido/amido complex could be easily converted to the alkoxide (Scheme 1-30):⁶⁸

Scheme 1-30: Reaction of a tantalum imide with alcohol.

In fact, the germanium imide compound discussed earlier also forms an alkoxide upon reaction with methanol (Scheme 1-31):⁶⁶

Scheme 1-31: Reaction of a germanium imide with methanol.

In Section 1.3, the reaction of $\text{Co}_2(\text{CO})_8$ with $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was discussed. This reaction was found to produce the bridged isocarbonyl complex, $(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}[\text{Co}_3(\text{CO})_9]$. Surprisingly, when $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ ($\text{R} = \text{SiMe}_3, ^t\text{Bu}$) was allowed to react with $\text{Co}_2(\text{CO})_8$, the identical red, crystalline product was obtained (Scheme 1-32).

Scheme 1-32: Reaction of uranium(V) imides with cobalt carbonyl.

As mentioned earlier, the analogous C_5H_5 compound has been synthesized by Stutte and Schmid,⁴⁴ and is also bright red.

This uranium(IV) complex shows a typical ^1H NMR, with a 3:2:2 pattern for the MeC_5H_4 at $\delta = -10.19$ ppm (3H), $\delta = -1.49$ ppm (2H), and $\delta = +5.16$ ppm (2H). The infrared spectrum of the compound shows several overlapped stretches in a somewhat broad carbonyl region: 2080, 2015, and 1965 cm^{-1} are the most obvious peaks. The infrared spectrum was also recorded in Et_2O solution, and the carbonyl region appeared sharper; stretches were observed at 2080, 2050, 2020, 1960, 1930, 1900, and 1860 cm^{-1} . The spectra both as a Nujol mull and in solution are shown in Figure 1-30.

Figure 1-30: Infrared spectra of $(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}[\text{Co}_3(\text{CO})_9]$, showing the CO stretching region. The top spectrum was taken as a Nujol mull, the bottom as a diethylether solution.

The analogous reaction was also performed using $\text{Cp}_3\text{UNSiMe}_3$ and cobalt carbonyl. Red crystals were obtained from toluene, and the ^1H NMR showed a single sharp resonance at $\delta = -3.3$ ppm. This is identical to the value reported by Stutte and Schmid. The carbonyl region of the infrared spectrum (Nujol mull) was found to be almost identical to the methycyclopentadienyl derivative, with three easily identifiable stretches at 2080, 2020, and 1970 cm^{-1} . Stutte and Schmid report similar data; they find a sharp ν_{CO} at 2070 cm^{-1} , and four other bands at 2000, 1985, 1970, and 1940 cm^{-1} .

The reaction between $\text{Cp}_3\text{UNSiMe}_3$ and $\text{Co}_2(\text{CO})_8$ was also performed in an NMR tube in d_8 -toluene at room temperature, to see both how quickly the reaction proceeded and how cleanly. It was found that the reaction is essentially complete after one hour. The ^1H NMR is extremely clean, showing only two resonances (other than solvent): the diminishing peak at $\delta = -6.4$ ppm from $\text{Cp}_3\text{UNSiMe}_3$, and the growing resonance at $\delta = -3.3$ ppm from $\text{Cp}_3\text{U}-\mu\text{-OC}[\text{Co}_2(\text{CO})_9]$. The reaction has a $t_{1/2}$ of 15-20 minutes under these conditions.

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Chapter 2

Reactions of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Diazides

The subject of this chapter is the study of reactions of trivalent uranium with diazidobenzene derivatives. These reactions were designed to produce bridged, dinuclear uranium-diimides of the type shown in Figure 2-1 below, where R is an organic residue:

Figure 2-1: General structure of a bridged uranium diimide.

Several of these molecules have been synthesized by techniques analogous to those used for preparation of the mononuclear uranium imides, as discussed in Chapter 1. All the diazides used in these syntheses are some type of aryl diazide, with the exception of one silyl diazide, $\text{Me}_2\text{Si}(\text{N}_3)_2$. This latter material is the only one of the diazides used which produces the uranium(IV) azide as the product.

Our purpose in preparing and studying these bridged diimide complexes was to investigate whether the proper combinations of the electronic natures of the ligand and the metal could be used to observe electronic interaction across the bridge. A great deal of interest over the last twenty years or so has focused upon metal complexes linked by various

bridging groups. In particular, groups with delocalized π -systems have been used extensively to study electron transfer processes in dinuclear systems.¹ This is demonstrated by studies involving pyrazine, a ligand used by Creutz and Taube in early electron transfer studies on what is now called the Creutz-Taube ion (Figure 2-2).²

Figure 2-2: Structure of the Creutz-Taube ion.

Similar dinuclear cyclopentadienyl pyrazine complexes of uranium have been synthesized, by Raymond and Eigenbrot in 1982,³ with the general structure shown below (Figure 2-3):

Figure 2-3: Structure of a $(\text{Cp}_3\text{U})_2$ -pyrazine complex.

Their goal was to look for some type of electronic exchange between the actinide metal centers. However, the early magnetic susceptibility results on these compounds were somewhat inconclusive. According to the authors, "The magnetic behavior of the methylated compound has been investigated four times. Three times the data indicate the compound is only weakly paramagnetic, and that the paramagnetism varies slowly with temperature.

The fourth investigation produced results that suggest an abrupt spin-state change at very low temperature. Any further interpretation of the magnetic behavior of this compound will require further investigation."⁴

We have synthesized the uranium-pyrazine complex $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{pyrazine})$ by Raymond and Eigenbrot's procedure, and done a further investigation of its magnetic behavior. The data, shown in Figures 2-4 and 2-5, does not indicate the presence of any interaction between the uranium nuclei. Fitting this data to the Curie-Weiss law yields a magnetic moment $\mu_{\text{eff}} = 5.22$ B.M. ($\Theta = -277$ K; $\mu_{\text{eff}} = 3.69$ B.M. per uranium atom) in the low temperature region (5-40 K) and a value of $\mu_{\text{eff}} = 4.28$ B.M. ($\Theta = -154$ K; $\mu_{\text{eff}} = 3.03$ B. M. per uranium atom) in the high temperature region (160-300 K).

One of the problems with the pyrazine ligand in a uranium system involves the redox potentials of both the ligand and metal. The Raymond complexes, if viewed as simple Lewis base coordination adducts, are uranium(III) materials. However, the pyrazine ligand is capable of accepting an electron from one of the metal centers, reducing the ligand and oxidizing one of the uraniums to U(IV). The reduction potential for the ligand is shown below (Scheme 2-1):⁵

Scheme 2-1: One-electron reduction of pyrazine to the radical/anion.

This can be compared with the potential for oxidizing the uranium(III). In aqueous solution, the U(III)/U(IV) oxidation potential is reported to be +0.63

Fig. 2-4: Chi vs Temp. plot for the pyrazine complex.

Fig. 2-5: $1/\chi_m$ vs Temp. plot for the pyrazine complex.

V.⁶ However, in organometallic systems, higher values have been obtained for the reductions of $(\text{RC}_5\text{H}_4)_3\text{UCl}$, as shown below (Scheme 2-2):⁷

Scheme 2-2: Reduction potentials of $(\text{RC}_5\text{H}_4)_3\text{UCl}$.

If, as often occurs, the reduction potential of the base (pyrazine) is lowered upon coordination to the metal center, the uranium may indeed be capable of reducing the pyrazine ligand. It should be noted that in other work from our group, D. Berg found that Yb(II) [as $\text{Cp}_2^*\text{Yb}(\text{OEt}_2)_2$] was oxidized to Yb(III) by pyrazine,⁸ even though the Yb(II)/Yb(III) oxidation potential has been measured at only *ca.* +1.3 V in $\text{Cp}_2^*\text{Yb}(\text{MeCN})_2$.⁹

If a redox process like this occurs in the uranium compound, the reduction of the ligand could possibly destroy any electronic interactions between the uranium metal centers. Although the formal oxidation state of the uranium-pyrazine complex is difficult to determine unambiguously, we can easily imagine that at least one of the metal centers may have been oxidized to uranium(IV), and that this may be the reason no electronic exchange is observed in the system. Indeed, the rather narrow ^1H NMR linewidths for the cyclopentadienyl ring protons in $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{pyrazine})$ (Eigenbrot reports $\nu_{1/2} = 15$ Hz; we obtained a value of $\nu_{1/2} = 12$ Hz) help to support this idea; these linewidths seem somewhat intermediate between those expected for uranium(III) and uranium(IV). In addition, the shape of

the $1/\chi_M$ versus T curve does not resemble the curves obtained for other trivalent uranium compounds, and may again indicate that an oxidation took place.

This leaves us in a rather interesting position with our uranium(V) dinuclear diimides. Pyrazine, as stated above, is considered to be an excellent ligand for preparing linked dinuclear metal systems. But, in these uranium compounds, it may cause oxidation of the metal, therefore making it ineffective as a ligand which allows electron exchange between the metal centers. Our imide ligands, on the other hand, are already constrained in a system where they are stabilizing the uranium in a particular oxidation state. Moreover, these uranium(V) atoms have an f^1 configuration, and electron interaction which causes pairing of the spins may be quite favorable in the right system. This puts us in a unique position, as these imides are the only reported uranium(V) organometallic compounds.

It should be noted here that very few examples of magnetic interaction between actinide nuclei have been reported, and these examples occur in extended lattice systems rather than simple molecular materials. For example, the magnetism of the trivalent actinide halides (AnX_3) has been investigated.¹⁰ In the case of uranium, UCl_3 , UBr_3 , and UI_3 all become antiferromagnetic at low temperatures, with Néel temperatures of 22 K, 15 K, and 3.4 K, respectively. The decrease in the T_N predictably follows the increase in the minimum metal-ion to metal-ion distance in the lattice; in UCl_3 , the minimum U-U distance is ca. 4.3 Å, in UBr_3 , 4.4 Å, and in UI_3 , 5.4 Å. $PuCl_3$ also becomes antiferromagnetic, with a T_N of 4.5 K. Note that the ground state configurations of U^{3+} and Pu^{3+} are f^3 and f^5 , and that no magnetic interaction was observed for the neptunium(III) halides, whose ground state is f^4 .

Why do we feel that an f^1 electron configuration may favor electronic exchange? A quote from the paper above in which the magnetic behavior of AnX_3 was evaluated may help explain this:

"In a qualitative assessment of the factors that lead to cooperative magnetic phenomena -- ferromagnetism or antiferromagnetism -- electronic factors appear to be of major importance, crystal field splitting, and metal-ion to metal-ion distance are of secondary importance, and the detailed structure of the crystal appears to be a minor factor. With a single exception, cooperative magnetic phenomena were found for the two ions with half-integer values of J , U^{3+} ($J = 9/2$) and Pu^{3+} ($J = 5/2$). $5f^n$ ions with half-integer J values necessarily have a magnetically degenerate lowest crystal field level (Kramers doublet), and thus will have a finite magnetic moment at low temperatures. Magnetic ordering can occur at temperatures sufficiently low that the exchange energy is greater than the thermal energy of the lattice. For Np^{3+} ($J = 4$), the crystal field splitting leads to a singlet ground level which is magnetically inactive.¹¹ Cooperative magnetic phenomena may also occur for ions of integer J values with a multiplet lowest state split by the crystal field, such as in uranium dioxide ($T_N = 29 K$).^{12,13}

Thus, since we are dealing with a ground state $J = 5/2$, we should have an opportunity to observe magnetic interaction in our system. This, of course, also suggests that uranium(III) should be a good ion for seeing these effects (as it proves to be in UCl_3 etc.); the problem seems to be in producing a discrete, dinuclear uranium(III) molecule where the metal is stabilized in this oxidation state. Uranium(IV), on the other hand, would be a poorer choice for these systems, despite the apparently unique behavior of UO_2 .

What is the right bridging ligand to maximize the possibility of electron exchange in a dinuclear uranium(V) compound? It seems logical that the proper ligand to choose would have a π -conjugated system, and therefore the para-phenylenediimido ligand, $[\text{NC}_6\text{H}_4\text{N}]^{4-}$, seems a logical choice.

Several recent papers from Maatta *et. al.*¹⁴ have appeared utilizing this ligand. The first compounds were prepared by reaction of Mo(IV) with p-diazidobenzene, as shown below (Scheme 2-3):

Scheme 2-3: Preparation of a molybdenum(VI) diimide from p-diazidobenzene.

These dimolybdenum complexes may easily be reduced to form, in addition to the Mo(VI)-Mo(VI) system, the Mo(V)-Mo(V), Mo(IV)-Mo(IV), and Mo(III)-Mo(III) complexes. Unfortunately, no magnetic data has appeared concerning these materials. Maatta *et. al.* also synthesized several dirhenium complexes using the p-phenylenediimido ligand, but once again, no magnetic information is available.

The two-electron oxidation of the metal in the scheme shown above is precisely the reaction we would like to perform with a uranium system, and therefore this ligand seemed to be a good starting point for our study of diimide complexes.

In the remainder of this chapter, I will discuss the preparation and properties of our uranium diimide complexes. They will be presented one by one, with a particular focus on the comparison between the properties of the compounds using the para-phenylenediimido ligand and the meta-phenylenediimido ligand, shown below (Figure 2-6):

Figure 2-6: Structures of the para- and meta-phenylenediimido ligands.

Section 2.1: Preparation and Properties of $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,4\text{-N}_2\text{C}_6\text{H}_4)$

Our first attempt at preparation of a uranium diimide involved chemistry analogous to that utilized by Maatta in synthesizing the molybdenum diimides and our own work with the mononuclear uranium imides. Para-diazidobenzene is easily prepared by diazotization of the corresponding diamine as shown below (Scheme 2-4):¹⁵

Scheme 2-4: Preparation of p-diazidobenzene.

When a solution of this diazide in ether was added to two molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, immediate evolution of nitrogen was observed, and a deep purple solution with a purple precipitate was obtained. Purple flakes could then be crystallized from warm toluene in fairly good yield.

The color of this material seemed to indicate that this compound was unusual when compared with the other uranium(V) imides we had prepared. As mentioned in Chapter 1, every one of those mononuclear materials was a very deep red or red/brown in color; this material was dark purple. The color led us to wonder if this material was indeed an analogous

imide, but characterization of the complex (which will be described subsequently) confirmed that it is the diimide shown below (Figure 2-7):

Figure 2-7: Structure of the uranium diimide $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,4\text{-N}_2\text{C}_6\text{H}_4)$.

The ^1H NMR spectrum of this compound, which will be referred to as the "para-diimide," indicated a highly symmetric material. Four peaks are seen in the spectrum, which is shown later in this chapter in Figure 2-13. The 3:2:2 pattern of the MeC_5H_4 appears at $\delta = 4.69$ ppm (Me), $\delta = -2.46$ ppm (ring H) and $\delta = -9.01$ ppm (ring H). These values are very similar to those obtained in the ^1H NMR spectra of the mononuclear phenylimides discussed in Chapter 1 (see Table 1-6). The fourth resonance is observed at $\delta = +15.11$ ppm, and is due to the four chemically equivalent protons of the p-phenylenediimido ligand [which are magnetically inequivalent (AA'A'A'')] Since these protons may be viewed as being both ortho to one uranium(V) and meta to another uranium(V), we would expect this resonance to be intermediate between the usual ortho and meta resonances seen in the mononuclear phenylimide complexes, and this is indeed the case.

One particular feature of the NMR spectrum should be discussed. The linewidths of the protons in this spectrum are somewhat unusual when compared to other uranium(V) phenylimide complexes. The cyclopentadienyl methyl group has $\nu_{1/2} = 6$ Hz, while in $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, the analogous peak has $\nu_{1/2} = 20$ Hz. Similarly, the cyclopentadienyl ring proton resonances in $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ have $\nu_{1/2} = 60$ and 49 Hz, while in the para-

diimide, these resonances have $\nu_{1/2} = 23$ and 17 Hz. We will not try to read too much into these numbers, since the bridged complex of this sort represents a different system from the simpler $(\text{RC}_5\text{H}_4)_3\text{UX}$.

Other methods of characterization gave results consistent with the formulation of this material as $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{p-NC}_6\text{H}_4\text{N})$. The melting point, 261-263°C, was high relative to the mononuclear compounds, and suggested a dinuclear material. The compound exhibited a molecular ion in the electron impact mass spectrum, at 1054 amu. The elemental analysis was also consistent, and the infrared spectrum appeared to be similar to the other uranium phenylimides.

The interesting measurement made on this compound was the magnetic susceptibility. The data is shown in Figures 2-8 and 2-9 as plots of χ_M vs. temperature and $1/\chi_M$ vs. temperature, at magnetic fields of 5 kG and 40 kG. From linear regression performed on the high temperature region (140 - 280K) of the $1/\chi_M$ plot, a $\mu_{\text{eff}} = 2.94$ B.M. ($\Theta = -147$ K) was obtained. This yields a value of $\mu_{\text{eff}} = 2.08$ B.M. per uranium atom, consistent with the high temperature results obtained in the mononuclear uranium(V) imides [See Table 1-7; the value obtained for $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ from 140 - 280K was 1.96 B.M.].

The fascinating feature of the magnetic data is the antiferromagnetic coupling observed with a Néel temperature (T_N) of 18 K. This is the first example of antiferromagnetic exchange observed in a discrete compound of the actinides (as opposed to in the extended lattices of UCl_3 or PuCl_3). The low temperature behavior of this material has been modeled by calculations performed by Dr. Norman Edelstein at the Lawrence Berkeley Laboratory. His calculations indicate an exchange interaction of approximately $J = -19 \text{ cm}^{-1}$.

Fig. 2-8: Chi vs Temperature plot for the para-diimide.

Fig. 2-9: $1/\chi_i$ vs Temperature plot for the para-diimide.

These calculations are discussed in more detail at the end of this chapter (Section 2.5).

The exchange interaction observed is fairly considerable when one takes into account the large distance between the metal centers. We can estimate this distance, based on the crystal structure of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ reported by Brennan and Andersen,¹⁶ and using a very simple modeling program for the Apple® Macintosh® called the "Molecular Editor."¹⁷ The model of the core of the compound is shown in Figure 2-10, and the U-U distance is ca. 9.6 Å. This distance should be kept in mind for comparisons later in this chapter.

It should be noted that the magnetic behavior of this material is strongly dependent on the purity. Six independent magnetic susceptibility measurements were made on different samples, and although the T_N remained consistent at ca. 16-18 K, the data for the various runs differed considerably at extremely low temperatures (below 5-7 K). Because the susceptibility of the antiferromagnetic material $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{p-NC}_6\text{H}_4\text{N})$ becomes extremely small at these low temperatures, very small amounts of paramagnetic impurities will greatly affect the data, and in fact should dominate. This is an occurrence that is not uncommon in attempting to measure the susceptibility of antiferromagnetic materials;¹⁸ Ginsberg, in a review on magnetism, states that, "The largest effect [of a paramagnetic impurity] is found for clusters with antiferromagnetic exchange...In this case the impurity causes a minimum to appear in the susceptibility versus temperature curve at a temperature below the susceptibility maximum."¹⁹ Repeated attempts at recrystallizing the compound did not alleviate the problem. The consistency of the T_N , and the reproducibility of the higher temperature data, however, give us great confidence in these results. Plots of

Figure 2-10: Para-Dimide Molecular Editor[®] Model

the runs made using several samples to show the variation are shown in Figure 2-11.

The observation that the spins on each uranium of the para-diimide antiferromagnetically couple may be rationalized by a super-exchange pathway. This can be demonstrated by examining several possible resonance structures that may be drawn for this compound. Two of these structures are shown in Figure 2-12. These resonance forms are not meant to suggest any type of ground state structure for the material, but instead are used to show the way a completely conjugated π -system may be drawn which extends from one uranium center across the bridging ligand to the other metal. It is possible that the presence of this π -conjugation is what allows the two uranium f^1 centers to "communicate" electronically. (Please note that a large number of other resonance structures may be drawn to represent this compound; these three are simply meant to illustrate a point and are by no means exclusive.)

Additionally, Hendrickson *et. al.* have done considerable magnetic investigations on compounds containing related ligands.²⁰ They found that dinuclear copper complexes containing a p-phenylenediamine bridging ligand ($p\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$) exhibit antiferromagnetic coupling. For example, the complex $[\text{Cu}_2(\text{tren})_2(\text{PPD})][\text{NO}_3]_4$ ($\text{tren} = 2,2',2''\text{-triaminotriethylamine}$; $\text{PPD} = p\text{-phenylenediamine}$) becomes antiferromagnetic with $T_N = 67\text{K}$ and an exchange interaction $J = -35.1 \text{ cm}^{-1}$. The authors discuss possible exchange mechanisms in some detail using molecular orbital calculations, and conclude that the pathway for the exchange is primarily a σ -type pathway. However, it must be noted that this bridging ligand is a σ -donating ligand with sp^3 hybridized nitrogens and therefore should have Cu-N-C angles which are far from linear, with no p-orbital on the nitrogen parallel to the

Fig. 2-11: Chi vs T plot for six para-diimide samples.

Figure 2-12: Resonance structures of the para-diimide attempting to demonstrate the existence of a completely conjugated π -system across the ligand.

aromatic system to conduct the exchange. This should not be the case in a system like ours in which each amine has been doubly deprotonated.

It is possible that both the unusual color and the NMR linewidths observed for the para-diimide complex of uranium reflect the unusual electronic nature of this compound. We decided that it would, of course, be interesting to synthesize a second uranium diimide that does not have the same type of conjugated π -system. We hoped to answer the following questions by performing this experiment: Does the non-conjugated material exhibit electronic exchange between the uranium centers? Will the non-conjugated diimide show the same surprising color and NMR linewidths? What other differences in properties will we observe in a diimide made with a non-conjugated bridge? These questions are answered in the next section.

