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ORGANOACTINIDE CHEMISTRY: SYNTHESIS, STRUCTURE, AND SOLUTION DYNAMICS

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J.G. Brennan
(Ph.D. Thesis)

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Organoactinide Chemistry: Synthesis, Structure, and Solution Dynamics

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ABSTRACT

The bidentate phosphine ligand DMPE kinetically stabilizes $Cp_2MX_2(DMPE)$ (X=halide) complexes with respect to ligand redistribution. Substitution of X results in thermally or kinetically unstable complexes. Ligand lability in these complexes is examined with the conclusion that halide is more labile than Cp in noncoordinating solvents. A fluctional molecular process in these pseudo tetrahedral molecules has been attributed to dissociation of one arm of the phosphine ligand from the metal coordination sphere.

The trivalent uranium coordination complexes $(RC_5H_4)_3U$-L (R=H, Me, $SiMe_3$) have been prepared to study the relative basicity of donor ligands toward low-valent uranium. It is found that the relative order of increasing basicity is $PMe_3 > P(OR)_3 \geq py > SR_2 \approx OR_2 \approx NR_3$. The series is found to be measurably sensitive to the steric and electronic properties of the metal coordination sphere as well as electronic perturbations of the donor ligand. A combination of data from solution measurements, crystallographic analysis, and gas phase PES, leads to the conclusion that trivalent uranium engages in a considerable degree of M→L π-backbonding toward ligands such as CO, CNR, PR_3, and $P(OR)_3$. Electronic saturation of the metal enhances this interaction.

The trivalent uranium complexes Cp_3U-L reduce PhNCO, CS_2, SCO, and YPR_3 (Y=S, Se, Te) to form the (IV) complexes $[Cp_3U]_2[X]$ (X= Y, CS_2, PhNCO). A comparison of the μ-S and μ-CS_2 structures indicates that U←S π-donation contributes to the stability of the sulfido complex. The reaction between Cp_3U and C_8H_8 or O_2 results in isolation of ligand redistribution products: in the C_8H_8 reaction, $(C_8H_8)U(Me_3SiC_5H_4)_2$ has been isolated, while in the O_2 reaction, $(Me_3SiC_5H_4)_4U$ has been isolated and structurally characterized; all Cp rings are η^5-coordinated to the metal. In the presence of organic azides, trivalent uranium acts as a two electron reducing agent to form U(V) imides $X_3U{=}NR$ (X = Cp, $(Me_3Si)_2N$). The μ-imido dimers $[Cp_3U{=}NR]_2$ (R=Ph, $SiMe_3$) have been isolated from the reaction of Cp_3UNR and Cp_3U. The Ph compound contains an asymmetric bridge with single and double U-N bonds, while the $SiMe_3$ complex is symmetrically bridged.

Richard A. Andersen

to my family

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INTRODUCTION

Organoactinide chemistry represents one of the greater challenges available to both experimental and theoretical chemists. Unlike the lanthanide series, where valence f-electrons appear immune to perturbation by the metal coordination sphere, the actinide valence f-electrons play a significant role in determining the physical and spectroscopic properties of the actinide ion. For example, absorption spectra of lanthanide complexes, if unobscured by charge transfer bands, consist of sharp resonances due to f-f transitions, with little observed broadening due to coupling with ligand vibrational modes. Organolanthanide magnetic susceptibility data indicate very little change in magnetic moment from that observed for the free ion[1]. In contrast, the absorption spectra and magnetic susceptibility data of actinide complexes are currently intractable in all but the most symmetric cases[2]. The large number of orbitals (5f, 6d, 7s) available for bonding interactions in the actinide series complicates spectroscopic interpretation and makes it difficult to predict which orbitals will participate in bonding with a given metal coordination sphere. The relatively low 5f-6d promotion energy is also given as an explanation for the large range of oxidation states available to the first half of the actinide series relative to the lanthanides.

The two actinide metals amenable to pratical large scale synthetic organometallic work are thorium and uranium. While thorium has only the tetravalent oxidation state available, uranium oxidation states range from +3 to +6, with most of the organometallic work

containing a +4 metal. The degree of covalent character in the various oxidation states is dependent on the radial extension of the valence orbitals; f-orbitals will contract relative to d-orbitals upon increasing the metal oxidation state, and there exists a balance between contracting spatially diffuse f-orbitals to the extent that overlap with ligand based orbitals is feasable, and contracting to the extent that the f-orbital is buried beneath the existing upper s and d-electrons.

Given the wide variety of accessable orbitals available for bonding in the actinides, it is logical to expect uranium complexes to appear ionic. With two valence electrons in U(IV), electron density contour plots appear virtually spherical[3], generating a shallow potential energy surface. This results in a decreased (relative to transition metals) barrier to ligand exchange or coordination sphere rearrangements. The rehybridization barriers that render some transition metal complexes kinetically inert are also lessened due to the large number of closely spaced energy levels. The size of the metal ion also permits coordination of additional ligands, which further minimizes barrier to exchange between possible geometries.

The desire to interpret the physical properties of certain organouranium complexes in terms of a covalent model has served as a convenient source of debate for decades. In 1956, the relative non-lability of Cp ligands in Cp_3UCl vs. Cp_3La (Reactions 1&2)[4] was given

1 $2\ Cp_3Ln + 3\ FeCl_2 \longrightarrow 3\ FeCp_2 + 2\ LnCl_3$

2 $Cp_3UCl + FeCl_2 \longrightarrow$ no reaction

as evidence for the more covalent nature of the uranium complex. The possible ramifications of an open coordination site in the lanthanide complex on the relative rate was not addressed. A decade later, Fischer proposed that a uranium compound with $C_8H_8^{--}$ could be isolated[5]. Subsequent preparation of uranocene[6] by Mueller-Westerhoff and Streitweiser initiated numerous research efforts to determine the extent that overlap between f-orbitals and ligand based orbitals stabilized uranocene. The apparent chemical stability (e.g. hydrolysis experiments, ligand exchange reactions) of $U(COT)_2$ has often been interpreted as evidence for additional covalent stability in uranocene relative to $Th(COT)_2$ or related lanthanide complexes, but alternative descriptions (i.e. kinetic vs. thermodynamic) of the chemistry based on size arguments exist, and it is difficult to separate size and covalent effects. Certainly one of the most convincing arguments for the existence of covalent bonding in uranocene is the photoelectron spectroscopic analysis of Paine and Green[7]. The synthesis of uranocene seems to have inspired an extensive analysis of non COT based systems; the possibly unique effects f-orbital covalency may have on organometallic chemistry is the principal reason for studying synthetic organoactinide chemistry.

This Thesis considers three aspects of organoactinide chemistry. In chapter one, a bidentate phosphine ligand was used to kinetically stabilize complexes of the type Cp_2MX_2. Ligand redistribution processes are present throughout the synthetic work, as has often been observed in uranium cyclopentadienyl chemistry. To gain an understanding of how these redistributions proceed and what alters the

relative ligand exchange rates, halide and cyclopentadienide ligand exchange processes were studied in a number of situations. In addition, the lability of the coordinating bidentate phosphine was examined in a number of molecular environments.

The hyperfine coupling between an actinide ion and flouride ion spin in PuF_3 is unequivocal evidence for covalent interactions in a low-valent actinide compound[8]; in the analogous lanthanide complexes, this coupling is greatly reduced. Chapter two considers the effects of covalent M-L bonding on the solution and solid state properties of U(III) coordination complexes. In particular, the nature of the more subtle interaction between the metal and the neutral ligand are examined. Using relative basicity data obtained in solution, and solid state structural data (and supplimented by gas phase photoelectron measurements), it is demonstrated that the more electron rich U(III) centers engage in significant U→L π-donation. Ligands classically considered capable of π-acceptance such as PR_3, $P(OR)_3$, CNR, and CO were examined and compared to sulfur, oxygen and nitrogen donor ligands.

The data in chapter two make it clear that trivalent uranium, when surrounded with strongly electron donating Cp ligands, is an electronically saturated metal center; synthetically, this translates into an extensive reaction chemistry. In Chapter three, trivalent uranium is shown to be capable of acting either as a one- or two-electron reducing agent toward a wide variety of unsaturated organic and inorganic molecules, generating molecular classes unobtainable via traditional synthetic approaches, as well as offering an alternative

synthetic approach to molecules accessable via metathesis reactions. Ligand redistribution processes are again observed, but given the information concerning ligand lability in chapter one, this reactivity pattern is applied to the synthesis of pure materials inaccessable from redox chemistry.

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CHAPTER ONE: $Cp_2MX_2(DMPE)$ Complexes

Following the first characterization of a stable organoactinide complex by Wilkinson in 1956[1], organometallic chemistry of the actinides was primarily limited to studying compounds of the type $(C_5H_5)_3MR$ (M = Th, U; R= alkyl, aryl, amide, alkoxide, etc.)[2]. Attempts at characterizing the thermolysis or photolysis products of the alkyl or aryl complexes provided little information about the nature of the reactivity of actinide-carbon σ-bonds. For M= uranium, no decomposition products containing the metal have been unequivacally characterized, but the predominant decomposition pathway was shown by analysis of the organic products to be homolytic fission of the U-C bond with formation of R-H via proton abstraction from the Cp ligands (trace amounts of deuterium abstraction from solvent was noted)[3]. In the Cp_3ThR thermolysis, the hydrocarbon products were found to be identical to those of the uranium complexes[4]. In addition, the predominant metal containing product has been isolated and the stoichiometry is shown in Reaction 1, confirming the abstraction of a

1 $2\ (C_5H_5)_3Th(n\text{-butyl}) \longrightarrow (C_5H_5)_2Th(C_5H_4)_2Th(C_5H_5)_2 + C_4H_{10}$

proton from a Cp ligand[5]. The reported photolysis of $(C_5H_5)_3Th(i\text{-}C_3H_7)$ to yield dark green $(C_5H_5)_3Th(III)$[6] has not been verified, and the physical properties of this compound conflict with those of the reported synthesis of purple $(C_5H_5)_3Th(III)$[7] from Reaction 2:

2 $(C_5H_5)_3ThCl + NaC_{10}H_8 \longrightarrow (C_5H_5)_3Th(III)thf + NaCl + C_{10}H_8$

Photolysis of Cp_3UR compounds generates the trivalent uranium compound Cp_3U-thf[8]. The actinide-carbon σ-bonds in Cp_3M-X compounds have recently been shown to insert carbon monoxide[9] and alkyl isocyanides[10] to form η^2-carbamoyl and iminoalkyl compounds; the CO reaction appears to be reversible, and is first order in CO and U-R. No reaction with H_2 has been noted. The problem in studying these materials stems from the great thermal stability of the actinide carbon σ-bond. For example, the complex $(C_5H_5)_3UCH_3$ dissolved in toluene has a half life of 6300 hours at 97°C[3]; bond disruption energies in several $(C_5Me_5)_2ThR_2$ compounds range from 75-90 kcal/mol[11]. Incorporation of a more sterically demanding coordination sphere does not appreciably destabilize the U-C bond; attempted thermolysis of $(Me_3SiC_5H_4)_3UCH_2C_6H_5$ (m.p. 60°C) at 150°C for 24 hours produced no measurable decomposition (by ^1H NMR spectroscopy). Clearly the development of an actinide ion coordination environment with either an increased number of reactive ligands, or a more accessible primary coordination sphere, was necessary to successfully broaden the understanding of organoactinide reactivity patterns.

The synthesis of dialkyl organoactinide complexes has preoccupied a number of research efforts, in attempts to observe whether actinide alkyls display the same types of reactivity patterns (β-hydride elimination, reductive elimination, or metallation reactions) characteristic of alkyl transition metal compounds. Early reports[12] of the synthesis of Cp_2UCl_2 were later shown[13] by synthetic work and

spectroscopic analysis (NMR, IR) to be incorrect; in solution, the compound undergoes a ligand redistribution process shown in Reaction 3. The driving force of this reaction is not maximization of

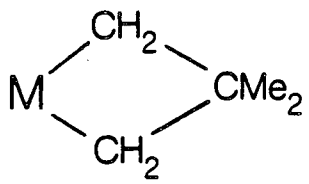
3 $$2\ Cp_2UCl_2 \longrightarrow CpUCl_3 + Cp_3UCl$$

coordinating ligands; two Cp_2UCl_2 can accommodate four thf ligands, while $CpUCl_3$ is known to coordinate two thf ligands[11], and Cp_3UCl remains base free. The observed instabliity of Cp_2UCl_2 can instead be attributed to the kinetic stability of Cp_3UCl. The demonstrated nature of "Cp_2UCl_2" casts doubt on the reported synthesis of the diphenyl derivative[14], and might have inspired a more detailed characterization of the recently published Cp_2NpCl_2[15].

A number of ligands have been employed in actinide chemistry to circumvent the problem of ligand redistribution. The first successful approach used a ligand with two cyclopentadienyl groups connected by an alkyl chain, in the expectation that redistribution would not only be kinetically less facile, but also redistribution resulting in the formation of a Cp_4U compound would be thermodynamically unfavorable[12]. Synthesis of the dialkyl derivatives (neopentyl, n-butyl) gave compounds unstable at room temperature, evolving alkane and alkene, the result of β-elimination[16]. Saturation of the metal coordination sphere imparts additional thermal stability to the dialkyls[17] since the coordination complexes are thermally stable.

By far the most fruitful ligand system studied to date utilizes the pentamethylcyclopentadienyl $(C_5Me_5)^-$, or Cp^* ligand. In this

case, redistribution of $Cp^*_2UCl_2$[18] to Cp^*UX_3 and Cp^*_3UX is apparently impossible due to the large steric requirements of Cp^* which prevents the placing of three Cp^* ligands around a metal center. This permits an extensive study of the chemistry of $Cp^*_2MX_2$ complexes (M= Th, U; R= halide, alkyl, aryl, hydride, amide, alkoxide)[19]. The M-C bond readily reacts with protic sources, adds across $R_2C{=}O$ groups[20] (unlike Cp_3UR compounds), and is readily hydrogenated[18]. Thermolysis studies (M=Th, R= CH_2CMe_3, CH_2SiMe_3) have demonstrated facile elimination of R-H with formation of a four-member metallacycle shown below[21].



A perturbation of this steric saturation approach is found in the recent study of actinide complexes using the bis(trimethylsilyl)cyclopentadienide $((CH_3)_3Si)_2C_5H_3^-$ group[22]. This ligand is also sufficiently large to prevent redistribution processes, while at the same time greatly changing the electronic nature of the Cp group relative to Cp^*. The chemistry is not yet as developed as that of the pentamethylcyclopentadienyl system, but it might be expected that substitution of ten methyl groups by four trimethylsilyl groups should preferentially enhance the stability of the trivalent oxidation state of uranium or the transuranium elements. For example, the trivalent uranium alkyls $(C_5Me_5)_2UR$ are reported to be unstable above -20°C, unless the alkyl group is sterically large, as when R= $CH(SiMe_3)_2$[23]. Substitution of $(Me_3Si)_2C_5H_3$ ligands may permit isolation of less bulky or more electron donating alkyl derivatives by

decreasing the electron donating ability of the Cp ligand toward the low-valent metal center.

Another method of stabilizing a biscyclopentadienyl actinide coordination sphere is to incorporate chelating ligands that 1) saturate the sphere with respect to bimolecular rearrangements or 2) make the rearrangement process thermodynamically unfavorable. The ability to synthesize organoactinide phosphine complexes increased in significance when it was shown that bis(1,2-dimethylphosphino)ethane (DMPE) quantitatively displaces the bidentate nitrogen analog tetramethylethylenediamine (TMEDA)[24]. Given the apparent thermodynamic strength of the uranium phosphine bond, and the inability of phosphine ligands to coordinate alkaline earth cations (permitting the use of alkyl lithium reagents), $MCl_4(DMPE)_2$ seemed a reasonable starting material for the synthesis of Cp_2MCl_2 compounds.

Synthesis

Addition of two equivalents of sodium cyclopentadienide to a thf solution of $MCl_4(DMPE)_2$ resulted in the formation of $Cp_2MCl_2(DMPE)$, 1a, M=U; 1b, M=Th) which was isolated from toluene in 50-60% yield; the reaction was not quantitative, as the formation of Cp_3MCl was also observed. It is important to maintain the solution at -70°C throughout the reaction time, and addition of the sodium cyclopentadienide should be dropwise to minimize formation of the side products. Once isolated, both 1a and 1b were completely stable over a period of days in toluene with respect to ligand redistribution (by ^1H NMR spectroscopy). The presence of bidentate phosphine ligands in

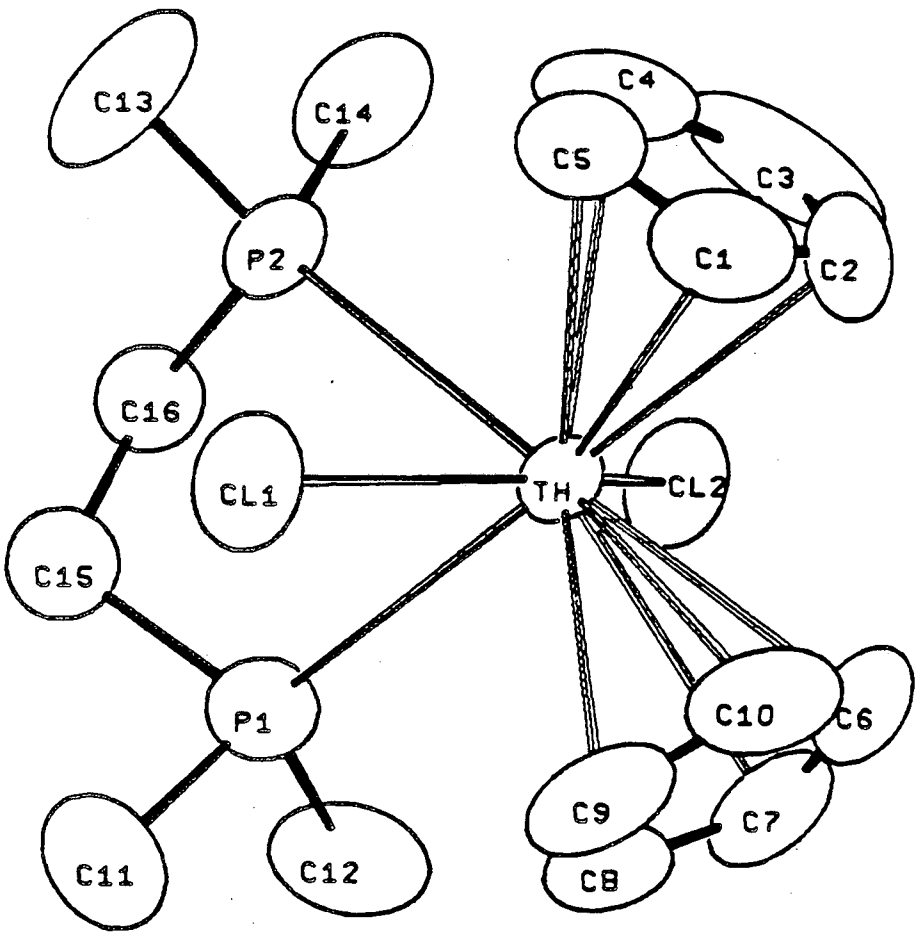
solution did not appear to kinetically activate Cp_3UCl toward substitution or ligand redistribution reactions, but the formation of $Cp_2UCl_2(DMPE)$ (Reaction 4) was observed in the reaction of Cp_3UCl

4 $\quad 2\ Cp_3UCl + UCl_4(DMPE)_2 + DMPE \longleftrightarrow 3\ Cp_2UCl_2(DMPE) + \ldots$

and $UCl_4(DMPE)_2$ in refluxing toluene, with ca. 5% conversion in 48 hours. This is not a trivial yield considering the relative non-lability of the coordinated Cp anion in toluene, as will be discussed later. The melting point of the thorium compound was higher than the uranium analog, reflecting the more polar nature of the thorium lattice; this has been noted previously in a number of organoactinide systems[4]. While spectroscopic and analytical data for both compounds (M= Th, U) were consistent with the formulation $Cp_2MCl_2(DMPE)$, the mass spectrum of the uranium compound did not give a parent ion, and a peak for Cp_3UCl was observed. The numerous errors noted in the early characterization of "Cp_2MCl_2" made structural characterization of these complexes desirable. Adequate crystals of 1b were obtained first, and X-ray crystallography confirmed the stoicheometry of the compound. The uranium compound has an identical IR spectrum, and was therefore presumed to be isostructural with the thorium compound (Figure 1). The Th-C distance average, 2.81A (distances range from 2.81 to 2.86 A), is similar to the Th-C distance found to the terminal Cp ligands in $Cp_2Th(C_5H_4)_2ThCp_2$, 2.83A[5], and the Th-Cl distance, 2.709(3)A, is similar to the Th-Cl distances found in $ThCl_4(NMe_3)_3$, 2.64(1)-2.69(1)A[25], and $(indenyl)_3ThCl$, 2.664(2)A[26]. There has been

ORTEP Drawing of $Cp_2ThCl_2(DMPE)$

Figure 1



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only one other report of a structurally characterized thorium phosphine complex in the literature, $Th(CH_2Ph)_4(DMPE)$[27], containing a Th-P distance of 3.015(5)Å, substantially shorter than the distance of 3.122(2) Å found in 1b. Without knowing the relative electron donating abilities of benzyl and Cp ligands, it is impossible to interpret this observation using an ionic bonding model. The increased distance in the Cp compound could also result from the increased metal coordination number. If the Cp ligands are taken as point charges, the geometry about the metal can be considered a distorted octahedron, with the chlorides trans. This at first seems suprising, as the more sterically demanding ligands would be expected to occupy coordination sites as far appart from each other as possible. Keppert has analyzed the geometry of six coordinate molecules with a purely electrostatic bonding model, considering ligands to be simple points on a sphere, and found that, in compounds with one bidentate ligand, the preferred geometry is dependent on the normalized bite of the bidentate ligand[28]. This purely electrostatic model predicts that, given the bidentate phosphine ligand, the most sterically demanding ligand (defined as the ligand with the shortest M-L distance) will occupy the coordination site trans to the phosphine, simply to minimize ligand-ligand repulsions. If the centroid of the Cp ligand is used to define an octahedron of point charges about the Th center, then the Th-centroid distance, 2.55Å, is shorter than Th-Cl, and the observed geometry is that predicted by the electrostatic model. This geometry has previously been observed in the six coordinate silylamido actinide complex

$((Me_3Si)_2N)_2UCl_2(DME)$[29], where the larger silylamide ligands adopt cis geometries. The monomeric compound containing the chelating cyclopentadienyl ligand $(C_5H_4CH_2C_5H_4)^{2-}$, $Cp_2UCl_2(BIPY)$, adopts the alternative geometry, with the chloride ions in the cis positions[17] similar to the structure of $((Me_3Si)_2N)_2Eu(DME)_2$.[30]. This result is also predicted using the electrostatic model for six coordinate molecules with two bidentate ligands[28].

The dimethyl derivative of both Th and U can be isolated when methyllithium is the alkylating agent (Reaction 5). From the color

5 $$Cp_2MCl_2(DMPE) + MeLi \longrightarrow Cp_2M(Me)_2(DMPE) + 2\ LiCl$$

change of the uranium reaction solution, it appears that formation of the dimethyl compound is complete within 2 hours at -45°C. The thorium compound had sufficient thermal stablity to obtain a ^{13}C NMR spectrum, whereas the uranium derivative did not. Both compounds melted with decomposition and with apparent gas evolution at 139°C (Th) and 84-86°C (U). Attempted synthesis of the dimethyl compounds using Grignard reagents resulted only in isolation of the disproportionation product Cp_3UMe[3], which was characterized by elemental analysis, m.p. and ^1H NMR spectroscopy (the CH_3 protons appear at -194 ppm). The Grignard transmetalations proceeded slowly at -10°C in ether; this reaction rate apparently competes with ligand redistribution of the intermediate or final product in coordinating solvents. This was the first evidence that phosphines may not be capable of sufficiently stabilizing dialkylactinide complexes to allow

thermolysis studies. In toluene, both 1a and 1b were stable at room temperature with respect to ligand redistribution. Attempted syntheses of the diethyl, di-t-butyl, or di-neopentyl derivatives of Th or U resulted in formation of compounds that were unstable above -20 to -30°C.

The benzyl anion has been used to isolate sufficiently stable organoactinide complexes of a wide variety; early reports of the synthesis of homoleptic actinide alkyls showed that the tetrakisbenzyl derivative of Th was relatively stable for brief periods of time at room temperature[31]. One of the first structurally characterized uranium carbon sigma bonds was in $Cp_3UCH_2C_6H_4$-p-Me[32]. Since then, the tris benzyl compound $(Bz)_3M(C_5Me_5)$[33] as well as the tetrakisbenzyl derivative $M(Bz)_4(DMPE)$ and trisbenzyl-monomethyl compounds $(Bz)_3M(Me)(DMPE)$[27] have been synthesized and structurally characterized. Part of the stability of these compounds has been attributed to the delocalization of negative charge over the ortho and para positions in the aromatic ring; in addition, all contain at least one distorted benzyl ligand, described as multihapto, with close contacts to the α position of the ring (Table 1). The M-C distances are similar to the distances found in the two reported arene coordination complexes of uranium, $(C_6H_6)U(AlCl_4)_3$, U-C = 2.91 Å[34], and $\{[(Me_6C_6)UCl_2]\mu\text{-}AlCl_3\}AlCl_4$, U-C = 2.90 Å[35]. Simple Huckel theory predicts no delocalization of negative charge on the ipso carbon atoms.

The dibenzyl thorium compound was isolated from the reaction of benzyllithium and the $Cp_2ThCl_2(DMPE)$, but repeated attempts to isolate

the uranium analog proved unsuccessful. Material could be isolated

Table 1: Distorted Actinide Benzyl Ligands

Compound	M-C(Å)	M-C_α (Å)	M-C-C_α (°)
$(C_5Me_5)ThBz_3$	2.58(2)	2.91(2)	87(1)
	2.58(2)	2.87(2)	86(1)
	2.58(2)	2.98(2)	91(1)
$ThBz_4(DMPE)$	2.53, 2.53(2)	2.86, 2.90(2)	88, 90(1)
$U(Me)Bz_3(DMPE)$	2.54(1)	2.758(5)	83.0(4)

from the reaction of BzLi and $Cp_2UCl_2(DMPE)$ which had a melting point somewhat lower than the Th derivative, as expected, but repeated recrystallization to remove non-neglegible amounts of Cp_3UBz resulted only in isolation of Cp_3UBz. Dibenzyl complexes of both Th and U could not be isolated using benzyl Grignard as the alkylating agent. The relative instability of the uranium complex with respect to ligand redistribution suggested that the structure of the thorium compound would be interesting. An ORTEP diagram of $Cp_2Th(Bz)_2(DMPE)$ is shown in Figure 2, and bond lengths and angles are given in Table 2. The geometry about the Cp and Bz ligands are unexceptional, with no multihapticity in the benzyl bonding, but the phosphine ligand contains two distinctly inequivalent Th-P distances. Asymmetric bidentate phosphine ligands have been observed in a number of actinide complexes to date, but always in compounds where the asymmetric nature of the coordination sphere served as an obvious source of the inequivalent bond lengths. There are no obvious contacts between the

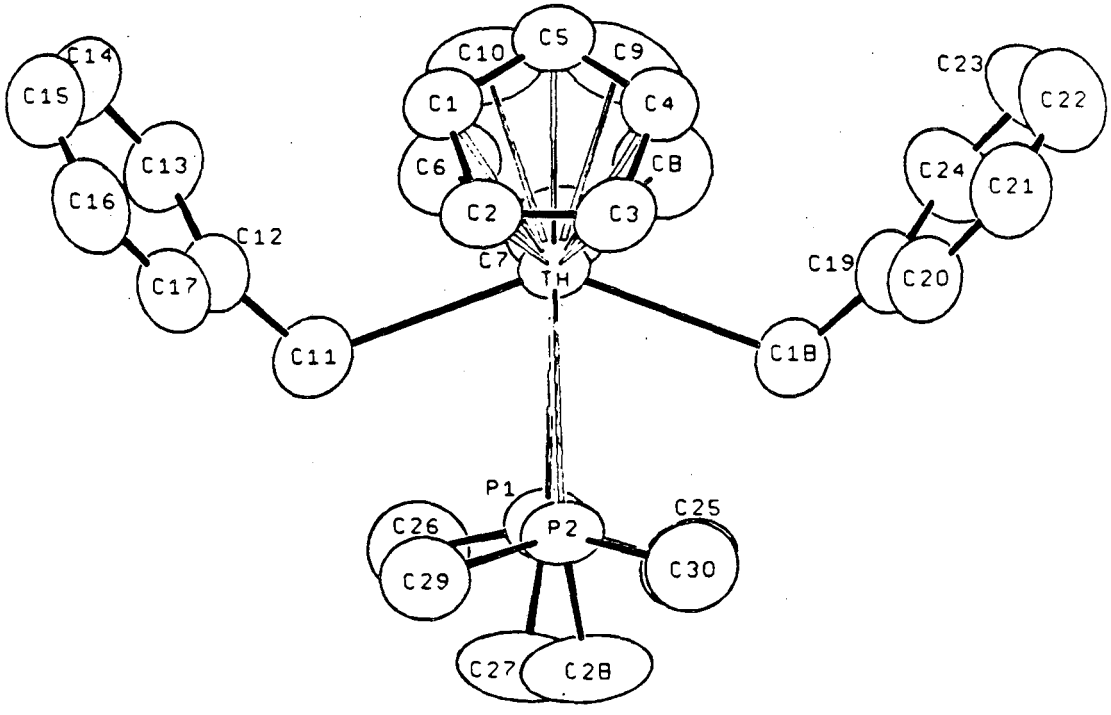

Figure 2

ORTEP Drawing of $Cp_2Th(Benzyl)_2(DMPE)$

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benzyl ligand and the phosphorus atoms, but without the positions of the hydrogen atoms, which were not located in the refinement, possible H-DMPE interactions cannot be discounted. This structure offers a plausible explanation for the instability of the uranium complex; with a decrease in metal radius on going from Th to U (Th=1.05Å, U=0.99Å), the surface area of the metal coordination sphere decreases by 10%, greatly increasing the steric interactions between the coordinating ligands. The presumed repulsive force responsible for the distortion from C_{2v} symmetry in this molecule must increase in the uranium compound, possibly to the extent that the phosphine ligand adopts a monodentate ligation in the ground state, facilitating ligand exchange by increasing the probability of complete dissociation of the phosphine from the metal.