Section 2.2: Preparation and Properties of $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,3\text{-N}_2\text{C}_6\text{H}_4)$

In deciding which diimide to synthesize in order to attempt to answer the questions posed above, we turned to an organic chemist's view of these materials. While a conjugated π -system may be drawn to bridge the metal centers using the *p*-phenylenediimido ligand, it is a basic organic chemistry fact that similar resonance structures may not be drawn for meta-disubstituted phenyl rings.

For this reason, we synthesized the compound meta-diazidobenzene by a similar diazotization method as that used to make other phenylazides.²¹ An ether solution of this diazide was then allowed to react with two molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, yielding immediate gas evolution and a color change to a very deep red. Crystallization of the material from warm toluene solution gave red/brown needles, presumably of the "meta-diimide," $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{m-NC}_6\text{H}_4\text{N})$.

The first indication that the meta- and para-diimides differed substantially in their properties was the color. However, a second indication was quickly seen in the ^1H NMR of the meta-diimide. The ^1H NMR spectra of both the meta-diimide and the para-diimide are shown in Figure 2-13. The most glaring differences between the two spectra are the linewidths of the resonances arising from the MeC_5H_4 groups. At room temperature, the resonances from these rings in this meta-diimide appear at $\delta = 4.46$ ppm (Me), $\delta = -2.57$ ppm (ring H), and $\delta = -10.53$ ppm (ring H), fairly similar positions to the matching resonances in the para-diimide spectrum. However, while the resonance from the methyl group has $\nu_{1/2} = 6$ Hz in the para-diimide, this resonance has $\nu_{1/2} = 18$ Hz in the meta-diimide. Similarly, the

Figure 2-13: ^1H NMR spectra of the para- and meta-diimides in C_6D_6 .

methylcyclopentadienyl ring protons, with widths of $\nu_{1/2} = 23$ and 17 Hz in the para-diimide, have $\nu_{1/2} = 57$ and 50 Hz in the meta compound. These linewidths are much more typical of those seen in the mononuclear uranium(V) imides, suggesting that there was indeed something particularly unusual about the para-diimide.

In order to assist us in looking at the ^1H NMR resonances of the phenylimide protons, they have been assigned as shown in Figure 2-14 below:

Figure 2-14: Proton designations in the meta-phenylenediimido ligand.

Proton H_A is meta to both of the imide functionalities. As we have seen in previous examples of uranium phenylimides, the meta proton is shifted downfield, to $\delta = \text{ca. } 18\text{--}21$ ppm in the mononuclear compounds. In this case, having two meta imido groups shifts the resonance even further; it is observed at $\delta = +29.58$ ppm at room temperature. The two equivalent protons on the phenyl ring, H_B , are para to one imide and ortho to the other. Their resonance is observed at $\delta = -6.54$ ppm.

The remaining phenyl ring proton, H_C , is ortho to both imide groups. Perhaps because of its close proximity to the two uranium(V) centers, the resonance for H_C is relatively broad at room temperature and is not observed in the spectrum. A variable temperature ^1H NMR spectrum helped to locate this resonance. At 59°C in perdeuterated toluene, it appears at $\delta = -0.46$ ppm with $\nu_{1/2} = 32$ Hz. The resonance gets somewhat sharper at higher

temperatures, shifting to $\delta = -0.77$ ppm at 80°C , $\delta = -0.98$ ppm at 96°C , and $\delta = -1.22$ ppm at 110°C . A plot of δ (ppm) vs. $1/T$ (K^{-1}) is linear, showing that the material follows Curie-Weiss behavior in the VT-NMR experiment.

Extrapolating the data to 30°C , we find a value of *ca.* $\delta = +0.09$ ppm for the H_C resonance. Assuming that this resonance is fairly broad, and since it arises in a region of the spectrum where we may find small diamagnetic impurities, it is not surprising that it is difficult to observe at room temperature.

Other characterization techniques were both interesting as a contrast with the para-diimide as well as consistent with our formulation of the meta compound. The melting point was again high, $213\text{--}215^\circ\text{C}$, as expected for a dimetallic uranium compound. Interestingly, a gas phase EI mass spectrum could not be obtained for this material; no molecular ion was observed. This suggests that the para-diimide may have some type of extra stability imparted by the π -conjugation of the bridging ligand which is unavailable to the meta-diimide, allowing the para compound to remain intact in the gas phase while the meta disproportionates. Air-sensitive techniques for Fast Atom Bombardment Mass Spectroscopy were utilized, using 18-crown-6 and tetraglyme as solvents. This yielded a strong M^+ at 1054 amu.

The measurement of the magnetic susceptibility of the meta-diimide seems to strongly support our theory that the π -conjugation of the bridging ligand is vital to electron exchange in these compounds. The data is shown in Figures 2-15 and 2-16 (χ_M vs. T and $1/\chi_\text{M}$ vs. T ; magnetic fields of 5 and 40 kG). The linear regression on the high temperature region (140-280 K) of the $1/\chi_\text{M}$ plot yields a $\mu_\text{eff} = 3.00$ B.M. ($\Theta = -134$ K), or $\mu_\text{eff} = 2.12$ B.M. per uranium. This is once again consistent with the high temperature data on $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ ($\mu_\text{eff} = 1.96$ B.M.) and the para-diimide ($\mu_\text{eff} = 2.08$ B.M.).

Fig. 2-15: Chi vs Temperature plot for the meta-diimide.

Fig. 2-16: $1/\chi_i$ vs Temperature plot for the meta-diimide.

Obviously, the most striking feature of the magnetic measurements on the meta-diimide is the lack of antiferromagnetic coupling, even down to temperatures of 2 K. In the low temperature region (5-40 K), the linear regression yields a value of $\mu_{\text{eff}} = 1.84$ B.M. ($\Theta = -4.0$ K; $\mu_{\text{eff}} = 1.30$ B.M. per uranium). Again, this may be favorably compared with the mononuclear $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, which showed a low temperature $\mu_{\text{eff}} = 1.25$ B.M.

By modelling the distance between the metal centers using the same software used for the para-diimide, a uranium-uranium distance of *ca.* 8.3 Å was obtained (Figure 2-17). This is a shorter distance than in the para-diimide, strongly suggesting that the electronic nature of the bridge, rather than simply the distance between the metals, is the dominant cause for whether antiferromagnetic exchange will or will not occur.

The differences between the susceptibilities of these compounds is graphically demonstrated in Figures 2-18 and 2-19, showing the overlaid $1/\chi_M$ vs. T and χ_M vs. T plots for the para- and meta-diimides. Note the extremely strong similarity in both the shapes and magnitudes of the curves for temperatures greater than *ca.* 80 K. It is at this point where the curves begin to separate, with paramagnetism continuing to dominate the behavior of the meta-diimide, while the antiferromagnetism begins to become dominant in the para-diimide.

Two other plots (Figures 2-20 and 2-21) show how strongly the magnetic behavior of the meta-diimide mirrors that of the typical mononuclear complex. The scale on the left of these plots is for $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$, while that on the right is for $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{m-NC}_6\text{H}_4\text{N})$. Note the extreme similarity between the two data sets.

Figure 2-17: Meta-Diumide Molecular Editor[®] Model

Fig. 2-18: $1/\chi_m$ vs T plot for the para- and meta-diimides.

Fig. 2-19: χ_i vs T plot for the para- and meta-diimides.

Fig. 2-20: χ_m vs T plot for UNPh and the meta-diimide.

Fig. 2-21: $1/\chi_i$ vs T plot for UNPh and the meta-diimide.

To sum up these results, it certainly appears that using the π -conjugation of the bridging para-phenylenediimido ligand gives us a very plausible explanation of the magnetic exchange observed in the para-diimide uranium(V) system. The lack of a similar conjugation in the meta-phenylenediimido ligand and the subsequent finding that the meta-diimide uranium(V) complex shows no electron exchange strongly supports this argument.

In the next section, we take a brief look at two other dinuclear uranium(V) diimides. Both of these diimides were synthesized to see whether other conjugated materials could produce any electronic exchange.

Section 2.3: Two Other Diimides of Uranium(V)

Before going into details about the synthesis and properties of these two other diimides, it should be mentioned that these compounds were synthesized with only the magnetic susceptibility measurements in mind. The compounds were recrystallized prior to measuring the susceptibility, however additional characterization was not done for either of the materials. We are quite confident that the compounds are what we claim them to be, especially for three main reasons: the organic and organometallic starting materials were quite pure, the reactions are directly analogous to those used to product the para- and meta-diimides, and the ^1H NMR spectra of the materials are, by comparison, quite similar to the other imides and diimides.

3.3.1: Preparation and Properties of a Diuranium Stilbene Diimide

The first of our other diimides was based upon the stilbene (1,2-diphenylethylene) unit. It is well known in organic chemistry that an extended π -conjugation exists in the trans form of stilbene, although steric effects from the interaction of the two phenyl rings greatly decreases this conjugation in the cis-stilbene.²²

Figure 2-22: The trans and cis forms of stilbene.

4,4' diazidostilbene (Figure 2-23) is easily prepared from the corresponding diamine by diazotization (cis and trans isomers).

Figure 2-23: 4,4'-diazidostilbene.

When the stilbene diazide was allowed to react with two molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, gas evolution was observed instantly and the color darkened to a deep red. Crystallization from toluene afforded brown needles. The high melting point of these needles ($241\text{--}245^\circ\text{C}$) suggested that we had successfully synthesized the desired "stilbene-diimide". Similarly with the meta-diimide, the stilbene-diimide gave no molecular ion in the E.I.-M.S. Air-sensitive F.A.B.-M.S. was performed on the sample using crown ether, and a molecular ion was observed at 1156 amu, in agreement with the calculated molecular weight. The ^1H NMR spectrum of the material was again consistent with the formulation of a stilbene-diimide. The 3:2:2 pattern typical of the MeC_5H_4 was observed at $\delta = 3.99$ ppm, $\delta = -3.33$ ppm, and $\delta = -10.68$ ppm. The ring methyl had $\nu_{1/2} = 22$ Hz, and the methylcyclopentadienyl ring protons had $\nu_{1/2} = 60$ and 62 Hz. These values are quite similar to those observed in the meta-diimide.

There should be three other resonances in the spectrum, labelled as H_A , H_B , and H_C below (Figure 2-24):

Figure 2-24: Labelling of protons in the stilbene-diimide.

The meta protons of the phenyl rings (H_B) appear to be at $\delta = +19.40$ ppm. This is consistent with the mononuclear, para-substituted uranium phenylimides discussed in Chapter 1, not a surprising result since the paramagnetic metal centers are so far apart and we may expect this material to behave like a simple para-substituted phenylimide. Using this assumption, the ortho protons (H_A) should be found in the vicinity of +2 to +5 ppm. A shoulder on the large peak at $\delta = +3.99$ is observed, and is assigned to the ortho protons. Recall that (at room temperature) the ortho protons in $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ overlap with the cyclopentadienyl methyl resonance (see Chapter 1). The ethylene protons (H_C) are observed at $\delta = +9.48$ ppm.

The magnetic susceptibility of the stilbene-diimide is shown in Figure 2-25 as χ_M vs. T and Figure 2-26 as $1/\chi_M$ vs. T (5 and 40 kG fields). The data, like that for the meta-diimide, shows no indication of magnetic interaction between the metal centers. Linear regression was performed on the $1/\chi_M$ plot. This yields a high temperature $\mu_{\text{eff}} = 2.73$ B.M. ($\Theta = -48$ K; $\mu_{\text{eff}} = 1.93$ B.M. per uranium), which compares favorably with the values obtained for the other uranium(V) imides, both mononuclear and dinuclear. The low temperature (5-40 K) value is $\mu_{\text{eff}} = 1.94$ B.M. ($\Theta = -6.3$ K; $\mu_{\text{eff}} = 1.37$ B.M.) per uranium. This is, once again, in the expected region for the uranium imides which show no unusual coupling.

Fig. 2-25: χ_i vs Temperature plot for the stilbene-diimide.

Fig. 2-26: $1/\chi_i$ vs Temperature plot for the stilbene-diimide.

As mentioned earlier, the stilbene unit may be drawn showing a conjugated π -system. This is indicated by the following two resonance structures for the stilbene-diimide (using the trans form; Figure 2-27):

Figure 2-27: Resonance structures of the stilbene-diimide.

Why, if we can draw such a conjugated resonance structure, is no electronic interaction between the uranium centers observed? One reason may be the long metal-metal distance; modelling this as described earlier with the $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ distances and standard C-C bond distances²³ (Figure 2-28) yields a U-U separation of *ca.* 16.0 Å. This is considerably longer than found in the *para*-diimide and may contribute to the lack of observed electronic exchange.

3.3.2: Preparation and Properties of a Diuranium Naphthalene Diimide

The second of our other diimides uses a naphthalene based system. This material was based upon the 1,5-diazidonaphthalene shown below (Figure 2-29):

Figure 2-28: Stilbene-Diimide Molecular Editor[®] Model

Figure 2-29: 1,5-diazidonaphthalene.

Like the other diazides, this one was prepared by a straightforward diazotization of the diamine. The diazide was then allowed to react with two molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ to give immediate gas evolution and a red/purple color. Crystallization from hot toluene gave black/purple needles of the naphthalene-diimide shown below (Figure 2-30).

Figure 2-30: Structure of the uranium(V) naphthalene-diimide complex

This material was not thoroughly characterized. The ^1H NMR spectrum could not be obtained in C_6D_6 due to its insolubility; instead it was taken in d_8 -thf. The pattern for the MeC_5H_4 was clearly seen at $\delta = +5.35$ ppm (ring Me), $\delta = -5.18$ ppm (ring H), and $\delta = -8.19$ ppm (ring H). The linewidths of the cyclopentadienyl ring protons were $\nu_{1/2} = 65$ and 49 Hz, consistent again with many of the uranium(V) imides, and much broader than the unusual

linewidths in the para-diimide. Only one of the three expected naphthalene ring proton resonances (Figure 2-31) was unambiguously identified; this is presumably from the meta protons H_B at $\delta = +16.95$ ppm.

Figure 2-31: Designation of protons in the naphthalene-diimide.

The other resonances presumably overlap with other peaks and this matter was not pursued further.

Magnetic susceptibility for this naphthalene-diimide was obtained at low temperatures only, in order to look for antiferromagnetic coupling. No such behavior was observed from 2-120 K, and the plots of χ_M vs. T and $1/\chi_M$ vs. T are shown in Figures 2-32 and 2-33. A $\mu_{eff} = 2.00$ B.M. ($\Theta = -5.5$ K) was obtained over the low temperature region (5-40 K), or $\mu_{eff} = 1.41$ B.M. per uranium. This is similar to the mononuclear uranium(V) imides, as well as the non-coupled dinuclear materials. No antiferromagnetic coupling is seen in this system, despite the fact that a conjugated π -system may again be drawn, as illustrated by the following example (Figure 2-34):

Fig. 2-32: Chi vs Temp. plot for the naphthalene-diimide.

Fig. 2-33: $1/\chi_m$ vs Temp. plot for the naphthalene-diimide.

Figure 2-34: Resonance structures of the naphthalene-diimide.

Modelling the structure of this compound (Figure 2-35) as described earlier gives a U-U distance of *ca.* 9.9 Å. This is close to that found in the para-diimide. Since the distance is similar and conjugation across the naphthalene ring should exist, what other reasons can we give for the lack of exchange? We assume that the *p*-phenylenediimido ligand and this naphthalene-diimido ligand are sufficiently different in their electronic natures to prevent electron exchange from occurring. The fact that two aromatic systems must be perturbed in both the naphthalene-diimide and the stilbene-diimide to arrive at completely conjugated resonance forms may play a role electronically. It is impossible to say anything more definitive on this subject, since the mechanism of exchange of this type is not well understood and varies widely from compound to compound.

A summary of all magnetic susceptibility measurements of the uranium(V) compounds studied in this work is presented in Table 2.1:

Figure 2-35: Napthalene-Diimide Molecular Editor[®] Model

Compound	μ_{eff} (B.M.) (Low Temp.)	μ_{eff} (B.M.) (High Temp.)
$(\text{MeC}_5\text{H}_4)_3\text{UNPh}$	1.25 (7-40 K)	1.96 (140-280 K)
$(\text{MeC}_5\text{H}_4)_3\text{UN}(p\text{-Me}_2\text{NC}_6\text{H}_4)$	1.40 (5-40 K)	2.21 (120-220 K)
$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,4\text{-N}_2\text{C}_6\text{H}_4)$ (para-diimide)	Antiferromagnetic $T_N = \sim 18$ K	2.08 (140-280 K)
$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,3\text{-N}_2\text{C}_6\text{H}_4)$ (meta-diimide)	1.30 (5-40 K)	2.12 (140-280 K)
$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[1,2\text{-(4-NC}_6\text{H}_4)_2\text{-C}_2\text{H}_2]$ (stilbene-diimide)	1.37 (5-40 K)	1.93 (140-260 K)
$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(1,5\text{-N}_2\text{C}_{10}\text{H}_6)$ (naphthalene-diimide)	1.41 (5-40 K)	-

Table 2.1: Summary of uranium(V) magnetic measurements (all μ_{eff} are given per uranium).

The plots of χ_M versus temperature all have similar appearances, with the exception of the unusual low temperature behavior of the para-diimide. By preparing several of these diimides, we have demonstrated that conjugation across the π -system of the bridging ligand seems important if electronic exchange is to occur in systems of this type. In addition, the results from the naphthalene-diimide suggest that this conjugation is most effective in conducting the super-exchange for systems containing only one aromatic ring.

Section 2.4: Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with $\text{Me}_2\text{Si}(\text{N}_3)_2$

The purpose of synthesizing dimethyldiazidosilane was to attempt to produce a uranium diimide that has no aryl system, once again showing that the electronic coupling must proceed through some sort of π -system rather than simply "through space."

Dimethyldiazidosilane was prepared by the method of Washburne and Peterson²⁴ as follows (Scheme 2-5):

Scheme 2-5: Preparation of a silicon diazide.

The compound has been found to be unpredictably explosive,²⁵ and thus caution was used in the handling of the reaction mixture. We found that the solvent hexamethylphosphoric triamide (HMPT) had to be dried over sodium slices prior to use in this reaction in order to minimize the production of silyl alcohols. By this technique, we were able to obtain fairly pure $\text{Me}_2\text{Si}(\text{N}_3)_2$ by fractional distillation. The material used in the reaction with uranium distilled at 50-53°C at 17 mm Hg. The infrared spectrum of this colorless liquid showed a strong N_3 stretch at *ca.* 2140 cm^{-1} , and in the ^1H NMR spectrum a single resonance at $\delta = -0.1$ ppm was observed. A small OH stretch from apparent silanol impurities was seen in the IR.

When this material was reacted with *ca.* 2.1 molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, a light green precipitate was immediately obtained. The ^1H NMR spectrum of the crude material from the reaction showed only $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ along with some small peaks in the diamagnetic region of the

spectrum. Green microcrystals of the compound were obtained in fair yield [29% based on total azide present, 53% based on $\text{Me}_2\text{Si}(\text{N}_3)_2$] from toluene recrystallization, and this material was found by ^1H NMR to be pure $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$.

Section 2.5: Model for the Interpretation of the Antiferromagnetism of the Para-diimide

The interpretation of the antiferromagnetic coupling observed in $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-NC}_6\text{H}_4\text{N})$ was evaluated by Dr. Norman Edelstein of the Lawrence Berkeley Laboratory.

For a U^{5+} compound with approximate C_{3v} symmetry the ground $J = 5/2$ term splits in a crystal field into six crystal field levels (μ), two $\mu_{1/2}$ states and one $\mu_{3/2}$ state plus their Kramers' conjugates. These states may be written as the following linear combinations of J, J_z states:

$$\begin{aligned}\mu = 1/2 \quad \psi_{1/2} &= a|5/2, \pm 1/2\rangle + b|5/2, \pm 5/2\rangle \\ \mu = 3/2 \quad \psi_{3/2} &= a'|5/2, 3/2\rangle + b'|5/2, -3/2\rangle\end{aligned}$$

It is likely in this system that the crystal field will be strong enough so that the higher-lying $J = 7/2$ state will not be mixed into the ground state. The important point to note is that for $\mu = 1/2$ both $g_{\parallel}$ (along the three fold axis) and $g_{\perp}$ may be non-zero but for the $\mu = 3/2$ state $g_{\perp} = 0$. Thus, no normal epr spectrum will be observed for the $\mu_{3/2}$ state because the intensity of the epr signal is proportional to $g_{\perp}^2$.

For the $(\text{RC}_5\text{H}_4)_3\text{UNR}$ mononuclear compounds, no epr signals were observed at low temperatures (*i.e.*, at $\sim 4\text{K}$). Therefore, we assume the ground state is $\mu_{3/2}$ and $g_{\perp} = 0$.

With this assumption and also assuming that only the ground state is populated, we can derive:

$$g_{\parallel} = 2.0 \mu_{\text{eff}}$$

This expression should be valid at low temperatures. Thus we can evaluate $g_{||}$ from the magnetic susceptibility data of a dinuclear $[(RC_5H_4)_3U]_2(NRN)$ which does not exhibit antiferromagnetic coupling. This was done using the meta-diimide, $[(MeC_5H_4)_3U]_2(m-NC_6H_4N)$, and a value of $\mu_{eff} = 1.30$ B.M. per uranium in the low temperature region (5-40 K) was obtained. From this, we calculate $g_{||} = 2.60$.

For a dinuclear uranium(V) diimide compound we assume the ground state does not change from the mononuclear species. This model assumes a one-dimensional exchange interaction along the three-fold or z axis, and this is called the Ising model for an isolated dimer.²⁶

The Hamiltonian for an interacting pair of spins is written as:

$$\mathcal{H} = -2JS_{z1}S_{z2} + g_{||} \mu_B H_z (S_{z1} + S_{z2})$$

The susceptibility along the three-fold axis for this system is

$$\chi_{||} = \frac{Ng_{||}^2 \mu_B^2}{kT} (1 - e^{-J/kT})^{-1}$$

for a dinuclear compound, or

$$\chi_{||} = \frac{Ng_{||}^2 \mu_B^2}{2kT} (1 - e^{-J/kT})^{-1}$$

per metal ion.

For a powder of this system (remember $g_{\perp} = 0$):

$$\chi_{Avg} = \frac{1}{3} \frac{Ng_{||}^2 \mu_B^2}{2kT} (1 - e^{-J/kT})^{-1}$$

Since all values in the above equation other than χ_{Avg} , T , and J are known, we can calculate χ_{Avg} versus T for various values of J . This is shown, along with the experimental data from two magnetic susceptibility runs on the para-diimide, in Figure 2-36. From this model we conclude $J = \text{ca. } -19 \text{ cm}^{-1}$, the antiferromagnetic state is lowest, and that there is a small impurity [probably uranium(III)] which is the primary contribution to the paramagnetism at low temperatures. The deviations at higher temperatures could be due to the thermal population of higher-lying crystal field states.

Figure 2-36: Experimental magnetic susceptibility of the para-diimide along with Ising model susceptibilities calculated for $J = -18 \text{ cm}^{-1}$, $J = -19 \text{ cm}^{-1}$, and $J = -20 \text{ cm}^{-1}$ [with a uranium(III) impurity]. Note that $g_{II} = 2.60$.

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Chapter 3

Tris(cyclopentadienyl)uranium Amine, Amide, and Hydrazide Compounds

Most of the chemistry involving the tris(cyclopentadienyl) systems of trivalent uranium has revolved around compounds of the type $\text{Cp}_3\text{U}(\text{L})$, where L is a Lewis base. The earliest report described the preparation of the compounds with $\text{L} = \text{thf}$, nicotinamide, and cyclohexylisocyanide.¹ Because of the relative insolubility of these compounds, work has more frequently focused on the methyl substituted cyclopentadienyl derivatives.² However, very little information has appeared concerning non-heterocyclic amine complexes of trivalent uranium. Brennan has prepared the compound $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{quin})$ [quin = quinuclidine, $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$],^{2a,2b} utilizing this "tied back" tertiary amine, but he was unable to prepare stable uranium(III) coordination complexes using either Me_3N or Et_3N .

We had an interest in examining compounds similar to the uranium(V) imides discussed in Chapter 1, but utilizing different oxidation states of the metal. This should allow us to make a "family" of related molecules like those shown below (Figure 3-1):

Figure 3-1: A family of uranium(III), uranium(IV), and uranium(V) compounds with U-N bonds.

By synthesizing such a group, we could compare the properties of these compounds, which can be referred to as uranium(III) amines, uranium(IV) amides, and uranium(V) imides. Additionally, we were interested in seeing whether the compounds could be interconverted formally by either addition or removal of an H $\cdot$ as shown below (Scheme 3-1):

Scheme 3-1: Interconversion of uranium amines, amides, and imides.

This chapter describes the preparation and properties of the uranium amine and amide complexes which have been synthesized, as well as some reactions involving the related hydrazine species.

Section 3.1: Preparation and Properties of (MeC₅H₄)₃U(NH₂R) Compounds

Several amine complexes of trivalent uranium have been prepared of the general formula (MeC₅H₄)₃U(NH₂R). These compounds and some of their properties are listed below in Table 3-1.

R	color	m.p. (°C)	ν_{N-H} (cm ⁻¹)	δ_{N-H} (ppm)
H	red-brown	206-210 (dec)	3312, 3239	-137
Me	red-brown	dec > 170	3290, 3245	-128
Ph	red-brown	155-157 (dec)	3310, 3225	-121
p-MeC ₆ H ₄	red-brown	166-169 (dec)	3324, 3221	-121

Table 3.1: Properties of (MeC₅H₄)₃U(NH₂R) compounds.

Preparation of these compounds is straightforward, proceeding by displacement of the thf ligand in (MeC₅H₄)₃U(thf) by the amine (Scheme 3-2):

Scheme 3-2: Preparation of uranium amine complexes.

In the cases where R = Ph or p-MeC₆H₄, one molar equivalent of the amine was added to a solution of the thf complex in toluene. Dark brown needles of the compounds (MeC₅H₄)₃U(NH₂Ph) and (MeC₅H₄)₃U(NH₂-p-MeC₆H₄) could then be crystallized from the toluene solution. For R = H or Me, two methods of preparation were employed: either a saturated toluene solution of the

amine was added to $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ or *ca.* 1.5 - 2 molar equivalents of the gaseous amine was condensed onto a frozen toluene solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$. Once again, the amine coordination compounds could then easily be obtained by crystallization from toluene as brown needles. All four of these materials are rather insoluble in common organic solvents. None of the compounds are soluble in hexane, though slightly soluble in ether, and more soluble in toluene.

The compounds all exhibit two N-H stretches in their infrared spectra. The spectrum of the compound with $\text{R} = \text{p-MeC}_6\text{H}_4$ is shown in Figure 3-2. The ^1H NMR spectra of these compounds are typical of uranium(III) coordination compounds. The spectra show the expected 3:2:2 pattern of the MeC_5H_4 rings with ring proton linewidths of $\nu_{1/2} = 16 - 20$ Hz. The positions and linewidths of these resonances are shown in Table 3-2. All of the compounds show a upfield shifted resonance for the amine protons, at $\delta = -121$ to -137 ppm (see Table 3-2). This is a typical result for uranium compounds in which protons are attached to an atom that is directly σ -bonded to a uranium center. For example, in $\text{Cp}_3\text{U}^n\text{Bu}$, the ^1H NMR resonance of the protons on the α -carbon is found at *ca.* -200 ppm.³ This resonance is relatively sharp in uranium(IV) compounds, and we find it to be broad but observable in our uranium(III) complexes. The positions of these resonances reflect the donating ability of the substituent on the amine. For the electron-withdrawing arylamines (PhNH_2 and $\text{p-MeC}_6\text{H}_4\text{NH}_2$), the resonances are further downfield (deshielded), consistent with less electron density on the nitrogen of these amines. In addition, the arylamine complexes have broader N-H resonances than the ammonia or methylamine compounds. The resonances due to the amine substituents are also shown in Table 3-2. A typical spectrum, that of $(\text{MeC}_5\text{H}_4)_3\text{UNH}_3$, is shown in Figure 3-3.

Figure 3-2: Infrared spectrum of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{NH}_2)_p\text{-MeC}_6\text{H}_4$.

R	Ring Me	Ring H	Ring H	NH ₂	Substituent
H	-15.5 ($\nu_{1/2}$ = 6 Hz)	-9.3 ($\nu_{1/2}$ = 16 Hz)	-18.7 ($\nu_{1/2}$ = 16 Hz)	-137 ($\nu_{1/2}$ = 39 Hz)	
Me	-17.1 ($\nu_{1/2}$ = 8 Hz)	-11.5 ($\nu_{1/2}$ = 19 Hz)	-15.1 ($\nu_{1/2}$ = 17 Hz)	-129 ($\nu_{1/2}$ = 70 Hz)	-30.3 ($\nu_{1/2}$ = 34 Hz)
Ph	-19.8	-10.7 ($\nu_{1/2}$ = 16 Hz)	-13.9 ($\nu_{1/2}$ = 16 Hz)	-121 ($\nu_{1/2}$ = 115 Hz)	-15.20 (2H) +0.75 (2H) +2.16 (1H)
p-MeC ₆ H ₄	-19.6	-10.6 ($\nu_{1/2}$ = 17 Hz)	-13.7 ($\nu_{1/2}$ = 17 Hz)	-121 ($\nu_{1/2}$ = 200 Hz)	-15.09 (2H) +0.59 (2H) -0.78 (3H)

Table 3-2: Chemical shifts (ppm) of the resonances in the ¹H NMR spectra of the uranium(III) amine complexes (MeC₅H₄)₃U(NH₂R).

Figure 3-3: ^1H NMR spectra of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$.

The compound $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NH}_3$ was also synthesized, by condensing 1.5 molar equivalents of $^{15}\text{NH}_3$ onto a frozen solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and crystallizing the compound from toluene. This material showed $\nu_{\text{N-H}}$ in the infrared spectrum at 3320 and 3241 cm^{-1} , as opposed to 3312 and 3239 cm^{-1} in the unlabelled material. The N-H resonance in the ^1H NMR spectrum was observed as a broad doublet at $\delta = -136$ ppm with $J_{^{15}\text{N-H}} = 60$ Hz. It should be noted that $J_{^{15}\text{N-H}}$ is actually negative due to the negative gyromagnetic ratio of ^{15}N ; the coupling constants are reported as absolute values in this chapter. This value may be compared with the coupling constant in free $^{15}\text{NH}_3$, which has been measured to be $J_{^{15}\text{N-H}} = 61$ Hz.⁴ The ^1H NMR spectra in the N-H region of both the labelled and unlabelled species is shown in Figure 3-4.

Andersen *et. al.*^{2a} and Fabiano^{2c} have done extensive studies on ligand base-competition studies involving trivalent uranium cyclopentadienyl compounds. They have found that compounds of the type $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{L})$ will rapidly exchange with additional free ligand (L). When this process is observed by ^1H NMR spectroscopy, the resonances from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{L})$ due to the ligand L shift towards the position of the resonances of free L. This phenomenon is also observed in the case of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$. When a small amount of p-toluidine was added to a d_6 -benzene solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$, the resonances from the p-toluidine ligand shifted towards the diamagnetic region of the NMR spectrum. While the MeC_5H_4 resonances at $\delta = -19.6$ ppm, -10.6 ppm, and -13.7 ppm remained constant, the ligand resonance at $\delta = +0.60$ ppm shifted to $\delta = +2.44$ ppm, the one at $\delta = -15.1$ ppm shifted to $\delta = -8.7$ ppm, and the one at $\delta = -0.80$ ppm shifted to $\delta = +0.10$ ppm. The N-H protons not observed, presumably because they are broadened by the chemical exchange.

Figure 3-4: ^1H NMR spectra showing the N-H resonances of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$ (top) and $(\text{MeC}_5\text{H}_4)_3\text{U}(^{15}\text{NH}_3)$ (bottom).

A similar process can be used with a second ligand, L', to gauge the relative affinity of the ligands towards uranium(III). A large number of these experiments have been performed,² and the following order for the strengths of Lewis bases toward trivalent uranium has been established (Figure 3-5):

Figure 3-5: Order of Lewis base strengths toward trivalent uranium (thf = tetrahydrofuran, tht = tetrahydrothiophene)

It is of interest to place NH_3 in this ligand displacement series. To a solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$ in C_6D_6 was added approximately two molar equivalents of PMe_3 . From the observed spectrum at 30°C , it can be calculated that 55-62% of the material is in the form $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$, while the remaining 38-45% is $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{PMe}_3)$ (Scheme 3-3):

Scheme 3.3: Equilibrium between the uranium amine and trimethylphosphine complexes.

An equilibrium constant for the reaction was calculated, and found to be in the range $K_{\text{eq}} = 4 - 7$. Thus ammonia is a better base towards trivalent uranium than PMe_3 .

A small needle-shaped crystal of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$ suitable for X-ray diffraction was obtained by slowly cooling a saturated ether solution to -20°C . The crystal was sealed in a quartz capillary under argon, and the X-ray diffraction analysis was performed by Dr. A. Zalkin of Lawrence Berkeley Laboratory.⁵ The crystal was found to be in the monoclinic space group Im , with $a = 12.129(3) \text{ \AA}$, $b = 24.197(3) \text{ \AA}$, $c = 8.725(3) \text{ \AA}$, and $\beta = 92.85^\circ$. There are

six molecules in the unit cell, of two different types. Four of the molecules lie on a general position (Figure 3-6), and the other two sit astride a mirror plane (Figure 3-7). Although the orientation of components in the two types of molecules is different, the bond distances and angles are comparable within the estimated statistics (Tables 3-3 and 3-4).

Bond	Distance (Å)	Bond	Distance (Å)
U1-Cp1	2.54	U2-Cp4	2.53
U1-Cp2	2.57	U2-Cp5	2.51
U1-Cp3	2.58	U2-N2	2.633(19)
U1-N1	2.595(12)		

Table 3-3: Distances in $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$.

Bond	Angle (°)	Bond	Angle (°)
Cp1-U1-Cp3	118.1	Cp4-U2-Cp4'	114.4
Cp2-U1-Cp3	118.1	Cp4-U2-Cp5	120.5
N1-U1-Cp1	98.1	N2-U2-Cp4	98.5
N1-U1-Cp2	97.4	N2-U2-Cp5	94.5
N1-U1-Cp3	97.6		

Table 3-4: Angles in $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$.

The average U-N distance of 2.61(3) Å in the ammonia complex may be compared with other trivalent uranium coordination complexes with nitrogen-containing donor ligands: 2.64(2) Å in $(\text{MeC}_5\text{H}_4)_3\text{U}(4\text{-NC}_5\text{H}_4\text{NMe}_2)^6$ and 2.764(4) Å in $(\text{MeC}_5\text{H}_4)_3\text{U}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$.^{2a} The large variation in these distances reflects the relative steric demands of the ligands,

Figure 3-6: ORTEP view of the molecule on the general position from the X-ray crystal structure of (MeC₅H₄)₃U(NH₃).

Figure 3-7: ORTEP view of the molecule on the mirror plane from the X-ray crystal structure of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$.

since NH_3 is smaller than either pyridine or quinuclidine. The average Cp-U-Cp and Cp-U-N angles also reflect the steric differences between these ligands, although the differences are small. In $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$, these angles are 118° and 97° respectively, while in $(\text{MeC}_5\text{H}_4)_3\text{U}(4\text{-NC}_5\text{H}_4\text{NMe}_2)$ and $(\text{MeC}_5\text{H}_4)_3\text{U}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$ the Cp-U-Cp angles are 117° and 116° and the Cp-U-N angles are 100° and 101° .

The electron impact mass spectra of these amine coordination compounds fail to yield molecular ions in all but one case. This is for the ammonia complex, which exhibited a weak M^+ at 492 amu. However, this compound showed an unusually large M-1 peak (491 amu), with an intensity 54% that of the M^+ . For the other compounds, only the M-1 peak was observed. Presumably, this is due to a thermal reaction of the molecule that occurs when it is heated in the mass spectrometer source (Scheme 3-4).

Scheme 3-4: Thermal decomposition of the uranium amine.

We indeed find that the observed spectra obtained from these amines are consistent for the corresponding uranium(IV) amides. The spectrum obtained for $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{Ph})$ is shown in Figure 3-8, along with the simulation for the molecular ion of the corresponding amide, $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$. Note that the simulation predicts an M+1 with intensity 27% that of the M^+ ; we observe the M+1 with an intensity of 29%. Thus the observed spectrum is in excellent agreement with that expected for the uranium(IV) amide.

Figure 3-8: Mass spectrum of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{Ph})$ and the simulation of the isotopic cluster for the M^+ of $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$.

These results are less surprising when we observe the melting behavior of these amine complexes. As noted in Table 3-1, all of the amine compounds melt with decomposition. This is easily observed when the materials are melted in sealed capillaries. At the point where melting begins, the compounds all evolve a gas and the color changes. For the arylamines, the color change is from the dark red-brown of the uranium(III) amine to a very bright cherry red. For the methylamine and ammonia compounds, the color changes from red-brown to a greenish-brown. The methylamine compound behaves slightly more oddly than the others since it "softens" from 170-200°C, then slowly changes color and melts at 237-238°C.

Because gas evolution was seen in the melting behavior and the M-1 peaks of the amides were observed in the mass spectra, we decided to repeat this procedure on a preparative scale in an attempt to isolate the uranium(IV) amide. The compound $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{NH}_2\text{Ph})$ was heated in a Schlenk tube to 160°C under a nitrogen atmosphere. The dark solid melted, bubbled, and turned bright red. After cooling, the residue was extracted with hexane and bright red bricks were crystallized from the solution. These were found to be the amide, $(\text{MeC}_3\text{H}_4)_3\text{UNHPh}$. The properties of these amides as well as further details on their methods of preparation will be discussed in Section 3.2.

We should note that the melting behavior of the uranium(III) amines follow the order expected based on how difficult it should be to oxidize the compounds to uranium(IV). In this process, the amine ligand must be reduced to the negatively charged amide, $(\text{NHR})^-$. When R is an electron withdrawing group such as an aryl, the negative charge will be stabilized, thus the arylamine ligands should be easier to reduce (with concurrent oxidation of the metal center) than methylamine or ammonia. This is seen in the

melting behavior; the PhNH_2 and $\text{p-MeC}_6\text{H}_4\text{NH}_2$ compounds decompose below 170°C , while the MeNH_2 and NH_3 compounds require somewhat higher temperatures.

It should be noted that the ammonia complex is the most difficult of the group to oxidize. As stated earlier, this is the only compound of the group which gave an M^+ in the mass spectrum. Additionally, when the compound was heated under vacuum (*ca.* 10^{-4} torr) to approximately 100°C , the material sublimed without decomposition, although the yield was poor.

The thermolysis reaction of the uranium(III) amines were studied in more detail by ^1H NMR spectroscopy. The goal of this study was to, at least crudely, measure the rate of conversion of the amine to the amide. We chose the *p*-toluidine complex, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{p-MeC}_6\text{H}_4\text{N}_2)$, for this study because of its desirable solubility properties as well as the favorable positions of the ^1H NMR resonances of the compound and the amide derived from it.

A d_8 -toluene solution of the amine of known concentration was prepared in the drybox, and the compound was thermolyzed in a constant temperature bath. After designated time intervals, the compound was removed from the heating bath, cooled briefly in an ice water bath, and the ^1H NMR spectrum obtained. The integration of the methyl resonance of the cyclopentadienyl ring was used to compare the relative amounts of the uranium(III) and (IV) species present. The experiments were continued to *ca.* 2 1/2 half-lives, rather than the customary three. This was due to the fact that the resonances from the uranium(III) species are somewhat broad, and when the concentration is relatively low, the integration is difficult to measure accurately. An example of the ^1H NMR spectrum obtained partway along one of these experiments is shown in Figure 3-9, and a plot of the logarithm of the uranium(III) concentration ratio versus time is shown in Figure 3-10. Note

from this plot that the reaction follows first-order kinetics. The rate constants were obtained from measuring the slopes of these first-order plots, and the values are:

$$k(120^{\circ}\text{C}) = 6.2 \pm 0.6 \times 10^{-4} \text{ sec}^{-1}$$

$$k(110^{\circ}\text{C}) = 2.7 \pm 0.3 \times 10^{-4} \text{ sec}^{-1}$$

$$k(102^{\circ}\text{C}) = 1.4 \pm 0.3 \times 10^{-4} \text{ sec}^{-1}$$

The error values were obtained simply by using a best estimate for the integration accuracy, applying these errors, and then finding the maximum and minimum slopes that could be obtained in the plot. An Arrhenius plot of $\ln k$ vs. $1/T$ was then used to obtain the activation energy of this reaction, and a value of $E_a = 24 \pm 6 \text{ kcal mol}^{-1}$ was obtained.

Figure 3-9: The ^1H NMR spectrum of the thermolysis of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$ after 1200 seconds at 120°C . The peaks marked "IV" are from the uranium(IV) amide, those marked "III" are from the uranium(III) amine, and those marked "s" are from solvent.

Figure 3-10: Kinetics plot of the thermal decomposition of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$.

Section 3.2: Preparation and Properties of (MeC₅H₄)₃UNHR Compounds

A number of cyclopentadienyl uranium(IV) amides have been previously reported. The first of these was Cp₂U(NEt₂)₂, which was synthesized in 1974 by Jamerson and Takats.⁷ More recently, several reports of triscyclopentadienyl uranium amides of the form Cp₃UNR₂ have appeared, with R = Et or Ph.⁸ The insertion chemistry of the various bis- and triscyclopentadienyl uranium amides has also been investigated to some extent.⁹ However, it should be noted that all of these materials are amides derived from secondary amines.

Several methods were used to prepare the uranium(IV) amides described in this work. One of the compounds had been prepared previously by Brennan,^{2b} (MeC₅H₄)₃UNHPh. He made this material by a reduction of the uranium(V) imide using ethylisocyanide, as described in Chapter 1. Table 3.5 below summarizes the properties of the (MeC₅H₄)₃UNHR compounds that have been synthesized:

R	color	m.p. (°C)	δ _{N-H} (ppm)
H	green	dec > 260	-135.4
Me	green-red	215-220	-103.8
Ph	red	128-129	-164.6
p-MeC ₆ H ₄	red	92-94	-1588

Table 3.5: Properties of (MeC₅H₄)₃UNHR compounds.

The most common technique used to prepare these amides was the thermal decomposition of the corresponding amines, as described in the previous section. For the arylamides, this technique works extremely well at relatively low temperatures (ca. 160°C). The bright red residue formed on heating can be extracted with hexane and red blocks of $(\text{MeC}_5\text{H}_4)_3\text{UNHAr}$ ($\text{Ar} = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) were crystallized from the solutions. Isolated yields from this procedure were typically on the order of 50%.

This solid phase thermolysis reaction also works for formation of the methylamide, $(\text{MeC}_5\text{H}_4)_3\text{UNHMe}$. However, this compound is much less soluble than the arylamides, and the material must be extracted with hot toluene. In addition, this reaction required a somewhat higher temperature (ca. 200°C). In contrast, $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ could not be prepared from the ammonia complex by a solid phase reaction.

These pyrolysis reactions may also be accomplished in solution. This was described in Section 3.1 for the kinetics measurements of the decomposition of the uranium(III) arylamines. For the compound $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-}p\text{-MeC}_6\text{H}_4)$, this reaction is reasonably rapid at 100-120°C. However, when an analogous reaction was performed on a preparative scale with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$, it was found to be somewhat slower. The ammonia complex was dissolved in toluene and heated to reflux (~110°C) for several hours, but at the end of this period the material still seemed to be the dark color of the trivalent uranium species. The reaction may be done using xylenes as solvent (b.p. ~140°C) and in less than two hours of reflux $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ can be isolated.