To see whether this structural feature was common to other dialkyls, the structure of $(C_5H_5)_2Th(Me)_2(DMPE)$ was determined (Figure 3). Here, the phopshine ligand was found symmetrically disposed, with no evidence for distortion from C_{2v} symmetry. The Th-Cp and Th-Me distances are in the expected range, and the Cp ligands are again found in a cis configuration. Important distances in the three Th structures are listed in Table 2. A bonding model that calculates expected metal-ligand distances entirely from the summation of ionic radii predicts that the Th-P distances in the three Th structures would all be equal[36], this is clearly not the case. As can be seen in the benzyl structure, small perturbations in the coordination environment may have a substantial effect on observed bond lengths of actinides to a coordinating ligand. There is an increase in the

ORTEP Drawing of $Cp_2ThMe_2(DMPE)$

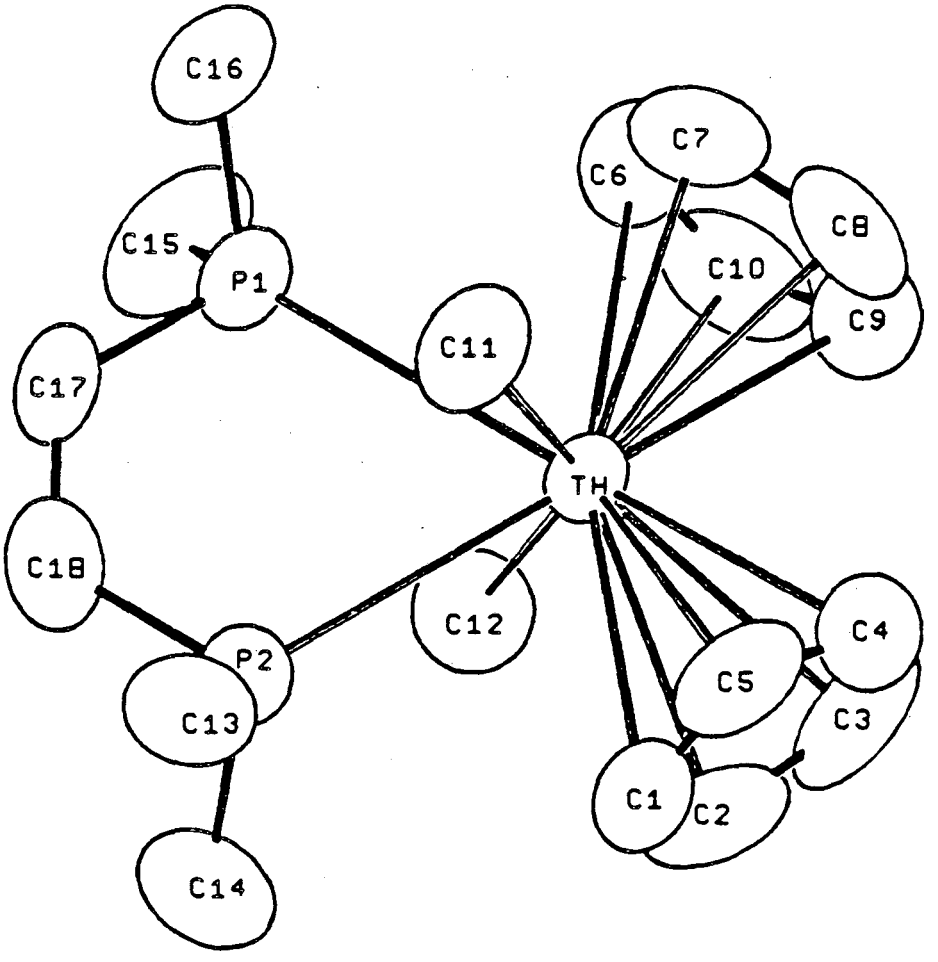

Figure 3

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average Th-P distances in the dialkyl compounds relative to $Cp_2ThCl_2(DMPE)$; this can be interpreted as either a decreased metal-ligand electrostatic attraction resulting from the superior

Table 2: Distances in $Cp_2ThX_2(DMPE)$ compounds.

X	Th-Cp Range(A),	avg.	Th-X(A)	Th-P
$CH_2C_6H_5$	2.770-2.914(7)	2.83	2.649(6)	3.140(2)
			2.665(7)	3.238(2)
CH_3	2.802-2.866(7)	2.83	2.57(1)	3.147(2)
Cl	2.775-2.835(7)	2.80	2.707(2)	3.121(2)

electron donating ability of R relative to Cl, or an increase in interligand repulsions resulting from the larger ionic radius of CH_3 (2.0 A) or Benzyl relative to Cl (1.8 A)[37].

The bis-trimethylsilylmethyl derivatives of both Th and U were impossible to isolate reproducibly, but ^1H NMR analysis of the products isolated from $LiCH_2SiMe_3$ alkylation reactions suggest that the compounds are similar in geometry to the dimethyl derivatives. The CH_2Si ^1H NMR chemical shift in the uranium compound, (127.8 ppm, -70°C), is similar to the shift found in the the dimethyl uranium complex (135.6 ppm, -70°C). These chemical shifts are similar to other U(IV) CH_2R shifts that have have been reported, all far from the -194 ppm found in Cp_3UMe[3]. As the temperature of the sample is raised, the alkyl resonances broadened into the baseline; at room temperature, only the peaks due to the Cp and DMPE ligands were observable. Above 80°C, the inequivalent sets of resonances due to

the Me_3Si protons have coalesced, but the CH_2 protons are still too broad to observe. If the resonances due to the P-CH_2 protons are not shifted too greatly, then the data is consistent with the formation of a trigonal bipyramidal structure in solution, with one half of the phosphine ligand completely dissociated (an extreme form of the dibenzyl DMPE distortion). The freezing out of the inequivalent alkyl resonances without seeing inequivalence of the phosphine sites is presumably due to the larger chemical shift difference of the protons bound to a coordinating atom. Isolation of the bis-trimethylsilylmethyl compounds was difficult as the ligand redstribution products (Reaction 6) are thermally stable (unlike the

6 $$2\ Cp_2MR_2(DMPE) \longrightarrow Cp_3MR + CpMR_3(DMPE) + DMPE$$

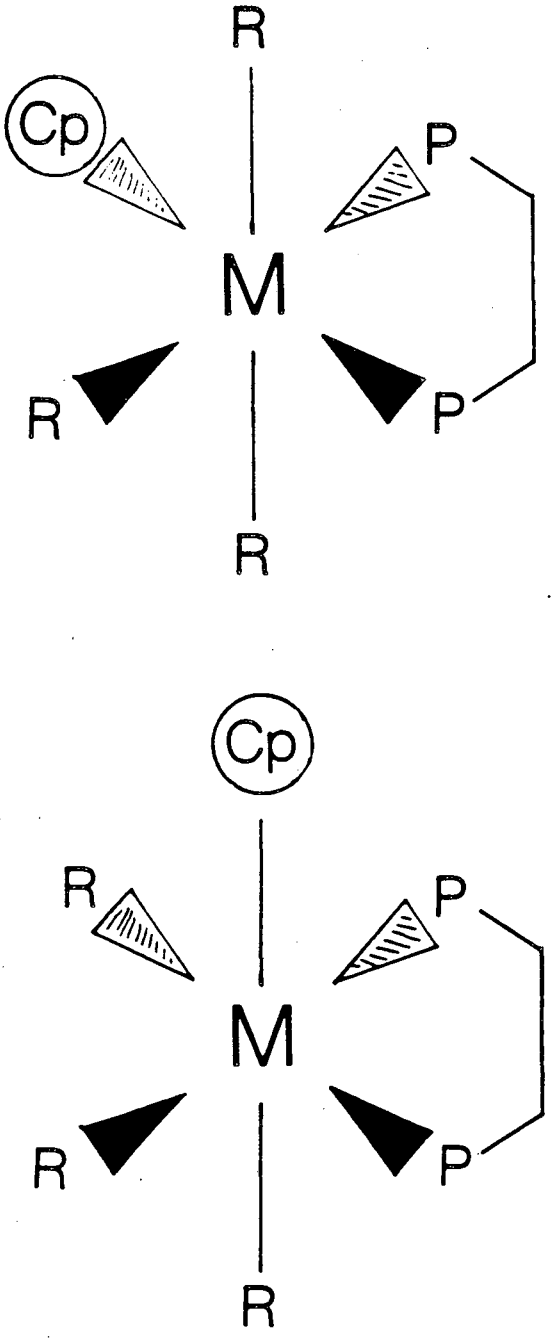
methyl derivatives) and easily isolated from aliphatic solvents (unlike the benzyl derivatives), eliminating fractional crystallization as a possible method of isolation.

In order to verify that the redistribution was indeed yielding mono-cyclopentadienide tris-alkyl species, the Th and U compounds were synthesized independently by the addition of three equivalents of $LiCH_2SiMe_3$, followed by one equivalent of Cp anion to $MCl_4(DMPE)_2$. Crystallization of the Th or U compounds from hexane produced in high yield products which were identical in physical and spectroscopic properties to the occasional side product isolated from the redistribution reaction. The formulation of these compounds cannot be considered complete, although elemental analysis is consistent, and

there is rarely a case where the carbon analysis of a uranium organometallic compound is found to be higher than expected. The melting points for both compounds were sharp, but the NMR suggests that, at least in solution, there is either no symmetry whatsoever in the molecule, or there is more than one isomer present. The two possible isomers that can be constructed from the assumed stoichiometry of the product (assuming that both phosphorus atoms are coordinated) are shown in Figure 4. There is precedence in f-block metal chemistry for monodentate coordination of a chelating ligand in $(C_5Me_5)_2YbCl(DMPM)$[38]. There appears to be a temperature dependence of the relative intensities in the spectrum, supporting the postulate that more than one isomer exists in solution. Further, there is a dynamic process, as monitored by ^1H NMR that effectively broadens every resonance in the spectrum, with the limiting high temperature spectrum consistent with the $CpUR_3(DMPE)$ formulation. Thermolysis of these trialkyls in toluene (80°C) resulted in the formation of Me_4Si (by ^1H NMR), but the metal containing product has not been identified. Elimination of alkane, with the formation of a four membered metallacycle is the probable decomposition route, as has been previously noted.[21]

Attempted syntheses of the tris-benzyl derivatives $CpM(Bz)_3(DMPE)$ (M=Th, U) resulted in the formation of oils that could not be induced to crystallize from hexane, ether, or toluene and these were not pursued further. Attempted syntheses of the tris-methyl compounds were more informative; the compounds must be synthesized by addition of three equivalents of MeLi, followed by addition of NaCp to

Two Possible Isomers of $CpMR_3(DMPE)$



XBL 8512-4978

Figure 4

$MCl_4(DMPE)_2$. An NMR sample of the uranium reaction product contained no resonances attributable to the presence of $Me_4U(DMPE)_2$, $Cp_2UMe_2(DMPE)$, or Cp_3UMe. The pattern of peaks was similar to that found for $CpU(CH_2SiMe_3)_3(DMPE)$. The compound decomposed above -20°C in toluene solution, and a singlet at δ = 0.55-0.60 ppm was observed in the ^1H NMR spectrum which is presumably methane. This singlet increased in intensity over a period of hours, although the amount was less than one molar equivalent relative to the amount of starting material. The multiplicity of the product resonance precludes the possibility of D abstraction from solvent. Not suprisingly, no olefinic resonance attributable to ethylene was observed.

The thorium trimethyl compound was prepared on a large scale, and allowed to decompose over 24 hours in diethyl ether. Filtration of the ether solution, followed by cooling, gave a 30% yield of the dialkyl compound $Cp_2Th(Me)_2(DMPE)$, thus adding another equilibrium to consider (Reaction 7) when discussing thermal decomposition

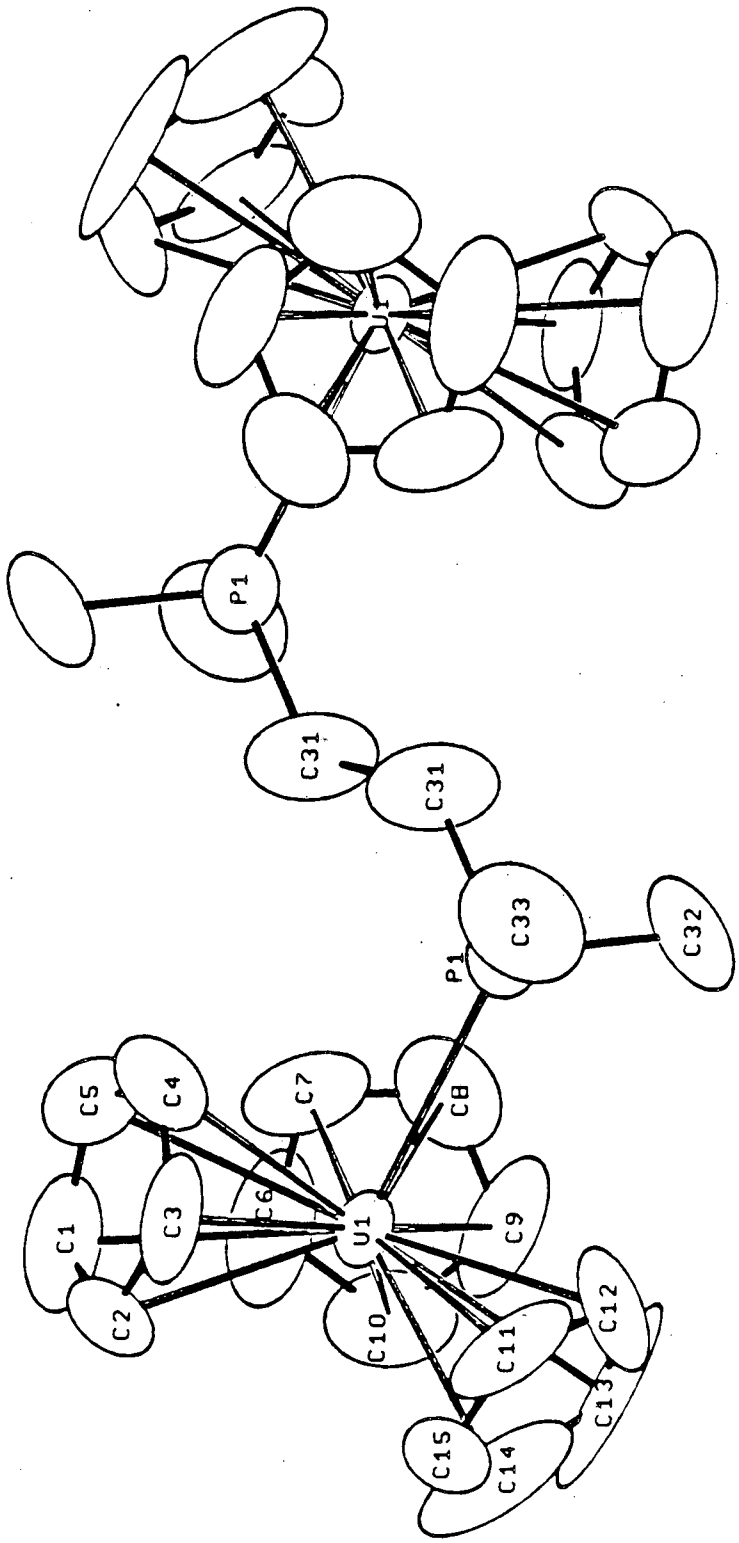
7 $\quad 2\ CpTh(Me)_3(DMPE) + DMPE \longleftrightarrow Cp_2Th(Me)_2(DMPE) + Me_4Th(DMPE)_2$

pathways. This redistribution was not observed in toluene solution by NMR, thus the solvent dependence of redistribution rates can be important.

A different reaction pathway was followed in the analogous uranium reaction. The initial formation of $CpUMe_3(DMPE)$ was shown to be quantitative by ^1H NMR. After removal of the thf at -20°C, the red solid was stirred in toluene at room temperature for 24 hours. The

color of the mixture darkened considerably over this period, and pressure increased in the reaction vessel. Hexane was added, and the red solution was filtered and cooled, after which a small crop of dark red crystals formed. Once isolated, the crystals did not redissolve in toluene, and 600 scans were necessary to obtain a trace of signal in the ^{1}H NMR spectrum. The IR spectrum indicated only that there were Cp and phosphine ligands present, but without a reliable integration it was impossible to determine the stoichiometry of the compound. The structure (Figure 5) was later shown to be $[Cp_3U]_2$(DMPE), a formulation consistent with the limited data available. Yield of the compound, based on Cp ligands, was roughly 10%. Interpretation of the structural data was not straightforward at the time; the possibility of a hydride ligand trans to the phosphorus atom fit the data as well as the U(III) formulation. One structurally characterized $Cp_3U(III)$[39] compound, $Cp_3U\cdot thf$, was known and the U-C distances were similar to the distance found in the dimer, but the values of the U-C range was also in the range for the eleven coordinate $Cp_3U(IV)XY$ compounds[40]. No U-P distances were available for comparison, only one other trivalent uranium phosphine complex had been reported[41], and the inequivalence in the U-P distances within the molecule made M-P distance comparisons in such dissimilar structures meaningless. The extreme insolubility of the compound precluded further spectroscopic characterization, and an independent synthesis of the compound from starting materials of known oxidation state was requried to put the structure on a firmer foundation.

Figure 5



ORTEP Drawing of $[Cp_3U]_2(DMPE)$

The uranium hydride Cp_3U-H had never been reported in any state other than as a decomposition product in mass spectroscopy experiments[42]; apparently the existence of uranium (IV) hydrides is thermodynamically unfavourable with respect to formation of H_2 (Reaction 8). The only exception to this rule is the compound

8 $$2\ X_3U(IV)H \longrightarrow 2\ X_3U(III) + H_2$$

$((Me_3Si)_2N)_3U$-H[43], where the kinetic stability can be attributed to the size of the silylamide ligands, as electronically the silylamide ligand puts less electron density on the metal than a Cp ligand, relatively stabilizing the trivalent oxidation state. The dihydride compound $(C_5Me_5)_2UH_2$ is reportedly stable in the solid state, but in solution an equilibrium between $(C_5Me_5)_2UH$ and $(C_5Me_5)_2UH_2$ is observed[18].

The assumed instability of Cp_3UH made it necessary to trap immediately the species with phosphines; coordination of another ligand would be expected to decrease the rate of H_2 elimination, and the insolubility of the dimeric compound would preclude further decomposition. Abstraction of BH_3 by Lewis bases has often been noted in uranium borohydride chemistry (Reaction 9)[44], but the prolonged reaction of Cp_3UBH_4 with DMPE in refluxing toluene yielded starting

9 $$UBH_4 + :L \longrightarrow U\text{-}H + H_3B{:}L$$

material quantitatively. Hydrogenation of uranium alkyls has been well documented for both $(C_5Me_5)_2UR_2$ and $(C_5Me_5)_2UClR$ systems[18], but never for the more sterically saturated Cp_3UR compounds. No apparent reaction between Cp_3UCH_3 and H_2 (150 psi, 50°C) in the presence of excess DMPE was observed. The reaction between Cp_3UCl and $LiAlH_4$ is reported to yield a trivalent uranium complex[45], presumably via initial formation of a uranium hydride, which then eliminates H_2. The reaction of Cp_3UCl in thf with $LiAlH_4$ produced a light green compound which had limited toluene solubility; light green crystals which desolvate when exposed to vacuum were isolated and recrystallized from thf. Elemental analysis of the completely desolvated powders suggested the ration of $Al:Cp_3U = 1:1$; the large number of bands which shift to lower frequency in the IR spectrum upon substitution of $LiAlD_4$, and the narrow NMR linewidths are consistent with the formula $Cp_3U(IV)AlH_4$. In the presence of DMPE, a solution of Cp_3UAlH_4 turned red, but the reaction product appeared to be too soluble to isolate from toluene, a property inconsistent with that of the structurally characterized dimer.

Having attempted the obvious approaches to $[Cp_3UH]_2$DMPE with no success, the possibility of the uranium atom being trivalent was considered. Reduction of UCl_4 with either sodium hydride[46] or sodium naphthalide[47], followed by addition of three equivalents of NaCp in thf produced a dark brown mixture from which Cp_3U-thf was isolated. This compound has been reported previously as a brown powder that does not readily crystallize[48], and the isolated product appears grossly impure (the ^1H NMR spectrum contained two broad, equally intense

peaks, with no resonances attributable to coordinated thf). Crystals of Cp_3U-thf adequate for X-ray analysis were obtained in Reaction 10[39], which again underscores the unpredictability of working with labile

10 $U[N(SiEt_3)_2]_2Cl_2 + 2NaCp \xrightarrow[thf]{} Cp_3U\text{-thf} + \text{unspecified products}$

systems. Addition of DMPE to a toluene solution of Cp_3U-thf resulted in immediate precipitation of a red-brown compound whose IR and NMR spectra suggested that the compound in question may contain U(III). The impure nature of Cp_3U-thf made it necessary to find an alternative starting material. The thf complex was heated at 100°C under dynamic vacuum to remove coordinated thf, and PMe_3 was added to a hexane suspension of the brown solid. From this hexane solution red crystalline Cp_3U-PMe_3 was isolated, and slow diffusion of DMPE into a toluene solution of this complex produced red needles which had virtually identical IR and NMR spectra to the structurally characterized dimer.

Given the large number of ligand redistribution reactions that have been observed (Table 3), it is impossible to acertain at which

Table 3

			Reaction
$Cp_3UCl + UCl_4(DMPE)_2$	⟶	$2\ Cp_2UCl_2(DMPE)$	4
$2\ Cp_2ThR_2(DMPE)$	⟶	$Cp_3ThR + CpThR_3(DMPE)$	6
$2\ CpThR_3(DMPE)$	⟶	$Cp_2ThR_2(DMPE) + ThR_4(DMPE)_x$	7

point the uranium is reduced or the molecularity of the reduction. Isolation and characterization of the uraniun containing products in a thermolysis study is rare; this is an uncommon example of the reduction of an organoactinide compound with an alkyl substituent containing no β hydrogens, the first being a report that UCl_4 reacts with four equivalents of 4 MeLi, forming uranium metal[49]. The possibility that Cp anion was the reducing agent must be considered; in the initial report of the synthesis of Cp_3UCl, it was noted that in the presence of excess Cp anion, insoluble reduced products of varying stoichiometry were isolated[1]. The Cp anion was also presumably the reducing agent in Reaction 10. The most common reaction pathway involving reduction of the metal is β-hydride elimination, followed by bimolecular elimination of either R-H or H_2. Evidence for the intermediate formation of uranium(III) hydrides was obtained in the reaction of UCl_4 with four equivalents of n-BuLi[50]. Photolysis of Cp_3Th-i-Pr is reported to yield Cp_3Th-thf (β-hydride elimination, followed by bimolecular reductive elimination of C_3H_8), but characterization of the metal containing product has been questioned[6]. The only example of a reaction yielding elimination products is in the thermolysis of $UO_2Cl_2(C_6H_5)_2$, with the isolation of biphenyl and UO_2; subsititution of other alkyl substituents gave evidence for β hydride elimination or abstraction of solvent protons by alkyl radicals.[51]. One final reaction pathway available to orgaonactinides is the abstraction of γ hydrogen occuring in $((Me_3Si)_2N)_3U$-CH_3,[43] and $(C_5Me_5)_2ThR_2$[20], with the formation of four membered metallacycles.

Ligand Lability

The overwhelming problem encountered in the isolation of bis cyclopentadienyl actinide dialkyls was the facility of ligand exchange. An understanding of the factors that influence redistribution rates would be enormously helpful in designing successful synthetic strategies, and the relative lability of the Cp_2MX_2(DMPE) system made it an ideal candidate for studying the relative exchange rates of anionic (Cp or X) and coordinating (DMPE) ligands. The ability to alternate between diamagnetic and paramagnetic systems greatly enhances the range of rates amenable to an NMR analysis.

Cp exchange

The rate of bimolecular exchange of a Cp ligand between metals should be slower than the other ligands due to the presumed inability of Cp to act as a bridging ligand. The structural evidence for the bridging of a Cp group between f-metal centers is in the structures of the Cp_3M[52] and $(MeC_5H_4)_3M$[53] compounds, where there is no alternative in saturating the metal coordination sphere but to interact with a neighboring Cp_3M group. These two examples can be compared with the large body of data available on f-metal compounds containing bridging halide, hydride, or alkyl groups. A transition state involving the transfer of a Cp group must either localize negative charge in the Cp ligand or greatly diminish the electrostatic attractions of the metal and ligand, whereas a bridging halide transition state requires neither.

The labeled Cp compound $(MeC_5H_4)_2UCl_2(DMPE)$ was synthesized to study the rate of Cp exchange in these systems. The methyl groups greatly increase the toluene solubility of the compound, with the melting point decreasing. The ^1H NMR resonance of the PCH_3 group shifted 8.6 ppm downfield from that of the C_5H_5 derivative, while the PCH_2 resonance is shifted downfield by 0.8ppm. Analysis of a toluene NMR sample of $(C_5H_5)_2UCl_2(DMPE)$ and $(MeC_5H_4)_2UCl_2(DMPE)$ at room temperature revealed peaks due only to the individual compounds, with no trace of the mixed Cp compound present. Further, the DMPE resonances remained well separated, showing that bimolecular exchange of the bidentate phosphine is slow on the NMR timescale. The solution temperature had to be increased to 95°C before new resonances attributable to the mixed Cp compound were observed (Reaction 11).

11 $Cp_2UCl_2(DMPE) + (MeC_5H_4)_2UCl_2(DMPE) \longrightarrow 2\ Cp(MeC_5H_4)UCl_2(DMPE)$

In refluxing thf, a completely random mixture of bis-Cp compounds (Cp_2:$Cp(MeC_5H_4)$: $(MeC_5H_4)_2$= 1:2:1, K_{eq}=4) was achieved in 24 hours. There is no significant deviation from a purely statistical distribution of Cp ligands. Resonances attributed to the mixed Cp compound could be identified by subtraction of known resonances. After 4 hours in toluene at 95°C, the ratio of integrated intensity of the methyl protons on the MeC_5H_4 groups was $[(MeC_5H_4)_2U]$:$[(MeC_5H_4)CpU]$ = 15:3, or 28.5% exchange product, but traces of decomposition (formation of a precipitate) at this temperature precluded a more detailed analysis of the data. That thf

should enhance the rate of exchange is understandable; any sort of ligand dissociation process would be stabilized by coordination of a solvent molecule to the intermediate metal complex. The rate of formation of the mixed Cp compound was faster here than in the reaction between $Cp_2UCl_2(DMPE)$ and $(MeC_5H_4)_3UCl$ in toluene; after 9 hours at 95°C, the ratio of bis-Cp compounds in solution was roughly Cp_2U: $Cp(MeC_5H_4)U$: $(MeC_5H_4)_2U$ = 5:1:1.

Halide Exchange

The rate of halide exchange was found to be considerably faster than Cp exchange. The dibromide derivative $Cp_2UBr_2(DMPE)$ was prepared in a fashion identical to the chloride, and found to be much less soluble in toluene. The DMPE resonances are again shifted, but in this case the methylene protons are shifted only 0.55 ppm downfield, while the PCH_3 resonance is shifted 11.5 ppm downfield and the Cp resonance is shifted upfield 2.7 ppm. There was no obvious band in the IR spectrum which decreased in frequency upon substituting Br for Cl. Formation of $(C_5H_5)_2UClBr(DMPE)$ (Reaction 12) was also monitored with ^1H NMR by

12 $$Cp_2UCl_2(DMPE) + Cp_2UBr_2(DMPE) \text{-----} > 2\ Cp_2UClBr(DMPE)$$

integrating the distinct set of resonances (10:12:4) that developed as a function of time. The low solubility of the bromide complex hindered a detailed analysis, but using the method of initial rates, the reaction was found not to be first order in either dichloride or dibromide, $\partial[Cp_2UClBr(DMPE)]/(\partial 1/T) = k[Cp_2UCl_2(DMPE)]^{1.4}x$

$[Cp_2UBr_2(DMPE)]^{2-}$[1]. The rate of formation of the mixed halide complex at 25°C is roughly five times as fast as the rate of formation of the mixed Cp compound at 95°C. The nonintegral order of the reaction indicates a more complicated reactivity than simple bimolecular exchange thorough a bridging halide transition state, but the accuracy of the experiment precludes further speculation. Over a period of four days, purely random distribution of halide was approached, as in the Cp exchange, with K_{eq}= 3.6.