Several other reactions have been used to produce the uranium(IV) amide compounds. In general, these reactions were used to prepare one or two of the compounds rather than the whole group of amides. The first of

these reactions was displacement of the methyl group of a uranium(IV) alkyl using aniline (Scheme 3-5):

Scheme 3-5: Preparation of a uranium amide by reaction of an alkyl with aniline.

This reaction is accomplished simply by refluxing $(\text{MeC}_5\text{H}_4)_3\text{U}^{\text{IV}}$ with excess aniline in hexane solvent. The reaction appeared to be quite slow, as the color change from the green of the uranium methyl compound to the bright cherry red of the amide occurred over *ca.* 2 1/2 days. The amide $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$ was isolated in 38% yield. One apparent problem with this process that may account for the low yield is the instability of $(\text{MeC}_5\text{H}_4)_3\text{UMe}$ at elevated temperatures. Although Cp_3UMe is reported to be quite stable at high temperatures,³ we have found that $(\text{MeC}_5\text{H}_4)_3\text{UMe}$ decomposes fairly rapidly below 100°C when heated in a sealed capillary. Indeed, in the reaction of the methyl compound with aniline in refluxing hexane, a considerable amount of insoluble material was produced. Attempts to speed up this reaction using a higher boiling solvent such as toluene were futile; in this case, even more decomposition was noted and the yield of the uranium(IV) amide was far poorer. The driving force for this reaction should be the pK_a of aniline vs. methane; aniline has a pK_a of *ca.* 28, while MeH has a pK_a of ~58.¹⁰ Thus aniline should be deprotonated.

A second reaction used to prepare the uranium(IV) amides was oxidation of the corresponding amine using the trityl radical. In particular, this reaction was used for the conversion of the ammonia complex to the amide (Scheme 3-6):

Scheme 3-6: Reaction of the uranium(III) ammonia complex with trityl radical.

Preparation of the trityl dimer was accomplished by a previously described procedure (Scheme 3-7):¹¹

Scheme 3-7: Preparation of the trityl radical.

It was found that "molecular" silver was necessary to get complete reduction of the chloride; the electrochemical preparation of this material has been described by Brauer.¹² We found that when the toluene solvent was removed, the trityl dimer contained one molecule of solvent. Thus, the material was used as though it had the composition $(\text{Ph}_3\text{C})_2(\text{PhMe})$. When one-half molar equivalent of this material was added to a toluene solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)_3$, the color immediately changed from deep red-brown to pale green. After filtration and removal of the solvent, the ^1H NMR spectrum of the residue showed a mixture of the compounds $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ and Ph_3CH . Attempts at fractional recrystallization of this mixture were futile. Thus, oxidation of the uranium(III) amine using the trityl radical is favored, but purification of the uranium(IV) product is difficult. This reaction is not surprising: the oxidation from uranium(III) to uranium(IV) and the formation of a C-H bond (even a weak C-H bond as should exist in Ph_3CH) should be enough of a driving force to make the

reaction occur. In addition, the U-N bond in the tetravalent uranium product should be stronger than in the trivalent uranium coordination complex.

It should briefly be noted here that attempts to oxidize an amide to the uranium(V) imide using this procedure were unsuccessful. In one attempt, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$ and two molar equivalents of $\text{Ph}_3\text{C}\cdot$ were mixed in an NMR tube in C_6D_6 . The ^1H NMR spectrum of this material after the initial mixing indicated the presence of three compounds: $(\text{MeC}_5\text{H}_4)_3\text{UNH-p-MeC}_6\text{H}_4$ (from oxidation of the amine by the trityl radical), Ph_3CH , and $\text{Ph}_3\text{C}\cdot$. After the NMR tube had been heated to 120°C for twenty minutes, another spectrum was taken. No $(\text{MeC}_5\text{H}_4)_3\text{UN-p-MeC}_6\text{H}_4$ had been formed, and the amount of $\text{Ph}_3\text{C}\cdot$ remaining seemed to have slightly decreased. After 9 1/2 hours of heating at 120°C , there was still no uranium(V) imide in the solution, and the trityl radical had completely decomposed. Again this is not a surprising result, since the oxidation of uranium(IV) to uranium(V) is an endothermic process.

One final method used to prepare uranium(IV) amides was the reaction of a uranium(III) amine with a uranium(V) imide. This reaction was described in Section 1.4.B, and was performed with the p-tolyl compounds $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-MeC}_6\text{H}_4)$ and $(\text{MeC}_5\text{H}_4)_3\text{UN-p-MeC}_6\text{H}_4$ to form $(\text{MeC}_5\text{H}_4)_3\text{UNH-p-MeC}_6\text{H}_4$. The driving force for this process is apparently the energy gain from conversion of uranium(III) and uranium(V) to uranium(IV).

The ^1H NMR spectra of these uranium amides are typical of tetravalent uranium cyclopentadienyl compounds. The chemical shifts and linewidths of the compounds are shown in Table 3-6. The resonance due to the amide N-H proton is shifted far upfield, as was seen for the amine protons in the uranium(III) compounds. A typical spectrum is shown in Figure 3-11. J.

R	Ring Me	Ring H	Ring H	NH	Substituent
H	+0.39	-5.73	-17.07	-135.4 (t, J = 44 Hz)	
Me	+1.44	-10.71 ($\nu_{1/2}$ = 7 Hz)	-14.98 ($\nu_{1/2}$ = 7 Hz)	-103.8 ($\nu_{1/2}$ = 50 Hz)	+7.29 (d, J = 6 Hz)
Ph	+4.20	-1.03 ($\nu_{1/2}$ = 8 Hz)	-18.56 ($\nu_{1/2}$ = 9 Hz)	-164.6 ($\nu_{1/2}$ = 24 Hz)	-33.58 (d, 2H) -2.10 (t, 2H) -5.18 (t, 1H)
p-MeC ₆ H ₄	+4.38 ($\nu_{1/2}$ = 2 Hz)	-1.91 ($\nu_{1/2}$ = 7 Hz)	-18.46 ($\nu_{1/2}$ = 7 Hz)	-158.8 ($\nu_{1/2}$ = 19 Hz)	-32.78 (d, 2H, J = 8 Hz) -1.80 (2H) +1.04 (3H)

Table 3-6: Chemical shifts (ppm) of the resonances in the ¹H NMR spectra of the uranium(IV) amide complexes (MeC₅H₄)₃UNHR.

Figure 3-11: ^1H NMR spectra of $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$.

Stewart observed a similar shift in the compound

$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{UNH-p-MeC}_6\text{H}_4$, with $\delta_{\text{N-H}} = -213$ ppm.¹³ It is interesting to note that the arylamine N-H resonances are shifted the furthest upfield in these tetravalent species, which is opposite to that seen in the trivalent compounds. It is difficult to explain what causes these shifts, but one possible explanation is that the more the lone pair on the nitrogen in these amides is involved in donation to the metal center, the less negative the nitrogen will be and the further downfield the N-H resonance should shift. When the substituent on the amide is electron-donating such as a methyl, the nitrogen lone pair will be destabilized and the lone pair will be more likely to interact with the uranium. Conversely, in the arylamides, the lone pair will be stabilized by the electron-withdrawing nature of the substituent, leaving the nitrogen with more partial negative charge and shifting the N-H resonance upfield.

The most interesting feature of the ^1H NMR spectra of the amides was seen in the spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$. The peak due to the NH_2 protons was observed as a 1:1:1 triplet, due to coupling between the protons and the ^{14}N , which has a nuclear spin of 1. The coupling constant was measured to be $J_{^{14}\text{N-H}} = 44$ Hz. The compound $(\text{MeC}_5\text{H}_4)_3\text{U}(^{15}\text{NH}_2)$, discussed earlier in this chapter, was oxidized using the trityl radical technique to prepare the labelled tetravalent amide, $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NH}_2$. The ^1H NMR spectrum of the labelled material showed a doublet for the NH_2 resonance, with $J_{^{15}\text{N-H}} = 65$ Hz. These resonances are shown in Figure 3-12. It is very unusual to observe ^{14}N coupling in molecules of this nature, and it is interesting that it is not seen in the substituted amides. The observation of this coupling is directly related to the relaxation time of the ^{14}N nucleus.¹⁴ These data prove that the 1:1:1

Figure 3-12: ^1H NMR spectra showing the N-H resonances of $(\text{MeC}_3\text{H}_4)_3\text{UNH}_2$ (top) and $(\text{MeC}_3\text{H}_4)_3\text{U}^{15}\text{NH}_2$ (bottom).

triplet is due to $^{14}\text{N-H}$ coupling since $|J_{14\text{N-H}}| = 0.713 \cdot |J_{15\text{N-H}}|$,¹⁵ and the values obtained for these uranium amides fit this formula.

The value of $J_{15\text{N-H}}$ in $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$ is 60 Hz and in $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ it is 65 Hz, indicating that the amount of s-character (hybridization) at nitrogen in both compounds is similar. This can be stated because the coupling constant is directly related to the amount of s-character in the N-H bonds; an empirical result is given by $\% s = 0.34 [J_{15\text{N-H}}]$.¹⁵ This suggests that NH_2 is pyramidal in $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$, though we have no supporting evidence for this deduction.

No N-H stretches are observed in the infrared spectra of the amides, with the exception of the compound $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$. This material exhibits a single very weak stretch at 3315 cm^{-1} . Note that Stewart also did not observe an N-H stretch in the uranium amide complex $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{UNH-p-MeC}_6\text{H}_4$.¹³ All of the amides exhibit parent molecular ions in the electron impact mass spectra.

Very few reactions involving these uranium amides were carried out, although several reactions were attempted using $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$. When this material was dissolved in toluene and placed under ca. 15 atmospheres of CO or D_2 , tan insoluble precipitates were obtained, and the reactions were not pursued further. Interestingly, $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ reacted with trimethylaluminum to give the known tetravalent uranium alkyl, $(\text{MeC}_5\text{H}_4)_3\text{UMe}$. When the reaction was performed with dichloromethane as solvent, a mixture of the methylated material and $(\text{MeC}_5\text{H}_4)_3\text{UCl}$ was obtained (as observed by ^1H NMR spectroscopy). We believed that the uranium(IV) chloride was being formed by reaction of the methyl compound with the CH_2Cl_2 solvent, since the uranium amide is stable in this solvent. To test this, $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ and AlMe_3 were allowed to react for three days

in toluene. The ^1H NMR spectrum of the green residue indicated that relatively pure $(\text{MeC}_5\text{H}_4)_3\text{UMe}$ was formed. Presumably, the mechanism of this reaction involves coordination of the AlMe_3 aluminum to the nitrogen lone pair and attack of a methyl group on the uranium through a μ -methyl bridge, resulting in the uranium(IV) methyl product and Me_2AlNH_2 (Scheme 3-8):

Scheme 3-8: Possible mechanism for the methylation of the UNH_2 compound with AlMe_3 .

Section 3.3 Preparation and Properties of (MeC₅H₄)₃U-N(R)NH₂ Compounds

A number of reactions between both trivalent and tetravalent uranium and hydrazines have been studied in this work, and these reactions are described in this section. Most of the work has focused on phenylhydrazine; this system has been the most well-behaved and thus easiest to study. The goal of this research was to see whether uranium(III) hydrazine coordination compounds could be prepared in an analogous manner to the uranium amines, and whether these could then be oxidized to the uranium(IV) hydrazide species.

One reason why we were particularly interested in hydrazines as ligands is the variety of different forms this species can take; compounds utilizing neutral hydrazines, hydrazido(1-), and hydrazido(2-) have all been reported.¹⁶ In addition, these compounds exhibit both η^1 and η^2 types of bonding, leading to interesting molecules.

Our earliest attempts at preparation of these compounds involved the reaction of (MeC₅H₄)₃U(thf) with PhNHNH₂ in toluene solution. When one molar equivalent of phenylhydrazine was added to the thf-complex, an immediate lightening of the color to bright red was observed. After one hour, the volatile materials were removed, and the residue extracted with ether. Attempts to crystallize a product from this extract yielded only red oily material. The ¹H NMR spectrum of this material indicated that two products formed; one was a new material with linewidths in the NMR spectrum that indicated tetravalent uranium (this was, by integration, *ca.* 2/3 of the product) and the second was the uranium(IV) amide, (MeC₅H₄)₃UNHPh. Recrystallization of the oily solid from an ether/hexane mixture gave

orange/red crystals whose ^1H NMR spectrum showed it to be the unknown product, formulated as a uranium(IV) hydrazide, as shown below (Figure 3-13):

Figure 3-13: Proposed structure of the uranium(IV) phenylhydrazide.

Formation of this product, with loss of a proton from the nitrogen containing the aryl group, is not surprising. The proton on the phenyl nitrogen should be more acidic than those on the the NH_2 end of phenylhydrazine, due to the presence of the electron withdrawing aryl group which can help stabilize the negative charge.

The properties of this molecule and detail on its characterization will be discussed later in this section.

The observation that this reaction also produced $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$ led us to wonder whether the hydrazide compound could be forced to rearrange to this molecule. Heating some of the pure $(\text{MeC}_5\text{H}_4)_3\text{UN(Ph)NH}_2$ to 100°C in a Schlenk tube for several hours and subsequent examination of the ^1H NMR spectrum showed that the hydrazide was completely converted to the amide. This thermolysis reaction will be discussed in more detail later in this section.

The fact that the phenylhydrazide was converted to the amide at 100°C led us to attempt the preparation at lower temperatures. Thus, $(\text{MeC}_5\text{H}_4)_3\text{U(thf)}$ and phenylhydrazine were allowed to react in ether at 0°C for less than five minutes. The ether was then removed, and the reaction mixture extracted with ether while keeping the temperature below 0°C .

Crystallization at -80°C gave brown crystals in very low yield, which the ^1H NMR spectrum showed to be the uranium(III) ammonia complex, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$. Further concentration of the remaining ether solution and addition of hexane to this solution eventually gave orange crystals of the pure uranium(IV) phenylhydrazide in $<20\%$ yield.

Although it is difficult to speculate on how the uranium(III) ammonia complex was formed in this reaction, it was evident that the isolation of the phenylhydrazide by this method was tedious, complicated by the formation of other products, and accomplished in very poor yield. We therefore decided to take advantage of the acidity of the phenylhydrazine to prepare the compound by reaction with a uranium alkyl as shown in Scheme 3-9:

Scheme 3-9: Formation of the uranium(IV) phenylhydrazide from alkyls.

Note that this reaction is directly analogous to the reaction of the uranium(IV) methyl compound with aniline discussed in Section 3.2.

Two different alkyls were used in this reaction. The compound with $\text{R} = \text{t-Bu}$ has been prepared by Brennan^{2b}. This material was found to react with phenylhydrazine in either toluene or ether for about one hour to give the phenylhydrazide. However, it was again difficult to obtain the product in high purity and in crystalline form; an oily product was repeatedly obtained. One reason for this may be that the tert-butyl alkyl slowly decomposes in solution,¹⁷ thus excess phenylhydrazine in the reaction mixture will lead to impure products. An attempt was made to substitute the uranium(IV) methyl compound for the t-butyl; this reaction was also found to produce the

uranium(IV) hydrazide, however the reaction required elevated temperatures (ca. 80-100°C) and again nicely crystalline product was difficult to obtain. Thus we conclude that replacement of the alkyl group with the phenylhydrazide by a protonation reaction is, as we'd expect, favored, however it is a poor synthetic route to give us $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{Ph})\text{NH}_2$ in high yield and purity.

An additional attempt to prepare this compound was then made using the tetrakis(cyclopentadienyl) uranium species, $(\text{MeC}_5\text{H}_4)_4\text{U}$. A good preparation for this material has recently been developed by Weydert¹⁷, and we felt that relief of the steric congestion in this molecule might be a driving force for the removal of one cyclopentadienyl ring by protonation (Scheme 3-10).

Scheme 3-10: Preparation of the uranium(IV) phenylhydrazide from $(\text{MeC}_5\text{H}_4)_4\text{U}$.

The acidities of the phenylhydrazine versus methylcyclopentadiene (pK_a ca. 18), however, made this reaction seem unlikely to proceed [the pK_a of phenylhydrazine should be greater than that of aniline (~ 28), since the protonated form of phenylhydrazine (PhNHNH_3^+ , $\text{pK}_a = 7.95$) is less acidic than the protonated form of aniline (PhNH_3^+ , $\text{pK}_a = 4.60$)¹⁰]. When $(\text{MeC}_5\text{H}_4)_4\text{U}$ and phenylhydrazine were allowed to react in toluene, a gradual lightening of the solution color from red to orange was observed over a period of two days. Removal of volatile materials and crystallization from an ether/hexane mixture gave $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{Ph})\text{NH}_2$ in >50% yield as red-

orange bricks. The material was found to be pure and this is the best preparation of the phenylhydrazide we have found thus far.

The characterization of this material was accomplished mainly through infrared and ^1H NMR spectroscopy, with the aid of a labelling experiment using an ^{15}N -substituted phenylhydrazine that will be described shortly. The infrared spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{Ph})\text{NH}_2$ is shown in Figure 3-14. Two N-H stretches are observed, at 3285 and 3223 cm^{-1} . The ^1H NMR spectrum of the compound is shown in Figure 3-15. The typical 3:2:2 pattern from the MeC_5H_4 rings is seen at $\delta = -0.03$ ppm, -5.7 ppm, and -18.3 ppm. Only two of the resonances from the phenyl ring were observed at room temperature; these appear as a doublet at $\delta = 10.9$ ppm and a doublet of doublets at $\delta = 8.2$ ppm. These resonances both integrate to two protons, and are assigned as the ortho and meta protons, respectively. The para proton is probably under the solvent signal at $\delta = 7.15$ ppm at room temperature; the variable temperature NMR spectrum of this compound will be discussed later. The NH_2 resonance is seen as a sharp singlet at $\delta = -9.3$ ppm. The position of this resonance seems to suggest that this nitrogen is not interacting strongly with the metal center, since we have observed large upfield shifts for protons on atoms directly bonded to the uranium (as mentioned earlier for the uranium amines and amides).

To confirm our formulation of the compound, a ^{15}N labelling study was performed. $\text{PhNH}^{15}\text{NH}_2$ was allowed to react with $(\text{MeC}_5\text{H}_4)_4\text{U}$ in toluene, and the product was again crystallized from an ether/hexane mixture. This material was not as nicely crystalline as the material obtained from the unlabelled phenylhydrazine; this may be due to problems with water in the labelled phenylhydrazine provided by Cambridge Isotope Laboratories, and some insoluble material was produced in this reaction. The

Figure 3-14: Infrared spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$.

Figure 3-15: ^1H NMR spectrum of $(\text{MeC}_3\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$.

^1H NMR spectrum of this product showed a change in only one resonance, and is shown in Figure 3-16. This is the resonance assigned to the NH_2 protons at -9.3 ppm, which splits into a doublet due to ^{15}N -H coupling. The coupling constant $J_{\text{N-H}}$ was measured to be 76 Hz; this may be compared to the value of 65 Hz found in $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NH}_2$. Note in the spectrum that a smaller peak between the two peaks of the doublet was also observed; we believe that this peak is due to unlabelled material contaminating the labelled product. A comparison of the ^{15}N -H coupling constant may be made with a tungsten hydrazido(1-) compound prepared by Sutton *et. al.*; in the molecule $[\text{Cp}_2\text{W}(\text{H}_2^{15}\text{NN-p-C}_6\text{H}_4\text{Me})][\text{BF}_4]$, the $J_{\text{N-H}} = 88 \text{ Hz}$.¹⁸

A low temperature ^1H NMR experiment was performed on $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{Ph})\text{NH}_2$, with spectra obtained from 30°C to -72°C . As the temperature is lowered, the peak from the para proton of the phenyl ring appears to shift downfield from under the solvent resonance. However, the interesting feature of this experiment is seen when plots of chemical shift versus T^{-1} are made for the various resonances. One such representative plot is shown in Figure 3-17, for the cyclopentadienyl ring methyl group. Note that the compound does not obey the Curie Law; this plot is not linear. In fact, plots of chemical shift vs. $1/T$ for the cyclopentadienyl ring protons also exhibit curvature, as do the phenyl ring resonances. This is consistent with some type of exchange process occurring in solution;¹⁹ two such processes are monomer-dimer equilibrium or η^1 - η^2 interconversion as shown in Scheme 3-11:

Figure 3-16: ^1H NMR spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UN}(^{15}\text{NH}_2)\text{Ph}$.

Figure 3-17: Variable temperature ^1H NMR data for $(\text{MeC}_6\text{H}_4)_2\text{UN}(\text{NH}_2)\text{Ph}$.

Scheme 3-11: (Top) Possible solution monomer/dimer equilibrium in the uranium(IV) phenylhydrazide. (Bottom) Possible $\eta^1\text{-}\eta^2$ interconversion in the uranium(IV) phenylhydrazide.

The mass spectrum of the phenylhydrazide compound exhibits a small molecular ion at 582 amu. However, a much larger peak is found for M-15, presumably due to $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$.

Thermolysis of the labelled and unlabelled phenylhydrazide compounds in an NMR tube with d_8 -toluene as solvent was done at 120°C . In both cases, the uranium(IV) amide was formed (Scheme 3-12):

Scheme 3-12: Thermolysis of the uranium phenylhydrazide.

The ^1H NMR spectra showed relatively clean conversions to the amide, although the times required for complete conversion are irreproducible and further investigation is warranted. The N-H resonance of the amide from the thermolysis using the ^{15}N labelled phenylhydrazide appeared as a singlet in the NMR spectrum, showing that no ^{15}N remains. Thus, the nitrogen that is lost is the one from the NH_2 group of the phenylhydrazide, and no

rearrangement is taking place. The thermolysis was also performed with some trans-stilbene present in the NMR tube. However, no trapping of the "NH" species could be observed by this technique.