Phosphine Lability

There are a number of dynamic processes that can be observed when a bidentate ligand coordinates to a metal. In addition to the possibility of semi or complete dissociation of the ligand, the 5 membered ring contains inherent asymmetry derived from the staggered geometry of the organic backbone. The ^1H NMR spectrum of $UCl_4(TMEDA)_2$ consists of two sets of equal intensity signals for the N-CH_2 and N-CH_3 protons[54]. A solution geometry containing all the chloride ions on one side of a square prismatic geometry accounts for the observed inequivalence; alternatively, the two signals could arise if the motion of the five membered ring is restricted due to extreme repulsion between the chloride ions and the N-Me groups[24] (Figure 6). This NMR behaviour is not observed in $UCl_4(DMPE)_2$; substitution of the phosphorus for nitrogen increases the M-L distance, diminishing the repulsive interactions and lowering the barrier to site exchange. At low temperatures, the P-CH_2 protons in $UBr_4(DMPE)_2$ begin to broaden into the baseline, but a limiting spectrum was not obtained. Additional support for the nonfluctional ring interpretation of the

Site Inequivalence in $UCl_4(TMEDA)_2$

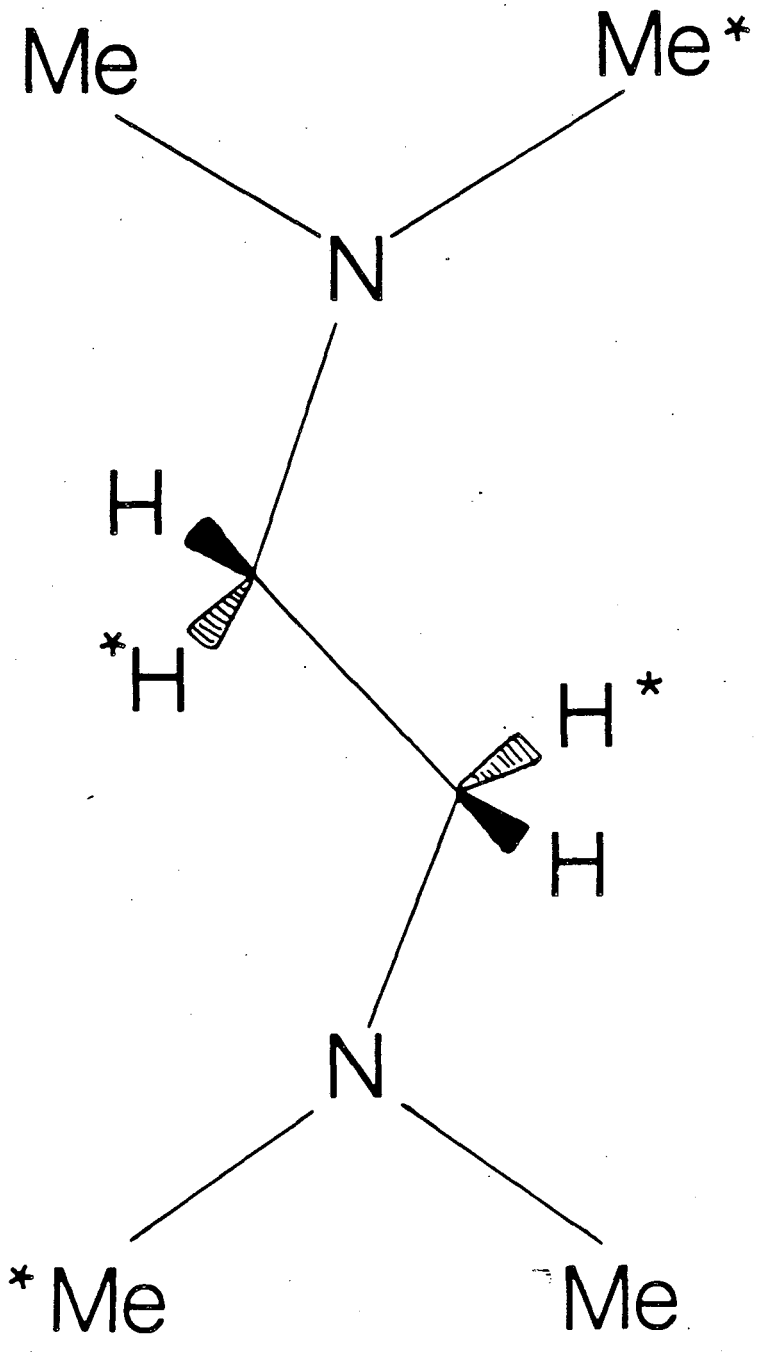


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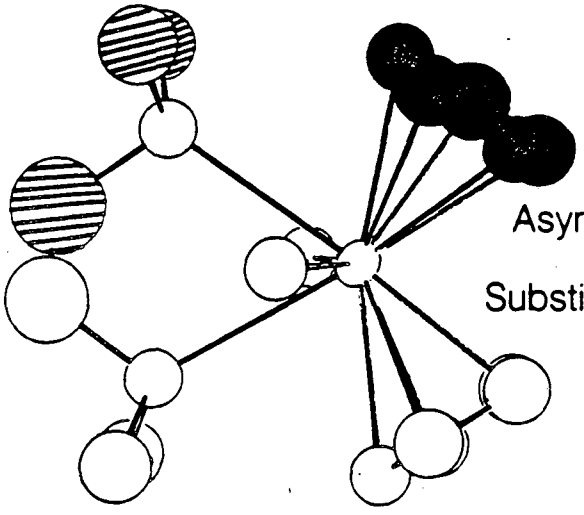
Figure 6

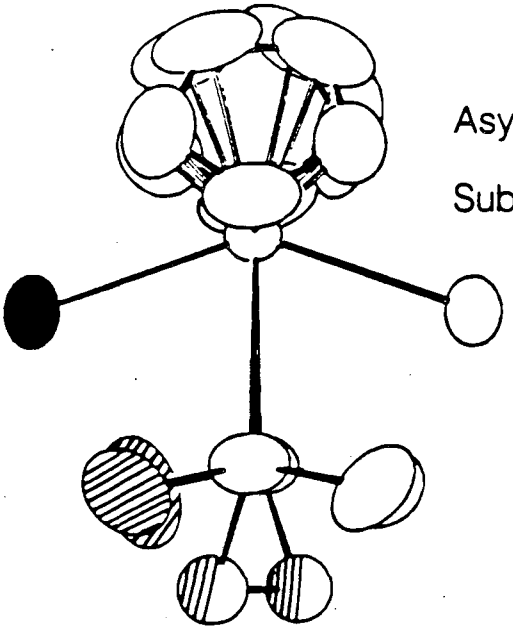
$UCl_4(TMED)_2$ NMR spectra comes from analysis of the P-CH_2 ^1H NMR signals in $Cp_2UX_2(DMPE)$ compounds. As low as -94°C, the CH_2 protons in $Cp_2UCl_2(DMPE)$ remained slightly broader than the other resonances. Upon substitution with the larger Br ion, the CH_2 signal almost broadened into the baseline by -78°C. In $(MeC_5H_4)_2UCl_2(DMPE)$, substitution of a sterically demanding but distal methyl group on the Cp ligand had no measurable effect on the spectral lineshape. That an increase in interligand steric repulsion near the PCH_2 protons should slow down a site exchange process is consistent with the restrained ring motion interpretation of the $UCl_4(TMED)_2$ spectrum. The syntheses of the $Cp_2UI_2(DMPE)$ or $Cp_2UCl_2(TMED)$ have not been attempted.

The formation of both the mixed Cp and mixed halide complex result in elimination of the molecular C_2 axis; in a static system, this renders sites on the phosphine ligand magnetically inequivalent. In the ClBr compound, there is no mirror plane containing the metal and P atoms, thus the top and bottom of the phosphine ligand are inequivalent (i.e each PCH_2 group contains two magnetically inequivalent sites). A mirror plane containing the U, Cl, and Br atoms renders the Cp ligands equivalent (Figure 7). Upon substitution of one C_5H_5 by MeC_5H_4, there is no longer a plane of symmetry bisecting the phosphine ligand, resulting in two inequivalent Me_2PCH_2 environments. In solution, the low symmetry of these molecules becomes evident as the temperature is lowered; the ^1H NMR spectrum of $CpMeCpUCl_2(DMPE)$ integrates 5:3:2:2:6:6:2:2, and $Cp_2UClBr(DMPE)$ is 10:6:6:2:2.

Induced site inequivalence in $Cp_2MX_2(DMPE)$



Asymmetry Resulting From Substitution of Cp by MeC_5H_4



Asymmetry Resulting From Substitution of Cl by Br

Figure 7

XBL 8512-5000

In both cases, upon increasing the temperature of the solution, a concentration independent dynamic site exchange process rendered the phosphine sites magnetically equivalent. Additionally, in the thorium compound $Cp_2ThCl_2(DMPE)$, at low temperatures coupling from P to the protons on the Cp (J_{PH}= 0.55Hz) ligand was resolved in the ^1H NMR spectrum. Upon increasing the solution temperature, the triplet collapsed into a singlet. This loss of coupling was also noted in $Cp_2ThMe_2(DMPE)$, where the coupling from P to the CH_3 groups (J_{PH}= 4.8Hz) dissipates at room temperature. The Th spectra are also concentration independent, and thus can be treated as a simple site exchange process. In all examples, the calculated barrier to exchange $\Delta G^{\pm}$ is approximately 14 kcal/mol[55]. The different temperatures at which the individual barriers were calculated prohibits an absolute comparison of $\Delta G^{\pm}$ values without knowledge of their temperature dependence.

The loss of coupling in this exchange process can only be attributed to a dissociative mechanism. That decoupling to both the Cp and methyl protons was observed requires that the phosphine ligand be the one to leave the coordination sphere of the metal. This would be predicted on electrostatic arguments; the uncharged ligand should more readily dissociate than an anion. Evidence for the proposal that only one arm of the bidentate phosphine ligand dissociates is obtained from analysis of the ^{31}P NMR spectrum of $Cp_2ThCl_2(DMPE)$ in the presence of added DMPE. If complete dissociation of the bidentate ligand were the rate determining step in the observed site exchange processes, then an identical barrier to exchange should be observed in

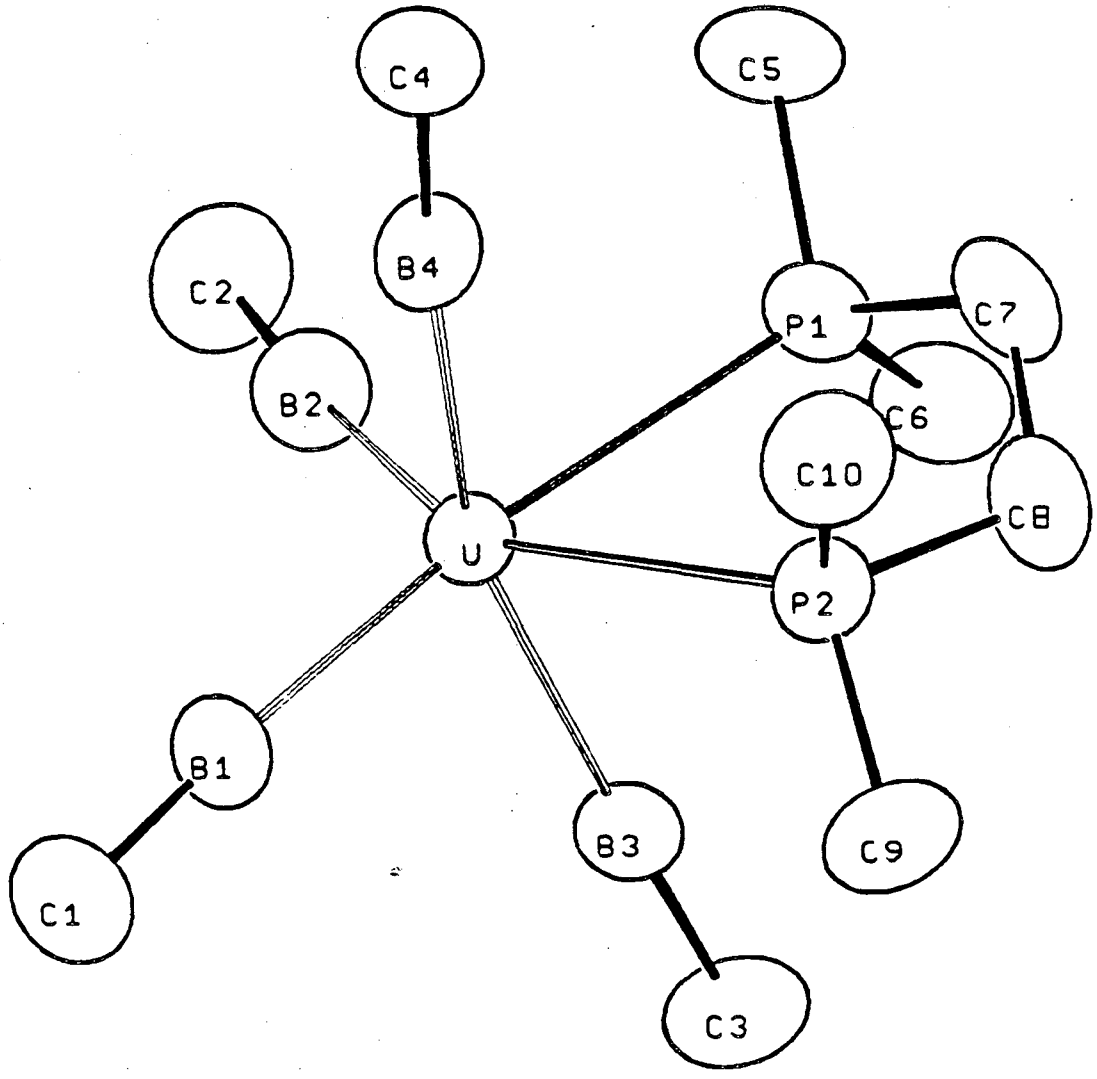
the exchange of free and coordinated DMPE ligands. The ^{31}P NMR spectrum of a 1:1 mixture of $Cp_2ThCl_2(DMPE)$ and DMPE contained two resonances, one for free ligand (by addition of additional ligand) and one for the complexed species. No exchange was observed up to 95°C until ca. 20 equivalents of DMPE were added; here the coordinated ligand peak broadened considerably. This concentration dependent exchange rules out the possibility of complete phosphine dissociation in the observed site exchange processes.

The lability of bidentate phosphine ligands has been previously reported; in the first report of a structurally characterized U(III) phosphine complex, $(C_5Me_5)_2UH(DMPE)$[41], comprehensive NMR analysis showed that two dynamic processes were operative. At low temperatures, either a rotation about the phosphine ligand or dissociation of one of the phosphorus atoms from the coordination sphere rendered the inequivalent sites of the methyl and methylene protons indistinguishable. Coupling from the phosphine ligand to the hydride could not be observed. At higher temperatures, a much slower dynamic process, as detected by spin saturation experiments, exchanges the environments of free and coordinated bidentate ligands. The presence of both free and coordinated DMPE in an NMR sample of $Th(Bz)_4(DMPE)$ (by ^{31}P NMR) has been claimed (Reaction 13)[27], but this

13 $$Th(Bz)_4(DMPE) \longleftrightarrow Th(Bz)_4 + DMPE \quad ?$$

observation conflicted with the description of the NMR spectrum of the U analog, which contained no free phosphine resonances although there

is a larger frequency difference between free and coordinated ligand resonances. An alternative explanation for the Th spectrum is the presence of phosphine ligand due to sample hydrolysis. A similar barrier to site exchange has been observed in the pseudo-octahedral complex $(CH_3BH_3)_4U(DMPE)$[44]. Structural characterization of this molecule revealed no statistically significant trans effect of the phosphine on the bond length of the borohydride ligand, with U-B(cis)= 2.58(1), 2.56(1)A and U-B(trans)= 2.56(1), 2.58(1)A (Figure 8). The inequivalent methylborohydride ligands cis and trans to the phosphorus atoms are evident in the NMR spectra, with BH_3 protons at 450.14 and -32.97 ppm at -66°C (the low field resonance shifts 1 ppm/°C). A plane of symmetry containing the U and P atoms as well as a molecular C_2 axis bisecting the phosphine ligand renders all the phosphine methyl and all methylene protons magnetically equivalent. As the solution temperature is raised, the cis and trans borohydride methyl groups coalesce, and the borohydride protons broaden into the baseline, with the limiting fast exchange spectrum not observed (90 MHz, 95°C,). A calculated barrier to site exchange of 10 kcal/mol can be obtained, similar to the barriers previously discussed. A twist mechanism has been proposed[56] based on a comparison of the relative rates of other $(MeBH_3)_4U$(bidentate ligand) complexes with relative basicity studies, but extreme steric repulsion in the TMEDA comples is relieved by a bidentate ligation of one of the methylborohydride ligands, complicating the argument. Additionally, the varied coalesence temperatures invalidates the comparison between relative ligand basicity and the barrier to site exchange without knowing the $\Delta G^{\pm}$



ORTEP Drawing of $(MeBH_3)_4U(DMPE)$

Figure 8

XBL 834-9360A

temperature dependence. A twist mechanism has also been proposed for the site exchange process in $MeTiCl_3(LL)$ (LL= DME, TMED, BMTE)[57], after correlating relative site exchange rates with measured $-\Delta H_f$ of $TiCl_4$ with monodentate O, N, and S donor ligands[58]. The 1-2 kcal/mol difference in the measured enthalpies of formation of the monodentate ligand complexes makes such comparisons tenuous, as relative ring strains have not been taken into account. Further studies on the temperature dependence of the J_{PH} or J_{PB} coupling in the isostructural Th compounds would be particularly informative, as would be the DMPE complex of $MeTiCl_3$. The decrease in exchange barrier upon increasing the coordination number of the metal is also inconsistent with a twist mechanism, whereas Cp or halide ligands are more stable anions than methylborohydride, thus increasing the electrostatic attraction between the metal and the donor ligand and raising the dissociation barrier.

Reactivity of $(MeC_5H_4)_3UCMe_3$

T-Butyllithium has frequently been found to reduce tetravalent uranium; the reaction of $(C_5Me_5)_2UCl_2$[59], $((Me_3Si)_2N)_3UCl$, or $(Me_3SiC_5H_4)_3UCl$, with LiC_4H_9 yields the trivalent compounds and LiCl. Side products in the silylamide reaction are the metallacycle and uranium hydride, in 5-10% yields. The isolation of the trivalent uranium silylamide complex does not rule out the possibility of β-hydride elimination as the initial reduction step, although $((Me_3Si)_2N)_3U$-H is reportedly stable. Reaction with a second

equivalent of t-butyllithium (Reaction 14), followed by coupling with a uranium chloride (Reaction 15), is also possible.

14 $(R_2N)_3U\text{-}H + LiBu^t \longrightarrow (R_2N)_3ULi + C_4H_{10}$

15 $(R_2N)_3ULi + (R_2N)_3UCl \longrightarrow 2(R_2N)_3U + LiCl$

Initial formation of a t-butyl complex, followed by homolytic U-C bond scission and coupling of t-butyl radicals or reaction with a solvent molecule must also be considered. In less sterically saturated compounds, formation of the uranium t-butyl compound has been observed; $(Indenyl)_2U(C_4H_9)_2$ is reportedly stable[60], $(C_5H_5)_3UC_4H_9$ has been characterized and found to be the least stable of a series of alkyl derrivatives[3] and $(MeC_5H_4)_3UCMe_3$ was easily isolated as needles from diethyl ether. This dark green compound (m.p. 220-226°C) slowly decomposes in toluene solution, with evolution of various hydrocarbons and only a trace (5%) of olefinic hydrogens, thus radical coupling or abstraction of a proton from solvent, a Cp ring, or another molecule is fast relative to β hydride elimination. Addition of PMe_3 to a toluene solution of this compound resulted in immediate reduction and formation of $(MeC_5H_4)_3U\text{-}PMe_3$; there are a number of aliphatic hydrocarbon products, with NMR resonances at 1.13, 0.83, and 0.56 ppm, as well as a trace of olefinic hydrogen products (singlet at 4.6ppm which did not shift with a change in temperature). The reduction proceeded less rapidly in the presence of thf. Both $(MeC_5H_4)_3UCMe_3$ and $(MeC_5H_4)_3U\text{-}thf$ react with PF_3 (Reaction 16) to form the tetravalent uranium flouride complex $(MeC_5H_4)_3UF$. Presumably the

16 $(MeC_5H_4)_3UCMe_3 + PF_3 \longrightarrow (MeC_5H_4)_3UF \longleftarrow PF_3 + (MeC_5H_4)_3U\text{-thf}$

t-butyl complex is reduced, forming the PF_3 complex, which then abstracts flouride. In the presence of CO, reduction unfortunately was not observed; instead insertion of CO into the U-C bond to form a presumably η^2 acyl complex occurs (a number of reports concerning the insertion of CO[9] or isocyanides[10] into the U-C σ-bonds in Cp_3U-R bonds have recently appeared). The decomposition pathways of the above reactions are not necessarily identical; in the PMe_3 reaction, a quantitative conversion to the PMe_3 complex is observed, whereas in the base free thermolysis, a precipitate formed which would not redissolve in the presence of excess trimethylphosphine.

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CHAPTER TWO: Tris Cyclopentadienyl Uranium (III) Complexes; Synthesis, Structure, and Relative Basicity.

In contrast to the large body of knowledge available concerning the relative affinity of transition metal ions for donor ligands, there is little known about the relative preferences actinide ions may have toward various Lewis bases. Synthetic chemists often cite the large coordination numbers and participation of f-orbitals in bonding as the reason f-metals may show unusual reactivities not available in transition metal chemistry. An understanding of the electronic nature of the central metal to ligand bond is manditory in the design of rational synthetic strategies.

The repeated failure over the years to unequivocally characterize an actinide phosphine complex led to the conclusion that the U-P bond must be thermodynamically weaker than U-O or U-N bonds. The successful isolation and structural characterization of the tertiary phosphine complex $U(OPh)_4(DMPE)_2$ was initially attributed to the synthetic conditions; no competitive bidentate solvents such as DME were used throughout the initial preparation, thus permitting isolation of the phosphine adduct[1]. Later, it was shown that the bidentate phosphine ligand DMPE quantitatively displaces the analogous nitrogen donor ligand tetramethylethylenediamine (TMEDA) from UCl_4 in hydrocarbon solvents[2]. The largest problem in interpreting this experiment concerned the nature of $UCl_4(TMEDA)_2$; the ligands on the metal surface are so tightly packed that the five membered ring is rigid on an NMR timescale, and inequivalent methyl and methylene

proton signals can be observed in the room temperature ^1H NMR spectrum. It is impossible to say whether the U-P bond is stronger than the U-N bond, thus driving the equilibrium, or the relaxation of steric congestion about the metal is a dominating force. The equilibrium constant could not be measured and thus relative enthalpic and entropic contributions to the reaction could not be assessed. Further, attempts to examine the kinetics of the displacement were apparently hindered by measurable concentrations of the mixed ligand complex, UCl_4(TMEDA)(DMPE). Shinomoto has prepared a series of methylborohydride complexes with coordinating bidentate ligands, finding again that DMPE quantitatively displaced TMEDA[3]. Unfortunately, in this example the steric demands of the TMEDA ligand are such that one of the CH_3BH_3 ligands is forced into a bidentate configuration (judging by the nonlinear U-B-C angle), whereas in the analogous phosphine complex all the BH_3CH_3 groups are tridentate. Again, no quantitative measurements were obtained. An analysis of the formation constants of Lewis bases with $(C_5H_5)_3Yb$ has been reported; in contrast to the widely held belief that the lanthanide ions are "hard" acids preferring "hard" bases, trialkyl phosphines and amines were found to preferentially coordinate to the metal, followed in base strength by pyridines, ethers, and thioethers[4]. This experiment was not monitored as a function of temperature, but the judicious selection of bases to minimize the inteference from steric restrictions permits the conclusion that the phosphine-Yb bond is one of the strongest studied.

When it was finally understood that the trimethylphosphine complexes of $(C_5H_5)_3U$ and $(MeC_5H_4)_3U$ had been synthesized starting from the thf complexes, the question of relative basicity again surfaced. The observation that a given ligand complex can be isolated from another ligand complex proves nothing about the relative stability of ligand complexes in solution, as isolation of a more weakly bound complex can result from the relative complex solubilities dependent on functions of complex-solvent interactions, relative crystal packing forces, or the synthetic route involved. The molecule $(RC_5H_4)_3U$ is ideal for studying relative basicity, as there is sufficient room to coordinate one monodentate ligand, and the hydrocarbon solubility allows the molecule to be studied over a large temperature range in a relatively noninteracting solvent. Additionally, synthetic modification of either the steric or electronic nature of the cyclopentadienyl ligand seemed relatively simple, permitting a detailed study of the effects influencing the stability of a coordination complex.

Synthesis

The first report of $Cp_3U{\cdot}X$ coordination compounds described the properties of the thf, nicotinamide, and cyclohexylisocyanide adducts, characterized by IR, melting point, mass spectrum, and elemental analysis[5]. The extreme difficulty in obtaining the pure thf compound and the low solubility in aromatic solvents probably discouraged further exploration in the area. In the work described here, coordination complexes of trismethylcyclopentadienyl uranium were

used, as they have solubility properties ideal for both synthetic work and solution study. The thf complex, $(MeC_5H_4)_3U\cdot thf$, is known; magnetic susceptibility data has been reported[6], as well as ^1H NMR data[7]. The compound is best prepared by reaction of UCl_3 (from UCl_4 and $NaC_{10}H_8$[8] or NaH[9]) with $NaMeC_5H_4$ in thf, removing solvent (and naphthalene) under reduced pressure, and crystallizing the residue from ether. The yield is roughly 60%. The observed ^1H NMR spectrum is inconsistent with that previously reported. The monodentate phosphine complex $(MeC_5H_4)_3U\cdot PMe_3$ can be isolated by adding PMe_3 to a hexane solution of the thf complex, followed by crystallization from hexane. The phosphine complex of $(C_5H_5)_3U$ was isolated similiarly. Both compounds melted with decomposition at 228-232°C (MeC_5H_4) and 283-288°C (Cp), evolving a gas (PMe_3) which condensed at the top of the capillary. These complexes were suprisingly stable; the trimethylphosphine complex of $(C_5Me_5)_2UCl$[10] is reported to desolvate upon standing, and $UCl_4(PMe_3)_3$ was not sufficiently stable under vacuum to afford a satisfactory elemental analysis[1]. Addition of PMe_3 to an NMR sample of either $(C_5H_5)_3U\cdot PMe_3$ or $(MeC_5H_4)_3U\cdot PMe_3$ did not yield signals due to coordinated and free base protons, but instead, a time averaged resonance was observed down to -70°C. The barrier to dissociation of a monodentate phosphine ligand from a trivalent uranium atom would be interesting to measure for comparison with the observed barriers of site exchange measured for the U(IV) complexes described in chapter one, but it appeared that free phosphine was displacing coordinated ligand through an associative process. An attempt was made to measure the barrier of dissociation of the

phosphine ligand by mixing $(C_5H_5)_3U\cdot PMe_3$ and $(MeC_5H_4)_3U\cdot PMe_3$, as here the rate determining step in the site exchange process must be dissociative, not associative. Unfortunately, the frequency difference between the phosphine protons in these complexes is never greater than 30 Hz on a 90 MHz instrument, and only an averaged signal was observed, generating a minimum dissociation barrier of 9.6 kcal/mol[11]. Two possible methods of increasing the frequency difference in these compounds are use of a high field instrument or designing a system with a larger chemical shift difference between exchanging sites. The later was accomplished by coordination of the bidentate phosphine ligand $(Me)_2PCH_2P(Me)_2$ (DMPM); monomeric uranium DMPM complexes can be isolated from pentane. Examination of the low temperature ^1H NMR spectrum of $(MeC_5H_4)_3U$-DMPM revealed that the methyl protons of the phosphine ligand are in two different sites, with one at -36.18 ppm (-70 °C), similar to the shift found in the PMe_3 complex, and the other farther from the uranium atom at -8.92 ppm. Upon increasing the sample temperature, the two PMe_2 peaks broaden and coalesce at 0.0°C, and at higher temperature only an averaged signal is observed. The calculated barrier to exchange, 11.5 kcal/mol, is similar to the observed 10-14 kcal/mol barriers in Cp_2UClBr(DMPE) and $(CH_3BH_3)U$(DMPE), suggesting that a similar mechanism is involved. Caution must be exercised when discussing the mechanism to a site exchange process, however, as small changes in the metal coordination sphere can greatly change the relative contribution of a given reaction pathway to the measured rate. When $(C_5H_5)_3U\cdot$DMPM was examined at low temperature, only a fast exchange spectrum was

observed. It was tempting to immediately attribute this increase in the exchange rate to a relatively weaker M-P bond, but upon careful examination, it was found that the lineshape of the phosphine methyl groups at low temperature is concentration dependent, unlike the behavior of the $(MeC_5H_4)_3U\cdot DMPM$ compound. Increasing the concentration lowers the temperature at which the limiting fast exchange spectrum is observed, consistent with a nonunimolecular or associative process. Clearly both types of exchange mechanisms are energetically accessable, and small changes in the coordination environment can have a large effect on relative rates. Until a thorough lineshape analysis of the exchange process in $(MeC_5H_4)_3U$-DMPM is obtained to generate a value for the entropy change in the transition state, it will be impossible to differentiate between a dissociative or unimolecular associative exchange process.

In contrast to the DMPM complexes, addition of DMPE to solutions of $Cp_3U\cdot L$ ($Cp = C_5H_5$, MeC_5H_4) complexes resulted in immediate formation of the dimeric bridging phosphine complexes. The extra methylene carbon produces a sufficient distance between Cp_3U groups to relieve steric restraints presumed responsible for the monomeric DMPM complexes. There is either no substantial slowing of rotation about the methylene C-C bond, as might be anticipated considering the size of the uranium groups, or the solution conformation is one with four equivalent (trans $(MeC_5H_4)_3U$'s) methyl groups.

Phosphite complexes have also been isolated and characterized. Initially, Vercaide's phosphite, $P(OCH_2)_3CEt$, was used, with the expectation that the terminal ethyl group would weaken the lattice

energy of the complex, rendering it soluble in ether or hexane. However, addition of an ether solution of the phosphite to a solution of $(MeC_5H_4)_3U\cdot thf$ resulted in immediate precipitation of a red solid. The compound was sparingly soluble in hot toluene, from which it was crystallized. The solubility characteristics were consistent with some type of dimerization product, of the type observed in the reaction of bispentamethylcyclopentadienyluraniumhydride and trimethylphosphite to form a bridging phosphinidine complex[12] as in reaction 1. The ^1H NMR spectrum indicated the compound was instead

1 $(C_5Me_5)_2UH + P(OMe)_3 \longrightarrow (C_5Me_5)_2U(OMe)\text{-}PH\text{-}U(OMe)(C_5Me_5)_2$

an extremely insoluble coordination complex. The solubility of this complex made it unsuitable for competition studies, and the trimethyl phosphite complex was prepared by displacement of thf from $(MeC_5H_4)_3U\cdot thf$. This complex has convenient solubility in hexane, from which red plates were isolated. Upon standing in a sealed Schlenk tube in a drybox for months, the dark red color of the compound turned to a lighter green, presumably forming $(MeC_5H_4)_3UOMe$. The melting point of the trimethylphosphite complex was almost identical to that of the triethylphosphine complex, and the chemical shift of the methyl group is equally similar to the shift observed for the methyl protons of the phosphine ligand. Upon addition of excess ligand to solutions of either the triethylphosphine or trimethylphosphite complex, rapid exchange was observed in the NMR spectrum at room temperature, but below -20°C, the signal due to the

rapidly exchanging ligands broadens considerably for the triethylphosphine ligand. At -50°C, coalesence was observed, but individual resonances for free and coordinated phosphine ligand could not be resolved to -80°C.

Isolation of a thiophene complex of $(MeC_5H_4)_3U$ was not as facile as the isolation of the phosphine or phosphite complexes. Addition of SC_4H_8 to a solution of the thf complex produced no observable color change. After removal of the solvent, the sulfur complex was isolated from ether in low yield. Other than the sulfur coordination complexes of $(MeBH_3)_4U$ that has recently been characterized[3], there is only one other uranium complex which contains a sulfur atom as a coordinating ligand[13], and in that case the sulfur atom was part of a tridentate ligand, with two oxygen donor ligands.

Pyridine complexes of actinide ions are far more common than P or S donor ligands, and isolation of $(MeC_5H_4)_3U\cdot py$ as needles from ether and $(C_5H_5)_3U\cdot py$ as plates from toluene was straightforeward. The later is the preferred starting material for the redox chemistry described in chapter 3. The dark green color of these complexes is unlike any other base complex yet isolated, suggesting the possibliity of a charge transfer band in the visible region. Consistent with this hypothesis the colors of $(MeC_5H_4)_3U\cdot NC_4H_4NMe_2$ and $(MeC_5H_4)_3U\cdot NC_4H_4CN$ are red and violet respectively. The electron donating group (NMe_2) should raise the energy of a metal to ligand charge transfer absorption (assuming the substituent effect alters the energy levels of the ligand to a greater extent than it perturbs the ionization potential of the metal), while the electron withdrawing CN group

should lower the transition energy by stabilizing the excited state. The dimethylamino complex readily crystallized from ether, whereas the cyano complex had limited solubility in toluene, perhaps due to aggregation in solution or in the solid state. This may also explain the origin of the observed colors in toluene solution, or the ligating atom may be either the amine or cyano nitrogen. The color of the bridging pyrazine dimer $(MeCp_3U)\cdot NC_4H_4N\cdot U(MeC_5H_4)_3$ was described as red[7]. In solution, the pyridine ligand exchanges rapidly with excess pyridine, as does the p-dimethylaminopyridine. In the case of the latter, a set of resonances is observed in the ^1H NMR spectrum at low temperatures which may be due to a measurable concentration of uranium complex coordinated to the tertiary amine portion of the pyridine ligand.

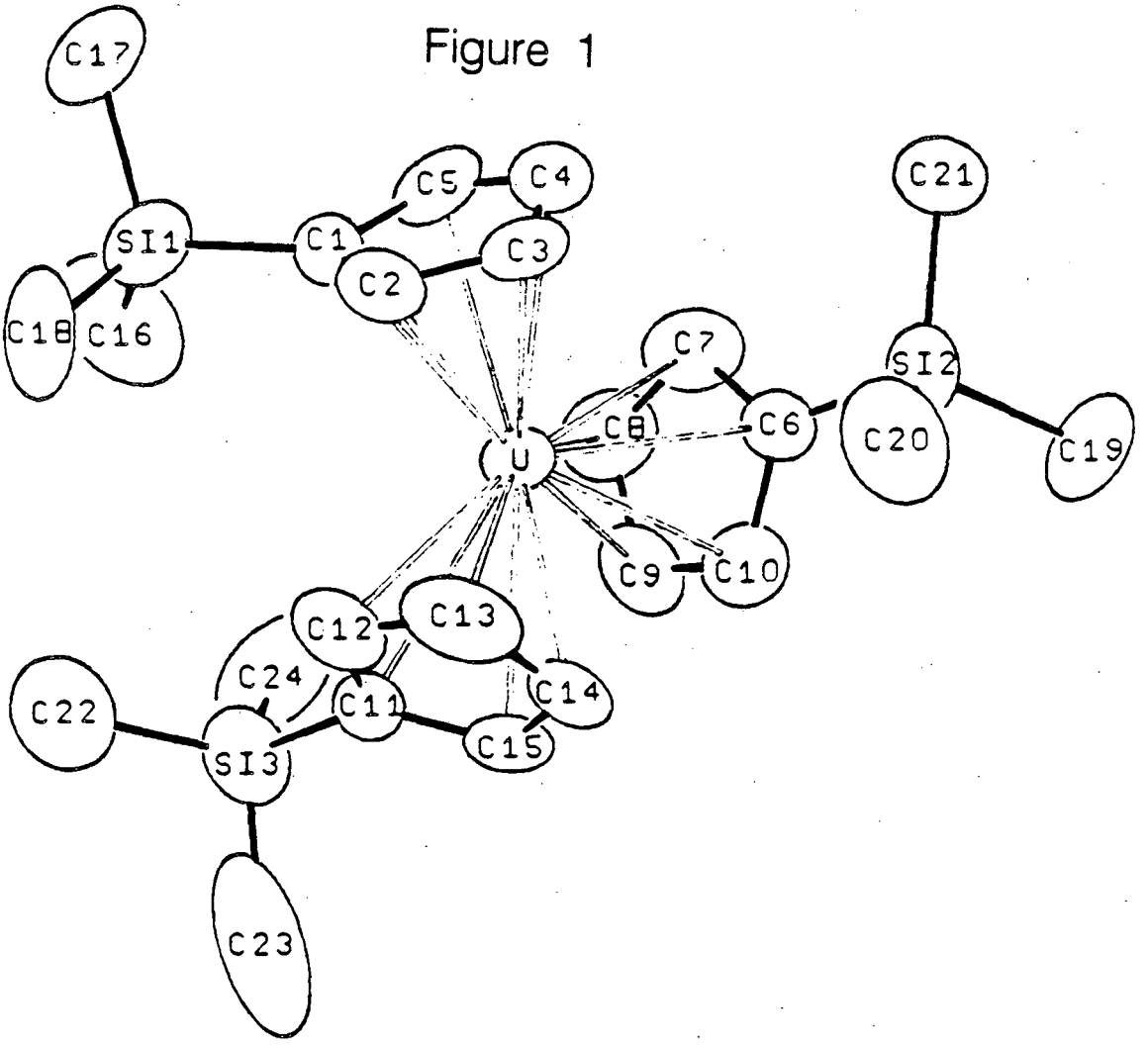
Attempts to isolate a trimethylamine complex were unsuccessful. Upon purging a toluene solution of the thf complex with a stream of NMe_3, the thf resonances in the NMR spectrum were shifted downfield, but upon taking a solution of the NMe_3/thf mixture to dryness, the equilibrium was shifted in the direction of the starting material as the amine ligand, with such a high vapor pressure, was removed from the system. If the solution was not taken to dryness but simply cooled, no material was isolated. A similar lack of success was achieved in attempting to isolate the triethylamine adduct. Fortunately, the nonvolatile tertiary amine quinuclidine (quin), $N(CH_2CH_2)_3CH$, can be used to form a stable tertiary amine complex with $(MeC_5H_4)_3U$. Upon addition of quin to a toluene solution of the thf complex, followed by slow removal of the solvent under reduced

pressure gave good yields of the quin complex as brown bars from diethyl ether. In solution coordinated quinuclidine does not exchange rapidly with added quin, unlike the behaviour found in the other complexes. For temperatures as high as +15°C, separate resonances for free and coordinated quin were observed in the ^{1}H NMR spectrum. Above +15C, the signals broaden and coalesce, with a calculated barrier to site exchange of 11.7 kcal/mol[9]. The lineshape appeared independent of the concentration of the species in solution; dilution of either the uranium complex or the ligand concentration by a factor of ten produced no observable change in the lineshape about the coalesence temperature, where line widths are particuliarly sensitive to rate changes. Additionally, in the presence of ca. 1-5 equivalents of either OC_4H_8 or SC_4H_8, there is still no perceptible change in the NMR lineshape of the quin resonances near the coalesence temperature. The addition of ca. 20-fold excess of thf decreases the quinuclidine coalesence temperature to -5°C. These observations are consistent with a purely dissociative exchange mechanism at moderate free-ligand concentrations, suggesting that ligand dissociation can be treated as a simple site-exchange process, if the reverse reaction is sufficiently fast such that no appreciable concentration of uncoordinated species exists in solution.

Red ethylisocyanide complexes $(RC_5H_4)_3U\cdot CNEt$ (R=H, Me) were isolated more readily than the corresponding proprionitrile adducts. The CNR stretching frequencies (2170, 2160; R=H: 2155; R=Me) were similar to the reported $(C_5H_5)_3U\cdot$cyclohexylisocyanide complex (2160 cm^{-1})[5].

The reaction of three equivalents of $K(Me_3SiC_5H_4)$, or KTMSCp, with UCl_4 in thf yielded the pentane soluble compound $(TMSCp)_3UCl$[14]. The thorium compound was isolated similiarly. Addition of two equivalents of KTMSCp to a solution of UCl_4 resulted only in isolation of the tris compound. The other redistribution product, presumably $TMSCpUCl_3 \cdot thf_x$, had moderate solubility in toluene, unlike $C_5H_5UCl_3$-2thf[15]. When red $TMSCp_3UCl$ dissolved in hexane was stirred over Na/Hg or Na/K, the red color turned green over a period of hours, and a green crystalline compound was isolated from hexane. The compound tested negative for halide ($AgNO_3$), and NMR analysis revealed a single type of TMSCp resonance with broad lines ($\nu_{1/2}$= 20-30 Hz), typical of trivalent uranium compounds. The compound did not react with H_2 (IR, NMR), and there was no change in the IR spectrum when exposed to D_2 (150 psi) for 24 hrs. The mass spectrum contained a parent ion M^+= 649 amu expected for $(TMSCp)_3U$, and the 78-80°C melting point was far lower than any other reported Cp_3M complex. X-Ray analysis (Figure 1) revealed that the complex was monomeric in the solid state, in contrast to the structures observed for $(C_5H_5)_3M$[16] and $(MeC_5H_4)_3M$[17]. Base free $(C_5H_5)_3Sc$ is eight coordinate in the solid state, with two η^5 Cp and two bridging η^1,η^5 ligands, and the Pr complex is described as polymeric, with three η^5 ligands, one of which is also η^2 coordinated to the next metal, whereas $(MeC_5H_4)_3Nd$ crystallizes in a tetrameric unit, with all three Cp's η^5, one of which also bridges in an η^1-fashion. In monomeric $TMSCp_3U$, the uranium atom is bound η^5 to the three TMSCp ligands, with the metal in the plane defined by the cyclopentadienyl centroids. The Cp-M-Cp angles are 120.2, 120.9, and

Figure 1



ORTEP Drawing of $(Me_3SiC_5H_4)_3U$

XBL 834-9361A

118.0°, and the metal-carbon distances range from 2.71 to 2.84Å, averaging 2.78Å. This is longer than the distances found in most 10 coordinate U(IV) compounds[18], and is closer to the observed average in $Cp_3U(DMPE)UCp_3$ lending structural support to formulation of the latter as a U(III) complex. In solution, there is no unusual dynamic behaviour as judged by ^1H NMR. If a mixture of the $TMSCp_3U$ and the $TMSCp_3U(IV)Cl$ are dissolved in toluene, only one Cp resonance is observed in the ^1H NMR spectrum while at -95°C, it appears as if the protons separated by the largest chemical shift difference are broadening into the baseline. This is consistent with a bimolecular exchange of halide ion between U(III) and U(IV) species. The rate of halide ion/electron-transfer is faster than that found for the bimolecular reaction between $(C_5H_5)_3U\cdot thf$ and $(C_5H_5)_3UCl$[19]; the latter exchange was monitored in a coordinating solvent (thf), and the observed barrier, ascribed to a prohibitive rehybridization energy, can more reasonably be explained if the rate determining step is assumed to be dissociation of thf from the metal complex. This reinterpretation is consistent with the observed barriers to ligand exchange processes described thus far. There is no measurable interaction between an equimolar mixture of $TMSCp_3ThCl$ and $TMSCp_3U(III)$, with no shifts in the ^1H NMR resonances of either the uranium or the thorium compound. Unlike $Cp_3U\text{-}F\text{-}UCp_3$[20] or $(MeC_5H_4)_3U\text{-}F\text{-}U(MeC_5H_4)_3$, which immediately precipitate upon mixing the respective $Cp_3U\cdot thf$ and Cp_3UF compounds, the $TMSCpU_3Cl$ complex was separated from the U(III) complex by fractional crystallization from hexane. The reaction between $(MeC_5H_4)_3U\text{-}F$ and $(MeC_5H_4)_3U\cdot py$ yielded no

precipitate; either pyridine remains coordinated to the metal upon dimerization and destabilizes the lattice, or the lone pair of electrons on pyridine is a better base towards $(MeC_5H_4)_3U$ than is the lone pair of the flouride atom.

The reduced uranium complex was also isolated in almost quantitative yield from the reaction of $TMSCp_3UCl$ with tertiary butyllithium in hexane. Reactions with other alkyl lithium reagents yielded only the uranium alkyl complexes (alkyl = benzyl, neopentyl), which could not be decomposed thermally to yield the trivalent compound.

Upon addition of PMe_3 to a solution of $TMSCp_3U$ in hexane, an immediate color change from green to red was observed. A stable monodentate complex was isolated from pentane at -80°C, but adequate X-ray quality crystals were not obtained due to the extreme solubility of the complex. The complex did not appear to lose PMe_3 under vacuum (10^{-2} torr) at room temperature, but decomposed when melted, regenerating the base-free complex. Upon addition of free phosphine ligand to a solution of $TMSCp_3U \cdot PMe_3$ in toluene, the free and coordinated ligands were resolved in the ^1H NMR spectrum below 0°C. Above this temperature, exchange between free and coordinated phosphine is fast on the NMR timescale, leading to a time averaged signal.

Unlike the phosphine complex, $TMSCp_3U \cdot NC_5H_5$ has a limited solubility in hexane, from which large red blocks (often greater than .2x.2x.2 cm.) were isolated. The pyridine ligand exchanges with free pyridine roughly as fast as the phosphine site exchange occurs.

Initially, the thf complex of $TMSCp_3U$ did not appear to be stable with respect to ligand dissociation under reduced pressure. When $TMSCp_3U$ was prepared by the reaction of UCl_3 (from UCl_4 and $NaC_{10}H_8$ in thf[8]) with KTMSCp, followed by extraction with ether, long green needles were isolated which decomposed upon exposure to vacuum. The product was found to be the base-free material. No attempt was made to establish whether the green crystals were in fact the thf complex, or if thf had been removed earlier along with the sublimed naphthalene, and a diethyl ether complex had then been isolated. Experiments by others suggest that the thf complex is stable until melted under vacuum +70°C, where the thf is lost[21], and thus the diethylether complex desolvated at room temperature.

There exist a number of trigonal bipyramidal tris cyclopentadienyl bis-ligand f-metal complexes, most of which are tetravalent uranium complexes with at least one anionic axial ligand[18]. Recently, a number of $Cp_3M(L)_2$ (M = early lanthanide, L = RCN) complexes have been isolated and structurally characterized[22]. To determine whether the trimethylsilyl substituent was sufficiently large to inhibit formation of the Cp_3UL_2 species, $TMSCp_3U$ was allowed to react with a two-fold excess of ethyl cyanide or ethyl isocyanide. Addition of EtCN to a hexane solution of $TMSCp_3U$ produced an immediate color change to red, and crystals of the monoligand complex $TMSCp_3U{\cdot}NCEt$ were isolated from hexane. The stoichiometry was established by elemental analysis and integration of the ^1H NMR spectrum. The C-N stretch, 2240 cm^{-1}, is exceedingly weak in the IR, as has been noted often in transition metal nitrile compounds, to the

point of being unobservable[23]. The near zero shift in ν_{CN} from that of free ligand (2242 cm^{-1}) is atypical of coordination to an electropositive metal; shifts to low frequency have often been attributed to an η^2 ligation[24]. In the presence of additional cyanide, exchange between free and coordinated cyanide ligands is faster than that observed for the pyridine or trimethylphosphine complex. The increased rate of ligand exchange could result from two postulated mechanisms. First, if an associative process is dominant, then the less sterically demanding cyanide ligand should more easily form an associated complex. If the site exchange is dissociative, then the pyridine and phosphine ligands could be more tightly bound than the cyanide, slowing down the observed rate of exchange.

In a similar fashion the monoligand complex $TMSCp_3U{\cdot}CNEt$ was isolated from hexane. The color of the complex is very similar to the phosphine complex, best described as burgundy, while the cyanide and pyridine complexes are brick red. The stoichiometry of the complex was again established by elemental analysis and ^1H NMR spectrosopy. The 112-115°C melting point of the compound was significantly lower than that of the isostructural propioitrile complex, 130-132°C. The IR spectrum of the complex as a Nujol mull contains two bands of equal intensity at 2178 and 2159 cm^{-1}, suggesting more that one independent molecule in the solid state. The cyclohexylisocyanide complex of $(C_5H_5)_3U$, with a ν_{CN}= 2160 cm^{-1}, has previously been reported[5]. A lower CN stretching frequency in the uranium complexes is always found relative to the isostructural lanthanide or heavier actinide complexes. Upon complexation of an isocyanide to a positively charged

metal, σ-donation from metal to ligand increases the CN stretching frequency as in the cyanide complexes, whereas if a metal is capable of π-backbonding, the CN stretch can decrease upon coordination by accepting electron density into accessable C-N antibonding orbitals[25]. The lower CN stretching frequency of the uranium complex has been attributed to both a weaker metal ligand bond, with no mention of the possibility of π-backbonding producing a lower observed stretch[26], as well as a bonding scheme involving back donation from metal to ligand[27]. Upon dissolving $TMSCp_3U$ and an equivalent amount of $TMSCp_3Ce$-CNEt in toluene d^8 (Reaction 2), the observed ^1H NMR spectrum contains peaks for only $TMSCp_3U$-CNEt and base free $TMSCp_3Ce$. The

$$2 \qquad U + Ce{\cdot}CNEt \longrightarrow U{\cdot}CNEt + Ce$$

equilibrium is driven entirely to the right, and no measurable concentration of the cerium isocyanide complex is present, thus proving the U·CNEt bond is stronger than the Ce·CNEt bond, and is the thermodynamically favored product. If the lowered isocyanide stretching frequency in the uranium complex is not the result of a weaker metal-ligand interaction, then the possibiltiy of π-backbonding must be considered. In the number of reported CNR complexes of uranium (Table 1), there is a definite trend of increasing CN stretching frequency as the metal oxidation state increases. This can be rationalized as a product of two inseparable effects; metal oxidation will increase the electrostatic attraction felt by the ligand, decreasing CN antibonding density, while concurrently

decreasing the propensity to engage the remaining f-electrons in π-backbonding with the CN antibonding orbital.

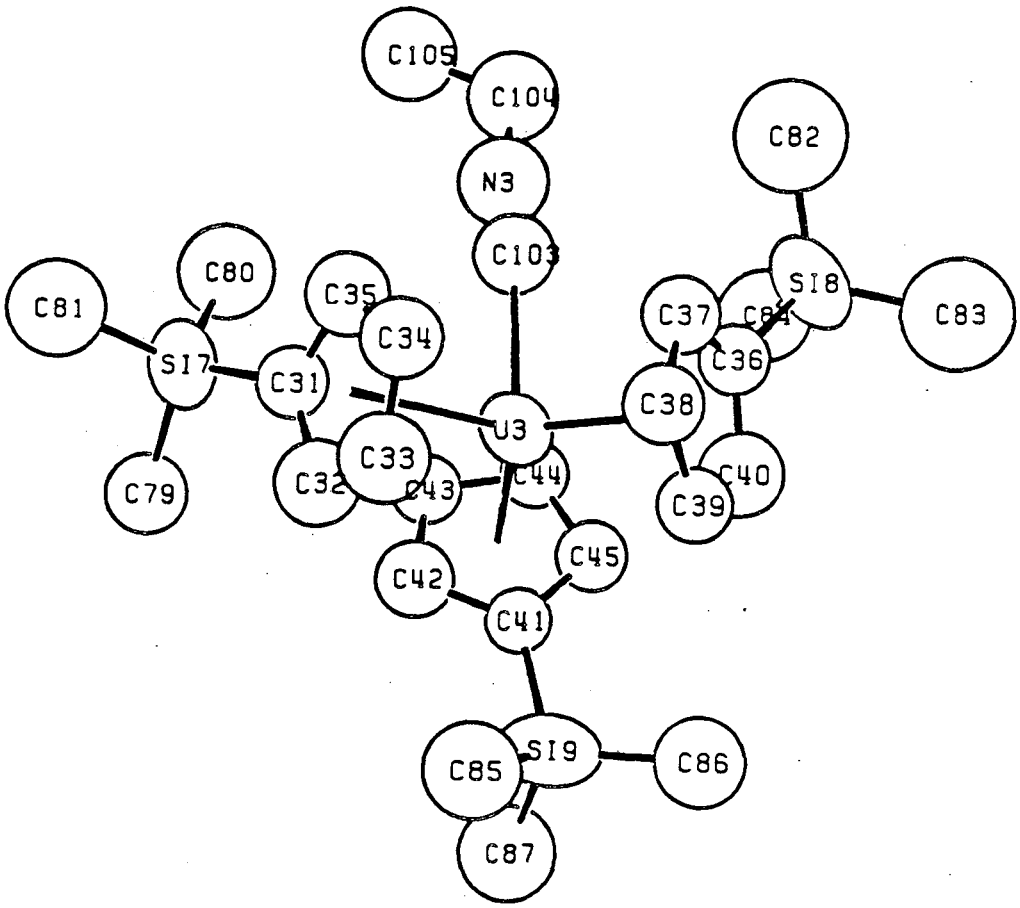
Table 1: Isocyanide Complexes of Uranium

Compound	M^+	$\nu_{CN}(cm^{-1})$	ν^{free}_{CN} ligand(cm^{-1})	Δ	Ref.
$Cp_3UCNC_6H_{11}$	+3	2160	2135	25	5
Cp_3UCNEt	+3	2170, 2160	2151	19, 9	Ch.2
$(MeC_5H_4)_3UCNEt$	+3	2155	2151	4	Ch.2
$(Me_3SiC_5H_4)_3UCNEt$	+3	2178, 2159	2151	27, 8	Ch.2
$UCl_4(CNC_6H_{11})_4$	+4	2196	2135	61	28
$UBr_4(CNC_6H_{11})_4$	+4	2193	2135	58	28
$UI_4(CNC_6H_{11})_4$	+4	2190	2135	55	28
$UO_2Cl_2(CNC_6H_{11})_2$	+6	2213	2135	78	28

$\Delta = \nu_{CN(coord)} - \nu_{CN(free)}$ in cm^{-1}

Similar dependence of CN stretch on metal oxidation state has been noted in transition metal chemistry[29].

The effects of this stronger M-L bond can be observed in the structure of the $(TMSCp)_3U{\cdot}CNEt$ (Figure 2) when compared with the previously determined structure of $(C_5H_5)_3Pr{\cdot}CNC_6H_{11}$.[30] While the average distance from the uranium atom to the Cp carbons, 2.81(3)Å, is 0.03Å larger than the average Pr-Cp distance of 2.78(2)Å, the uranium isocyanide carbon distance of 2.57(2)Å is 0.08Å shorter than the Pr-C distance. If ionic radii could simply be summed to yield bond distances[31], then the bond differences in the two ligand types should be consistent, dependent only on the relative metal ionic radii.



ORTEP Drawing of $(Me_3SiC_5H_4)_3U$-CNEt

XBL 8512-4997

Figure 2

Instead, what is seen is the relative shortening of the U-C σ-bond due to an increase in bond strength.

Exposure of $TMSCp_3U$ dissolved in hexane to a CO atmosphere resulted in an immediate change in solution color from green to burgundy. The solution color was indistinguishable from that of the isocyanide or PMe_3 complex, all of which were distinct from the pyridine or cyanide complexes. Upon exposure to vacuum or purging of the solution with an inert atmosphere, the color reverts to the original green; the cycle may be repeated many times. A solution IR spectrum of the complex under a CO atmosphere in hexane contains a ν_{CO} at 1976 cm^{-1}; this shifts to 1932 cm^{-1} with ^{13}CO, and 1931 cm^{-1} with $C^{18}O$. Isolation of this material from solution has proved difficult; crystals of what were assumed to be the CO complex were examined by X-ray analysis, but decompostion of the crystal, as judged by diffraction intensity changes, was complete within 5 minutes. The CO complex can exist in the solid state[32], with ν_{co} = 1969 cm^{-1}; substitution of ^{13}CO gives a stretch at 1922 cm^{-1}. The stoichiometry of the solution reaction was established by volumetric gas uptake studies[33], which showed that only one mole of CO was adsorbed per mole of uranium complex. The data are consistent with the formation of the first molecular CO complex of an f-metal, $(Me_3SiC_5H_4)_3U{\cdot}CO$. The CO is presumed to bond through the carbon atom as in the structure of the isocyanide complex. Exposure of a hexane solution of $MeCp_3U{\cdot}thf$ to an atmosphere of CO resulted in a similar color change from red to burgundy, and a solution IR spectrum contained a weak band at 1953cm^{-1}. Saturation of a toluene solution of $MeCp_3U{\cdot}thf$ with CO

produced an 8 ppm shift of the high field thf resonance towards the diamagnetic portion of the spectrum, consistent with a 25% displacement of thf by CO. There was no color change nor reduced CO stretch observed when $((Me_3Si)_2N)_3U$, $(Me_3SiC_5H_4)_3Ce$[21], or $(Me_3SiC_5H_4)_3Nd$[21] was exposed to CO. There are few reports in the literature concerning the coordination of CO to a uranium atom. A uranium carbonyl compound, $U(CO)_x$, formed by the reaction of uranium atoms with CO in an argon matrix at 4K[34], is described to be unstable above 30K. The CO stretching frequency reported, 1961 cm^{-1}, displays the same greatly reduced (free CO = 2143 cm^{-1}) stretching frequency found for $(Me_3SiC_5H_4)_3U{\cdot}CO$. The uranium carbonyl stretching frequencies are lower than those of other group VI metal carbonyls[35] under similar conditions, for example $Cr(CO)_6$, ν_{CO}= 1990 cm^{-1}, and $Mo(CO)_6$, ν_{CO}= 1992 cm^{-1}. At 20K, adsorbtion of CO by tetravalent UO_2 has been reported[36], and $UF_4(CO)$[37] in an argon matrix has a ν_{CO}= 2284 cm^{-1}, indicating that CO is acting as a σ-base towards UF_4. The possibliity that a CO complex of Cp_3U^{+6} could exist has been the subject of a theoretical study, with the conclusion that an acid will react with a base[38]. The extent of π-backbonding was found to be neglegible in contributing to the stability of the complex, a prediction not too suprising for a metal with no valence electrons (U(VI) is f^0). The facility with which CO is removed from the metal indicates that the CO ligand is either labile (as have been all other traditional complexes) or the U-C bond is thermodynamiclaly weak. Our inability to evaluate the loss of entropy upon coordination prohibits a rough calculation of a minimum $-\Delta H_f$.

A number of trivalent uranium complexes have been examined by gas phase photoelectron spectroscopy, in an attempt to understand the formation of CO complexes in the Cp compounds but not in $((Me_3Si)_2N)_3U$ compounds, as well as to determine the electron donating or withdrawing nature of the $SiMe_3$ group. Values for the assigned f-electron ionization band and the ionizations due to the Cp groups are given in Table 2. The values for Cp_3U were obtained in the analysis of a sample of Cp_3U-PMe_3; the base

Table 2

Compound	f e^- (EV)	Cp ionizations (EV)			Reference
Cp_3U-thf	6.42	7.58	8.18	8.73	39a
$MeCp_3U$-thf	6.25	7.51	7.93	8.47	39b
Cp_3U	5.94	7.54	8.17	8.55	39b
$TMSCp_3U$	5.77	7.30	7.74	8.17	39b
$((Me_3Si)_2N)_3U$	6.96				39c
Cp_3UCl	7.01	7.99	8.56	9.20	39d
$(MeC_5H_4)_3UCl$	6.91	7.92	8.32	8.95	39d
Cp_3UBH_4	6.35, 6.75	8.10	8.45	8.85	39e
$(MeC_5H_4)_3UBr$	6.95	8.20	8.50	8.85	39e

(These values have been assigned an accuracy of ± 0.05 ev.)

complex is apparently unstable in the gas phase, with complete ligand dissociation occuring before a spectrum of the complex could be obtained. The ionization energy (IE) of the Cp ligand in the $TMSCp_3U$ complex is significantly lower in energy than the C_5H_5 complex; this

is interpreted as $SiMe_3$ acting as an electron donating group, putting more density in the Cp ring, thus lowering the energy necessary to remove an electron. The same effect can be noted to a lesser extent in the IE of the metal valence electrons. This trend is also seen in the reported photoelectron spectra of $(C_5H_5)_3U\cdot thf$ and $(MeC_5H_4)_3U\cdot thf$, where to a lesser degree the methyl group acts as an electron donor relative to H. The values reported for the $(C_5H_5)_3U\cdot thf$ complex are inconsistent with the IE obtained for the base-free compound; coordination of an electron donating ligand will lower a metal IE. It is possible that sublimation of the thf complexes resulted in thermal decomposition; in refluxing thf, $(C_5H_5)_3U$ is known to react with solvent[40] forming $(C_5H_5)_3U\text{-}OCH_2CH_2CH_2CH_3$ while, in the absence of a proton source, sublimation of $(MeC_5H_4)_3U\cdot thf$ gives a green compound in low yield that contains a parent ion for $(MeC_5H_4)_3U\text{-}OCHCH_2$ in the mass spectrum, although the broad signals in the ^1H NMR spectrum were consistent with the isolation of $(MeC_5H_4)_3U(III)$. The U-thf ionization potentials are in the range found for other tetravalent species. The lower values of the metal IE in the $(C_5H_5)_3U$ and $(Me_3SiC_5H_4)_3U$ compounds relative to $((Me_3Si)_2N)_3U$ demonstrate that Cp ligands are more electron donating than silylamide, reducing the energy necessary to remove an electron by over 20 kcal/mol. This is consistent with the observation that the π-electron accepting CO ligand coordinates only to the more electron rich metal center.

The contribution of π-bonding to the total complex stability can be examined by comparing the bulk magnetic susceptibility of a series of $Cp_3U\cdot L$ compounds. The extent of electron donation is not

sufficient to alter the electronic ground state of the metal; magnetic susceptibility measurements demonstrate the insensitivity of magnetic moment to the coordinating ligand. Trivalent uranium has a $^4I_{9/2}$ ground state, whereas U(IV) is $^3H_4$, with temperature independent behaviour at low temperature (kT< crystal field splitting). Comparison of the susceptibility curves for $Cp_3U{\cdot}L$, L=thf[6], CNC_6H_{11},[6] pyridine, or PMe_3 reveals no consistent change in χ_m upon coordination of π-accepting ligands, indicating dominance of the σ-bond in defining metal electronic structure.

Structural Characterization

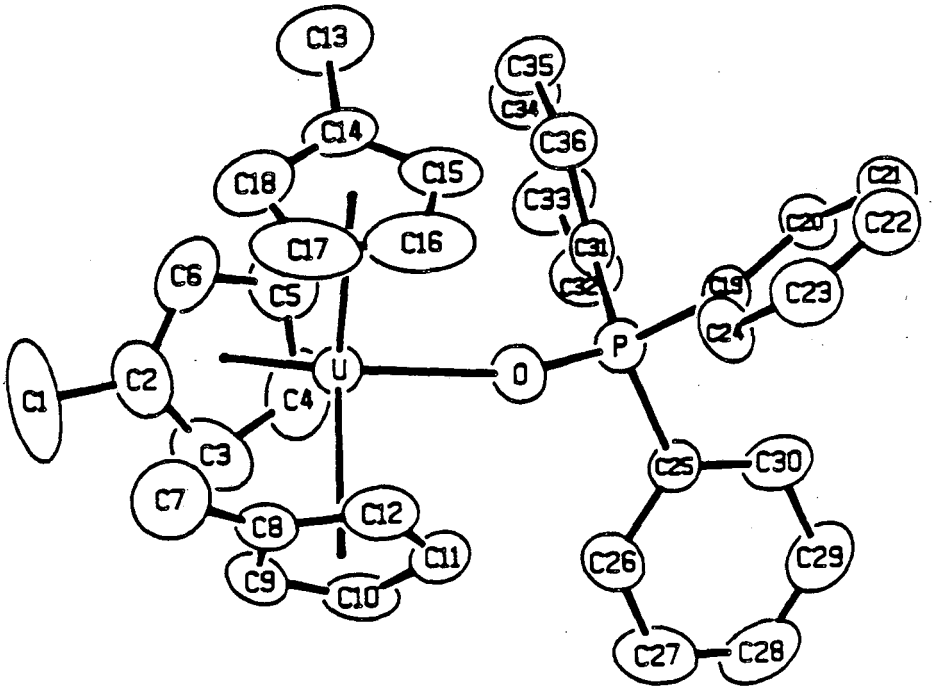
The intensity of interaction between a metal and a ligand is governed not only by the electronic nature of the ligand or metal, but also by the interligand repulsions in the metal coordination sphere. Bonding between large, low valent metals and neutral ligands should be particularly susceptible to ligand-ligand repulsive forces, first because the charged ligands are expected to dominate the forces dictating surface geometry, second, the high coordination numbers common in such systems produce a geometry with a poorly defined local minimum on a potential energy surface, resulting in facile ligand lability, and most importantly, the lower metal charge results in a lessened electrostatic attraction toward electron donors, potentially increasing the importance of the first two interactions. The effect of local steric environments upon metal-ligand bonding was detected in the first report of a trivalent uranium phosphine complex, $(Me_5C_5)_2UH(DMPE)$[41]; the structure consists of a uranium atom between

two Me_5C_5 groups, with the bidentate phosphine and the hydride in the equatorial girdle defined by the Me_5C_5 rings. The U-P distances are 3.092(8) and 3.211(8)Å, with the longer distance to the phosphorus atom whose methyl groups are closer to the Me_5C_5 methyl groups.