Although cleavage of the N-N bond in coordinated hydrazido(2-) species by protonation with acid has been reported,^{16a} no such reaction has yet been observed for hydrazido(1-) compounds. For example, McCleverty *et. al.* reported that the acidolysis of $[\text{Mo}(\text{HB}(\text{Me}_2\text{pz})_3)(\text{NO})(\text{I})(\text{NHNH}_2)]$ (Me_2pz = 3,5-dimethylpyrazolyl) with HCl yielded hydrazine and the molybdenum dihalide, while the reaction of $[\text{Mo}(\text{HB}(\text{Me}_2\text{pz})_3)(\text{NO})(\text{I})(\text{NHNHPh})]$ with HI gave the dihalide and $(\text{PhNHNH}_3)(\text{I})$.^{16f}

Several other reactions of trivalent uranium with hydrazines were attempted, with poor results. As in the case of the reaction of PhNHNH_2 with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, the reactions gave several products, and these were not vigorously pursued. A brief summary of these reactions and what products were observed is given below.

When MeNHNH_2 was allowed to react with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ at 0°C in ether, the material obtained was predominantly the uranium(III) amine, $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{Me})$. This is similar to the result noted in the phenylhydrazide reaction at low temperature, where a small amount of the ammonia complex was isolated. It is conceivable that coordination of the hydrazine to the trivalent metal center occurs, followed by a 1,2-hydrogen shift and concurrent breaking of the N-N bond giving this product. The formation of this product may reflect the relative difficulty in deprotonating this species; methylhydrazine should be somewhat less acidic than phenylhydrazine.

When 1,1-diphenylhydrazine (Ph_2NNH_2) was allowed to react with the uranium thf-complex (at room temperature in toluene), the dominant

product in the ^1H NMR spectrum appeared to be the diphenylamide, $(\text{MeC}_5\text{H}_4)_3\text{UNPh}_2$. This compound has been previously prepared^{8a,d} and was identified by comparison of the NMR spectrum with the reported values.

The reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with hydrazine, H_2NNH_2 , was complex and not reproducible. It appears that a hydrazide complex was formed, but two different species are observed in separate reactions run under similar conditions. One of these species converts slowly to the other upon heating in an NMR tube, and, eventually, all the material converts to the uranium amide, $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$. The purity of the hydrazine, which can easily become hydrated, may play a large role in these reactions, and the matter was not pursued further. It should be noted, however, that when hydrazine was allowed to react with $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ in thf for several days, $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ was isolated.

The development of the reaction using $(\text{MeC}_5\text{H}_4)_4\text{U}$ to prepare the uranium(IV) phenylhydrazide will help to extend the chemistry of these hydrazide compounds, as they can now be prepared in good yield and in high purity.

Section 3.4: Preparation of a Dinuclear Uranium Amine

In order to look for magnetic interactions between uranium(III) nuclei, a dinuclear uranium diamine complex was synthesized, using *p*-phenylenediamine as the bridging ligand. This compound is similar to the para-diimide discussed in Chapter 2. One of the reasons for investigating this system was that antiferromagnetic coupling had been observed in copper complexes using the same bridging ligand; as mentioned in Chapter 2, the compound $[\text{Cu}_2(\text{tren})_2(\text{PPD})][\text{NO}_3]_4$ ($\text{tren} = 2,2',2''\text{-triaminotriethylamine}$, $\text{PPD} = p\text{-phenylenediamine}$) exhibits an antiferromagnetic coupling with $T_N = 67 \text{ K}$.²⁸

The diamine complex is straightforwardly synthesized by reaction of two molar equivalents of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with *p*-phenylenediamine in toluene (Scheme 3-13):

Scheme 3-13: Preparation of a bridged dinuclear uranium diamine.

The compound is insoluble in toluene, and precipitates out of the reaction mixture as brown microcrystals.

A ^1H NMR spectrum of this compound could not be obtained, due to its insolubility in either C_6D_6 or C_7D_8 . An attempt to obtain the spectrum in

d_5 -thf was unsuccessful; although the material dissolved, the spectrum showed only the MeC_5H_4 resonances due to $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$. Thus, the bridging interaction is not strong, and the amine is displaced by the large excess of thf.

The infrared spectrum of the compound showed two N-H stretches at 3281 and 3228 cm^{-1} . This is similar to the results obtained for the mononuclear amine coordination compounds discussed in Section 3.1. An electron impact mass spectrum of the compound could not be obtained; the material apparently fragmented in the gas phase. The elemental analysis was also consistent with the proposed structure of the compound.

Magnetic susceptibility measurements were obtained on a sample of the diamine. Freshly prepared and recrystallized $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ was reacted with a sublimed, zone-refined sample of p-phenylenediamine;²¹ slightly more than two molar equivalents of the uranium species were used to ensure that no excess base was present and prevent the formation of mononuclear species. The product was washed several times with toluene and ether before measurement of the susceptibility.

The results of these measurements are shown in Figures 3-18 and 3-19 as plots of χ_M vs. T and $1/\chi_M$ vs. T. Note that no antiferromagnetic coupling is observed for the compound. Linear regression performed on the $1/\chi_M$ data yielded $\mu_{\text{eff}} = 4.17$ B.M. ($\Theta = -69$ K) for the high temperature region (140-300K) and $\mu_{\text{eff}} = 2.95$ B.M. ($\Theta = -3.1$ K) for the low temperature region (5-40K). This works out to values of $\mu_{\text{eff}} = 2.95$ and $\mu_{\text{eff}} = 2.09$ per uranium for the high and low temperature regions, respectively. These values may be compared to those obtained for other $(\text{RC}_5\text{H}_4)_3\text{U}(\text{L})$ compounds. For the pyridine complex, $\text{Cp}_3\text{U}(\text{py})$, values of $\mu_{\text{eff}} = 3.20$ (110-300 K) and $\mu_{\text{eff}} = 2.33$ (6-90 K) were measured, while in $\text{Cp}_3\text{U}(\text{PMe}_3)$, the values were $\mu_{\text{eff}} = 2.82$ (120-300 K) and

$\mu_{\text{eff}} = 2.21$ (5-40 K).²² Thus the magnetic susceptibility of the bridged uranium(III) complex was found to be quite similar to mononuclear materials.

Fig. 3-18: Chi vs Temperature plot for the para-diamine.

Fig. 3-19: $1/\chi_i$ vs Temperature plot for the para-diamine.

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Chapter 4

Experimental Details

General

All manipulations involving air-sensitive materials were carried out under nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere dry box under argon. Diethylether, tetrahydrofuran, and hexane were dried and deoxygenated over sodium benzophenone ketyl, toluene was dried over sodium, and dichloromethane was dried over CaH. All solvents were distilled from these drying agents under nitrogen prior to use.

Infrared spectra were recorded on either a Perkin-Elmer 283 grating spectrometer or a Matson Polaris F.T.I.R. spectrometer as Nujol mulls between CsI windows. Melting points were measured in sealed capillaries and are uncorrected. NMR spectra were recorded on a JEOL FX-90Q spectrometer in perdeuterated benzene or toluene which had been dried over sodium and distilled under nitrogen. ^1H NMR spectra (89.6 MHz) were referenced to residual protons in the solvent; in $\text{C}_6\text{D}_5\text{H}$, $\delta = 7.15$ ppm, in $\text{C}_6\text{D}_5\text{CD}_2\text{H}$, $\delta = 2.09$ ppm. ^1H NMR resonances are reported as δ -values, with positive values at higher frequencies than Me_4Si ($= 0$ Hz). ^{119}Sn NMR spectra (33.3 MHz) were referenced to Me_4Sn , $\delta = 0.00$ ppm. Mass spectroscopy and elemental analyses were performed by the University of California, Berkeley, Department of Chemistry mass spectral and microanalytical laboratories. The isotopic cluster of the parent molecular ion was simulated for many of the

compounds and the experimental and simulated results are reported as follows: (experimental intensity; simulated intensity).

Magnetic susceptibility measurements were made using either a S.H.E. Model 905 or a Quantum Design Model MPMS superconducting magnetometer. A typical sample preparation is as follows: 50 - 100 mg of the compound was ground with mortar and pestle in an argon dry box and weighed into the bottom half of a Kel-F sample container. The two halves of the container were sealed using a small amount of silicone grease and removed from the dry box. The container was then tied together using nylon thread and suspended in the sample container with cotton thread. Measurements were taken at magnetic fields of 5 kG and 40 kG at the following temperatures: 5 - 9 K (every 2 K), 12 - 21 K (every 3 K), 25 - 50 K (every 5 K), 60 - 100 K (every 10 K), and 120 - 300 K (every 20 K). When lower temperatures were desired on the Quantum Design magnetometer, the measurements were also taken from 2 - 4.5 K (every 0.5 K). All data were corrected for sample and container diamagnetism. Samples exhibiting Curie-Weiss behavior were fit to the Curie-Weiss law $1/\chi = (T - \Theta)/C$ using a linear least-squares program written by Dr. E. Gamp and modified by Dr. N. Edelstein.

Commercially obtained uranium tetrachloride (Cerac) was treated with refluxing SOCl_2 for *ca.* 7 days, followed by washing of the green powder with CH_2Cl_2 until the extracts were colorless and heating of the powder under reduced pressure (1 mTorr) at *ca.* 150°C for 12 hours. $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$, $(\text{MeC}_5\text{H}_4)_3\text{UCl}$, $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UCl}$, $\text{Cp}_3\text{UNSiMe}_3$, and $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ were prepared as described by Brennan¹. $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\text{pyrazine})$ was prepared as described by Eigenbrot and Raymond.²

The cyclopentadienide and methylcyclopentadienide anions were prepared from the freshly cracked C_5H_6 or MeC_5H_5 monomers as the sodium salts in tetrahydrofuran. Trimethylsilylcyclopentadiene was prepared as described by Brennan¹ and used as the potassium salt in tetrahydrofuran.

$tBuN_3$,³ Me_3GeN_3 ,⁴ Me_3SnN_3 ,⁴ Ph_3SnN_3 ,³ and Ph_2CHN_3 ⁶ were synthesized from the appropriate halides. Me_3SiN_3 (Petrarch) was dried over $MgSO_4$ and distilled before use. PhN_3 ⁷ was synthesized by diazotization of aniline, and the substituted phenylazides $p-MeC_6H_4N_3$,⁸ $p-MeOC_6H_4N_3$,⁸ $p-Me_2NC_6H_4N_3$,⁸ $p-CF_3C_6H_4N_3$,⁹ $o-MeC_6H_4N_3$,⁸ $o-^iPrC_6H_4N_3$,¹⁰ $o-CF_3C_6H_4N_3$,¹¹ $2,6-Me_2C_6H_4N_3$ ¹⁰ were synthesized by analogous procedures.¹² The aryl azides that were solids at room temperature were recrystallized from ether or toluene, and liquids were distilled under vacuum (10^{-3} torr) through a $-20^\circ C$ trap. A typical azide preparation by diazotization is given in Section 4.1. $Ph^{15}NNN$ was prepared by diazotization of $Ph^{15}NH_2$ (99% ^{15}N , Cambridge Isotope Laboratories). $p-(N_3)_2C_6H_4$,¹³ $m-(N_3)_2C_6H_4$,¹⁴ 4,4'-diazidostilbene,¹⁵ and 1,5-diazidonaphthalene¹⁶ were prepared by diazotization routes and $Me_2Si(N_3)_2$ ¹⁷ was prepared from the dichloride.

Section 4.1: Chapter 1 Experimental Details

p-MeOC₆H₄N₃ (typical azide preparation by diazotization)

p-Anisidine (p-methoxyaniline, recrystallized from hot H₂O, ca. 7.5 g, 61 mMol) was suspended in 50 mL of H₂O. Concentrated HCl (15 mL) was added; all of the solid dissolved to give a pale orange solution. The solution was cooled to 0°C, then a solution of NaNO₂ (4.4 g, 64 mMol) in H₂O (30 mL) was added dropwise over ca. 15 minutes, resulting in a yellow-orange solution. While still maintaining a temperature of below 0°C, NaN₃ (4.2 g, 65 mMol) in H₂O (30 mL) was added dropwise over ca. 30 minutes. During the addition, gas evolution occurred and the solution became cloudy. After the addition was complete, the solution was warmed to room temperature and stirred for 30 minutes. Ether was added (100 mL), the mixture poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted with an additional 50 mL of ether, the ether layers were combined, washed with H₂O (50 mL), and dried over MgSO₄ with a small amount of decolorizing carbon. The solution was filtered and rotovapped to give an orange oil, which was then distilled at ca. 10⁻³ torr through a cold trap maintained at -20°C to give a pale yellow liquid. ¹H NMR (C₆D₆, 30°C): 3.2 (s, 3H), 6.6 (m, 4H).

(MeC₃H₄)₃UN₃

Method A: (MeC₃H₄)₃UCl (2.0 g, 3.9 mmol) was suspended in 75 mL of deoxygenated H₂O and stirred vigorously. A light green color developed in the solution. NaN₃ (0.80 g, 12 mmol) in 15 mL of H₂O was added by cannula, resulting in an immediate green precipitate. The mixture was stirred for 24 hours and then allowed to settle. The water was decanted and the green solid

was dried under reduced pressure. Dichloromethane (30 mL) was added and the green-brown solution was filtered. Concentration of the filtrate to ca. 20-25 mL and cooling to -80°C resulted in green microcrystals, which were isolated by filtration and dried in 90% (1.82 g) yield, m.p. $152-160^{\circ}\text{C}$. ^1H NMR (C_6D_6 , 30°C): -3.11 (3H), 11.08 (2H), -17.43 (2H). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_3\text{U}$: C, 41.8; H, 4.09; N, 8.12. Found: C, 40.7; H, 4.61; N, 6.88. Mass spectrum: 517 (100; 100), 518 (17; 21). IR: 2112 vs br, 1239 w, 1093 w, 1065 w, 1050 w, 1034 m, 930 w, 846 m, 782 s, 727 m, 700 m, 638 w, 606 w cm^{-1} .

Method B: To $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.69 g, 1.3 mmol) dissolved in 20 mL of Et_2O was added by syringe 6.0 mL of a 0.21 M solution of HN_3^{18} in Et_2O (1.3 mmol). A bright green precipitate immediately formed, with very little color remaining in the solution. The mixture was stirred for one hour, then taken to dryness under reduced pressure. The solid that remained was sublimed (10^{-4} torr, $120-130^{\circ}\text{C}$) to yield 0.17 g of a green solid. The ^1H NMR spectrum showed this solid to be $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The material that did not sublime was extracted with CH_2Cl_2 (50 mL), filtered, and taken to dryness to yield 0.08 g of additional $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$; the total yield was 38% (0.25 g)

$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$

To a mixture of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (1.01 g, 1.55 mMol) and Me_3SnN_3 (0.40 g, 1.9 mMol) was added 30 mL of Et_2O . The brown-green solution was stirred for 18 hours, then the volatile materials were removed under reduced pressure. The residue was extracted with hexamethyldisiloxane (25 mL), the solution was filtered, and the filtrate was concentrated to ca. 20 mL and cooled to -20°C . Brown crystals were isolated by filtration and dried in 41% (0.44 g) yield, m.p. $103-105^{\circ}\text{C}$. ^1H NMR (C_6D_6 , 30°C): -7.07 (9H), -15.10 (2H), -13.69 (2H). Anal. Calcd for $\text{C}_{24}\text{H}_{39}\text{N}_3\text{Si}_3\text{U}$: C, 41.7; H, 5.68; N, 6.07. Found: C, 37.6; H, 5.83;

N, 5.44. Mass spectrum: 691 (100; 100), 692 (41; 43), 693 (15; 19), 694 (3; 5). IR: 2082 vs, 1249 s, 1174 m, 1046 m, 902 m, 836 vs, 795 s, 753 m, 723 , 689 w, 633 m, 625 m cm^{-1} .

This reaction was also performed in an NMR tube with C_7D_8 as solvent. The ^1H NMR spectrum obtained from this reaction showed that the reaction cleanly formed $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$. Several peaks were also observed between 0.3 ppm and -0.1 ppm.

$(\text{MeC}_5\text{H}_4)_3\text{UNCO}$

$(\text{MeC}_5\text{H}_4)_3\text{UCl}$ (2.9 g, 5.7 mmol) was suspended in 100 mL of deoxygenated H_2O and stirred vigorously. A light green color developed in the solution. KOCN (1.42 g, 17.5 mmol) in 20 mL of H_2O was added by cannula, resulting in an immediate green precipitate. The mixture was stirred for 48 hours and then allowed to settle. The water was decanted and the green residue was dried under reduced pressure. Dichloromethane (50 mL) was added and the green solution was filtered. The filtrate was concentrated to ca. 20-25 mL and then cooled to -80°C . Green crystals were isolated by filtration and dried in 23% (0.82 g) yield. ^1H NMR (C_6D_6 , 27°C): 2.67 (3H), 13.23 (2H), -19.16 (2H). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NOU}$: C, 44.1; H, 4.06; N, 2.71. Found: C, 44.3; H, 4.08; N, 2.64. IR: 2180 vs, 1070 w, 1050 w, 1030 m, 930 w, 860 w, 840 m, 800 m, 785 s, 620 m, 605 m, 345 w, 310 w, 265 m, 255 m cm^{-1} .

$(\text{MeC}_5\text{H}_4)_3\text{UNCMe}_3$

To $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.47 g, 0.86 mMol) dissolved in 20 mL of diethyl ether was added 0.95 mL of 0.90 M *t*-butylazide (0.86 mMol) in cyclohexane. Gas was instantly evolved, and the color changed from brown-red to a deep

red. The solution was stirred for 24 hours, then the volatile material was removed under reduced pressure. Hexane (20 mL) was added, the solution was filtered, and the filtrate was concentrated to ca. 10 mL, and then cooled to -20°C . Fine black-red needles were isolated and dried in 49% (0.23 g) yield, m.p. $232\text{--}237^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6 , 30°C): 13.56 (9H, $\nu_{1/2} = 54$ Hz), 4.18 (9H, $\nu_{1/2} = 30$ Hz), -4.21 (6H, $\nu_{1/2} = 150$ Hz), -9.87 (6H, $\nu_{1/2} = 135$ Hz). Mass spectrum: 546, 547 (24.8; 21.9), 548 (3.0; 2.1). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{NU}$: C, 48.4; H, 5.53; N, 2.56. Found: C, 47.3; H, 5.50; N, 2.30. IR: 1348 m, 1260 m, 1210 s, 1090 w, 1040 m, 850 m, 800 m, 780 m, 760 s, 600 m, 525 w, 320 w cm^{-1} .

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Me_3GeN_3

To 0.50 g of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.91 mMol) dissolved in 20 mL of Et_2O was added 0.2 mL of Me_3GeN_3 . The reaction mixture was stirred for 3 days with no obvious color change. At the end of this time, the volatile materials were removed under reduced pressure. The red/brown residue was extracted with hexane, the red solution was filtered, and the filtrate was concentrated and cooled to -20°C . Brown flakes were isolated and dried (0.15 g). A second crop of 0.09 g was obtained by further concentration and cooling of the hexane solution. The total yield of $(\text{MeC}_5\text{H}_4)_3\text{UNGeMe}_3$ was 44% (0.24 g), m.p. $187\text{--}189^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6 , 30°C): 6.46 (3H, $\nu_{1/2} = 11$ Hz), 2.86 (3H, $\nu_{1/2} = 15$ Hz), -1.53 (2H, $\nu_{1/2} = 54$ Hz), -11.10 (2H, $\nu_{1/2} = 51$ Hz). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{GeNU}$: C, 41.5; H, 4.98; N, 2.31. Found: C, 41.4; H, 5.13; N, 2.19. Mass spectrum: 604 (52; 52), 605 (13; 3), 606 (72; 83), 607 (37; 35), 608 (100; 100), 609 (23; 22), 610 (23; 26), 611 (5; 5), 612 (1; 1). IR: 1261 w, 1231 w, 1170 w, 1098 w, 1029 m, 918 m, 808 s, 771 s, 628 w, 599 m, 564 w, 535 w cm^{-1} .

The material that was insoluble in hexane was extracted with CH_2Cl_2 (20 mL), the yellow-green solution was filtered, and the volatile materials

were removed under reduced pressure, giving 0.08 g of material. ^1H NMR spectroscopy showed this to be primarily $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Me_3SnN_3

A solution of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (1.90 g, 3.47 mMol) in 75 mL of Et_2O was added to Me_3SnN_3 (0.90 g, 4.4 mMol). A light precipitate formed immediately. After stirring for one week (one day is probably sufficient), the precipitate was allowed to settle and the ether was removed by filtration. The green solid that remained was extracted with dichloromethane (50 mL), the solution was filtered, and the filtrate was concentrated to ca. 10 mL. Hexane (3 mL) was added to this solution, and it was cooled to -80°C . Green microcrystals were isolated by filtration and dried in 18% (0.32 g) yield. ^1H NMR spectroscopy indicated that this material was $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The volatile materials were removed from the remaining dichloromethane solution under reduced pressure, and the ^1H NMR spectrum of the green residue (0.16 g) showed it to be fairly pure $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$. The volatile materials from the original ether solution were removed under reduced pressure. ^1H NMR spectroscopy showed that the remaining solid consisted mainly of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, with several other peaks observed in the diamagnetic region (probably tin-containing materials).