In discussing relative ligand basicities, it is helpful to know the distance from the metal to the donor atom as well as the geometry about the coordinating ligand in order to describe possible steric influences on metal-ligand bond strengths. The structural characterization of monodentate Lewis base complexes of actinide elements has focused primarily on oxygen donor (for example, there are at least 12 structurally characterized thf complexes of uranium, yet only one thioether complex), and to a lesser extent, nitrogen donor ligands coordinated to either tetravalent or hexavalent metals.

For these reasons, the compounds $(MeC_5H_4)_3U$-L, where L = PMe_3, $P(OCH_2)_3CEt$ ($P(OR)_3$), SC_4H_8 (SR_2), $NC_5H_4NMe_2$ (PYR), and $N(CH_2CH_2)_3CH$ (QUIN) were fully characterized by X-ray crystallography. All compounds contain uranium atoms in a distorted tetrahedral geometry with three η^5 methylcyclopentadienyl groups, and one coordinating atom from the base. Table 3 and Table 4 list the important distances and angles.

The PMe_3 complex is most distorted from C_{3v} symmetry, with one Cp ring displaced away from the metal and bent toward the phosphine ligand. The U-P distance is the shortest yet observed for a uranium phosphine complex, several of which (Table 5) have been characterized, predominantly containing bidentate ligands.



ORTEP Drawing of $(MeC_5H_4)_3U\text{-}OPPh_3$

XBL 8512-5002

Figure 3

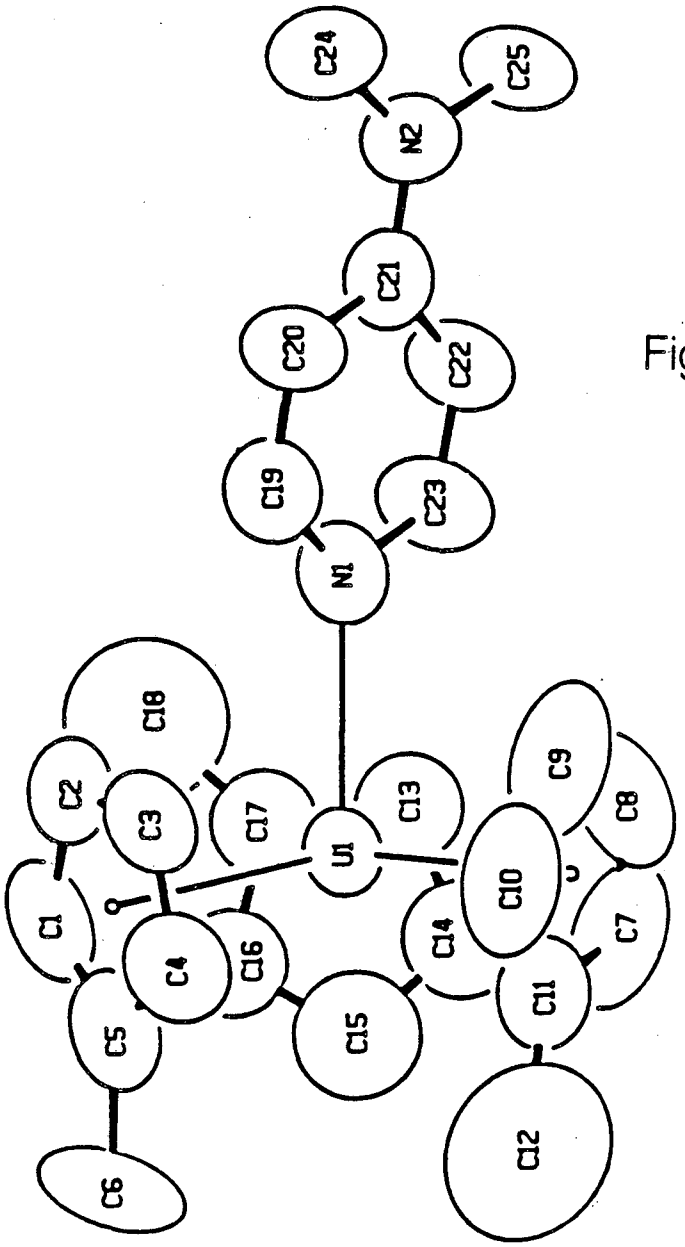
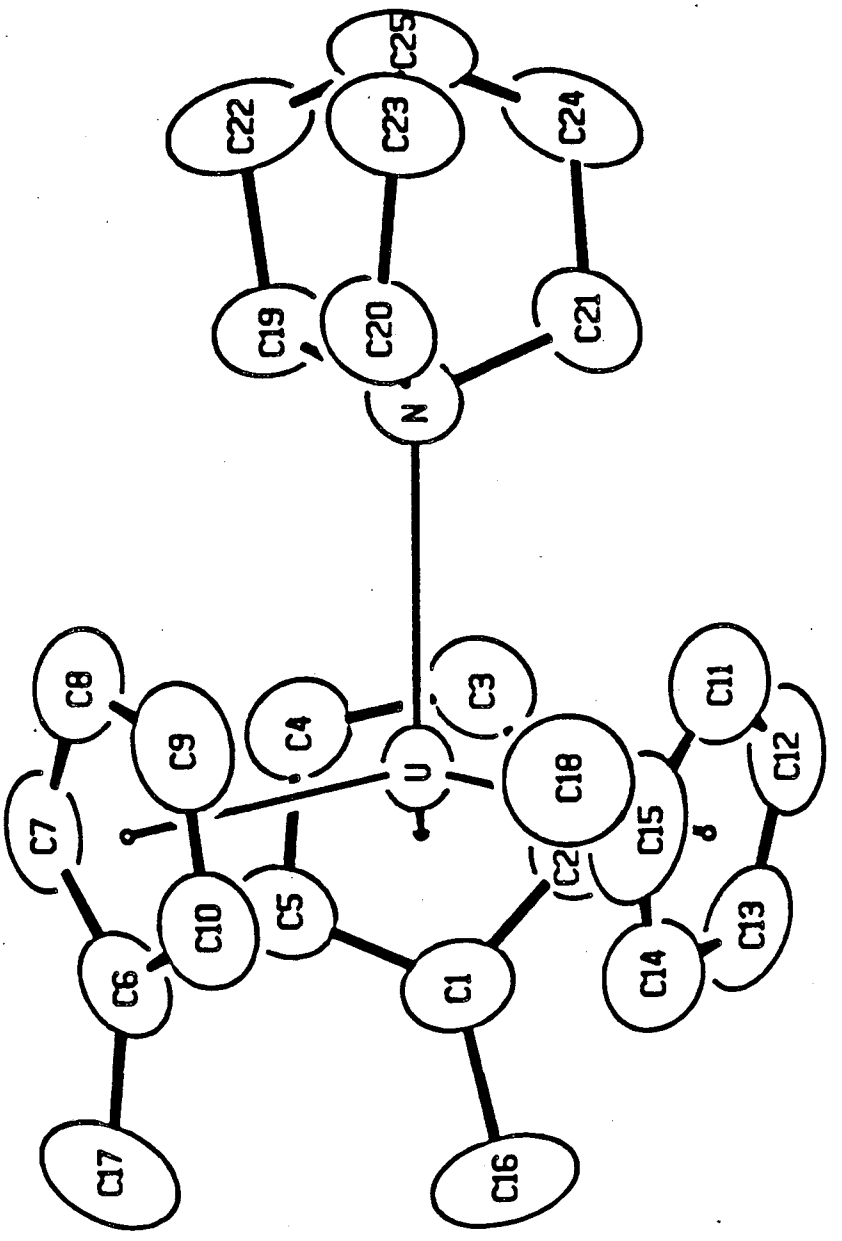


Figure 4

ORTEP Drawing of $(MeC_5H_4)_3U\text{-}NC_5H_4\text{-}p\text{-}NMe_2$

XBL 8512-4988

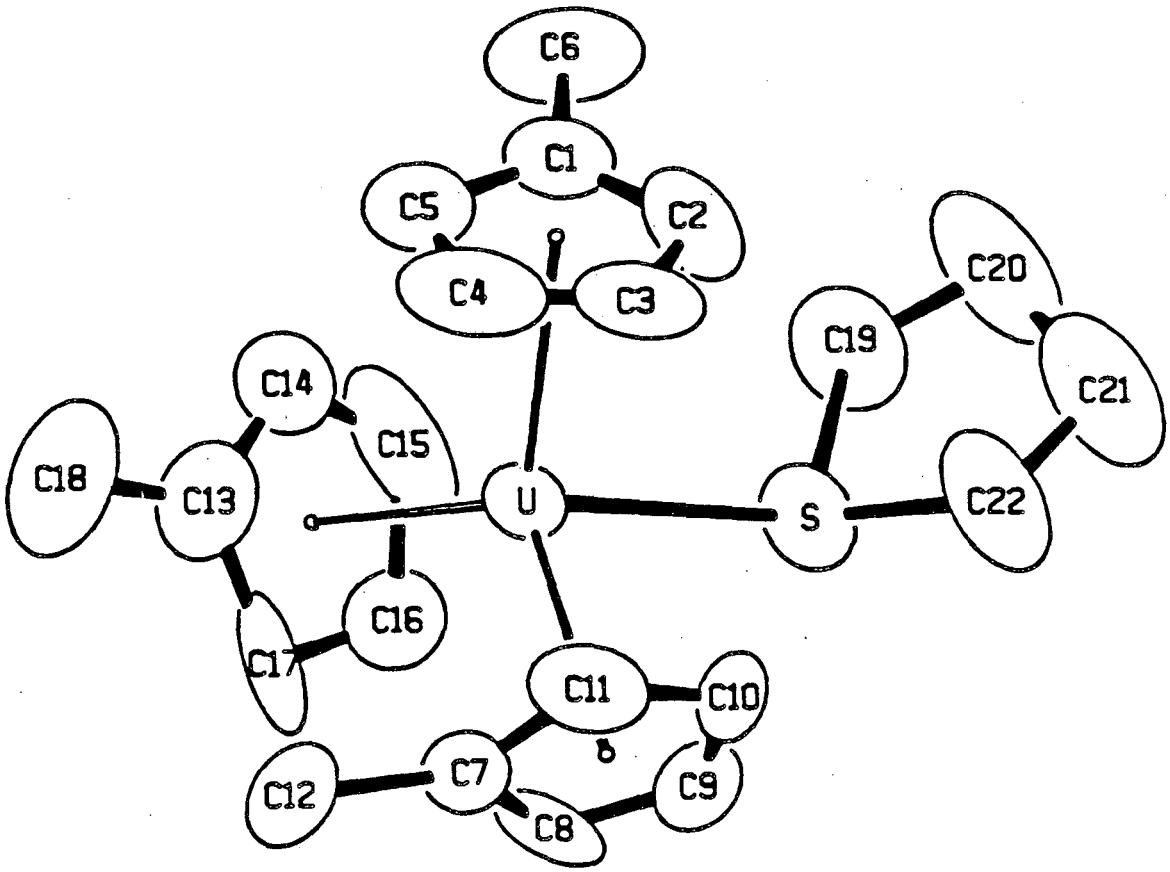


ORTEP Drawing of $(MeC_5H_4)_3U\text{-}N(CH_2CH_2)_3CH$

Figure 5

XBL 8512-4991

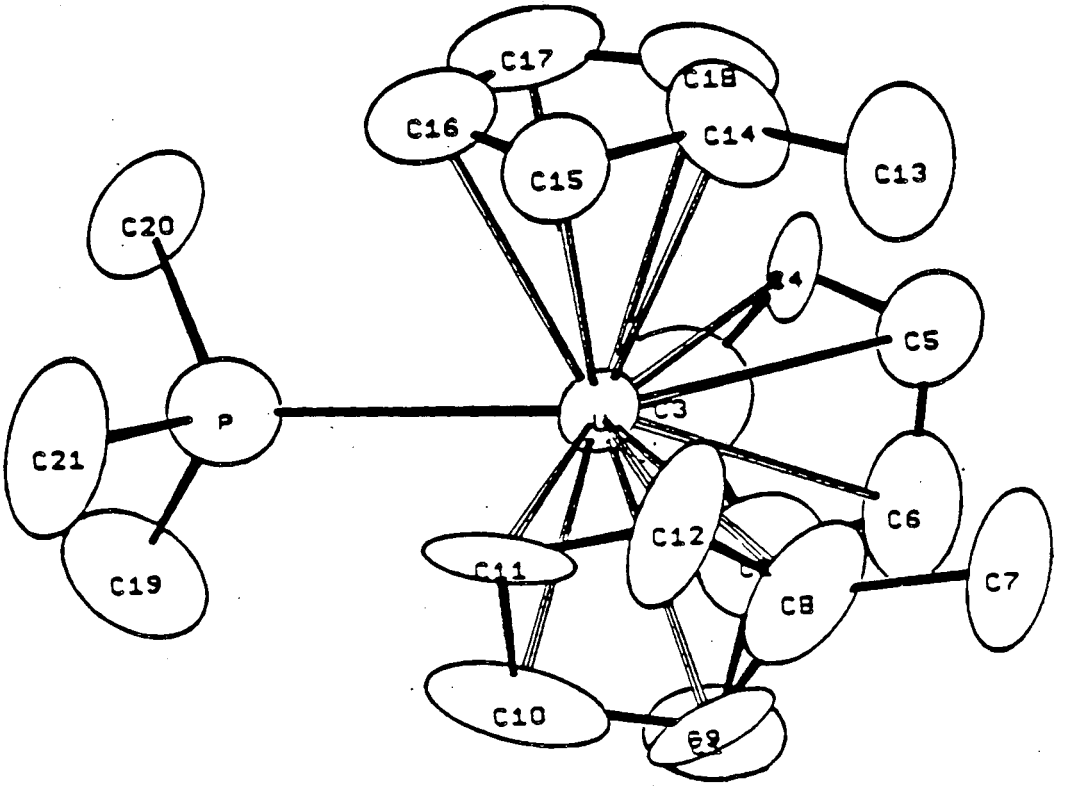
Figure 6



ORTEP Drawing of $(MeC_5H_4)_3U\text{-}SC_4H_8$

XBL 8512-4992

ORTEP Drawing of $(MeC_5H_4)_3U\text{-}PMe_3$



XBL 8512-4986

Figure 7

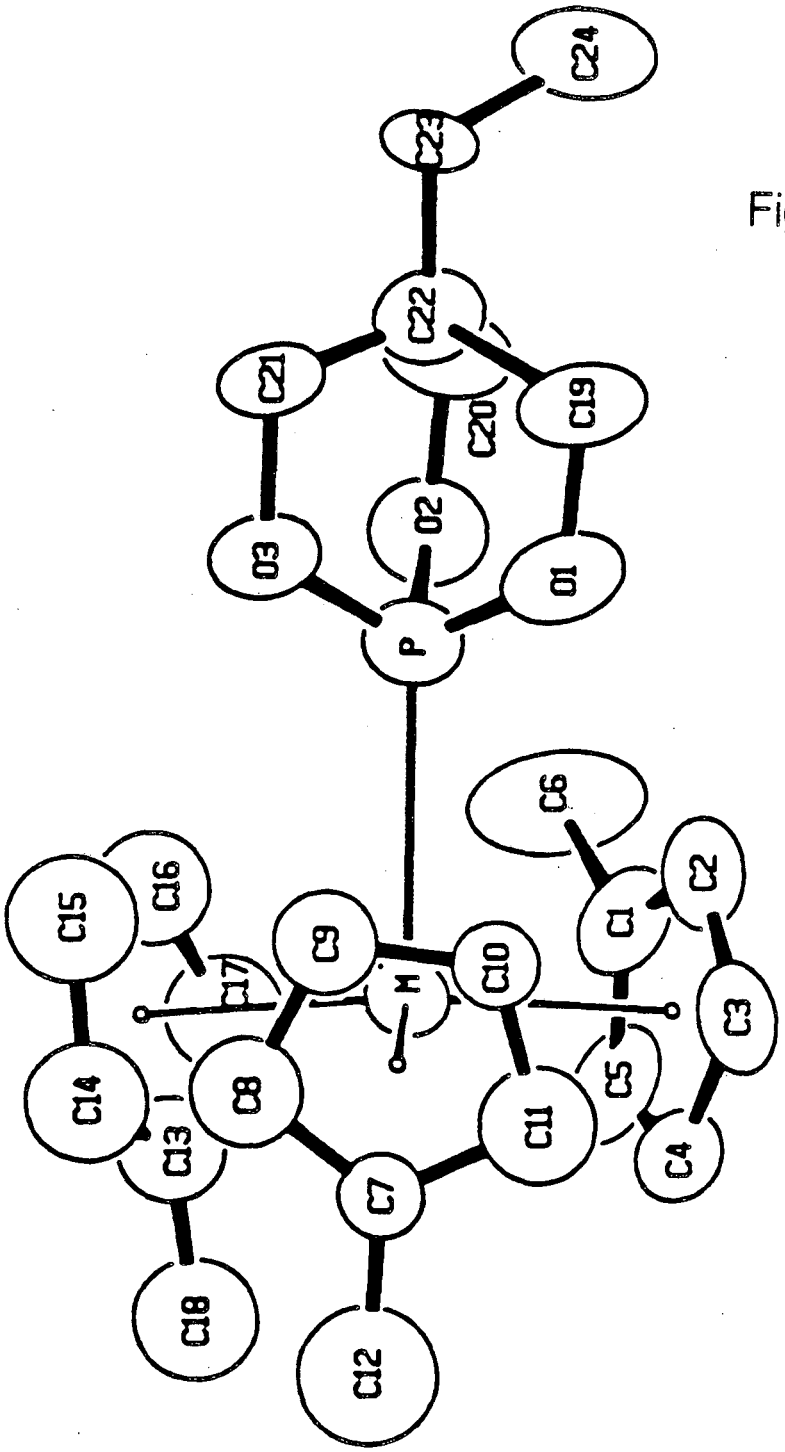


Figure 8

ORTEP Drawing of $(MeC_5H_4)_3U\text{-}P(OCH_2)_3CEt$

XBL 8512-4999

Table 3 Significant Distances in $(RC_5H_4)_3U$-L

$(MeC_5H_4)_3U$-L	U-L (A)	U-C avg.(A)	U-C range	Figure
$OPPh_3$	2.389(6)	2.82(4)	2.77-2.94	3
Py	2.63(2)	2.82(4)	2.75-2.93	4
	2.66(2)			
QUIN	2.764(4)	2.82(3)	2.78-2.88	5
SR_2	2.987(5)	2.81(4)	2.75-2.89	6
PMe_3	2.972(6)	2.79(6)	2.67-2.89	7
$P(OR)_3$	2.988(5)	2.80(6)	2.66-2.91	8
$(TMSCp)_3U$		2.78(4)	2.71-2.84	1
$(TMSCp)_3U$-CNEt	2.57(2)	2.81(3)		2

Table 4 Significant Angles in $(RC_5H_4)_3U$-L

U-L	X-U-Cp (°)	Avg.	Cp-U-Cp (°)	Avg.
$OPPh_3$	97.8, 99.3, 100.7	99.6	116.9, 117.4, 117.6	117.3
Py	99.4, 101.7, 103.2	101.4	115.9, 117.7, 117.7	117.7
	95.8, 100.5, 101.0	99.1	115.3, 118.0, 119.3	117.5
QUIN	100.9, 101.3, 101.4	101.2	115.7, 116.2, 117.0	116.3
SR_2	92.8, 95.4, 104.9	97.7	117.8, 118.4, 118.4	118.2
PMe_3	96.7, 109.7, 112.7	106.4	106.0, 109.8, 119.4	111.7
$P(OR)_3$	93.5, 95.5, 98.2	95.7	115.7, 120.6, 120.7	119.0
$TMSCp_3U$			118.0, 120.2, 120.9	119.7
$TMSCp_3U$-CNEt		97.0		118.5

Table 5 Structurally Characterized Uranium Phosphine Complexes

Compound	M-P(Å)	C.N.	M^+	Ref.
$(C_5Me_5)_2UH(DMPE)$	3.092(8), 3.211(8)	9	+3	41
$(Cp)_3U(DMPE)UCp_3$	3.008(7)	10	+3	Ch.1
$U(BH_4)_3(PEt_3)_2$	3.02	11	+3	42a
$U(BH_4)_3(Ph_2Ppy)_2$	3.162(1)	13	+3	42b
$U(BH_4)_3(DMPE)_2$	3.057(9), 3.139(9)	10	+3	42c
$U(BH_3CH_3)_3(DMPE)_2$	3.085(3), 3.174(3)	11	+3	42d
$U(OPh)_4(DMPE)_2$	3.014(6)	8	+4	1
$U(Bz)_3Me(DMPE)$	3.020(2), 3.010(2)	6	+4	42e
$U(BH_3Me)_4(DMPE)$	3.017(2), 3.029(2)	14	+4	Ch.1
$(MeC_5H_4)_3UPMe_3$	2.972(6)	10	+3	Ch.2

In the table, M^+ is the metal oxidation state, and C.N. is the coordination number.

From the table, it is clear that there is no consistent change in the metal-phosphine distance upon alteration of the metal oxidation state; the effect of local ligand-ligand repulsion is evident in the asymmetric geometries of some of the complexes with bidentate ligands. The 2.972(6)Å U-P distance in $(MeC_5H_4)_3U{\cdot}PMe_3$ is also significantly shorter than the 3.008(7)Å distance observed in $[(C_5H_5)_3U]_2(DMPE)$, contrary to what would be predicted from steric arguments, as the MeC_5H_4 complex is obviously far more congested (if distortion of the Cp-M-Cp angles from that expected for a base-free complex can be used as an indicator) than the DMPE compound. The average 2.79(6)Å U-C distance in $(MeC_5H_4)_3UPMe_3$ is identical to that found in $(C_5H_5)_3U{\cdot}thf$

and, as previously noted, is shorter than that predicted by summation of the ionic radii established for 10 coordinate U(III) and the Cp ligand. The U-C distance in $(MeC_5H_4)_3U{\cdot}PMe_3$ is larger by 0.02Å than in the $(C_5H_5)_3U(DMPE)U(C_5H_5)_3$ compound, opposite what would be predicted based on a comparison of U-P distances. Apparently methyl substituents on the Cp ring enhance M-P bonding relative to M-Cp bonding, resulting in a shorter U-P distance and longer U-C distance.

In contrast to the abundance of phosphine complexes in the literature, there are no phosphite complexes currently available with which to compare bond distances. In $(MeC_5H_4)_3U{\cdot}P(OCH_2)CEt_3$, the phosphorus atom is slightly (but significantly) further away from the uranium atom than in the phosphine complex. The origin of this increased bond distance must be electronic, as the phosphite ligand is sterically less demanding than the trimethylphosphine ligand, with calculated ligand cone angles[43] of 101(2)° and 118(4)° respectively. This is also reflected in the average Cp-M-Cp angles of 111° [PMe_3] and 117° [$P(OCH_2)CEt_3$]. The bond length difference in metal phosphine and phosphite complexes has been the subject of a number of crystallographic studies. Initially, the chromium complexes $Cr(CO)_5L$, L = PPh_3 and $P(OPh)_3$, were structurally characterized and the Cr-P distance in the phosphite complex was found to be shorter by 0.113Å[44]. The shorter distance was attributed to enhanced π-backbonding in the phosphite complex; this explanation was supported by an increase in the Cr-C bond distance in the carbonyl <u>trans</u> to the phosphite relative to the phosphine complex. However, in <u>trans</u>-$Pd(NCS)_2(PPh_3)_2$ vs. <u>trans</u>-$Pd(SCN)_2[P(OPh)_3]_2$, the Pd-P respective distances of 2.3404(9)Å

and 2.312(2)Å were attributed to a combination of steric and σ-donating properties, and π-backbonding was dismissed as unnecessary in describing the structural data[45]. More recently, an isostructural set of rhodium dimers, $Rh_2(O_2CCF_3)_4L_2$,[46] and $Rh_2(O_2CCH_3)_4L_2$, L= PPh_3 and $P(OPh)_3$, have been described[47]. In both cases, the phosphite complex was the shorter M-P bond, by 0.016 Å in the triflouroacetate complex, and 0.007Å in the acetate complex. Subsequent theoretical analyisis of the complex $Rh_2(O_2CH_3)_4(PH_3)_2$ found no evidence for significant M-P π-interaction.[48]

Unfortunately, no structural data have been reported concerning the relative M-P distances in phosphite vs. bicyclicphosphite transition metal complexes. The gas phase proton affinity of $P(OMe)_3$ is 17.5 kcal/mol[49] more exothermic than the PA of $P(OCH_2)_3CCH_3$; this has been attributed to a combination of the lower ionization potential of the acyclic phosphite (Δ I.P.= 20kcal/mol) and a stereoelectronic effect the oxygen lone pairs have in stabilizing the $P\text{-}H^+$ bond[50]. While $P(OMe)_3$ is less of a σ-base, it is considered a stronger π-acceptor than trialkylphosphines[51]. Thus it is impossible to make a definitive statement about the possibility of π-backbonding in the uranium phosphine or phosphite complexes by comparison of the two U-P distances. The longer U-P distance in the uranium-bicyclic phosphite complex must be the result of a weaker M-P interaction, as the "covalent radius" of the phosphorus atom is smaller due to the presence of the electronegative oxygen atoms.

Detailed analysis of the thiophene complex $(MeC_5H_4)_3U{\cdot}SC_4H_8$ also suffers from a lack of comparable structures in the literature. There

exists only one other structurally characterized sulfur coordination complex of uranium, cis-dichloro-[meso-bis(trans-2-hydroxycyclohexyl) sulfide-OOS] dioxouranium (VI), a uranyl complex with a tridentate O-S-O coordinating ligand[13]. The U-S distances for the ten coordinate U(III) and the seven coordinate U(VI) complex, 2.987(5)Å, and 2.94(1)Å, are remarkably similar. Raymond's adaption of Pauling's structural definition of ionic bonding has recieved considerable attention for being able to predict, on the basis of coordination number and oxidation state, the bond distances in organoactinide compounds by simple addition of ionic radii. In this case, the ionic radius of U(III) is larger than U(VI) by 0.295Å, and the effect on the increase in coordination number from 7 to 10 would lead us to predict a U-S distance of 3.33 Å for the U(III) complex, 0.36Å larger than observed. The same invariance of bond distance with oxidation state has been noted in the analysis of uranium-phosphine complexes. The thiophene ligand is in an envelope configuration similar to that of $(C_5H_5)_3U\cdot thf$, the result of bonding one pair of electrons to the metal.

Phosphine oxides have been used to form stable coordination complexes of uranium for decades; the ability of these ligands to extract actinide ions from aqueous solutions has inspired numerous solution and crystallographic studies. In aqueous solution trimethylphosphine oxide was shown to be intermediate in donor strength between Cl and Br anion[52]. Triphenyl phosphine oxide is the only ligand for which there exists structural characterization of uranium complexes with $+4$[53], $+5$[54], and $+6$[55] metal oxidation states,

and the trivalent complex described here, $(MeC_5H_4)_3U\cdot OPPh_3$, completes the set, allowing a broader examination of the effect of oxidation state on the M-L bond length. Table 6 lists the important distances and angles found for some of the known $OPPh_3$ complexes, along with metal oxidation state and coordination number. Most of the complexes not listed are uranyl compounds with unexceptional geometries. The uranyl species $UO_2Cl_2(OPPh_3)_2$ contains trans $OPPh_3$ ligands as does $UBr_4(OPPh_3)_2$, whereas $UCl_4(OPPh_3)_2$ is a distorted octahedron with cis $OPPh_3$ groups. Uranium pentachloride is reported to form base complexes with a large variety of Lewis bases, but only $UCl_5(OPPh_3)$ has been structurally characterized, with the ligands in an octahedral geometry. In contrast, the $OPPh_3$ adduct of uranyl bisactetate is a dimeric compound with two bridging acetate groups, while the thioacetate analog is monomeric with the four sulfur atoms and $OPPh_3$ ligand in the equatorial positions.

Table 6 Selected Uranium $OPPh_3$ Coordination Complexes

Compound	M^+	C.N.	U-O (Å)	U-O-P (°)	Ref.
$U(MeC_5H_4)_3OPR_3$	+3	10	2.39	163	Ch.2
$UCl_4(OPR_3)_2$	+4	6	2.242	165.1	53a
$UBr_4(OPR_3)_2$	+4	6	2.21, 2.24(3)	160, 168(1)	53b
UCl_5OPR_3	+5	6	2.10	164	54
$UO_2Cl_2(OPR_3)_2$	+6	6	2.300	159	55a
$[UO_2AcAc_2OPR_3]_2$	+6	7	2.37	143	55b
$UO_2(SacSac)_2OPR_3$	+6	7	2.30	159	55c

Only the uranyl acetate dimer contains a U-O-P angle less than 159°. As can be readily seen, there is again no obvious trend in the observed bond distances with oxidation state; of the six coordinate U(IV), (V), and (VI) complexes, the U(V)-O distance is shortest, followed by U(IV), and U(VI). A trend based only on oxidation state predicts U(VI) < U(V) < U(IV). If the U(III) complex bond length could legitimately be adjusted to the distance predicted for a six coordinate molecule, the new bond length, 2.29 Å, would be comparable to the U(IV) and U(VI) distances.

Structural data on nitrogen donor complexes of the actinide elements is also limited, and by far, most data relates to pyridine complexes (Table 7). There exists one report of an asymmetric bidentate ligand complexe with both pyridine and phosphine functionalities, $U(BH_4)_3(o\text{-}Ph_2P\text{-}C_6H_4N)_2$, a complex similar in ligand environment to the bis-DMPE complexes. Comparison of U-N distances is

Table 7 Pyridine Complexes of Uranium (III) and (VI)

Compound	U-N(Å)	C.N	O.S	Ref.
$(MeC_5H_4)_3UNC_5H_4NMe_2$	2.64(2)	10	+3	Ch.2
$U(BH_4)_3(Ph_2P\text{-}C_6H_4N)_2$	2.659(4)	13	+3	42b
$UO_2(tropolonate)_2py$	2.61(1)	7	+6	56a
$UO_2(AcAc)_2py$	2.47(1)	7	+6	56b

reasonable with this complex, as the pyridine ligand is in the less sterically hindered site (as judged by the U-P distances in the isomorphous DMPE complexes). The U-N distance, 2.659(4)Å, is

identical within experimental error to that in $(MeC_5H_4)_3U{\cdot}NC_5H_4NMe_2$. Pyridine complexes of uranyl ions have also been examined. A striking difference in U-N distances reported for complexes of the type $UO_2L_2(py)$ is observed, as listed in Table 7. The structure of bis(pentane-2,4-dionate)pyridineuranium is particuliarly interesting, as the exceedingly short U-N distance (2.47(1)Å) is achieved at the expense of a relatively non-linear O-U-O geometry (173.5(8)°).

There are no known monodentate tertiary amine complexes of the trivalent actinide ions though the thorium complex $ThCl_4(NEt_3)_3$ has been crystallographically examined. This compound[57] has three inequivalent Th-N distances of 2.79(3), 2.83(3) and 2.66(3)Å, again demonstrating the sensitivity of bond distances to steric interactions. Corresponding data on monodentate tertiary amine complexes of uranium do not exist, but the observed 2.764(4)Å U-N bond distance in $(MeC_5H_4)_3U{\cdot}N(C_2H_4)_3CH$ is similar to the M-L distance in the thorium complex. Two bidentate trialkylamine complexes of uranium have been examined; in $UCl_4(TMEDA)_2$, the U-N distances range from 2.78(1) to 2.83(1)Å[2], while in $(MeBH_3)_4U(TMEDA)$, U-N = 2.72(1) and 2.74(1)Å[3]. Surprisingly, the tetravalent compound with the larger coordination number (13 vs. 8) contains the shorter U-N bond.

The quinuclidine complex is the least labile of all the U(III) base complexes studied thus far. The reason is unclear, though steric arguments are convincing. The complex contains an extremely short methyl-methyl contact (3.47Å) between C14-C18' (Figure 5) in the solid state. If the predominant mechanism for rapid (on an NMR timescale) site exchange in these complexes is associative, as has been

determined in the site exchange process in $(C_5H_5)_3U\cdot DMPM$, then the increased steric demands of the quinuclidine ligand may be inhibiting or effectively eliminating this mechanistic possibility, rendering ligand dissociation kinetically competetive.

Relative Basicity

Over the years, there have been numerous attempts to develop theoretical or empirical models to predict the enthalpy of formation of coordination complexes or explain observed trends in relative ligand basicity toward a metal ion[58]. To date, there is no model that predicts the preference of trivalent uranium for phosphine or phosphite ligands relative to oxygen or nitrogen donors. Very little is known about the relative stability of uranium complexes with coordinating ligands. The overwhelming abundance of nitrogen and oxygen donor ligand complexes described over the past 50 years leads to the conclusion that these must be the most stable ligand complexes, and thus M-O and M-N bonds are thermodynamically preferred. A relative basicity series of such 'hard' ligands in aqueous solution was established, and trimethylarsine oxide was found to displace most ligands, including negatively charged chloride and bromide ions. In non coordinating solvents, studies of the relative basicity of oxygen and nitrogen donor ligands toward uranyl bis(hexaflouroacetylacetonate) indicate that the uranyl ion behaves as a model Lewis acid[59]; the relative affinity series was found to correlate well with the Gutmans donor number[60], a quantity derived

from the enthalpy of formation of Lewis bases and the Lewis acid $SbCl_5$.

Less is known about the coordinative affinity of ligands commonly encountered in synthetic organometallic chemistry. A pioneering study of the formation constants of Lewis bases with $(C_5H_5)_3Yb$ was recently published, with suprising results. By using standard optical spectroscopy, the order of relative basicity was shown to be pyrrolidine $\geq PEt_3 >$ tht, thf, with no evidence for the formation of a bis-ligand adduct in benzene solution[4]. The observation that a tertiary phosphine will displace thf or rival a secondary amine would not have been predicted judging by the constant reference to lanthanide and actinide ions as 'hard' ions preferring 'hard' bases[61]. The observed formation constants, while not accurate enough to unequivocally establish a basicity order, were substantiated by sequentially displacing the weaker bases in the order $O<S<P\leq N$. Unfortunately, optical spectroscopy of actinide ions is less straightforward than that of the lanthanides. For this reason, NMR spectroscopy was used to obtain relative basicity data with trivalent uranium as the reference acid.

The simplest equilibrium to measure is the displacement of one monodentate ligand by another, as in reaction 3

3 $$L_3U{\leftarrow}A + :B \longleftrightarrow L_3U{\leftarrow}B + :A$$

The equilibrium constant is defined as

$$K_{eq} = \frac{[U\text{-}A][B]}{[U\text{-}B][A]}$$

There are a number of structurally characterized trigonal bipyramidal Cp_3ML_2 complexes reported, in most cases one of the L ligands is anionic. In measuring the above equilibrium, it was first necessary to insure that neither of the individual coordinating ligands involved in the competition was capable of forming a bis ligand complex to any measurable extent. This was accomplished by first recording the ^1H NMR spectrum of the paramagnetic compound at a set concentration as a function of temperature. Examination of a second sample of the compound at identical concentrations, but with additional ligand present in the solution, results in one of two observations. Either the chemical shift of the Cp ligand resonances remained unchanged from the initial measurement, indicating that only one base coordinates to the metal at any one time, or a shift difference is observed, indicating the presence of additional species in solution. Upon coordination of a second base, the Cp-Metal-Cp angles should approach those expected for a base-free complex (120°), and this geometric perturbation has a noticeable effect on the observed chemical shifts[62]. To date only sterically unencumbered ligands such as $O{=}PR_3$, RCN, and RNC have displayed this complicated type of behavior. For all other ligands, OR_2, SR_2, PR_3, and NR_3, addition of excess ligand caused no observable shift in the Cp resonance. Further, in these latter cases, the observed chemical shift of the coordinating species

was the arithmetic sum of the relative concentrations of the coordinated and free ligands in solution multiplied by their individual chemical shifts, i.e.,

$$\delta_{obs}=(\chi_1 \text{ free base})x\delta_{f.b.} + (\chi_2 \text{ complexed base})x\ \delta_{c.b.}/\text{total base}$$

where f.b. is free base and c.b. is coordinated base. As an example, upon additon of six A to a solution of one U-A the observed chemical shift of A should be given by

$$\delta A_{obs} = [6(\delta_A) + 1(\delta_{U-A})]/7$$

Once the behavior of the individual ligands was established, the competition could be examined. Ligand exchange is exceedingly facile in these systems (the rate of exchange between free and coordinating species is usually $>10^3$/sec), so determining whether the experiment should be U-A + B or U-B + A was simply a matter of deciding which base would be most easily manipulated in a drybox. For example, if one desired to study the competition between $P(Me)_3$ (P) and $N(CH_2CH_2)_3CH$ (N), the easiest way would be to add N (solid, easy to weigh) to a sample of U-P. Addition of P to U-N achieves the same result, but measuring quantities of $P(Me)_3$ (liquid, b.p. 33°C) in a glovebox (30°C) also generates a box filled with trimethylphosphine vapors.

The experiments have thus far has been done in the nonpolar, non hydrogen bonding solvent toluene; solvent effects could prove

interesting, but non coordinating alternatives with high dielectric constants were not readily available (U(III) reacts with chlorinated hydrocarbons).

It has been suggested that a consistent set of electron donors be used in studying the acidity characteristics of a given system[63]. Unfortunately, the study here is limited by the ability to isolate a given complex. A summary of equilibrium constant measurements for the reaction $(MeC_5H_4)_3U\text{-}L + L' \longleftrightarrow (MeC_5H_4)_3U\text{-}L' + L$ is given in Table 8.

Table 8 K_{eq} Values for the Reaction

$(MeC_5H_4)_3U\text{-}L + L' \longleftrightarrow (MeC_5H_4)_3U\text{-}L'$

L	L'	K_{eq}(ca. -50°C)
py	PMe_3	180
p-$Me_2NC_5H_4N$	PMe_3	5.0
quinuclidine	py	130
thf	tht	3.0
quinuclidine	thf	2.4
$P(OMe)_3$	PEt_3	20

It can be seen that for $(MeC_5H_4)_3U$, coordination of the trimethylphosphine ligand is thermodynamically favored in solution, quantitatively displacing pyridine. Pyridine quantitatively displaces thf or quin, and the oxygen, sulfur, and tertiary amine donor ligands were found to be roughly equivalent. The triethylphosphine complex was found to be more stable than the trimethylphosphite complex.

These results roughly parallel the observed formation constants reported for $(C_5H_5)_3Yb + L$[4], as listed in Table 9

Table 9 Formation constatants for $(C_5H_5)_3Yb + L$

Ligand	log K_f
pyrolidine (HNR_2)	5.0(4)
PEt_3	4.9(5)
tetrahydrothiophene	3.6(2)
thf	3.4(2)
$P(C_6H_5)_3$	<2
NEt_3	0

The most noticeable difference is found in the relative order of the phosphine and amine basicities, but changes in the steric requirements of the phosphine and amine ligands used account for the differences. The sterically encumbering tertiary amine in the uranium system may be less competitive relative to the secondary amine used in the Yb study due to the presence of the additional alkyl group. When triethyl amine is used, there is no measurable coordination to the Yb complex; this was attributed to an increase in ligand-coordination sphere repulsive forces, and underscores the sensitivity of equilibrium constant measurements to interligand repulsions. In the structures of $(MeC_5H_4)_3U{\cdot}L$, L = PMe_3 and SC_4H_8, the substitution of one lone pair on the coordinating atom with a demanding alkyl group severely distorts the geometry about the metal, presumably to relieve interligand repulsions. Of all the $(MeC_5H_4)_3U$-L complexes studied

thus far, the quin complex was unique in that, upon addition of excess L to a solution of U-L, the NMR spectrum of the quin complex contained resonances due to both free and coordinated ligand. This relatively slow site exchange has been attributed to the inability of a second quin ligand to displace the coordinated ligand via an associative pathway, implying that, as in the Yb complex, the relative influence of steric demands of the coordinating ligand is greater in the case of the tertiary amine complex.

The relative basicity series established here can be compared with basicitiy trends measured for the acids H^+, $AlMe_3$, or BMe_3. Table 10 lists the gas phase enthalpies of formation for these acids with a number of bases:

Table 10 ΔH_f for Acid + L ——> Acid-L

H^+		$AlMe_3$		BMe_3	
L	$-\Delta H^{64}$	L	$-\Delta H^{65}$	L	$-\Delta H^{65}$
quin	228.7	PMe_3	22.1	$EtNH_2$	18.0
PMe_3	223.5	NMe_3	19.8	py	17.0
py	218.1	py	17.4	PMe_3	16.5
$P(OR)_3$	208.0	thf	12.7	$P(OR)_3$	14.4
SEt_2	202.6	SEt_2	6.5		
thf	196.4				

If the quinuclidine complex of uranium is excluded due to possiblity of overwhelming steric problems, then the trend in equilibrium constants for uranium most closely resembles that of the

proton in the gas phase; for example, in the aluminum series, thf will displace tht, and in the boron compounds, B-pyridine has a larger ΔH_f than B-trimethylphosphine. There are a number of complications that preclude an absolute comparison of relative basicities; the inability to consistently separate the relative entropic and enthalpic contributions make the evaluation of steric effects qualitative at best, and the differences in interaction between solvent and either the uranium complexes or the free bases is assumed to be neglegible, whereas the H^+, $AlMe_3$ and BMe_3 measurements were done in the gas phase. Drago has stated that the comparison of metal acidity trends with ligand proton affinities to evaluate trends or characteristics of the acid are difficult, as the proton appears chemically different from most other acids[63]. From the development of a three parameter equation to describe the relative contributions of bonding schemes to an enthalpy of adduct formation, it was inferred that the proton-Lewis base complex gains considerable stability from transfer of electron density from the base to the proton, in addition to the usual electrostatic and covalent contributions that constitute a bond, making it a poor model of donor basicity trends.

The observation that PMe_3 will quantitatively displace all other bases studied thus far was suprising, as up until 1981, phosphine complexes of the actinide elements were thought to be too unstable to rigorously characterize. In the solid state, the primary coordination sphere of the phosphine complex appears to be the most sterically crowded, with the largest distortion in Cp-M-Cp angles from the base free complex; it was therefore suprising that the U-P distance is the

shortest yet observed. One possible explanation for the relative stability of the phosphine complex was that in increasing the distance from the metal to the coordinating atom, the alkyl groups of the ligand are also removed from the inner coordination sphere, and perhaps this decrease in secondary ligand-ligand repulsion contributed significantly to the driving force of the reaction. This hypothesis was tested by increasing the size of the Cp ligand, and again studying the relative affinity of the phosphine and pyridine ligands for the uranium center. Substitution of Me_3Si for Me on the Cp group yielded coordination complexes so congested that exchange between both free and coordinated pyridine or PMe_3 is now slow on an NMR timescale (a decrease in site exchange rate of at least 10^3/sec), and thus at -50°C, integration of the ^1H NMR spectrum yields an

$$K_{eq} = \frac{[(Me_3SiC_5H_4)_3U\text{-}P][py]}{[(Me_3SiC_5H_4)_3U\text{-}py][P]} = 0.1$$

equilibrium constant substantially shifted toward formation of the pyridine adduct, with $K_{eq} = 0.1$. This was as expected; coordination of the sterically less demanding ligand is relatively enhanced when the coordination sphere of the metal becomes too congested. To further explore this effect (or, using three points to define a straight line), the experiment was repeated with $(C_5H_5)_3U$ as the reference acid. Here, it seemed logical to expect an increase in the relative

affinity of the PMe_3 ligand, but instead, the equilibrium constant decreased to 80.

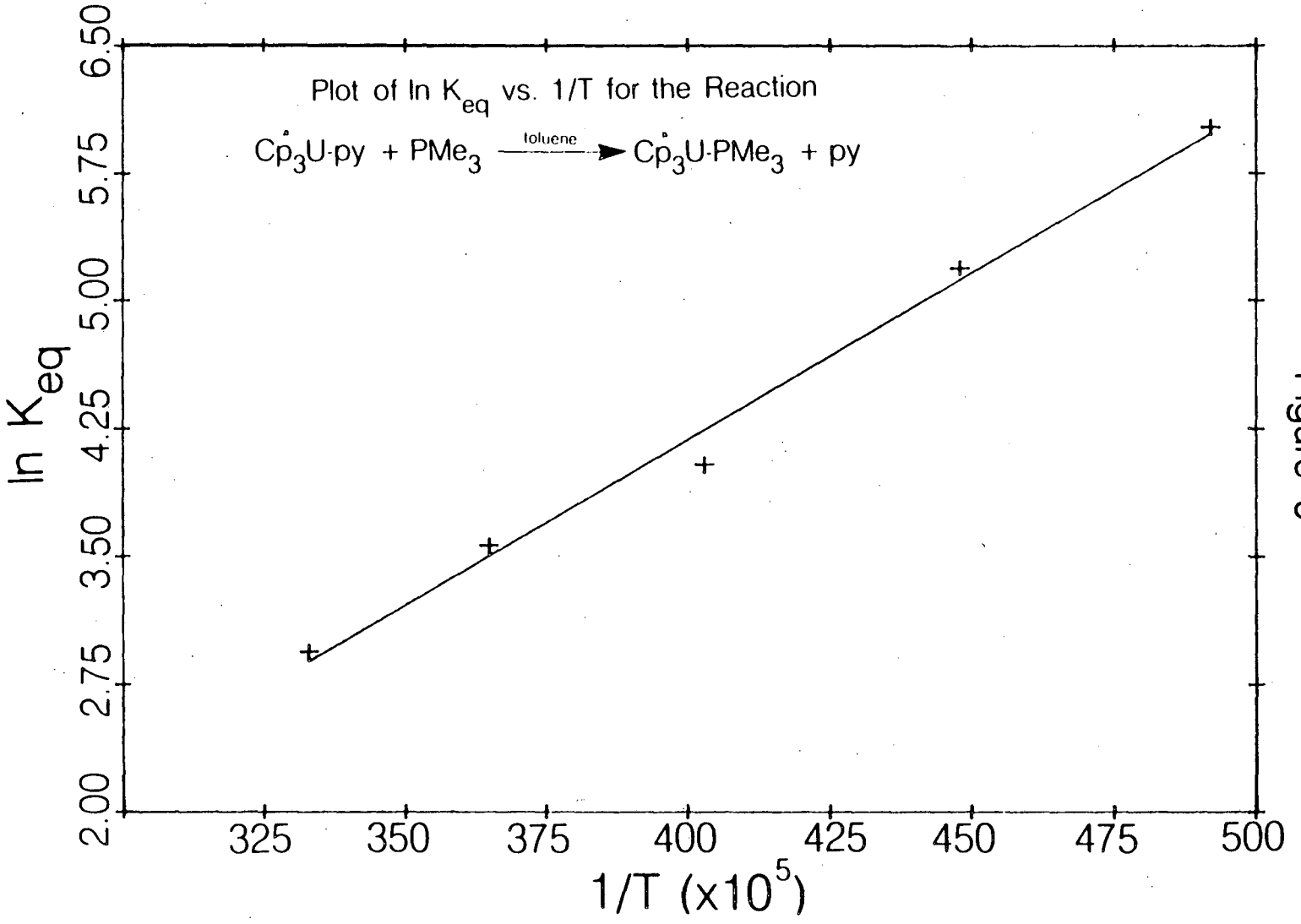
$$K_{eq} = \frac{[U\text{-}P][py]}{[U\text{-}py][P]}$$

$(CH_3C_5H_4)_3U$	$K_{eq} = 180$	$\Delta G = -2.3$ kcal/mol
$(C_5H_5)_3U$	$K_{eq} = 80$	$\Delta G = -1.9$ kcal/mol
$(Me_3SiC_5H_4)_3U$	$K_{eq} = 0.1$	$\Delta G = -1.0$ kcal/mol

Clearly, the assumption that steric influences were predominant was incorrect, and the equilibria must be examined in greater detail to determine the effect of electronic perturbations. A variable temperature analysis of the MeC_5H_4 and Cp complexes was performed; in the $Me_3SiC_5H_4$ experiment, the ligands are broadened into the baseline from -30°C to +25°C due to an intermediate rate of ligand site exchange and thus an accurate temperature dependence of K_{eq} was impossible to obtain by ^1H NMR spectroscopy. Plotting ln K vs. 1/T yields a straight line (Figure 9 is a plot of the MeC_5H_4 values) in both cases, with slope $-\Delta H/R$ and intercept $\Delta S/R$. From the enthalpy and entropy differences (listed below) the trend in

$(MeC_5H_4)_3U$	$\Delta H = -3.9(2)$ kcal/mol	$\Delta S = -7.2(8)$ eu
$(C_5H_5)_3U$	$\Delta H = -2.6(2)$ kcal/mol	$\Delta S = -2.8(8)$ eu

K_{eq} can be understood. In the C_5H_5 complex, coordination of the PMe_3 ligand results in loss of entropy, as expected for formation of more sterically saturated coordination complex. The driving force of the reaction is the negative enthalpy of the reaction. Upon switching to



XBL 8512-4947

Figure 9

the MeC_5H_4 ligand, again entropy is lost upon coordination of PMe_3, with the magnitude of the entropy loss reflecting the increased steric demands of the Me substituent. The surprising driving force of this reaction, overwhelming the loss of entropy, is the large increase in $-\Delta H$; apparently an increase in the electron donating ability of the metal coordination sphere preferentially enhances the interaction between the metal and the ligand that, in transition metal chemistry, is considered strongly capable of acting as a π-accepting ligand[66]. Of course, substitution of a Me group on the Cp ligand could be preferentially decreasing the strength of the U-N bond, and until absolute enthalpies are obtained from formation constant measurements it is impossible to distinguish which is occuring. However, additional support for the claim that U(III) is acting as an electron donor is obtained from a study of isostructural cerium complexes[21]. In the competition between PMe_3 and pyridine for $(MeC_5H_4)_3Ce$, K_{eq} was found to be significantly lower than that in the uranium system (Table 11). The entropy term behaves as expected; the slightly larger

Table 11 $\quad M\text{-}Py + PMe_3 \longrightarrow M\text{-}PMe_3 + py$

	$(MeC_5H_4)_3Ce$	$(MeC_5H_4)_3U$
ΔG(kcal/mol)	-0.5(1)	-2.3(2)
ΔH(kcal/mol)	-1.8(1)	-3.9(2)
ΔS(e.u.)	-4.0(2)	-7.2(8)

(ca. 0.03Å) radius of the Ce(III) ion in this system permits coordination of the larger base with measurably less loss of entropy. It is again the ΔH term driving the coordination of phosphine to uranium. Given the small alteration of metal size, one would predict on electrostatic arguments that the two metals would behave similarly; clearly there is an additional source of bonding stabilization available to the actinide ion. It is tempting to postulate that the relative increase in ΔH of the uranium phosphine complex is due to the contribution of π-bonding.

The ΔH values thus far obtained are consistently reflected in the observed change in M-L bond lengths. An increased $-\Delta H$ in the PMe_3 complex relative to pyridine in Cp_3U vs. $(MeC_5H_4)_3U$ is consistent with the observed M-P distances in $(MeC_5H_4)_3U \cdot PMe_3$ (2.972(6)Å) and $[(C_5H_5)_3U]_2DMPE$ (≈3.008(7)Å), where the shorter (stronger) M-P bond is found in the more sterically congested complex. This effect was previously discussed in comparison of the uranium and praseodymium isocyanide complexes, where the relative shortening of the U-L bond was attributed to an increase in bond strength, and π-backbonding was invoked to explain the lowered CN stretch in the IR spectrum. To further explore the possible effect of ligand π-acceptance on M-L bond lengths, Stults and Zalkin have structurally characterized a series of $(MeC_5H_4)_3Ce \cdot L$ compounds. Table 12 gives a list of M-C and M-L distances in known $Cp_3M \cdot L$ complexes, from which the effects of the nature of the metal-ligand bond upon the observed bond distance is illuminated. The parameter Δ has been defined as [(U-C)-(U-L)] - [(M-C)-(M-L)] and can be interpreted as a measure of the ability of ionic

radii summation to predict observed bond lengths. For ionic compounds where radius summation arguments appear valid, each set of metal values deletes the contribution of the metal radius to the bond lengths. The Cp and ligand radii will remain constant in a purely ionic model, resulting in a cancellation of the two sets of values, with Δ approaching zero. A positive value indicates a shortening of the uranium ligand distance relative to the lanthanide

Table 12 The Effect of U→L π-Donation on U-L Bondlength

Compound	M-C(Å)	M-L(Å)	Δ[1]	Ref.
$(C_5H_5)_3La\cdot thf$	2.82(4)	2.57(1)	-0.01	68a
$(C_5H_5)_3Pr\cdot thf$	2.80(2)	2.56(1)	0.00	68b
$(C_5H_5)_3Nd\cdot thf$	2.78(2)	2.54(1)	0.00	68b
$(C_5H_5)_3Gd\cdot thf$	2.74(3)	2.494(7)	-0.01	68c
$(C_5H_5)_3Y\cdot thf$	2.71(3)	2.451(4)	-0.02	68a
$(C_5H_5)_3Lu$ thf	2.69(4)	2.39(2)	-0.06	68d
$(C_5H_5)_3U\cdot thf$	2.79(3)	2.55(1)		68e
$(MeC_5H_4)_3Ce\cdot quin$	2.85(3)	2.786(4)	0.00	21
$(MeC_5H_4)_3U\cdot quin$	2.82(3)	2.764(4)		Ch.2
$(MeC_5H_4)_3Ce\cdot PMe_3$	2.82(3)	3.074(6)	**+0.07**	68f
$(MeC_5H_4)_3U\cdot PMe_3$	2.79(3)	2.972(6)		Ch.2
$(MeC_5H_4)_3Ce\cdot P(OCH_2)_3CEt$	2.82(3)	3.093(3)	**+0.09**	21
$(MeC_5H_4)_3U\cdot P(OCH_2)_3CEt$	2.80(5)	2.988(6)		Ch.2
$(C_5H_5)_3Pr\cdot CNC_6H_{11}$	2.78(2)	2.65(1)	**+0.11**	29
$(Me_3SiC_5H_4)_3U\cdot CNEt$	2.81(3)	2.57(2)		Ch.2

[1] $\Delta=[(U-C)-(U-L)]-[(M-C)-(M-L)]$

ligand distance. In the six known isostructural $(C_5H_5)_3M\cdot thf$ complexes, the observed M-O and M-C distance appears to be a simple function of the metal radius for the first half of the lanthanide series, with equivalent changes in M-C and M-L observed upon substitution of uranium for the lanthanides, and Δ approaches zero. This is also found for the quinuclidine complexes of Ce and U. As the smaller Y and Lu are substituted, there is a distinct change in Δ to negative values; without an accompanying study of relative metal acidity, attributing the reason for this change to either steric or electronic forces would be premature. The increased melting points across the lanthanide series cannot be used as a measure of complex stability; in the isostructural $(Me_3SiC_5H_4)_3U\cdot L$ (L=EtCN, EtNC) the thermodynamically prefered (K_{eq}= 180) isocyanide complex melts at a lower temperature. It is clear that when the metal ions are roughly the same size, Δ approaches zero. In contrast, when the ligand is capable of acting as a π-acceptor as well as a σ-donor, as in the phosphine, phosphite and isocyanide complexes, one observes a consistent decrease in the U-L distance relative to the Ce-L distance, $\Delta<0$. The isocyanide comparison is legitimate in spite of the difference in Cp ligands, as substitution of H by the electron donating Me_3Si group would be expected to increase the U-C distance from both steric and electronic arguments. The relative basicity measurements, supported with the IR data on the CO and CNR complexes of uranium, leave little doubt that U·L π-bonding is a useful postulate for the source of the decrease in U-L bond lengths.

This is not to say that π-bonding is the only effect in the ligand displacement series of U(III). The relative σ and π contributions have yet to be explored in a quantitative sense, but a rough estimate can be obtained by considering the stabilities of the various complexes. The substantial reduction in the CO stretching frequency upon coordination to $(RC_5H_4)_3U$ is unequivocal evidence for π-bonding in Cp_3U compounds, yet CO immediately dissociates upon exposure to less than an atmosphere of pure CO, whereas all other adducts are stable until heated under vacuum. In addition, susceptibility measurements indicated that the metal electronic levels were similar regardless of whether the ligand was a pure σ-donor or also a π-acceptor.

The effect of ligand-ligand repulsion on relative basicity can also be assessed by comparing K_{eq} values and the effect of Cp substituent on metal or Cp ionization energies. Both methyl and trimethylsilyl have been shown to donate electron density to the metal, having roughly the same effect on the f-orbital ionization potentials relative to the analogous unsubstituted compound. Thus, the drastic 10^3 decrease in relative metal affinity for PMe_3 vs. Py in the TMSCp complex can be entirely attributed to repulsion between the donor ligand and the Cp groups. The contribution of the entropy term in the pyridine vs. PMe_3 competitions range from 0.7 to 2.3 kcal/mol at room temperature. If the 10-14 kcal/mol barriers to site exchange in uranium phosphine adducts are an accurate estimation of the strength of the U-P bond, then this entropy term represents a substantial contribution to the overall complex stability.

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CHAPTER THREE: Reactivity of U(III) as a One or Two Electron Reducing Agent

Metal-ligand bonding in organoactinide chemistry is most accurately described as ionic; ligands are fluctional, bonding is nondirectional, with maximization of coordinative saturation, and there exist well-defined metal oxidation states with little question as to the location or definition of the localization of valence electrons. This contrasts with transition metal compounds, which are usually nonfluctional and 4-6 coordinate, with oxidation states that are a less accurate description of the electronic nature of the metal. There is rarely an example of a physical study producing unambiguous spectroscopic evidence for the effects of covalency in f-metal systems; certainly a pioneering effort in this regard is the correct interpretation of the uranocene photoelectron spectrum[1], where the effect of f-orbital participitation in bonding with the COT ligand accounts for the observed shift in energy levels of $U(COT)_2$ relative to $Th(COT)_2$. Discussion of the structural ramifications of ionicity in these compounds focused on a narrow selection of available data concerning anionic Cp or COT ligands, with the conclusion that bond distances can be predicted from the summation of metal and ligand ionic radii[2]. As mentioned in Chapter two, bond lengths in uranium-Lewis base complexes do not follow a predictable pattern that can be accounted for by simple electrostatic bonding models considering only the coordination number and oxidation state of the metal. It is not entirely fair to dismiss this model on data pertaining to neutral

ligand complexes, as these ligand-metal distances would be particuliarly susceptible to interligand repulsive interactions.

During the 1970's, a number of structural studies of Cp_3UX compounds revealed what was interpreted as a consistent M-C (Cp) distance, ranging from 2.68 to 2.74 , and averaging 2.71Å. Shannon's tabulation of 'ionic radii', obtained from the observed distances in metal flouride and oxide structures, predicts that an increase in M-C distance of 0.14Å should accompany a change in oxidation state from U(III) to U(IV), given identical coordination numbers[3]. The structural characterization of $(C_5H_5)_3U$-thf in 1981 contained the first evidence that the bond distance/metal oxidation state relationship may not behave quite as predicted in organoactinide systems[4]. The U-C distances average to 2.80Å, which is only 0.08Å longer than the average U(IV) distances, an increase of only 60% of the predicted value. The successive characterization of $Cp_3U(DMPE)UCp_3$, $(Me_3SiC_5H_4)_3U$, and the $(C_5H_4)_3U$-L compounds discussed in Chapters 1 and 2, provided additional examples of U(III) compounds, all having roughly the same M-C distance found in the thf complex. It thus became interesting to isolate and structurally characterize a $Cp_3U(V)$ complex to measure the effect that further change in oxidation state would have on the M-C distance.

Pentavalent organouranium complexes were not expected to possess great thermal stability; in Chapter one, the facile reductive decompostion of U(IV) alkyls was discussed, along with the numerous examples where the Cp anion acted as a reducing agent toward U(IV) halides. The only known U(V) organometallic compounds in the

literature were the salts $Li_3UR_8 \cdot 3$dioxane (R= Me, CH_2CMe_3, CH_2SiMe_3), characterized by hydrolysis experiments, IR and ^1H NMR spectroscopy[5]. Possible synthetic routes to $Cp_3U(V)$ complexes employ readily available, thermodynamically stable U(III) or U(IV) starting materials. Unfortunately, the chemistry of Cp_3UX has thus far been dominated by substitution of Y for X, although recently the reaction chemistry of the M-alkyl σ-bond has been the subject of a number of investigations[6]. The large metal coordination number in these compounds renders the metal center kinetically inert, a handicap in attempting to isolate what is expected to be an unstable complex. The use of trivalent starting materials is more satisfactory in this respect; ligand dissociation is facile in Cp_3U-L complexes, effectively rendering the metal coordinatively unsaturated. Selection of the proper substrate could induce U(III) to act as a two electron reducing agent, forming a kinetically inert U(V) compound.

Correctly predicting the products of the first reactions would have been fortuitous; there is scant information available concerning the reactivity of trivalent uranium as a reducing agent towards organic substrates. Not only is there a question of control of the oxidation, but ligand redistribution processes must also be considered in anticipitating a reaction outcome. In one of the first conscious reductions of an organic substrate by U(III) (Reaction 1), $(C_5Me_5)_2UCl$ was allowed to react with diphenylacetylene[7]; the expected reductive coupling of the acetylene was observed, but the final reaction product contained a mixture of redistribution products. A similar reaction with the cyclic ketone $OC(CPh)_4$ (Reaction 2) did not couple the

1 $(C_5Me_5)_2UCl + PhCCPh \longrightarrow (C_5Me_5)_2UC_4(Ph)_4 + (C_5Me_5)_2UCl_2$

2 $(C_5Me_5)_2UCl + O{=}C(CPh)_4 \longrightarrow (C_5Me_5)_2\eta^2\text{-}OC(CPh)_4 + (C_5Me_5)_2UCl_2$

radical anion formed upon initial reduction[8], instead the reaction yields a 50% mixture of $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2U\text{-}\eta^2\text{-}OCPh_2$. In the first attempted synthesis of a $Cp_3U(V)$ complex, phenyl isocyanate (PhN=C=O) was allowed to react with $(MeC_5H_4)_3U$. The anticipated reaction was abstraction of O to form the U(v)oxo compound concomitantly eliminating phenylisocyanide, similar to transition metal abstraction of sulfur from alkylisothiocyanates[9]. This reaction did not yield the expected product, but did lead to a diverse U(III) reaction chemistry.