This reaction was also performed in an NMR tube with C_6D_6 as solvent. The ^1H NMR spectrum obtained from this reaction showed that the predominant species are: $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$, thf , and several peaks between 0.5 ppm and -0.1 ppm.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_3CN_3

To 0.51 g $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.93 mmol) dissolved in 10 mL of Et_2O was added by cannula 0.32 g Ph_3CN_3 (1.1 mmol) dissolved in 10 mL of Et_2O . A bright green precipitate immediately formed. After stirring for 12 hours, the ether was removed by filtration, and the green powder dried under reduced pressure. ^1H NMR spectroscopy showed this powder to be $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$; 0.24 g, 50%.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_3SnN_3

To a mixture of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.25 g, 0.46 mMol) and Ph_3SnN_3 (0.18 g, 0.46 mMol) was added 20 mL of Et_2O , resulting in a light green solution with a green precipitate. The mixture was stirred overnight and the volatile materials were then removed under reduced pressure. The ^1H NMR spectrum of the green residue showed that it consisted of $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ and other materials with resonances in the diamagnetic region of the spectrum. No attempt was made to separate the uranium compound from the tin containing by-products.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with Ph_2CHN_3

Preparative scale reaction: To $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (1.0 g, 1.8 mMol) dissolved in 30 mL of Et_2O was added 0.38 g Ph_2CHN_3 (ca. 1.8 mMol). Gas evolution was immediately observed, and color turned dark red. After one hour, the volatile materials were removed under reduced pressure. The residue was extracted with hexane (50 mL), the solution was filtered, and the filtrate was concentrated and cooled to -20°C . Brown crystals were isolated by filtration and dried in 58% (0.70 g) yield, m.p. $89-91^\circ\text{C}$. ^1H NMR (C_6D_6 , 30°C): 4.27 (9H, $\nu_{1/2} = 24$ Hz), -4.6 (6H, $\nu_{1/2} = 65$ Hz), -10.3 ($\nu_{1/2} = 80$ Hz), 12.41 (4F), 8.62

(4H, d, $J = 7$ Hz), 7.65 (2H). The benzhydryl C-H resonance was not located. Mass spectrum: 656 (100; 100), 657 (35; 35). IR: 1262 m, 1162 w, 1010 m, 1073 m, 1030 s, 845 m, 776 s, 741 m, 702 s, 610 m cm^{-1} .

The hexane-insoluble material was extracted with dichloromethane, filtered, and the volatile materials removed under reduced pressure to give a green residue (0.05-0.06 g). The ^1H NMR spectrum of this residue showed the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UCl}$.

NMR tube reaction: To 20.5 mg of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ dissolved in ca. 1.5 mL of C_6D_6 was added by syringe 7.0 μL of Ph_2CHN_3 . Gas evolution was noted, and the color changed from red to dark brown/red. An aliquot of the solution was transferred by pipette to an NMR tube, and the ^1H NMR spectrum obtained. The ratio $(\text{MeC}_5\text{H}_4)_3\text{UNC}(\text{H})\text{Ph}_2 : (\text{MeC}_5\text{H}_4)_3\text{UN}_3$ was measured by integration to be ca. 8 : 1.

$(\text{MeC}_5\text{H}_4)_3\text{UNCH}_2\text{Ph}$

To 1.45 g of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (2.6 mmol) dissolved in 50 mL of diethyl ether was added 0.33 mL of benzylazide (2.65 mmol). Gas was immediately evolved, and the color of the solution changed from red-brown to a dark brown-green. The solution was stirred for 5 hours then the volatile material was removed under reduced pressure. The brown solid was extracted with 60 mL of hexane, the brown solution was filtered, and the filtrate was concentrated to ca. 30 mL and cooled to -20°C . Brown flakes were isolated by filtration and dried in 60% (0.91 g) yield, m.p. $57-59^\circ\text{C}$. ^1H NMR (C_6D_6 , 30°C): 3.42 (9H, $\nu_{1/2} = 23$ Hz), -2.81 (6H, $\nu_{1/2} = 94$ Hz), -11.33 (6H, $\nu_{1/2} = 78$ Hz), 123.5 (2H, $\nu_{1/2} = 450-500$ Hz), 12.73 (2H, $\nu_{1/2} = 27$ Hz), 8.60 (2H, $\nu_{1/2} = 12$ Hz), 7.63 (1H, $\nu_{1/2} = 16$ Hz). Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{NU}$: C, 51.7; H, 4.86; N, 2.41. Found: C,

51.9; H, 5.01; N, 2.44. Mass spectrum: 580 (100; 100), 581 (28; 28). IR: 1298 w, 1264 w, 1132 m, 1032 m, 972 w, 932 w, 850 m, 764 s, 729 m, 698 m, 615 w cm^{-1} .

$(\text{MeC}_3\text{H}_4)_3\text{UNPh}$

$(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.70 g, 1.28 mMol) was dissolved in diethyl ether (30 mL) and the solution cooled to 0°C . To this solution was added 0.81 mL of a 1.58 M solution of phenylazide (1.28 mMol) in toluene. Gas was immediately evolved, and the color of the solution turned deep red. After 10 minutes, the solvent was removed under reduced pressure and the red-brown solid was extracted with hexane (2×25 mL). The red solution was filtered, and the filtrate was concentrated to ca. 30 mL and cooled to -20°C . Red needles were isolated and dried in 45% (0.32 g) yield, m.p. $109\text{--}112^\circ\text{C}$. ^1H NMR (C_6D_6 , 60°C): 3.68 (9H, $\nu_{1/2} = 20$ Hz), -2.96 (6H, $\nu_{1/2} = 60$ Hz), -9.64 (6H, $\nu_{1/2} = 49$ Hz), 17.93 (2H, $\nu_{1/2} = 18$ Hz), 3.32 (2H), -2.31 (1H, $\nu_{1/2} = 20$ Hz). The ^1H NMR was recorded at 60°C because at room temperature the peak at 3.32 ppm is buried under the resonance at 3.68 ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{NU}$: C, 50.9; H, 4.63; N, 2.47. Found: C, 50.7; H, 4.60; N, 2.34. Mass spectrum: 566 (100; 100), 567 (27; 28), 568 (4, 12). IR: 1589 m, 1574 m, 1555 w, 1264 s, 1161 m, 1152 w, 1067 w, 1047 w, 1034 m, 1022 w, 992 w, 928 w, 907 m, 890 w, 860 w, 849 s, 799 s, 760 s, 723 m, 693 s, 600 w, 527 w cm^{-1} . Magnetic susceptibility (5 and 40 kG fields): $\mu_{\text{eff}} = 1.96$ B. M. (140–280 K; $\Theta = -110$ K), $\mu_{\text{eff}} = 1.25$ B.M. (5–40 K; $\Theta = 1.03$ K).

$(\text{MeC}_3\text{H}_4)_3\text{UN-p-MeC}_6\text{H}_4$

To 1.00 g of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (1.83 mMol) dissolved in 30 mL of diethyl ether was added 0.76 mL of 2.39 M p-tolylazide (1.82 mMol) in toluene. Gas was immediately evolved, and the color turned deep red. The mixture was stirred at room temperature for 45 minutes, then the solvent was removed

under reduced pressure. The dark red residue was extracted with 50 mL of hexane, filtered, and the filtrate was concentrated to ca. 25 mL and cooled to -20°C . Red-brown crystals were isolated in 66% (0.70 g) yield, m.p. $89-92^{\circ}\text{C}$. ^1H NMR (C_6D_6 , 30°C): 3.68 (9H, $\nu_{1/2} = 20$ Hz), -3.48 (6H, $\nu_{1/2} = 50$ Hz), -10.96 (6H, $\nu_{1/2} = 50$ Hz), 19.01 (3H, $\nu_{1/2} = 12$ Hz), 18.65 (2H, $\nu_{1/2} = 18$ Hz), 3.37 (2H). Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{NU}$: C, 51.7; H, 4.86; N, 2.41. Found: C, 51.7; H, 4.80; N, 2.41. Mass spectrum: 580 (100; 100), 581 (28; 35), 582 (4; 9). IR: 1491 s, 1348 w, 1273 s, 1240 w, 1165 w, 1101 w, 1067 w, 1034 m, 974 w, 932 w, 912 m, 895 w, 843 m, 814 s, 781 s, 768 s, 610 w, 554 w, 523 m cm^{-1} .

$(\text{MeC}_3\text{H}_4)_3\text{UN-p-Me}_2\text{NC}_6\text{H}_4$

To $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.71 g, 1.3 mMol) dissolved in 30 mL of diethyl ether was added 0.21 g (1.3 mMol) *p*-dimethylaminophenylazide in 10 mL of diethyl ether. Gas evolution was observed immediately, and the color of the solution changed from red-brown to a deep red. After 10 minutes, the volatile materials were removed under reduced pressure. The red-black solid was extracted with diethyl ether (50 mL), the extract was filtered, and filtrate was concentrated to ca. 30 mL and cooled to -20°C . Red-black bricks were isolated and dried (0.32 g), m.p. $147-148^{\circ}\text{C}$. An additional 0.12 g was isolated by concentrating the remaining ether solution to ca. 10 mL and cooling to -20°C . Total yield was 0.44 g, 55%. ^1H NMR (C_6D_6 , 30°C): 3.66 (9H, $\nu_{1/2} = 25$ Hz), -4.01 (6H, $\nu_{1/2} = 70$ Hz), -10.92 (6H, $\nu_{1/2} = 74$ Hz), 10.20 (6H, $\nu_{1/2} = 5$ Hz), 17.85 (2H, $\nu_{1/2} = 16$ Hz), 2.60 (2H, $\nu_{1/2} = 37$ Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{U}$: C, 51.2; H, 5.13; N, 4.60. Found: C, 51.3; H, 5.43; N, 4.90. Mass spectrum: 609 (100; 100), 610 (30; 31). IR: 1588 s, 1494 s, 1339 s, 1266 m, 1216 m, 1178 m, 1162 w, 1120 w, 1105 w, 1045 w, 1030 w, 941 m, 906 w, 858 w, 834 m, 818 s, 800 m, 766 s, 605 w, 556 w,

539 w, 517 w, 333 w cm^{-1} . Magnetic susceptibility (5 and 40 kG fields): $\mu_{\text{eff}} = 2.21$ B. M. (140-220 K; $\Theta = -120$ K), $\mu_{\text{eff}} = 1.40$ B.M. (5-40 K; $\Theta = -3.32$ K).

$(\text{MeC}_3\text{H}_4)_3\text{UN-p-MeOC}_6\text{H}_4$

To $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.50 g, 0.91 mMol) dissolved in 20 mL of diethyl ether was added 0.14 g (0.94 mMol) of p-methoxyphenylazide in 10 mL of diethyl ether. Gas evolution was immediately observed, and the color of the solution changed from red-brown to a deep red. The solution was stirred for 10 minutes, then the volatile materials were removed under reduced pressure. The solid residue was extracted with 50 mL of hexane, the extract was filtered, and the filtrate was concentrated to ca. 40 mL and cooled to -20°C . Red-brown crystals were isolated by filtration and dried under reduced pressure to give 0.25 g, m.p. $97-99^\circ\text{C}$. An additional 0.08 g was obtained by concentrating the hexane mother liquor to ca. 15 mL and cooling to -20°C . Total yield was 0.33 g, 60%. $^1\text{H NMR}$ (C_6D_6 , 30°C): 3.68 (9H, $\nu_{1/2} = 18$ Hz), -3.66 (6H, $\nu_{1/2} = 75$ Hz), -10.92 (6H, $\nu_{1/2} = 60$ Hz), 7.04 (3H, $\nu_{1/2} = 5$ Hz), 17.98 (2H, $\nu_{1/2} = 14$ Hz), 2.94 (2H, $\nu_{1/2} = 27$ Hz). Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{NOU}$: C, 50.3; H, 4.73; N, 2.35. Found: C, 50.0; H, 4.60; N, 2.35. Mass spectrum: 596 (100; 100). IR: 1586 m, 1482 s, 1435 m, 1290 w, 1260 m, 1233 s, 1178 w, 1155 w, 1095 w, 1030 m, 927 w, 908 w, 829 m, 763 s, 638 w, 601 w, 572 w, 538 w, 330 w cm^{-1} .

$(\text{MeC}_3\text{H}_4)_3\text{UN-o-MeC}_6\text{H}_4$

To $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.98 g, 1.79 mMol) dissolved in 40 mL of diethyl ether was added 0.25 mL of o-tolylazide (1.88 mMol). Gas evolution immediately occurred, and the color of the solution changed from red-brown to a darker red. The volatile materials were removed immediately under reduced pressure over a period of ca. 15 minutes. The brown solid residue

was warmed to 50°C under vacuum for 15 minutes to remove excess azide. The residue was then extracted into 40 mL of diethyl ether, the extract was filtered, and the filtrate was concentrated to ca. 10 mL and cooled to -20°C. Brown-red needles were isolated and dried in 75% yield (0.78 g), m.p. 118-120°C. $^1\text{H NMR}$ (C_6D_6 , 30°C): 4.73 (9H, $\nu_{1/2}$ = 18 Hz), -7.52 (6H, $\nu_{1/2}$ = 64 Hz), -8.67 (6H, $\nu_{1/2}$ = 67 Hz), 15.27 (3H, $\nu_{1/2}$ = 27 Hz), 19.95 (1H, $\nu_{1/2}$ = 24 Hz), 19.29 (1H, $\nu_{1/2}$ = 21 Hz), 5.14 (1H, partly overlapped with the large peak at 4.73), -3.15 (1H, $\nu_{1/2}$ = 17 Hz). Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{NU}$: C, 51.7; H, 4.86; N, 2.41. Found: C, 51.5; H, 4.97; N, 2.36. Mass spectrum: 580 (100; 100), 581 (28; 25). IR: 1580 w, 1555 w, 1246 s, 1109 w, 1164 w, 1035 m, 911 w, 845 m, 771 s, 758 s, 711 w, 601 w, 455 w, 336 w, 328 w cm^{-1} .

$(\text{MeC}_3\text{H}_4)_3\text{UN}-o\text{-}^i\text{PrC}_6\text{H}_4$

To $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.54 g, 0.99 mMol) dissolved in 20 mL of diethyl ether was added 0.16 mL of *o*-isopropylphenylazide (ca. 1.0 mMol). Gas evolution immediately occurred, and the color of the solution changed from red-brown to a darker red. The volatile materials were removed immediately under reduced pressure. The residue was then extracted with 30 mL of hexane, the extract was filtered, and the filtrate was concentrated to ca. 5-10 mL and cooled to -20°C. Black-red needles were isolated and dried in 65% yield (0.39 g), m.p. 77-83°C. $^1\text{H NMR}$ (C_6D_6 , 30°C): 4.71 (9H, $\nu_{1/2}$ = 23 Hz), -8.18 (12H, $\nu_{1/2}$ = 78 Hz), 1.81 (6H, $\nu_{1/2}$ = 12 Hz), 21.16 (1H, $\nu_{1/2}$ = 18 Hz), 19.27 (1H, $\nu_{1/2}$ = 18 Hz), 5.04 (1H, partly overlapped with the large peak at 4.71), -2.75 (1H, $\nu_{1/2}$ = 18 Hz), 9.24 (1H, $\nu_{1/2}$ = 65 Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{NU}$: C, 53.3; H, 5.30; N, 2.30. Found: C, 52.1; H, 5.05; N, 1.91. Mass spectrum: 608 (100; 100), 609 (32; 30), 610 (15; 4). IR: 1580 w, 1280m, 1245 m, 1085w, 1030 m, 910 w, 859 w, 839 w, 792 m, 768 s, 743 m, 606 w cm^{-1} .

(MeC₅H₄)₃UN-2,6-Me₂C₆H₃

To (MeC₅H₄)₃U(thf) (0.77 g, 1.41 mMol) dissolved in 30 mL of diethyl ether was added 0.21 mL of 2,6-dimethylphenylazide (1.43 mMol). Gas evolution immediately occurred, and the color changed from red-brown to deep red. The volatile materials were removed under reduced pressure, and the residue was extracted with 50 mL of diethyl ether. The ether extract was filtered, and the filtrate was concentrated to *ca.* 30 mL and cooled to -20°C. Red-black needles were isolated by filtration and dried in 51% (0.43 g) yield, m.p. 154-156°C. ¹H NMR (C₆D₆, 30°C): 5.67 (9H, *v*_{1/2} = 25 Hz), -4.60 (6H, *v*_{1/2} = 76 Hz), -14.23 (6H, *v*_{1/2} = 87 Hz), 19.79 (6H, *v*_{1/2} = 43 Hz), 20.58 (2H, *v*_{1/2} = 23 Hz), -5.49 (1H, *v*_{1/2} = 19 Hz). Anal. Calcd for C₂₆H₃₀NU: C, 52.5; H, 5.09; N, 2.36. Found: C, 50.9; H, 5.05; N, 2.17. Mass spectrum: 594 (100; 100), 595 (29; 28), 596 (4; 6). IR: 1490 m, 1260 w, 1230 w, 1090 m, 1068 w, 1044 m, 1030 m, 975 w, 929 w, 897 w, 889 w, 866 w, 845 m, 795 s, 788 s, 763 vs, 601 w, 385 w, 337 w cm⁻¹.

Reaction of (MeC₅H₄)₃U(thf) with p-CF₃C₆H₄N₃

To (MeC₅H₄)₃U(thf) (0.50 g, 0.91 mMol) dissolved in 15 mL of Et₂O was added 0.17 mL of p-trifluoromethylphenylazide. Gas evolution immediately occurred, and the solution turned dark red. After 5 minutes, the volatile materials were removed under reduced pressure and the residue was extracted with hexane (60 mL). The red solution was filtered, and the filtrate was concentrated to *ca.* 30 mL and cooled to -20°C. A small amount of brown powder was isolated (0.04 g). The volatile materials were then removed from the remaining hexane solution and the residue was extracted with diethyl ether (20 mL). The solution was filtered, and the filtrate was concentrated to *ca.* 10 mL and cooled to -20°C. Red-brown crystals (0.21 g) were isolated and

dried. Both crops were examined by ^1H NMR spectroscopy. Both spectra showed the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UN-p-CF}_3\text{C}_6\text{H}_4$ and $(\text{MeC}_5\text{H}_4)_3\text{UF}$ (by comparison with a spectrum obtained by Brennan¹), with the uranium(V) compound predominant. The ^1H NMR spectrum of $(\text{MeC}_5\text{H}_4)_3\text{UN-p-CF}_3\text{C}_6\text{H}_4$ is as follows: 3.59 (9H, $\nu_{1/2}$ = 16 Hz), -3.12 (6H, $\nu_{1/2}$ = 43 Hz), -11.29 (6H, $\nu_{1/2}$ = 37 Hz), 18.25 (2H, $\nu_{1/2}$ = 16 Hz), 3.16 (2H). Attempts to recrystallize the material always yielded a mixture of compounds and the reaction was not pursued further.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ with $\text{o-CF}_3\text{C}_6\text{H}_4\text{N}_3$

To $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.56 g, 1.02 mMol) dissolved in 20 mL of Et_2O was added 0.19 g of *o*-trifluoromethylphenylazide dissolved in 10 mL of Et_2O . The solution color immediately began to lighten, and a dark precipitate formed. After stirring for 14 hours, the volatile materials were removed under reduced pressure. The ^1H NMR spectrum of the green residue showed that it was primarily $(\text{MeC}_5\text{H}_4)_3\text{UF}$. A trace amount of what is probably $(\text{MeC}_5\text{H}_4)_3\text{UN-o-CF}_3\text{C}_6\text{H}_4$ was also observed in the spectrum. The reaction was not pursued further.

$(\text{MeC}_5\text{H}_4)_3\text{UN}_3(\text{AlMe}_3)$

To $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (0.84 g, 1.6 mMol) dissolved in 20 mL of dichloromethane was added trimethylaluminum (13 mL of a 1.3 M solution in hexane, 16.9 mMol). The solution immediately darkened. After 12 hours, the volatile materials were removed under reduced pressure, leaving a brown powder. This powder was extracted with toluene (25 mL), the solution was filtered, and the filtrate was concentrated to *ca.* 20 mL and cooled to -20°C . Brown crystals were isolated by filtration and dried; a second crop was

obtained an additional concentration and cooling of the solution. The total yield was 75% (0.72 g), m.p. 152-154°C. ^1H NMR (C_6D_6 , 30°C): -4.22 (3H), 12.04 (2H), -16.54 (2H), -7.62 (ca. 2.5 H). The integration of the peak at -7.6 appears to increase as the temperature of the NMR is lowered (it is close to 3 at -72°C).

Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{AlN}_3\text{U}$: C 42.8; H, 5.13; N, 7.03. Found: C, 38.9; H, 5.10; N, 7.03. The mass spectrum only showed a molecular ion for $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (517). IR: 2110 s br, 1268 m, 1169 m, 1048 w, 1030 m, 844 w, 791 s, 710 s, 610 w, 525 w, 425 w, 347 w, 248 m cm^{-1} .

Reaction of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ with $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$

To $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (0.15 g, 0.23 mMol) dissolved in 10 mL of hexane was added $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UN}_3$ (0.16 g, 0.23mMol) dissolved in 10 mL of hexane. The color immediately changed to deep brown. After stirring overnight, the solution was filtered, and the filtrate was concentrated to ca. 5 mL and cooled to -20°C. Brown crystals were isolated and dried, m.p. 83-86°C. ^1H NMR (C_6D_6 , 30°C): -8.79 (9H, $\nu_{1/2} = 7$ Hz), -16.52 (2H, $\nu_{1/2} = 7$ Hz), 0.9 (2H, $\nu_{1/2} = \text{ca. } 40$ Hz). IR: 2122 s, 2081 s, 1246 s, 1177 m, 1042 s, 903 s, 836 s, 785 s, 760 s, 750 s, 689 w, 635 m, 625 m cm^{-1} .