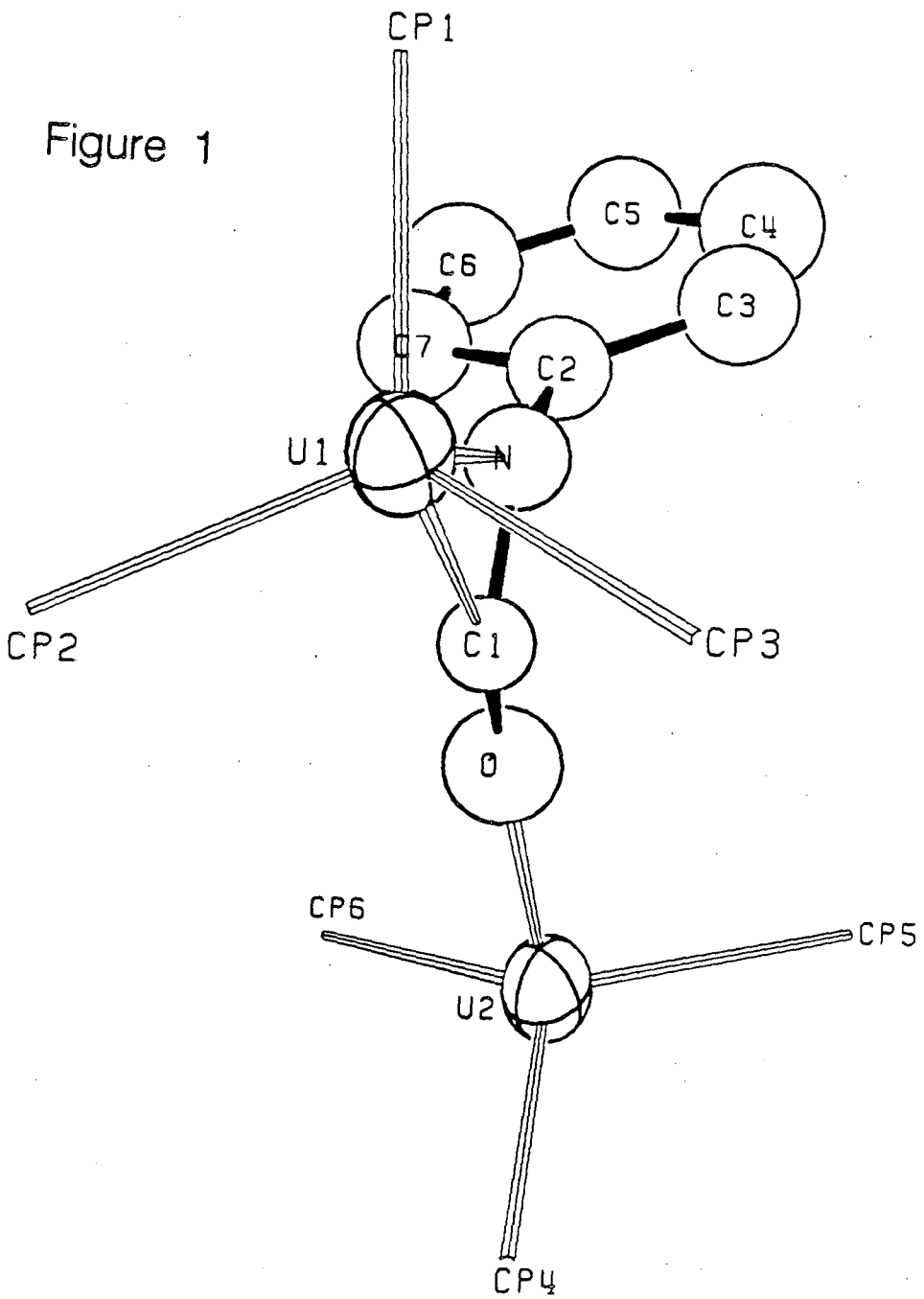
Redox Chemistry

Addition of PhNCO (one molar equivalent) to a green ether solution of $(MeC_5H_4)_3U\text{-py}$, resulted in an instantaneous color change to light red, and formation of a precipitate (the reaction is instantaneous at -80°C). The reaction product was insoluble in ether, and was crystallized from toluene. Two sets of Cp resonances (1:1 intensity) were observed in the ^1H NMR spectrum; addition of PhNCO to a sample of $(MeC_5H_4)_3U\text{-thf}$ in an NMR tube yielded a solution with an NMR spectrum identical to that of the isolated compound, proving this to be the sole reaction product. Elemental analysis was consistent with the formulation of 1 PhNCO : 2 $(MeC_5H_4)_3U$, and the NMR experiments indicated that phenylisocyanate was the nitrogen source. The relative chemical shifts of the two MeC_5H_4 groups were confusing.

One pattern (3:2:2) had shifts similar to those observed in other $(MeC_5H_4)_3UX$ compounds (X= Cl, C_4H_9), whereas the other set had chemical shifts in the region found for the trivalent complexes previously described. The observed linewidths (ca. 3-4 Hz) for both sets of signals were characteristic of U(IV) complexes, but a mixed valence dimeric compound with sufficiently proximate metal centers could also result in narrow linewidths for both $(MeC_5H_4)_3U$ resonances. No rational formulation could be deduced which contained $(MeC_5H_4)_3U(III)$, $(MeC_5H_4)_3U(IV)$, and a bridging PhNCO, thus the complex was examined crystallographically.

The structure (Figure 1) contains two $(MeC_5H_4)_3U$ groups, and a bridging n^1,n^2 PhNCO ligand, with the O atom coordinated to U(2) and the C and N atoms coordinated to U(1). Fischer has tabulated NMR chemical shift patterns of Cp_3UX compounds, observing that when X is flouride, alkoxide or dialkylamide, a substantial shift of Cp resonance to high field is observed; multidenticity of the X ligand produced the same effect, but to a significantly smaller degree[10]. Following Fisher's observation, the high field ^1H NMR resonances can be attributed to the Cp_3U-OR fragment. The bond distances and angles of the Cp_3UOR portion of the molecule are unexceptional; the U-O distance, 2.11(1)Å, is similar to the terminal uranium(IV) alkoxide distances reported for $[U(C_3H_5)_2(O\text{-}i\text{-}Pr)_2]_2$, 2.056(13)Å[11], $K[U_2(OCMe_3)_9]$, 2.13(1)Å[12], and $[(Me_5C_5)_2UOMe]_2PH$, 2.05(1)Å[13]. The nearly linear U-O-C angle, 164(1)°, is slowly being recognized as a consistent solid state feature of uranium alkoxides, possibly resulting from O→U π-donation, which will be discussed later. The

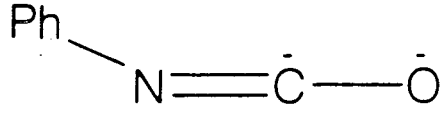
Figure 1



ORTEP Drawing of $[(MeC_5H_4)_3U]_2[PhNCO]$

XBL 847-3149A

interesting structural feature of the molecule is the η^2-coordination of the NC to U(2). The U-C distance, 2.42(2)Å, is intermediate between the U-C distances found for Cp_3UCCPh (2.33(1)Å)[14], and $Cp_3U(p$-xylyl), 2.54(2)Å[15], consistent with the sp^2 carbon hybridization. The U-N distance (2.36(2)Å) is significantly shorter than in the previously discussed coordination complex $(MeC_5H_4)_3U(III)\cdot N(CH_2CH_2)_3CH$, where U-N = 2.764(4)Å. In the related compound $Cp_3UN_2C_3H_3$, the identical 2.38(1)Å U-N distances[16] are also intermediate between typical anionic U-N distances and the distance expected for a simple coordination complex. The effect of the higher coordination number on the U-Cp distances is as expected; the average U-C distance is 2.80(3)Å for U(1), and 2.76(2)Å for U(2). Magnetic susceptibility measurements indicate no coupling between the metal centers across the two atom bridge to 5K. The χ vs. T curves are indistinguishable from those of monomeric Cp_3UX compounds. Above 110K, the susceptibility curve follows Curie Weiss behaviour; from 10K-110K, the slope changes due to depopulation of excited electronic states, and below 10K, becomes temperature independent, consistent with the description of two noninteracting U(IV) ions. The simplest chemical description of the complex is that of two one-electron reductions of PhNCO by trivalent uranium, with negative charges localized on the C and O atoms, as illustrated below.



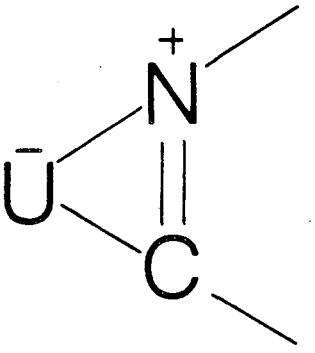
The compound is thermally stable to 95°C in toluene, and there is no observed reaction with either CO or D_2 (150 psi in toluene, 25°C). Given the kinetic inertness of $Cp_3U(alkyl)$ complexes toward CO, the lack of reactivity in this complex is expected. In the ^1H NMR spectrum, there is no line broadening at the high temperature extreme (80°C) to indicate the possibility of Cp site exchange, nor a broadening of any resonances at low temperaures (-80°C) attributable to a slowing Cp site exchange process, as was observed in the ^1H NMR spectrum of the structurally similar $(C_5H_5)_3U\eta^2\text{-}(Me)C{=}N(C_6H_{11})$.[17] This compound, the product of cyclohexylisocyanide insertion into the U-C σ-bond in $(C_5H_5)_3UCH_3$, contains a related η^2-bond to the uranium as described in Figure 2. The U-C and U-N distances, 2.36(2) and 2.40(2)A are equivalent, within experimental error, to those of the isocyanate reaction product. For some reason, the electronic structure of this complex was described as in Figure 2a, Figure 2b being ruled out due to the planarity of the U, C, N, C(Me) and C(cyclohexyl) atoms. An alternative description involves a simple dative U-N bond which reqires no charge separation, as shown in Figure 2c.

The $[(MeC_5H_4)_3U]_2[\eta^1,\eta^2\text{-}PhNCO]$ was the first unequivocal example of an aryl isocyanate ligand bridging two metal centers; subsequent reactivity of tne isocyanate within the metal coordination sphere usually precludes isolation of the initial reaction product. For example, the first report[18] of a transition metal isocyanate complex, $[Fe(CO)_3PhNCO]_2$, was later shown by X-ray analysis to be the bridging ureylene complex $[Fe(CO)_3]_2\mu[PhNC(O)NPh]$[19]. Synthetic reports of the

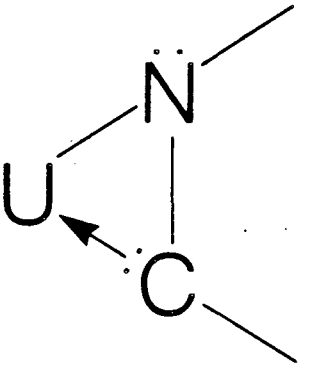
Valence Bond Descriptions of η^2-coordinating Ligands

Figure 2

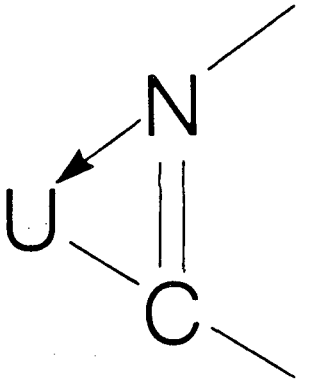
(a)



(b)



(c)

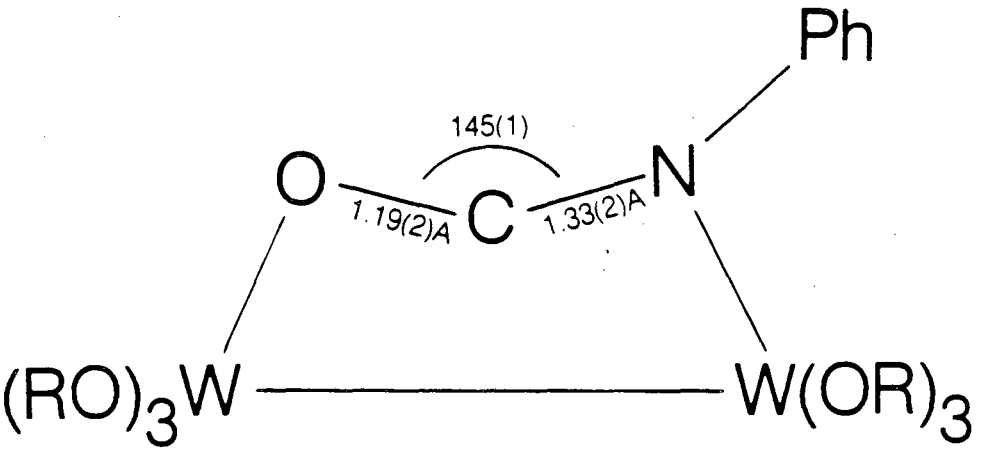


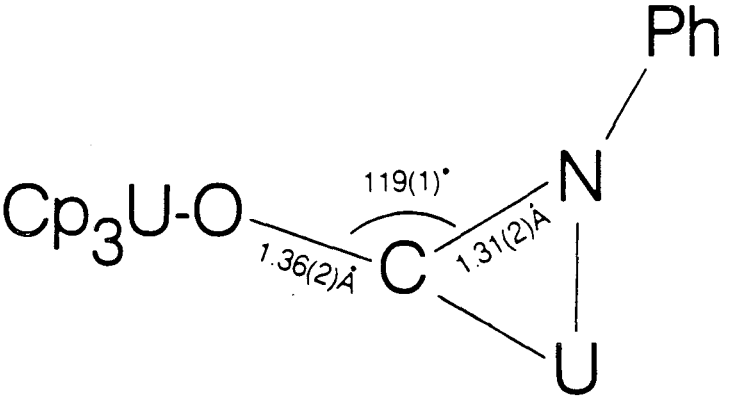
XBL 8512-4983

isolation of RNCO complexes of Ni, Rh, and Re exist[20], but the first structurally characterized example was the recently described tungsten alkoxide complex of PhNCO, $[(t\text{-}BuO)_3W]_2PhNCO$ (a)[21], shown in Figure 3, along with the low temperature solid state structure of H_3SiNCO[22]. The structure of the tungsten complex is described as resulting from a single bond from W to the N and O atoms, with a three center-two electron bond between the metals and the carbon atom. The uranium PhNCO complex has a long C=N bond relative to (a), but in comparison to the C-N bonds found in H_3SiNCO, or the negatively charged NCO ligands[23] in $Cp_2Zr(NCO)_2$, is consistent with the carbon hybridization.

The observation that U(III) reacts with an unsaturated organic substrate, putting two electrons into an X=Y=Z functional group, suggested a number of related reactions. Preliminary results of Henley indicated that $(C_5Me_5)_2Yb\text{-}OEt_2$ acts as a one-electron reducing agent toward carbon disulfide, S=C=S, with coupling of the radical anion to form a thiooxalate Yb dimer. This reactivity pattern parallels that of Na or K in dmf[24], but is rarely found in transition metal systems[25]. This coupling is different from that observed for the uranium PhNCO reaction; thus it was of interest to see whether uranium would also couple CS_2 radical anions. Upon addition of carbon disulfide to an ether solution of $(MeC_5H_4)_3U$-thf, a precipitate immediately formed, and crystallization from toluene yielded dark red needles. The same reaction was observed between $(Me_3SiC_5H_4)_3U$ and CS_2, with the product having good ether or slight hexane solubility. Elemental analysis was consistent with the stoichiometry of 1 CS_2: 2 Cp_3U, and analysis of the ^1H NMR spectrum of each complex showed that

Comparison of Uranium and Tungsten PhNCO Complexes.





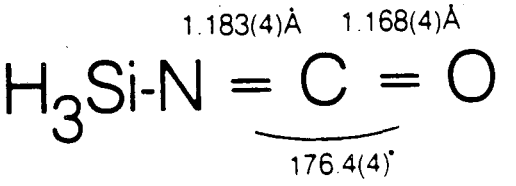


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Figure 3

there were again two inequivalent Cp resonances, with chemical shift differences similar to the PhNCO compound. There was no dynamic behavior exhibited in the MeC_5H_4 compound to ±90°C. The ($Me_3SiC_5H_4$) complex had one set of Cp resonances which were broad (ca. 30Hz) at room temperature and broaden into the baseline at -30°C, presumably from slowing a site exchange process similar to the proposed exchange of axial and equatorial Cp sites in the pseudo trigonal bipyramidal $(C_5H_5)_3U$-η^2-$MeCN(C_6H_{11})$[17]; the signals remain unresolved to -90°C (90 MHz). Two structural possibilities (Figure 4) were consistent with the available data. Geometry A could result from initial coordination at the carbon, producing a delocalized sulfur based radical anion, which then couples to the second U(III). This ligation is possibly found in the thiolate compound Cp_3US_2CMe. Alternatively, geometry B is likely to arise from initial coordination to a sulfur atom, with reduction producing a carbon centered radical anion which rapidly couples to the second U(III), resulting in a structure similar to the PhNCO reaction product. Analogous transition metal CS_2 complexes of both structural types, as well as a number of monomeric structural types have been observed[26].

From the large number of bands in the IR spectrum, it was impossible to distinguish between the two structural possibilities consistent with the observed data, and so the $(MeC_5H_4)_3U$ compound was characterized by X-ray crystallography. The structure was found to be consistent with geometry B, containing an η^1,η^2-SCS ligand bridging two $(MeC_5H_4)_3U(IV)$ groups (Figure 5). The U-C (Cp) distance, 2.76(4)Å, is similar to the U-C distance found in the PhNCO dimer.

Possible Bridging CS_2 Geometries

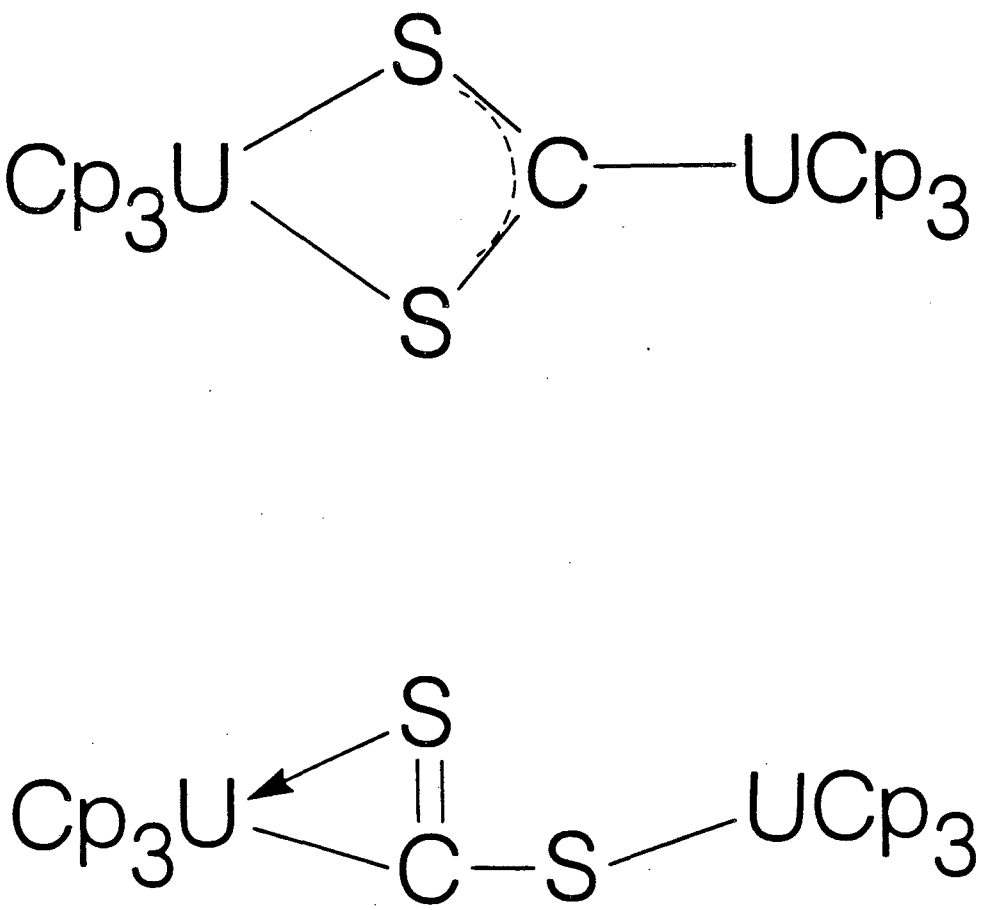

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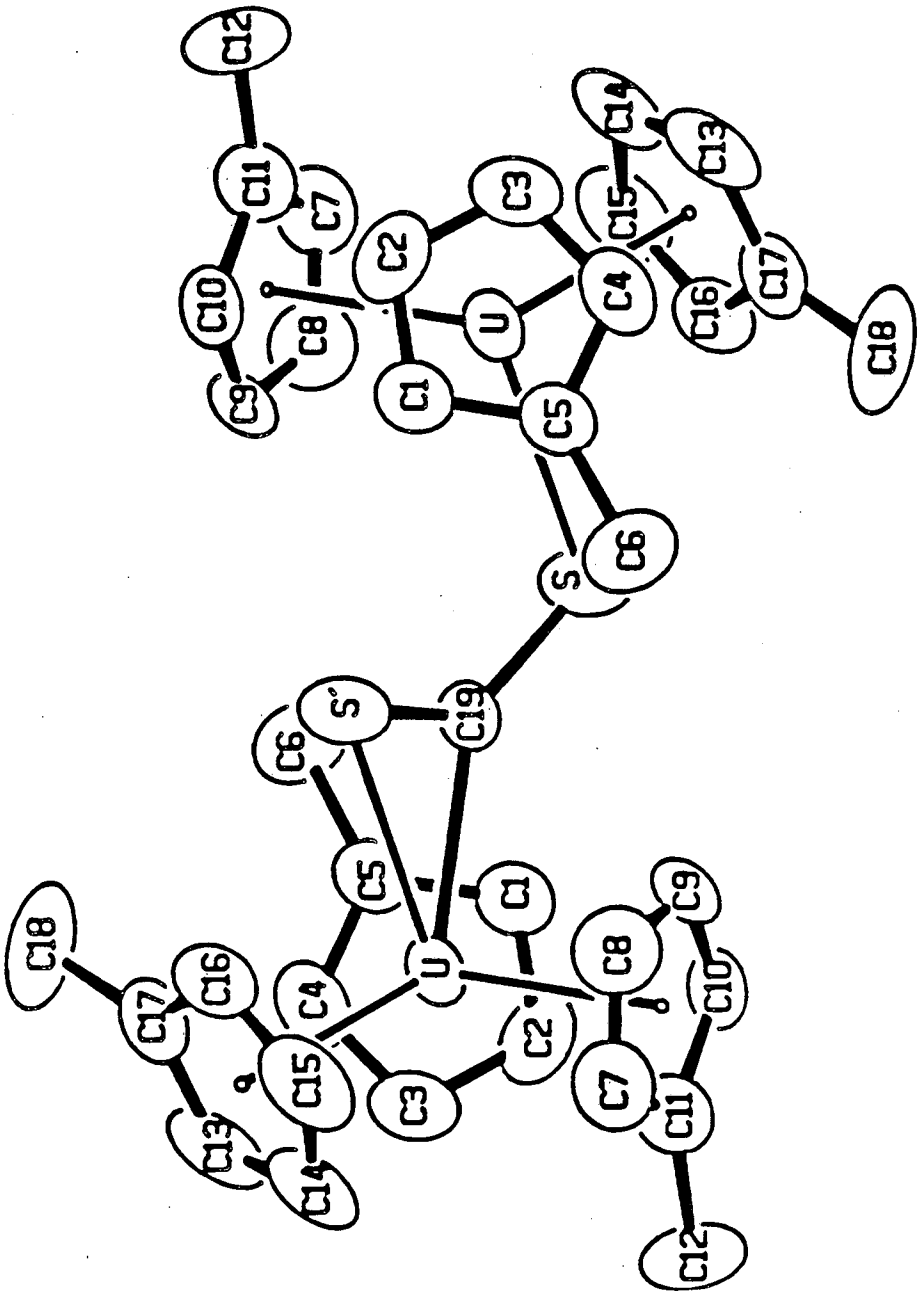
Figure 4



ORTEP Drawing of $[(MeC_5H_4)_3U]_2CS_2$

Figure 5

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The bridging carbon was crystallographically disordered, with equal probability that it would be bound to either uranium; the U-C(19) distance is 2.53(2)Å. This results in an apparent inversion center, and the U-S dative and U-S anionic bond lengths are equivalent; U-S=2.792(3)Å. Complexes of the type Cp_3USR are unavailable in the literature to date, and thus U-S distance comparisons are limited. The U-S bond is significantly shorter than the three known examples of U-S dative interactions; in $(MeC_5H_4)_3U\text{-}SC_4H_8$, U-S = 2.96(5)Å, in $[(MeBH_3)_4USC_4H_8]_2$, U-S = 3.120(4), 3.240(5), 3.164(4), and 3.276(4)Å[27], and in cis-dichloro-[meso-bis(trans-2-hydroxycyclohexyl)sulphide-OOS]dioxouranium(VI), U-S = 2.94(1)Å[28]. Molecular uranium sulfur σ-bonding is equally unexplored in the literature. There exists an interesting n^2 disulfide complex $[R_2NH_2]_2[UO_2((NC_3H_7)NCOS)_2S_2]$ with a U-S_2 distance of 2.711(3)Å[29], the U-S distance in $[(MeC_5H_4)_3U]_2S$ is found to be 2.60(1)Å, and in uranium sulfur complexes involving bonding of thiolate, dithiolate, or in mineral structures, U-S bonds range from 2.69 to 2.93Å[30]. The observed U-S distance in the CS_2 complex is consistent with these structural characterizations.

While these two Cp compounds represent the only CS_2 complexes of an f-block metal, a diverse CS_2 chemistry exists among transition metals[26]. The n^1,n^2 geometry adopted in the uranium compound is rare, the known examples are listed below, along with pertinent geometrical data. Of immediate interest is the variation in C-S bond distances. In contrast to the minor perturbations observed in the C-S distances upon coordination to d-metals, the CS_2 ligand is significantly altered

in the uranium complex, with a short C=S double bond and a long C-S single bond (in CS_2, C=S is 1.559(3)A[32], while in p-$Me_3CC_6H_4C(S)SMe$, C=S is 1.630(2)A and C-S is 1.788(3)A)[33]. While an evaluation of the change in C-S distances is difficult considering the possible effect of disorder on the absolute location of the carbon atom, the severe CS_2 distortion is consistent with the clearly tetravalent metals

Table 1 η^1,η^2-CS_2 Complexes

Compound	η^2C-S(A)	η^1C-S(A)	η^2-η^1	SCS<	MSC<	Ref.
$[MeC_5H_4)_3U]_2CS$	1.46(2)	1.83(2)	-.37	132	112	
$[Ph_3PNi(CS_2)]_2$	1.63(1)	1.68(1)	-.05	137	145	31a
$[(PhBu_2)PPt(CS_2)]_2$	1.674(6)	1.651(6)	.02	133	108	31b
$Fe(CO)_2(PMe_2Ph)_2$-$(CS_2)Mn(CO)_2Cp$	1.658(6)	1.642(6)	.02	140	120	31c
$HC(CH_2PPh_2)Co$-$(CS_2)Cr(CO)_5$	1.65(3)	1.63(2)	.02	136	113	31d

(by ^1H NMR and susceptibility), indicating a complete two electron reduction with the two electrons residing in a localized C-S antibonding orbital. As in the PhNCO complex, no reactivity with H_2 or CO was observed. The CS_2 compound could not be isolated from reaction of $(MeC_5H_4)_3U$-thf with CS_2-PMe_3; if this reaction is to be pursued, a more soluble phosphine should be used.