$(\text{MeC}_5\text{H}_4)_3\text{U}-\mu\text{-OC}(\text{Co}_2(\text{CO})_9)_2$

Method A: To $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ (0.44 g, 0.85 mMol) dissolved in 30 mL of dichloromethane was added $\text{Co}_2(\text{CO})_8$ (0.29 g, 0.85 mMol) dissolved in 15 mL of dichloromethane. The solution slowly turned from green to red. After 18 hours, the volatile materials were removed under reduced pressure. The solid was extracted with hexane (40 mL), the red solution was filtered, and the filtrate was concentrated and cooled to -20°C. Red microcrystals were isolated by filtration and dried in 77% (0.41g) yield (based on cobalt). ^1H NMR (C_6D_6 ,

30°C): -10.16 (3H), 5.14 (2H), -1.50 (2H). IR: 2080 m, 1960 s vbr, 1030 m, 855 m, 780 s, 580 s, 535 s, 509 s, 470 s, 430 s, 405 m, 355 w, 335 w cm^{-1} . The infrared spectrum was also obtained in Et_2O solution; the absorbances between 2100 and 1800 cm^{-1} are as follows: 2080 w, 2062 w, 2058 w, 2025 s, 2017 s, 1959 m, 1927 m, 1899 m, 1869 w cm^{-1} .

Method B: To $(\text{MeC}_5\text{H}_4)_3\text{UN}^t\text{Bu}$ (0.10 g, 0.18 mMol) dissolved in 20 mL of hexane was added $\text{Co}_2(\text{CO})_8$ (0.06 g, 0.18 mMol) dissolved in 20 mL of hexane. The solution slowly turned red and a red precipitate formed. After 24 hours, the dark red solution was filtered. The red precipitate that remained was extracted with 20 mL of hexane, the solution was filtered, and the two filtrates were combined. The filtrate was concentrated to ca. 50 mL and cooled to -20°C. Red crystals were isolated by filtration and dried, m.p. 130°C (dec.). ^1H NMR spectroscopy showed that this material was identical to that produced in method A

$\text{Cp}_3\text{U}-\mu\text{-OC}[\text{Co}_2(\text{CO})_9]$

To $\text{Cp}_3\text{UNSiMe}_3$ (0.62 g, 1.2 mMol) dissolved in 40 mL of ether was added $\text{Co}_2(\text{CO})_8$ (0.40 g, 1.2 mMol) dissolved in 30 mL of ether. A red precipitate slowly formed as the mixture was stirred over 20 hours. The volatile materials were removed under reduced pressure, the red solid was extracted with toluene (40 mL), the solution was filtered, and the filtrate was concentrated to ca. 30 mL and cooled to -20°C. Red plates were isolated by filtration and dried in 80% (0.57 g) yield (based on cobalt). ^1H NMR (C_6D_6 , 28°C): 3.32. IR: 2080 m, 2020 s, 1968 m, 1260 w, 1165 w, 1018 w, 1009 w, 817 w, 795 m, 720 m, 588 m, 540 m, 510 m, 477 m, 436 m, 412 w cm^{-1} .

$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2\cdot\mu\text{-PhNCO}$

A Fisher-Porter pressure apparatus containing $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ (0.15 g, 0.27 mMol) dissolved in 15 mL of Et_2O was charged with 185 psi of carbon monoxide. After several hours, the color of the solution appeared to be lightening from deep red to pale red-orange. After 18 hours, the solution was cannulated from the reactor and the volatile materials were removed under reduced pressure. The yellow-orange solid was extracted with ether (30 mL), the solution was filtered, and the filtrate was concentrated to *ca.* 10 mL and cooled to -20°C . A small amount of oily material precipitated from the solution. The mother liquor was refiltered and cooled to -80°C , resulting in the formation of orange microcrystals, which were isolated and dried in 43% (0.07 g) yield. ^1H NMR (C_6D_6 , 30°C): -3.42 (9H), -21.74 (9H), 12.64 (6H), 4.39 (6H), -7.87 (6H), -18.71 (6H), -25.00 (2H), 3.0 (2H), 6.4 (1H). The spectrum was found to be identical to that obtained by Brennan.¹

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with Me_3SnN_3

$(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ (0.15 g, 0.27 mMol) and Me_3SnN_3 (0.09 g, 0.44 mMol) were mixed in a Schlenk tube. Toluene (10 mL) was added and the solution was stirred for 24 hours. At the end of this time, the volatile materials were removed under reduced pressure and the green-brown residue was examined by ^1H NMR spectroscopy. The spectrum indicated the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ in a ratio of *ca.* 95 : 5.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with Me_3SiN_3

To $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ (0.15 g, 0.27 mMol) dissolved in 10 mL of toluene was added Me_3SiN_3 (0.06 mL, 0.46 mMol). The solution was stirred for 24 hours. At the end of this time, the volatile materials were removed under

reduced pressure and the brown residue was examined by ^1H NMR spectroscopy. The spectrum indicated the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ in a ratio of *ca.* 85 : 15.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with Me_3SnN_3

$(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ (0.15 g, 0.27 mMol) and Me_3SnN_3 (0.09 g, 0.44 mMol) were mixed in a Schlenk tube. Toluene (10 mL) was added and the solution was stirred for 24 hours. At the end of this time, the volatile materials were removed under reduced pressure and the green residue was examined by ^1H NMR spectroscopy. The spectrum indicated the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ in a ratio of *ca.* 93 : 7.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with Me_3SiN_3

To $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ (0.15 g, 0.27 mMol) dissolved in 10 mL of toluene was added Me_3SiN_3 (0.06 mL, 0.46 mMol). The solution was stirred for 24 hours. At the end of this time, the volatile materials were removed under reduced pressure and the brown residue was examined by ^1H NMR spectroscopy. The spectrum indicated the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ in a ratio of *ca.* 92 : 8.

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with Ph_3CN_3

To $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ (0.12 g, 0.21 mMol) was added Ph_3CN_3 (0.11 g, 0.37 mMol) dissolved in 10 mL of toluene. The solution was stirred for 24 hours. At the end of this time, the volatile materials were removed under reduced pressure and the brown residue was examined by ^1H NMR spectroscopy. The spectrum indicated the presence of both $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$ in a ratio of *ca.* 98 : 2.

$(\text{MeC}_5\text{H}_4)_3\text{UOMe}$

$(\text{MeC}_5\text{H}_4)_3\text{UCl}$ was generated *in situ* as follows: To UCl_4 (0.80 g, 2.1 mMol) dissolved in 20 mL of thf was added NaMeC_5H_4 (5.0 mL of a 1.25 M solution in thf, 6.25 mMol). The solution immediately turned red-brown, and a light precipitate formed. After one hour of stirring, the precipitate was allowed to settle and the solution of $(\text{MeC}_5\text{H}_4)_3\text{UCl}$ was filtered onto NaOMe (0.18 g, 3.3 mMol). The solution was stirred for 12 hours and the color changed from red to bright emerald green. The volatile materials were removed under reduced pressure, and the green solid was extracted with hexane (50 mL). The green solution was filtered, the filtrate was concentrated to ca. 15 mL and cooled to -20°C . Green flakes were isolated and dried in 47% (0.50 g) yield, m.p. $274\text{--}275^\circ\text{C}$ (the compound turns brown above 120°C). ^1H NMR (C_6D_6 , 30°C): -0.32 (9H), -10.61 (6H), -22.48 (6H), 45.2 (3H). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{OU}$: C, 45.1; H, 4.78. Found: C, 44.8; H, 4.78. Mass spectrum: 506 (100; 100), 507 (17; 21). IR: 1262 w, 1239 w, 1108 s, 1050m, 1030 m, 934 w, 826 m, 768 s, 632 w, 494 w cm^{-1} .

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with MeOH

To $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ (0.37 g, 0.66 mMol) dissolved in 30 mL of toluene was added MeOH (1.34 mL of a 0.49 M solution in ether). A reflux condenser topped with a gas inlet was placed on the flask and the solution was heated to reflux for 36 hours. At the end of this time, the solution was cooled and the volatile materials were removed under reduced pressure. The brown solid was extracted with hexane, the brown solution was filtered, and the filtrate was concentrated and cooled to -80°C . Brown bricks were isolated

by filtration and dried (0.12 g). ^1H NMR spectroscopy indicated that the product was a mixture of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UOMe}$ (ca. 1:1).

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ with PhOH

To $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ (0.37 g, 0.66 mMol) dissolved in 15 mL of ether was added PhOH (0.06 g, 0.6 mMol) dissolved in 15 mL of ether. The mixture was stirred for 24 hours. The volatile materials were removed under reduced pressure. The brown solid was extracted with hexane (25 mL), the solution was filtered, and the filtrate was concentrated to ca. 5 mL and cooled to -20°C . Brown crystals were isolated by filtration and dried. ^1H NMR spectroscopy indicated that the product was a mixture of $(\text{MeC}_5\text{H}_4)_3\text{UNSiMe}_3$ and $(\text{MeC}_5\text{H}_4)_3\text{UOPh}$. The major ^1H NMR resonances of $(\text{MeC}_5\text{H}_4)_3\text{UOPh}$ are as follows: -3.1δ (9H), -4.75 (6H), -12.01 (6H). This compound was identified by comparison with an authentic sample prepared by Stults.¹⁹

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ with $t\text{BuNC}$

To $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ (0.46 g, 0.81 mMol) dissolved in 20 mL of toluene was added *t*-butylisocyanide (0.10 mL, 0.88 mMol). The solution was stirred for 8 days with no obvious color change, then the volatile materials were removed under reduced pressure and the residue was extracted with hexane (50 mL). The pale red solution (a lot of the material was not hexane soluble) was filtered and cooled to -20°C , resulting in the formation of pale red-orange needles. The ^1H NMR spectrum (C_6D_6) of these needles was complex, and the spectrum changed over time. Anal. Found: C, 54.3; H, 5.52; N, 7.39. IR: 2180 m, 1590 m, 1455 s, 1290 m, 1263 m, 1235 m, 1218 m, 1167 w, 1068 w, 1030 w, 948 m, 880 w, 840 w, 772 m, 751 m, 745 m, 690 m cm^{-1} . Concentration and cooling of the remaining hexane solution yielded a dark solid; the ^1H NMR spectrum

of this material showed it to be $(\text{MeC}_5\text{H}_4)_4\text{U}$. The remaining hexane solution was filtered, and the volatile material removed under reduced pressure. The ^1H NMR spectrum of the residue indicated that the primary material in this residue was $(\text{MeC}_5\text{H}_4)_4\text{U}$, although resonances from $(\text{MeC}_5\text{H}_4)_3\text{UNPh}$ and $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$ were also observed.

Section 4.2: Chapter 2 Experimental Details

$[(\text{MeC}_3\text{H}_4)_3\text{U}]_2[\mu\text{-1,4-N}_2\text{C}_6\text{H}_4]$

To 0.68 g of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (1.24 mMol) dissolved in 30 mL of diethyl ether was added 0.10 g of 1,4-diazidobenzene (0.62 mMol) in 10 mL of diethyl ether. Gas was immediately evolved, and the color of the solution changed from red to deep purple with formation of a dark precipitate. After stirring for 15 minutes, the volatile materials were removed under reduced pressure, leaving a dark solid. This solid was extracted into toluene (60 mL), the purple solution was filtered, and the filtrate was concentrated to 40–45 mL and cooled to -20°C . Purple-black flakes were isolated by filtration and dried under reduced pressure, yielding 0.19 g of product. Concentrating the remaining solution to ca. 15 mL and cooling to -20°C allowed isolation of an additional 0.12 g of product. Total yield was 48% (0.31 g), m.p. $261\text{--}263^\circ\text{C}$. $^1\text{H NMR}$ (C_6D_6 , 30°C): 4.69 (9H, $\nu_{1/2} = 6$ Hz), -2.46 (6H, $\nu_{1/2} = 23$ Hz), -9.01 (6H, $\nu_{1/2} = 17$ Hz), 15.11 (4H, $\nu_{1/2} = 14$ Hz). Anal. Calcd for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{U}_2$: C, 47.8; H, 4.40; N, 2.66. Found: C, 48.1; H, 4.54; N, 2.64. Mass spectrum: 1054 (100; 100), 1055 (47; 36). IR: 1578 w, 1493 m, 1283 m, 1260 m, 1090 w, 1047 w, 1032 m, 928 w, 903 w, 849 m, 833 m, 764 s, 610m, 592 m, 538 w cm^{-1} . Magnetic susceptibility (5 and 40 kG fields): $\mu_{\text{eff}} = 2.94$ B. M. (140–280 K; $\Theta = -147$ K; $\mu_{\text{eff}} = 2.08$ B. M. per uranium). The compound is antiferromagnetic with $T_N = \text{ca. } 18$ K and $J = \text{ca. } -19$ cm^{-1} .

$[(\text{MeC}_3\text{H}_4)_3\text{U}]_2[\mu\text{-1,3-N}_2\text{C}_6\text{H}_4]$

To 0.47 g of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.86 mMol) dissolved in 15 mL of diethyl ether was added 2.2 mL of a 0.03 g mL^{-1} solution of 1,3-diazidobenzene (0.066 g, 0.41 mMol) in toluene. Gas evolution occurred immediately, and the solution color darkened to deep red. The volatile materials were

immediately removed under reduced pressure. The brown-red solid was extracted with 25 mL of hot toluene (55-60°C), the solution was filtered, and the filtrate was concentrated to ca. 10 mL and cooled to -20°C. Red-brown needles were isolated by filtration and dried in 37% (0.17 g) yield, m.p. 213-215°C. $^1\text{H NMR}$ (C_6D_6 , 59°C): 4.38 (18H, $\nu_{1/2}$ = 17 Hz), -2.27 (12H, $\nu_{1/2}$ = 62 Hz), -9.22 (12H, $\nu_{1/2}$ = 55 Hz), 28.23 (1H, $\nu_{1/2}$ = 25 Hz), -0.46 (1H, $\nu_{1/2}$ = 32 Hz), -6.89 (2H, $\nu_{1/2}$ = 32 Hz). The NMR was recorded at 59°C because the peak at -0.46 ppm was too broad to be observed at room temperature. Anal. Calcd for $\text{C}_{42}\text{H}_{46}\text{N}_2\text{U}_2$: C, 47.8; H, 4.40; N, 2.66. Found: C, 47.5; H, 4.41; N, 2.63. Mass spectrum: 1054 (observed by FAB MS using 18-crown-6 and tetraglyme). IR: 1545 m, 1490 w, 1292 w, 1250 m, 1200 m, 1148 m, 1048 w, 1029 m, 990 m, 861 w, 854 w, 842 m, 797 m, 765 s, 682 m, 604 w, 330 w cm^{-1} . Magnetic susceptibility (5 and 40 kG fields): μ_{eff} = 3.00 B. M. (140-280 K; Θ = -134 K; μ_{eff} = 2.12 B. M. per uranium), μ_{eff} = 1.84 B. M. (5-40 K; Θ = -4.0 K; μ_{eff} = 1.30 B. M. per uranium).

$[(\text{MeC}_3\text{H}_4)_3\text{U}]_3[\mu\text{-}1,2\text{-(}4\text{-NC}_6\text{H}_4)_2\text{C}_2\text{H}_2]$

To 0.50 g of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.91 mMol) dissolved in 10 mL of thf was added 0.12 g of 4,4'-diazidostilbene (0.46 mMol) in 10 mL thf. Gas evolution occurred immediately, and the solution color darkened to deep red. After 30 minutes, the volatile materials were removed under reduced pressure. The brown-red solid was extracted with 30 mL of toluene, the solution was filtered, and the filtrate was concentrated to ca. 25 mL and cooled to -20°C. Red-brown needles were isolated by filtration and dried in 64% (0.34 g) yield, m.p. 241-245°C. $^1\text{H NMR}$ (C_6D_6 , 30°C): 3.99 (18H, $\nu_{1/2}$ = 22 Hz), -3.33 (12H, $\nu_{1/2}$ = 60 Hz), -10.68 (12H, $\nu_{1/2}$ = 62 Hz), 19.40 (4H, $\nu_{1/2}$ = 18 Hz), 9.48 (2H, $\nu_{1/2}$ = 12 Hz). The peak from the ortho protons was not observed. Anal. Calcd for $\text{C}_{50}\text{H}_{52}\text{N}_2\text{U}_2$: C, 51.9; H, 4.53; N, 2.42. Found: C, 52.0; H, 4.81; N, 2.22. Mass

spectrum: 1157 (observed by FAB MS). Magnetic susceptibility (5 and 40 kG fields): $\mu_{\text{eff}} = 2.73$ B. M. (140-220 K; $\Theta = -48$ K; $\mu_{\text{eff}} = 1.93$ B. M. per uranium), $\mu_{\text{eff}} = 1.94$ B.M. (5-40 K; $\Theta = -6.3$ K; $\mu_{\text{eff}} = 1.37$ B.M. per uranium).

$[(\text{MeC}_3\text{H}_4)_3\text{U}]_3[\mu\text{-}1,5\text{-N}_2\text{C}_{10}\text{H}_6]$

To 0.75 g of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (1.37 mMol) and 0.14 g of 1,5-diazidonaphthalene (0.67 mMol) was added 10 mL thf and 30 mL ether. Gas evolution occurred immediately, and the solution color darkened to deep red-purple. After 10 minutes, the volatile materials were removed under reduced pressure. The brown-red solid was extracted with 75 mL of hot toluene (50-60°C), the solution was filtered, and the filtrate was cooled to -15°C. Black-purple needles were isolated by filtration and dried in 18% (0.26 g) yield. ^1H NMR ($\text{d}_8\text{-thf}$, 30°C): 5.35 (18H, $\nu_{1/2} = 22$ Hz), -5.18 (12H, $\nu_{1/2} = 65$ Hz), -8.19 (12H, $\nu_{1/2} = 49$ Hz), 16.95 (4H, $\nu_{1/2} = 18$ Hz), 9.48 (2H, $\nu_{1/2} = 12$ Hz). The other naphthalene ring resonances were not observed. Magnetic susceptibility (5 and 40 kG fields): $\mu_{\text{eff}} = 2.00$ B.M. (5-40 K; $\Theta = -5.5$ K; $\mu_{\text{eff}} = 1.41$ B.M. per uranium).

Reaction of $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ with $\text{Me}_2\text{Si}(\text{N}_3)_2$

To 1.05 g $(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (1.92 mMol) dissolved in 30 mL of ether was added 0.12 mL $\text{Me}_2\text{Si}(\text{N}_3)_2$ (0.90 mMol). A green-brown precipitate was observed immediately. The volatile materials were removed under reduced pressure. The green-brown solid was examined by ^1H NMR spectroscopy and found to be primarily $(\text{MeC}_3\text{H}_4)_3\text{UN}_3$. This solid was extracted with 50 mL of hot toluene (55-60°C), the solution was filtered, and the filtrate was concentrated to ca. 25 and then cooled to -80°C. Green microcrystals were

isolated by filtration and dried in 58% (0.27 g) yield [based on $\text{Me}_2\text{Si}(\text{N}_3)_2$]. The ^1H NMR spectrum of this material indicated that it was pure $(\text{MeC}_5\text{H}_4)_3\text{UN}_3$.

Section 4.3: Chapter 3 Experimental Details

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_3)$

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.45 g, 0.82 mmol) was dissolved in 30 mL of toluene, and the solution was frozen in a liquid nitrogen bath and the Schlenk tube evacuated. Into the vacuum line was expanded 9.4 cm of anhydrous ammonia (Volume = 0.32 L; 9.4 cm = ca. 1.6 mmol), and this gas was then condensed into the Schlenk tube. The tube was warmed to room temperature, filled with argon, and the reaction mixture was stirred for 24 hours. At the end of this time, the solution was warmed with a hot water bath to 55–60°C, then filtered while hot. The dark red filtrate was then concentrated and cooled to -20°C. Red needles were isolated by filtration and dried in 57% (0.23 g) yield, m.p. 206–210°C (with gas evolution and a color change from brown-red to brighter red). ^1H NMR (C_6D_6 , 29°C): -15.48 (9H, $\nu_{1/2}$ = 6 Hz), -9.28 (6H, $\nu_{1/2}$ = 16 Hz), -18.71 (6H, $\nu_{1/2}$ = 16 Hz), -137.25 (3H, $\nu_{1/2}$ = 39 Hz). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{NU}$: C, 43.9; H, 4.91; N, 2.84. Found: C, 43.6; H, 4.78; N, 2.71. Mass spectrum: 492 (100; 100), 493 (32; 20), 494 (30; 2). IR: 3315 m, 3241 m, 1594 m, 1212 s, 1026 m, 930 w, 830 m, 756 s, 617 w, 577 w cm^{-1} .

$(\text{MeC}_5\text{H}_4)_3\text{U}(^{15}\text{NH}_3)$

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.50 g, 0.91 mmol) was dissolved in 40 mL of toluene, and the solution was frozen in a liquid nitrogen bath and the Schlenk tube evacuated. Into the vacuum line was expanded 10.4 cm of $^{15}\text{NH}_3$ (Volume = 0.32 L; 10.4 cm = ca. 1.8 mmol), and this gas was then condensed into the Schlenk tube. The tube was warmed to room temperature, filled with argon, and the reaction mixture was stirred for 24 hours. At the end of this time, the solution was filtered and the volatile materials were slowly removed under

reduced pressure. Red-brown flakes were obtained. $^1\text{H NMR}$ (C_6D_6 , 30°C): -15.43 (9H, $\nu_{1/2} = 6$ Hz), -9.22 (6H, $\nu_{1/2} = 16$ Hz), -18.73 (6H, $\nu_{1/2} = 16$ Hz), -135.94 (3H, d, $J = 60$ Hz). IR: 3320 m, 3240 m, 1596 m, 1207 s, 1043 w, 1025 w, 973 w, 928 w, 834 m, 812 m, 770 s, 751 s, 617 w cm^{-1} .

$(\text{MeC}_3\text{H}_4)_3\text{U}(\text{NH}_2\text{Me})$

$(\text{MeC}_3\text{H}_4)_3\text{U}(\text{thf})$ (0.60 g, 1.10 mmol) was dissolved in 25 mL of toluene and the solution was frozen using a liquid nitrogen bath. The Schlenk tube was then evacuated and *ca.* 2.0 mmol of MeNH_2 from a constant volume bulb was condensed into the flask. The solution was warmed to room temperature, the tube filled with nitrogen, and the mixture was stirred for one hour. At the end of this time, the toluene was removed under reduced pressure to leave a red-brown solid. The solid was extracted with ether (2×30 mL), the red solution was filtered, and the filtrate was concentrated to *ca.* 50 mL and cooled to -20°C . Red/black flakes were isolated and dried. A second crop was obtained by concentrating the ether filtrate to 10-15 mL and cooling to -78°C . Overall yield was 70% (0.39 g). The compound does not exhibit a clear melting point. When heated slowly in a sealed capillary, the material begins to "soften" at *ca.* $170\text{--}175^\circ\text{C}$, continues softening to *ca.* 200°C , then appears to begin to change color to a brighter red-green and finally melts at $237\text{--}238^\circ\text{C}$. $^1\text{H NMR}$ (C_6D_6 , 30°C): -17.13 (9H, $\nu_{1/2} = 8$ Hz), -11.51 (6H, $\nu_{1/2} = 19$ Hz), -15.08 (6H, $\nu_{1/2} = 17$ Hz), -30.34 (3H), -129 (2H, $\nu_{1/2} = 70$ Hz). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{NU}$: C, 45.1; H, 5.17; N, 2.77. Found: C, 44.9; H, 5.03; N, 2.71. The mass spectrum exhibited an M-1 peak at 505. IR: 3290 m, 3245 m, 1588 m, 1234 w, 1200 w, 1032 m, 987 s, 928 w, 820 s, 758 s, 611 w, 327 w cm^{-1} .

(MeC₃H₄)₃U(NH₂Ph)

To 1.00 g of (MeC₃H₄)₃U(thf) (1.83 mmol) dissolved in 20 mL of toluene was added 0.50 mL of aniline (8.5 mmol; an excess). The solution was stirred at room temperature for 18 hours, then the toluene removed under reduced pressure. The dark red-brown residue was heated to 50-60°C under vacuum to remove excess aniline, then the residue was extracted with toluene (55 mL). The solution was filtered, and the toluene completely removed very slowly under reduced pressure. Dark red crystals were isolated in 84% (0.87 g) yield, m.p. 155-157°C (with gas evolution and a color change from brown to red). ¹H NMR (C₆D₆, 27°C): -19.81 (9H), -10.68, (6H, $\nu_{1/2}$ = 16 Hz), -13.85 (6H, $\nu_{1/2}$ = 16 Hz), 2.16 (t, 1H), 0.75 (t, 2H), -15.26 (2H), -121.45 (2H, $\nu_{1/2}$ = 115 Hz). Anal. Calcd for C₂₄H₂₈NU: C, 50.7; H, 4.96; N, 2.46. Found: C, 49.0; H, 4.88; N, 2.24. The mass spectrum exhibited an M-1 peak at 567. IR: 3300 w, 3215 m, 1592 m, 1578 m, 1257 m, 1225 m, 1020 s, 923 w, 821 s, 810 s, 795 s, 691 s, 608 w, 519 m cm⁻¹.

(MeC₃H₄)₃U(p-NH₂C₆H₄Me)

To 0.52 g of (MeC₃H₄)₃U(thf) (0.95 mmol) dissolved in 20 mL of toluene was added 0.11 g of p-toluidine (1.0 mmol) dissolved in 10 mL of toluene. No obvious color change was observed. After eight hours, the toluene was removed under reduced pressure, and the excess toluidine was sublimed from the flask using a warm water bath (50-60°C). The brown solid was then extracted with toluene (40 mL), the solution was filtered, and the filtrate was concentrated to ca. 20 mL and cooled to -20°C. Brown needles were isolated and dried in 69% (0.38 g) yield, m.p. 166-169°C (with gas evolution and a color change from brown to red). ¹H NMR (C₆D₆, 30°C): -19.64 (9H, $\nu_{1/2}$ = 6 Hz), -10.57 (6H, $\nu_{1/2}$ = 17 Hz), -13.70 (6H, $\nu_{1/2}$ = 17 Hz), 0.59 (2H, d, J = 6.8 Hz), -15.09

(2H), -0.78 (3H), -121 (2H, $\nu_{1/2}$ = 200 Hz). Anal. Calcd for $C_{25}H_{30}NU$: C, 51.5; H, 5.19; N, 2.40. Found: C, 51.4; H, 5.11; N, 2.45. IR: 3324 w, 3221 m, 1616 w, 1576 w, 1514 m, 1233 w, 1146 w, 1036 s, 972 w, 936 w, 928 w, 816 m, 760 s, 519 w cm^{-1} .

$(MeC_3H_4)_3UNH_2$

Method A: $(MeC_3H_4)_3U(NH_2)$ (0.25 g, 0.51 mMol) was dissolved in 25 mL of xylenes in a 100 mL round-bottomed Schlenk flask. A reflux condenser with a gas inlet was attached to the flask, and the solution heated to reflux for 1.5 hours. The color lightened to red-green over this time. The solution was allowed to cool slightly, then filtered. The volatile materials were removed under reduced pressure, and the residue was extracted with warm hexane (20 mL). The solution was filtered and cooled to $-80^\circ C$. Brown microcrystals were isolated by filtration and dried in 44% (0.11 g) yield. The compound did not exhibit a clear melting point; the material darkened and "softened" at $170-175^\circ C$, was very dark brown by $260^\circ C$, and did not melt up to $310^\circ C$. 1H NMR (C_6D_6 , $30^\circ C$): 0.39 (9H, $\nu_{1/2}$ = 3 Hz), -5.73 (6H, $\nu_{1/2}$ = 8 Hz), -17.07 (6H, $\nu_{1/2}$ = 8 Hz), -135.4 (2H, t, J = 44 Hz). Anal. Calcd for $C_{18}H_{23}NU$: C, 44.0; H, 4.72; N, 2.85. Found: C, 42.6; H, 4.44; N, 2.44. Mass spectrum: 491 (100; 100), 492 (21; 20). IR: 3315 w, 1495 m, 1258 w, 1235 w, 1150 w br, 1068 w, 1045 m, 1029 m, 970 w, 929 w, 830 m br, 760 s, 720 m, 652 m, 601 m, 497 m, 450 m, 327 m cm^{-1} .

Method B: To $(MeC_3H_4)_3U(NH_2)$ (0.56 g, 1.1 mMol) was added 0.33 g $(Ph_3C)_2PhMe^{20}$ (1.1 mMol of trityl monomer) dissolved in 30 mL of hexane. The solution immediately turned bright green-red. After three hours, the solution was filtered and the volatile materials were removed under reduced pressure. A cold finger was placed in in the flask and the solid heated to $100^\circ C$ under reduced pressure for three hours. A green-white solid sublimed onto the coldfinger; this material was discarded. 1H NMR spectroscopy

showed that the remaining solid (0.37 g) was a mixture of $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ and Ph_3CH (approximate molar ratio 1.0 : 0.6).

Method C: To $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.50 g, 0.91 mMol) dissolved in 20 mL of thf was added 28 μL of anhydrous hydrazine. The solution was stirred for 18 hours, during which time the color turned light green. The volatile materials were removed under reduced pressure and the solid extracted with toluene (30 mL), filtered, and the toluene removed under reduced pressure. To the green residue was added 10 mL of hexane, and the solution was stirred for 30 minutes and then cooled to -80°C . Red-green microcrystals were isolated by filtration and dried in 20% (0.09 g) yield. The ^1H NMR spectrum of this material showed it to be $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$.

$(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NH}_2$

$(\text{MeC}_5\text{H}_4)_3\text{U}(^{15}\text{NH}_3)$ (0.25 g, 0.51 mMol) and $(\text{Ph}_3\text{C})_2\cdot\text{PhMe}$ (0.15 g, 0.50 mMol of trityl monomer) were mixed and 6 mL of toluene was added. The solution was warmed to 60°C and stirred for 10 minutes. At the end of this time, the solution was filtered, allowed to cool to room temperature, then cooled to -80°C . A tan solid was isolated by filtration and dried; ^1H NMR spectroscopy indicated that this was a mixture of Ph_3CH and unreacted $(\text{MeC}_5\text{H}_4)_3\text{U}(^{15}\text{NH}_3)$. The volatile materials from the mother liquor were removed under reduced pressure to yield $(\text{MeC}_5\text{H}_4)_3\text{U}^{15}\text{NH}_2$ and additional Ph_3CH . ^1H NMR (C_6D_6 , 30°C): 0.39 (9H), -5.74 (6H), -17.03 (6H), -134.86 (2H, d, $J = 64$ Hz).

Reaction of $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ with AlMe_3

To $(\text{MeC}_5\text{H}_4)_3\text{UNH}_2$ (0.24 g, 0.49 mMol) dissolved in 15 mL of toluene was added AlMe_3 in hexane (0.35 mL of a 1.38M solution, 0.48 mMol). The

solution was stirred for four days, then the volatile materials were removed under reduced pressure. The green solid was extracted with toluene (20 mL), the solution was filtered, and the volatile materials were removed from the filtrate under reduced pressure. ^1H NMR spectroscopy indicated that this material was primarily $(\text{MeC}_5\text{H}_4)_3\text{UMe}$.

$(\text{MeC}_5\text{H}_4)_3\text{UNHMe}$

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{Me})$ (0.15 g; 0.30 mMol), in a Schlenk tube under N_2 , was immersed in an oil bath at 215-225°C. The dark brown solid melted and turned red. After 20 minutes, the flask was cooled to room temperature, and the solid was extracted with warm toluene (50-60°C). The red-green solution was filtered and the toluene removed to give a green-red solid in 80% (0.12 g) yield. ^1H NMR (C_6D_6 , 30°C): 1.44 (9H), -10.71 (6H, $\nu_{1/2} = 7$ Hz), -14.98 (6H, $\nu_{1/2} = 7$ Hz), 7.29 (3H, d, $J = 5.9$ Hz), -103.75 (1H, $\nu_{1/2} = 50$ Hz). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NU}$: C, 45.2; H, 4.98; N, 2.77. Found: C, 45.0; H, 4.99; N, 2.57. Mass spectrum: 505 (100; 100), 506 (33; 21). IR: 1492 w, 1408 w, 1258 m, 1238 w, 1056 s, 1027 s, 930 w, 840 m, 760 s, 606 m, 425 m br, 329 m cm^{-1} .

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NHPh})$

Method A: $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{C}_6\text{H}_5)$ (0.30 g, 0.53 mMol), in a Schlenk tube under N_2 , was immersed in an oil bath at 160°C. The dark brown solid melted, turned red, and gas was evolved. After one hour at 160°C, the flask was cooled to room temperature, and the solid was extracted with hexane (30;10 mL; the solution was warmed to dissolve the solid). The bright red solution was filtered, and the filtrate was concentrated and cooled to -20°C. Red bricks were isolated and dried in 53 % (0.16 g) yield, m.p. 128-129°C. ^1H NMR (C_6D_6 , 30°C): 4.20 (9H), -1.03 (6H, $\nu_{1/2} = 8$ Hz), -18.56 (6H, $\nu_{1/2} = 9$ Hz),

-2.10 (t, 2H), -5.18 (t, 1H), -33.58 (d, 2H), -164.57 (1H, $\nu_{1/2}$ = 24 Hz). Anal. Calcd for $C_{24}H_{27}NU$: C, 50.8; H, 4.80; N, 2.47. Found: C, 50.8; H, 4.84; N, 2.66. Mass spectrum: 567 (100; 100), 566 (27; 27). IR: 1582 s, 1347 m, 1253 s, 1210 m, 1168 m, 1148 w, 1063 m, 1026 m, 989 m, 928 m, 889 w, 840 s, 773 s, 747 s, 690 s, 607 m, 558 s, 543 w, 490 m, 340 s, 325 m, 252 m, 236 s cm^{-1} .

Method B: In a 100 mL Schlenk flask, 0.52 g of $(MeC_5H_4)_3U(OMe)$ (1.1 mMol) was dissolved in 30 mL of hexane, and 0.20 mL of aniline (2.2 mMol) was added. The flask was equipped with a reflux condenser topped with a gas inlet, and the solution was heated to reflux. The solution slowly turned from green-brown to red. After 60 hours, the flask was cooled and the condenser was removed. The bright red solution was filtered, and the filtrate was concentrated to ca. 10 mL and cooled to $-20^\circ C$. Red crystals were isolated by filtration and dried in 38% (0.23 g) yield. 1H NMR showed this product to be $(MeC_5H_4)_3U(NHPh)$.

$(MeC_5H_4)_3U(NH-p-tolyl)$

Method A: $(MeC_5H_4)_3U(NH_2-p-tolyl)$ (0.21g, 0.36 mMol), in a Schlenk tube under N_2 , was immersed in an oil bath at $160^\circ C$. The dark brown solid melted, turned red, and gas was evolved. After 20 minutes at $160^\circ C$, the flask was cooled to room temperature, and the solid was extracted with hexane (20 mL; the solution was warmed to dissolve the solid). The bright red solution was filtered, and the filtrate was concentrated to ca. 7 mL and cooled to $-20^\circ C$. Red crystals were isolated and dried in 53% (0.11 g) yield, m.p. $92-94^\circ C$. 1H NMR (C_6D_6 , $30^\circ C$): 4.38 (9H, $\nu_{1/2}$ = 2 Hz), -1.91 (6H, $\nu_{1/2}$ = 7 Hz), -18.46 (6H, $\nu_{1/2}$ = 7 Hz), 1.04 (3H), -1.80 (2H), -32.78 (2H, d, J = 7.9 Hz), -158.78 (1H, $\nu_{1/2}$ = 19 Hz). Anal. Calcd for $C_{25}H_{29}NU$: C, 51.6; H, 5.03; N, 2.41. Found: C, 51.5; H, 4.94; N, 2.38. Mass spectrum: 581 (100; 100), 582 (24; 28), 583 (2; 4). IR: 1603 m, 1501 s,

1252 s, 1208 m, 1175 m, 1102 w, 1047 m, 1032 m, 932 w, 889 w, 851 m, 768 s, 602 w, 523 m cm^{-1} .

Method B: To 0.35 g of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH}_2\text{-p-tolyl})$ (0.60 mMol) dissolved in 20 mL of toluene was added 0.35 g of $(\text{MeC}_5\text{H}_4)_3\text{UNC}_6\text{H}_4\text{CH}_3$ (0.60 mMol) dissolved in 10 mL of toluene. The solution immediately turned bright red. After 90 minutes, the solvent was removed under reduced pressure to give a bright red solid. The solid was extracted with hexane (60 mL), the red solution was filtered, and the filtrate was concentrated to ca. 30 mL and cooled to -20°C . Red crystals were isolated by filtration and dried in 69% (0.48 g) yield. ^1H NMR showed this product to be $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{NH-p-tolyl})$.

$(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$

Method A: To $(\text{MeC}_5\text{H}_4)_4\text{U}$ (0.27 g, 0.49 mMol) dissolved in 15 mL of toluene was added 45.5 μL of phenylhydrazine (0.46 mMol). The solution was stirred for 40 hours, during which time a color change from red to orange occurred. At the end of this time, the volatile materials were removed under reduced pressure and the red-orange oily solid was extracted with 20 mL of hexane and 5 mL of Et_2O . The orange solution was filtered, and the filtrate was concentrated to ca. 15-20 mL and cooled to -20°C . Red bricks were isolated by filtration and dried in 46% (0.12 g) yield, m.p. $81\text{-}87^\circ\text{C}$. An additional amount (ca. 0.03 g) was obtained by further concentration of the filtrate (7-10 mL) and cooling to -20°C . The total yield was 56%. ^1H NMR (C_6D_6 , 30°C): -0.03 (9H), -5.73 (6H, $\nu_{1/2} = 9$ Hz), -18.32 (6H, $\nu_{1/2} = 9$ Hz), 10.90 (2H, d, $J = 6.8$ Hz), 8.17 (2H, m), -9.24 (2H). The resonance from the para proton of the phenyl ring is buried under the solvent signal at room temperature, but can be observed in the variable temperature ^1H NMR spectrum. At -12°C , the following resonances were observed: 0.34 (9H), -5.36 (6H), -23.29 (6H), 10.01

(2H, d, $J = 7.7$ Hz), 7.81 (1H), 7.59 (2H), -6.79 ppm (2H). Anal. Calcd for $C_{24}H_{28}N_2U$: C, 49.5; H 4.84; N, 4.81. Found: C, 49.4; H, 4.91; N, 4.71. Mass spectrum: 582 (100; 100), 583 (26; 27). IR: 3285 w, 3223 w, 1589 s, 1561 s, 1491 s, 1298 s, 1260 vs, 1184 w, 1154 w, 1047 m, 1030 m, 988 m, 849 m, 779 vs br, 752 s, 694 m, 633 m, 592 m cm^{-1} .

Method B: $(MeC_5H_4)_3U(thf)$ (0.50 g, 0.91 mMol) was dissolved in 20 mL of Et_2O and the solution was cooled to $0^\circ C$. Phenylhydrazine (0.10 mL, 1.0 mMol) was added by syringe, and the solution immediately turned red. After two minutes, the volatile materials were removed under reduced pressure while keeping the material at $0^\circ C$. The brown solid was extracted with 40 mL of cold Et_2O ($0^\circ C$), and the solution was filtered into a pre-cooled flask and cooled to $-20^\circ C$. Brown crystals were isolated and dried in 15% (0.07 g) yield (based on uranium). 1H NMR spectroscopy indicated that this material was $(MeC_5H_4)_3U(NH_3)$. The mother liquor was concentrated to ca. 5 mL and cooled to $-80^\circ C$. A very small amount of brown powder formed. The solution was again filtered, ca. 10 mL of hexane was added, and the solution was cooled to $-20^\circ C$. Orange crystals were isolated by filtration and dried in 17% (0.09 g) yield. 1H NMR spectroscopy indicated that the material was $(MeC_5H_4)_3UN(NH_2)Ph$.

Method C: To $(MeC_5H_4)_3U^tBu$ (0.10 g, 0.19 mMol) dissolved in 10 mL of Et_2O was added 17.6 μL of phenylhydrazine (0.18 mMol). The solution was stirred for 1 1/4 hours, during which time a color change from green to orange occurred. At the end of this time, the volatile materials were removed under reduced pressure and the red-orange oily solid was examined by 1H NMR spectroscopy, indicating that the material was primarily $(MeC_5H_4)_3^+N(NH_2)Ph$.

Method D: To $(\text{MeC}_5\text{H}_4)_3\text{UMe}$ (0.04 g, 0.08 mMol) dissolved in 10 mL of toluene was added 8.4 μL of phenylhydrazine (0.09 mMol). The solution was heated to 70-75°C for 42 hours, during which time the color changed to orange. At the end of this time, the solution was cooled and filtered and the volatile materials were removed under reduced pressure. the red-orange oily solid was examined by ^1H NMR spectroscopy, indicating that the material was primarily $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$.

$(\text{MeC}_5\text{H}_4)_3\text{UN}(^{15}\text{NH}_2)\text{Ph}$

To $(\text{MeC}_5\text{H}_4)_4\text{U}$ (0.25 g, 0.45 mMol) dissolved in 15 mL of toluene was added 42.5 μL of $\text{PhNH}^{15}\text{NH}_2$ (0.43 mMol). The solution was stirred for 18 hours, during which time a color change from red to orange occurred. At the end of this time, the volatile materials were removed under reduced pressure and the red-orange oily solid was extracted with 20 mL of hexane and 5 mL of Et_2O . The orange solution was filtered, and the filtrate was concentrated to *ca.* 15-20 mL and cooled to -20°C. A red-orange powder were isolated by filtration and dried. ^1H NMR (C_6D_6 , 30°C): -0.03 (9H), -5.74 (6H), -18.30 (6H), 10.86 (2H, d), 8.13 (2H, m), -9.24 (2H, d, $J = 76$ Hz). IR: 3281 w, 3225 w, 1591 s, 1572 m, 1495 m, 1296 w, 1254 s, 1186 m, 1152 w, 1044 m, 988 w, 868 e, 833 m, 818 s, 791 vs, 764 vs, 694 m, 635 m cm^{-1} .

Thermolyses of $(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$ and $(\text{MeC}_5\text{H}_4)_3\text{UN}(^{15}\text{NH}_2)\text{Ph}$

$(\text{MeC}_5\text{H}_4)_3\text{UN}(\text{NH}_2)\text{Ph}$ was dissolved in d_8 -toluene. The ^1H NMR spectrum was obtained, then the NMR tube was heated in a constant temperature bath to 120°C. Spectra were obtained over various time intervals, and indicated the disappearance of the phenylhydrazide and the

appearance of $(\text{MeC}_5\text{H}_4)_3\text{UNHPh}$. For the labelled material, the ^1H NMR spectrum showed a singlet for the N-H resonance at -162 ppm.

$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-1,4-(H}_2\text{N)}_2\text{C}_6\text{H}_4]$

$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (0.65 g, 1.2 mMol) was dissolved in 30 mL of Et_2O . This solution was filtered onto 0.065 g p-phenylenediamine (0.60 mMol). A brown precipitate immediately began to form. The solution was stirred overnight, then filtered. The brown powder was dried under reduced pressure in 66% (0.42 g) yield, m.p. 193-197°C. The ^1H NMR spectrum could not be obtained due to the insolubility of the material. Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{N}_2\text{U}_2$: C, 47.6; H, 4.76; N, 2.65. Found: C, 47.4; H, 4.89; N, 2.64. IR: 3280 m, 3230 m, 1588 m, 1489 m, 1375 m, 1347 w, 1258 w, 1235 m, 1217 w, 1140 w, 1119 w, 1025 s br, 935 w, 927 w, 815 s, 755 s br, 610 w, 541 m, 329 w cm^{-1} . The material used for magnetic susceptibility measurements was made by an analogous procedure with toluene as solvent, an excess of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ (2.5 molar equivalents), and sublimed, zone-refined p-phenylenediamine (Aldrich Chem. Co.). The brown, microcrystalline precipitate was washed with 10 mL of toluene and 20 mL of Et_2O prior to the measurement of its magnetism.

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