The asymmetric CS_2 bridge suggested an interesting experiment. If CS_2 were replaced with carbonyl sulfide, two possible products could result. Initial coordination through the oxygen atom, followed

by ligand reduction and coupling of the second U(III) to the carbon centered radical intermediate, would produce an η^2-CS and η^1-O geometry. Alternatively, initial cordination through S, would yield a molecule containing η^2-CO and η^1-S (see Figure 6). Exposure of a diethyl ether solution of $(MeC_5H_4)_3U$-thf to an atmosphere of S=C=O gave an immediate precipitate as in the PhNCO and CS_2 reactions, but the ^1H NMR spectrum contained only one type of Cp resonance. This could result from a rapid site exchange process between η^2 and η^1-metal centers, or the molecule contains a symmetric bridge between the two $(MeC_5H_4)_3U$ groups. Elemental analysis indicated a S:U ratio of 1:2. The relatively weak C-S bond[34] in S=C=O results in a tendency to eliminate CO upon reaction with low-valent transition metal complexes[35], and such a reaction with the low-valent uranium, forming a bridging sulfido complex, would account for the NMR spectrum. The compound $[(C_5H_5)_3U]_2S$, obtained from the reaction between Cp_3UBr and K_2S or by thermolysis of Cp_3USH, has been mentioned in a review article, but no characterization has been reported[36]. If a bridging sulfido group were to have exceptional thermodynamic stability, then it should be accessable <u>via</u> other redox reactions. The reaction between $(MeC_5H_4)_3U$-thf and $^1/_2$ or $^1/_8$ molar equivalent S_8 in ether yielded no characterizeable material, but the reaction between $(MeC_5H_4)_3U$-thf and $S=P(C_6H_5)_3$ yielded a compound with identical spectral and physical properties to that isolated in the S=C=O reaction, further evidence that COS must be eliminating CO to form $[(MeC_5H_4)_3U]_2S$. The compound is nicely soluble in toluene from which it may be frequently recrystallized. It did not appear to react with

Anticipated Reaction Products of U(III) with COS

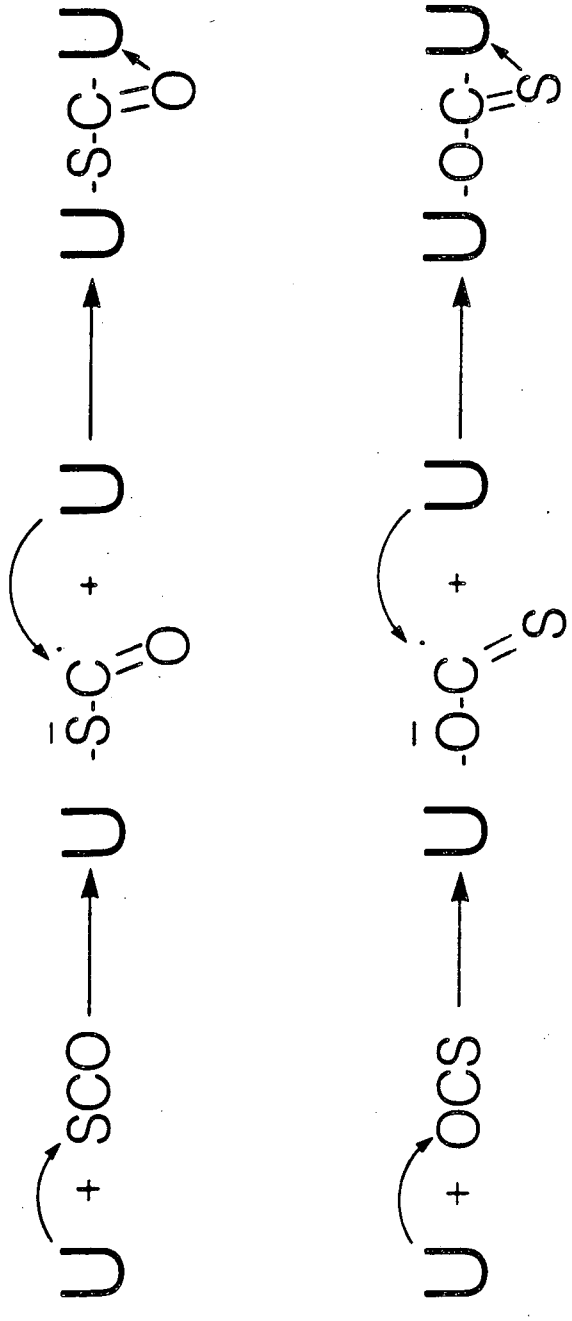

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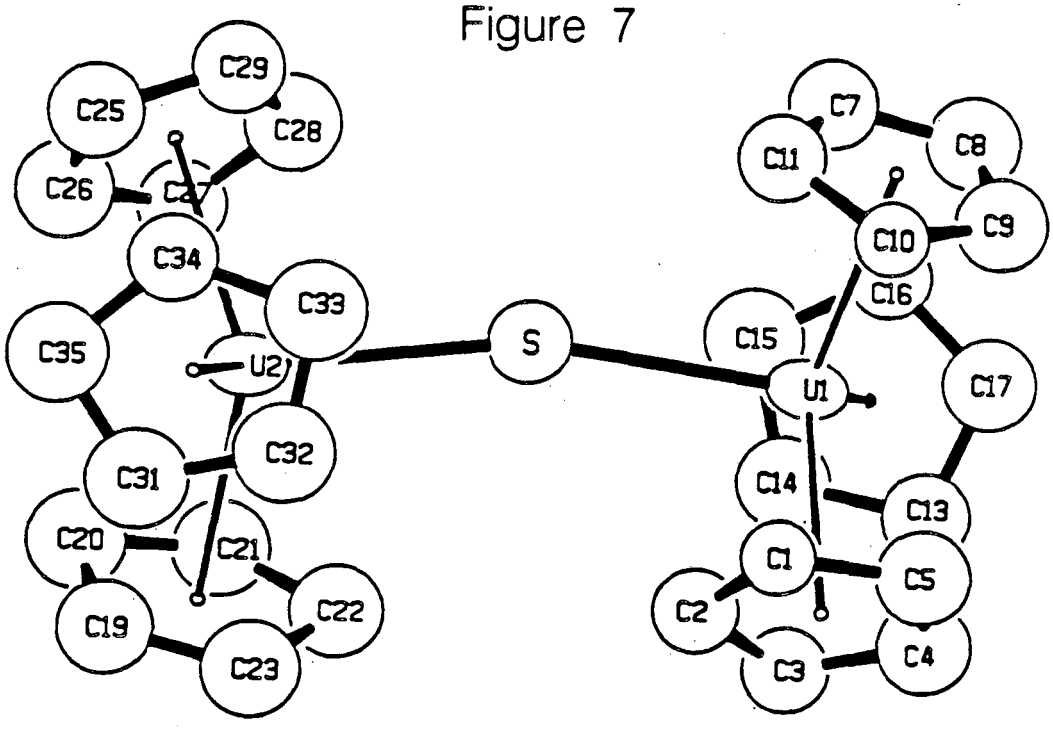
Figure 6

either H_2 or CO, but did react with Lewis acids such as $(MeBH_3)_4U$ or $Al(Me)_3$. The later reaction appeared to fragment the bridge, producing at least two U(IV) compounds, one of which had a 1:1 $S:(MeC_5H_4)_3U$ ratio. Structural characterization of $[(MeC_5H_4)_3U]_2S$ revealed some interesting solid state features (Figure 7). Both the U-S distance, 2.60(1)Å, (the shortest U-S distance observed by 0.09Å), and the nearly linear U-S-U angle [164.9(5)°], suggest that sulfur lone pairs are involved in the bonding to the metal. For comparison, the only other available structure is the CS_2 complex $(MeC_5H_4)_3U$-SR (R= $-n^1n^2CSU(MeC_5H_4)_3$); here the relatively long U-S distance (2.78Å) and bent geometry (U-S-R = 112.°) support the contention that some degree of S→M π-bonding is involved in the bridging sulfido compound. The geometry about the bridging sulfido ligand is remarkably similar to other sulfido complexes of group (VI) metals. In $[(C_5H_5)Cr(CO)_2]_2S$, the Cr-S-Cr angle [174.4(2)°] approaches linearity[37], and the Cr-S distances [2.067(2)-2.076(2)Å] are substantially shorter than the distances found in $(C_5Me_5)_2Cr_2S_5$, where Cr-S range[38] from 2.238(4) to 2.354(4)Å, or in $(C_5H_5)_2Cr_2(CO)_5S_2$, where Cr-S = 2.348(2), 2.466(2), and 2.399(2)Å[37b]. Similiarly, in the structure of $K_6[Mo_2(CN)_{12}]S$, the Mo-S-Mo angle is 169.5(2)°, and the Mo-S distance, 2.173(1)Å, was found to be identical to the terminal Mo=S distances in tetrathiomolybdates[39]. In both the Cr and Mo compounds, the short distance and nearly linear bridge was attributed to S→M π-donation. This argument is further substantiated by the structure of $[CpW(CO)_2]_2S$ which contains a non-linear M-S-M angle of

Figure 7



ORTEP Drawing of $[(MeC_5H_4)_3U]_2S$

XBL 8512-4989

127°, and a W-S distance, 2.53(1)Å, in the range found for W-S single bonds[40].

Bonding descriptions involving π-donation were first used in actinide chemistry to rationalize the near planar geometry about the nitrogen atoms in a series of uranium dialkylamido structures[41]. Apparently unaware of this work or the large body of work concerning structurally characterized U-O-R functionalities, other researchers have proposed identical arguments to explain the consistently observed near linear U-O-R geometry in U(IV), (V), and (VI) alkoxides, as well as the structural differences between dimeric bridging alkoxide uranium complexes and the analogous transition metal alkoxide complexes which contain M-M bonds[12]. The only previous example of a second row element possibly engaged in π-bonding is found in the planar phosphorus atom in $[(C_5Me_5)_2UOMe]_2PH$[13]. In Fischer's chemical shift arguments for the existence of π-donation in Cp_3UX compounds, second row elements were found not to significantly alter the Cp chemical shift[10]. Unfortunately, contributions from the geometric perturbation upon incorporation of a larger atom to the observed shift have not been separated from the possible effects of π-donation.

An alternative interpretation of the geometry in $[(MeC_5H_4)_3U]_2S$ describes the near linearity as a result of steric repulsion between the two uranium groups, predicting that substitution of Se or Te will result in a bent structure as the two $(MeC_5H_4)_3U$ groups are further displaced. While this model explains the near linear geometry, it is inconsistent with the U-S bond length. If steric repulsion is the predominant factor influencing molecular geometry, the U-S distance

would not be at least 0.09Å shorter than all other known U-S distances. Given the diversity of structural features consistent with some degree of L→M π-donation, it seems justifiable to attribute the short U-S distance and the nearly linear U-S-U angle to a stabilizing contribution from S→M π-bonding into available orbitals of appropriate symmetry.

As discussed in Chapter two, reaction of $(MeC_5H_4)_3U$-thf with $O=PR_3$ does not yield the bridging oxo complex, instead forming the phosphine oxide coordination complex. This is consistent with the measured strength of the P=O (137kcal/mol)[42] and P=S (91kcal/mol) bonds[43]. Reaction of the thf complex with trialkylphosphine selenide or telluride yielded the bridging uranium selenide or telluride. While addition of an excess of SPR_3 or $SePR_3$ did not seem to complicate isolation of the bridging chalcogenide complex, the bridging telluride complex could only be isolated using a stoichiometric amount of $TeP(n\text{-}Bu)_3$. What appears to be the bridging oxo complex was prepared from the thf complex and one equivalent of N_2O in ether (addition of N_2O to toluene solution of the thf complex results in a red precipitate which was intractable). The μ-oxo complex, which immediately precipitated as a light green microcrystalline solid upon addition of N_2O by syringe, was so insoluble in toluene (as intractable as the bridging flouride complex $([MeC_5H_4)_3U]_2F$[44]) that no ^1H NMR spectrum could be obtained over a period of hours. The hydrocarbon solubility of the U-X-U compounds increases in the order X= O<S<Se<Te, and the solubility is inversely related to the melting point temperature (Table 2). Characterization

of the oxo compound was by elemental analysis, mass spectrum and IR; the S, Se, and Te compounds were also studied by NMR and magnetic susceptibility. All bridging complexes show a parent ion in the mass spectrum, and the IR spectra are identical except for the position of one band, tentatively assigned to ν U-X-U, which shifts to lower frequency as the mass of X increases.

Table 2 Bridging Chalcogenide Complexes of $[(MeC_5H_4)_3U]_2$

$[(MeC_5H_4)_3U]_2\underline{X}$	ν U-X-U (cm^{-1})	m.p.(°C)	Color
O	610	>320	green
S	358	275	red
Se	216	240	red
Te	<200	200	green

The U-Te-U stretch would be expected below our IR detection limits. The shift in frequency is not a simple function of the relative masses of X, but is consistent with the limited number of assigned stretches in transition metal compounds[4,5]. The oxo complex has a light color typical of a U(IV) compound, while the others are far darker, suggesting a charge transfer band in the visible spectrum. The isolation of a compound with a direct bond from uranium to an element as electropositive as the semi-metal tellurium is remarkable, suggesting that direct bonds from uranium to such electropositive elements as Nb or W may be isolable, given an adequately designed metal coordination sphere devoid of bridging ligands.

Redox/Ligand Redistribution

Successful isolation of the dimeric bridging chalcogenides is extremely sensitive to the metal coordination sphere. When $(Me_3SiC_5H_4)_3U$ or $[(Me_3Si_2)N_3]_3U$ were allowed to react with one equivalent of $S=PPh_3$, roughly one half of the $S=PPh_3$ could be recovered by extracting the uranium product with hexane, leaving behind $S=PPh_3$ (by ^{31}P NMR spectroscopy). The uranium products were too soluble to recover from hexane at -80°C. The reaction between $(Me_3SiC_5H_4)_3U$ and N_2O is far more complex; upon addition of one equivalent of N_2O to a hexane solution of $(Me_3SiC_5H_4)_3U$, the solution color immediately turned light red, and after a few minutes, a precipitate formed (Reaction 3). The solution never developed the color intensity characteristic of U(V) compounds, possibly due to initial formation of a peroxo compound similar to $Lu_2[N(SiMe_3)_2]_4(OPPh_3)_2$.[46] After 2-3 hours the reaction appeared complete; the hexane soluable portion was crystallized as red diamonds, and ^1H NMR, elemental analysis, and mass spectra support the formulation $[(Me_3SiC_5H_4)_2UO]_2$. The remaining red precipitate was

3 $$(Me_3SiC_5H_4)_3U + N_2O \longrightarrow [(Me_3SiC_5H_4)_2UO]_2 + \text{ppt (X)}$$

insoluble in ether or toluene, but dissolved in toluene upon addition of bipyridine (Reaction 5). The dimeric μ-oxo compound was repeatedly

4 $$(X) + DMPE \longrightarrow \text{no reaction}$$

5 $$(X) + BPY \longrightarrow \text{toluene solubility}$$

recrystallized from hexane to remove a small (1-2%) impurity which carried over each time. Recrystallization of the product from diethyl ether yielded an entirely different product having properties

6 $$[(Me_3SiC_5H_4)_2UO]_2 \xrightarrow{\text{diethyl ether}} \text{red needles}$$

consistent with the formulation $[(Me_3SiC_5H_4)_3U]_2O$ (see Figure 8). The unit cell of this compound is rhombohedral, unlike the triclinic cell of $[(Me_3SiC_5H_4)_2UO]_2$, requiring that the molecule contain a threefold axis which can only exist if the U-O-U angle is rigorously linear. The melting point of this compound, 75°C, suggests that the bridging sulfido complex referred to earlier did not solidify upon removal of solvent due to a melting point close to or below room temperature. Elemental analysis of this compound has been particuliarly inconsistent, making it impossible to distinguish between $[(Me_3SiC_5H_4)_3U]_2O$ and $[(Me_3SiC_5H_4)_2UO]_3$, both of which could contain a threefold axis. In toluene, this bridging oxo compound slowly underwent a ligand redistribution process (by ^1H NMR spectroscopy), producing both $[(Me_3SiC_5H_4)_2UO]_2$ and a lesser amount of $(Me_3SiC_5H_4)_4U$, the properties of which will be described later.

Reaction 7

$$\text{red needles} \xrightarrow{\text{toluene}} [(Me_3SiC_5H_4)_2UO]_2 + (Me_3SiC_5H_4)_4U \text{ (minor product)}$$

If the structural assignments are correct, it is suprising that the polar coordinating solvent should favor the existence of the nonpolar

$$(Me_3SiC_5H_4)_3U + N_2O$$

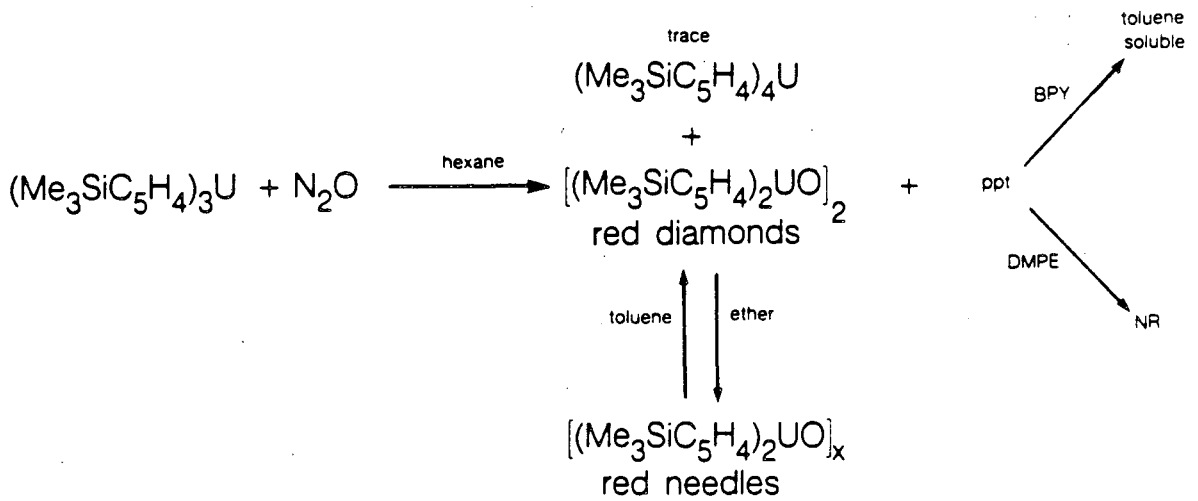


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Figure 8

complex least likely to admit a solvent molecule into the inner coordination sphere.

The reaction between diazocyclopentadiene (NNC_5H_4) and $(Me_3SiC_5H_4)_3U$ appeared to proceed with evolution of a gas, but the isolated product of this reaction had a ^1H NMR spectrum which contained resonances for only one type of ($Me_3SiC_5H_4$) ligand, with no trace of the protons from the NNC_5H_4 ligand. This material had physical properties that were identical to an occasional minor product from the N_2O reaction described above, and thus it was assumed that traces of oxygen had entered both reaction mixtures. The reaction between $(Me_3SiC_5H_4)_3U$ and a stoichiometric amount of oxygen produced a greater yield of this compound; the mass spectrum contained a peak at 771amu, indicating some type of oligiomerization, as the mass for $(Me_3SiC_5H_4)_3U + O_2 = 681$. Structural characterization of the complex showed it to be $(Me_3SiC_5H_4)_4U$, a formulation also in accord with the physical characterization. Isolation of this compound was particularly amusing as ($Me_3SiC_5H_4$) was first used with the expectation that the steric requirements of the Me_3Si group would kinetically stabilize $(Me_3SiC_5H_4)_2UCl_2$ with respect to ligand redistribution and the formation of $(Me_3SiC_5H_4)_3UCl$. In the structure (Figure 9a), all four Cp rings are n^5 bound to the metal, with U-C distances ranging from 2.81-2.87Å. There are two disordered positions in the molecule (Figure 9b). The Cp-M-Cp centroid angles are rigorously tetrahedral, with the $SiMe_3$ groups bent 20° out of the plane defined by the Cp rings. The average U-C distance, 2.85(3)Å, is longer than the U-C distance observed in $(C_5H_5)_4U$, 2.81(2)Å[47],

ORTEP Drawing of $(Me_3SiC_5H_4)_4U$

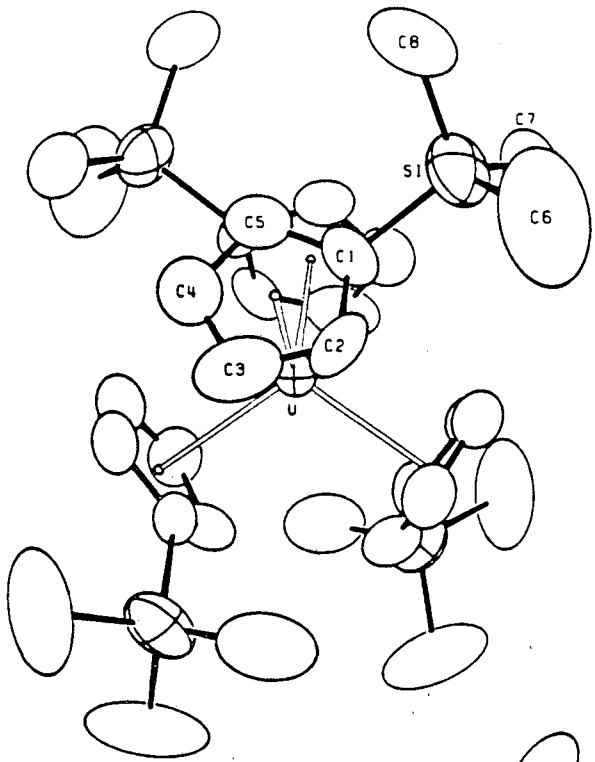
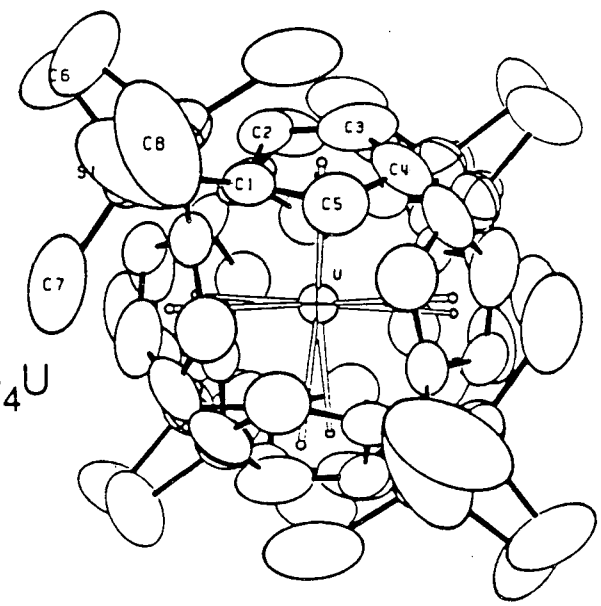


Figure 9



View of the Disordered Structure of $(Me_3SiC_5H_4)_4U$

XBL 8512-4993

although not significantly. This increase is most likeley a product of the steric demands imposed by the $SiMe_3$ group. Recall that in Chapter 2 the electron-donating ability of $SiMe_3$ relative to H was discussed; an increased electron density in the ring would increase the electrostatic potential between metal and ligand, resulting in a shorter M-C bond. $(Me_3SiC_5H_4)_4U$ cannot be obtained by reacting $(Me_3SiC_5H_4)_3UCl$ with $K(Me_3SiC_5H_4)$ in either refluxing toluene or thf; the starting materials are quantitatively recovered. Analysis of the low temperature NMR spectrum shows the Cp resonances to be undergoing some form of dynamic site-exchange process resulting in complete broadening of the C-H resonances into the baseline at -100°C. This site inequivalence conflicts with the solid state tetrahedral arrangement of Cp ligands, unless there is restricted movement between the disordered positions, or a solution geometry other than that found in the solid state (possibly an η^1 Cp). The low temperature of coalesence (and thus the low barrier to exchange) is evidence for a simple restricted ring rotation producing the NMR lineshape, as even in the less sterically saturated $Cp_3U(allyl)$, an 8-9 kcal/mol barrier to exchange via $\eta^1 \rightarrow \eta^3 \rightarrow \eta^1$ allyl ligation was observed[48]. The reaction between $[(Me_3Si)_2N]_3U(III)$ with 1/2 O_2 proceeds in a similar fashion. Upon addition of O_2 to a hexane solution of the amide, the solution color immediately lightens, and the previously isolated uranium metallacycle can be crystallized from hexane in 20-30% yield. Instead of acting as a simple four electron reducing agent to form a U(V) compound, one can postulate that decomposition of the initial product proceeds via elimination of a silylamide radical, which abstracts a

proton from the unreacted U(III)silylamide. This parallels the inability to isolate the $[(Me_3Si)_2N]_4U$ from UCl_4 and four equivalents of $NaN(SiMe_3)_2$, although in this case the fourth silylamide anion reacts to form $[(Me_3Si)_2N]_3UH$. In contrast to the Cp chemistry, the oxygen containing product in the reaction of $[(Me_3Si)_2N]_3U$ and O_2 is extremely soluble in hexane, and would probably form a stable crystalline complex with $OPPh_3$.[46]

The reaction of trivalent uranium compounds with neutral cyclooctatetraene (C_8H_8, COT) shed further light on the above reactions. Addition of COT to a hexane solution of $[(Me_3Si)_2N]_3U$ resulted in the formation of at least two compounds, one being the metallacycle referred to above, which was isolated by fractional crystallization. When COT was added to a benzene solution of $(Me_3SiC_5H_4)_3U$, and the reaction monitored by ^1H NMR, initial formation of a compound with exceedingly broad ^1H NMR linewidths was observed (indicating either a U(V) compound or a compound undergoing some form of slow site-exchange process). Over the course of hours, formation of a U(IV) complex could be deduced. When the reaction was done in hexane, the solution color slowly changed from green to red, and the uranium 'half sandwich' complex $(C_8H_8)U(Me_3SiC_5H_4)_2$ was isolated by crystallization. Samples of this compound suitable for X-ray analysis have not been obtained thus far as it crystallizes in thin sheets; it does not sublime (150°C, 10 millitorr); an occasional crystal of $(Me_3SiC_5H_4)_4U$ could be separated by hand from the isolated product. Spectroscopic characterization of $(C_8H_8)U(Me_3SiC_5H_4)_2$ was straightforward; the ^1H NMR spectrum contained peaks for the Cp

(18:4:4) ligands and the COT dianion, at -32 ppm. The ^{13}C [^{1}H] NMR spectrum contained resonances with chemical shifts typical of ($Me_3SiC_5H_4$) bound to a U(IV) ion, and one peak that splits to a doublet (J_{CH}= 159.7 Hz) in the absence of proton decoupling. Elemental analysis was consistent with the formulation $(C_8H_8)U((Me_3SiC_5H_4)_2$, and the IR spectrum had weak bands characteristic of COT dianion[49]. The mass spectrum was particuliarly satisfying, as the compound shows a parent ion for $C_8H_8U(Me_3SiC_5H_4)_2$= 616), $M^+-C_8H_8$ = 512, $M^+-(Me_3SiC_5H_4)$ = 479, as well as the C_8H_8 (104) and Cp+1 (138) ligands. As a solid the compound is stable to 180°C, and in noncoordinating solvents is stable with respect to ligand redistribution, showing no trace of uranocene or Cp_4U formation after 24 hours. Mono COT complexes of thorium are known to be accessable from the two routes[50] shown below, but $C_8H_8U(Me_3SiC_5H_4)_2$ represents

8 $$ThCl_4 + K_2COT \xrightarrow[thf]{} (COT)ThCl_2thf_2 + 2KCl$$

9 $$(COT)_2Th + ThCl_4 \xrightarrow[thf]{} 2(COT)ThCl_2thf_2$$

the first rigorous characterization of monoCOT complex of uranium. Previous attempts at isolation of the mono-ring complex of uranium used $U(C_8H_8)_2$ as starting material, with the intent of selectively cleaving one ring. Coordination of an acid to the metal[51] is thought to be the initial step in the hydrolysis of $U(C_8H_8)_2$, with cleavage of the first ring opening a number of vacant metal coordination sites. Kinetically, removal of the second ring should be facile due to these open coordination sites, making it virtually impossible for this

synthetic route to succeed. Using this electron-transfer approach to half sandwhich compounds, Streitweiser has developed a synthetic strategy involving NaH reduction of the ligand redistribution product UCl_4 to quantitatively synthesize the dichloride derivative $(C_8H_8)UCl_2$.

Uranium Imido Complexes

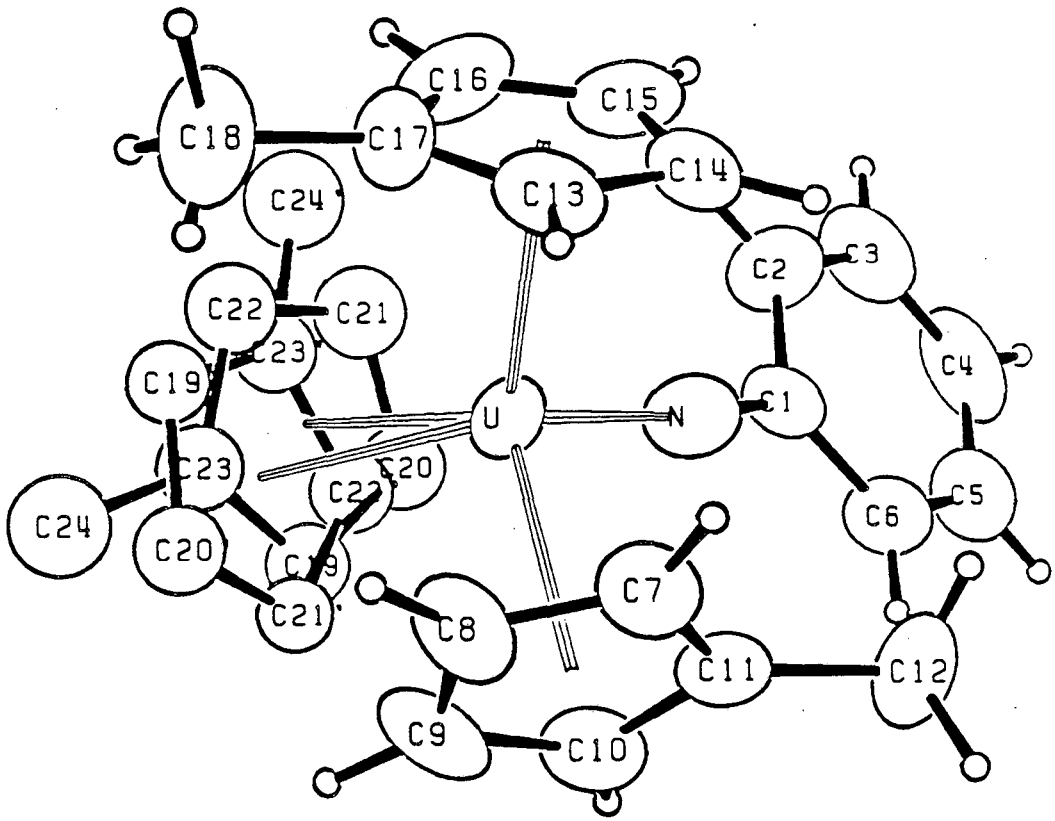
Thus far U(III) has been shown to be capable of acting as a one-electron reducing agent toward a wide variety of unsaturated molecules, where ligands clearly capable of existing as a dianion did so by accepting one electrom from two metal centers, or redistribution resulted in isolation of only U(IV) species. Alkyl azides might be expected to react differently, as (at least crystallographically) they are more reasonably represented by a dipolar valence bond structure containing a terminal N-N triple bond[52]. Addition of Me_3SiNNN to a diethyl ether solution of $(MeC_5H_4)_3U\cdot thf$ resulted in what appeared to be refluxing of the solvent. The reaction product was soluble in hexane, from which it was crystallized. The possibility of simple coordination complex formation, as reported for $[(Me_3Si)_2N)_2UN(SiMe_3)SiMe_2CH_2\cdot NNNSiMe_3$,[53] was immediately dismisssed when the IR spectrum showed no azide stretch, while the ^1H NMR spectrum indicated that the Me_3Si fragment was still present; the integrated intensities in the ^1H NMR spectrum were 1 Me_3Si:3 MeC_5H_4 ligands. Elemental analysis revealed that there was $1N/(MeC_5H_4)_3U$, and the parent ion observed in the mass spectrum confirmed that the reaction proceeded with evolution of N_2 to form a uranium imido

complex $(MeC_5H_4)_3U{=}NSiMe_3$. This formulation requires a pentavalent uranium ion, a fact consistent with the extremely fast relaxation time observed in the ^1H NMR spectra ($\nu_{1/2}$= 40-60 Hz), and the bulk magnetic susceptibility, which was temperature dependent to 5K. The compounds $(MeC_5H_4)_3U{=}NR$, R= Ph, $SiMe_3$, and $Cp_3U{=}NSiMe_3$, were synthesized and the $(MeC_5H_4)_3U{=}NPh$ complex characterized by X-ray crystallography (Figure 10). The U=N bond distance, 2.019(6)Å, was the shortest U-N distance measured at the time, and the U=N-C angle, 167.4(6)°, suggests that both nitrogen lone pairs are involved to some extent with bonding to the metal, giving what is formally a U-N triple bond. The average U-C distance, 2.75(3)Å, is surprisingly similar to the known $Cp_3U(IV)X$ distances. Table 3 contains a summary of the observed, average, bond-distance ranges for the known U(III), U(IV), and U(V) Cp_3U compounds,

Table 3 M-C distances in 10 coordinate Cp_3U-X compouonds.

Oxidation State	U-C average range (Å)	Metal Ionic Radius
U(III)	2.79 - 2.82	1.074
U(IV)	2.69 - 2.76	0.932
U(V)	2.75	0.796

as well as Shannon's metal ionic radii, adjusted from coordination number six to ten. While there is clearly a contraction observed in going from U(III) to U(IV), it is not as great as that predicted from ionic radii arguments. When the metal is further oxidized, this ionic bonding model completely disintegrates; the U(V) complex has a greater U-C distance average than most reported $Cp_3U(IV)X$ compounds.

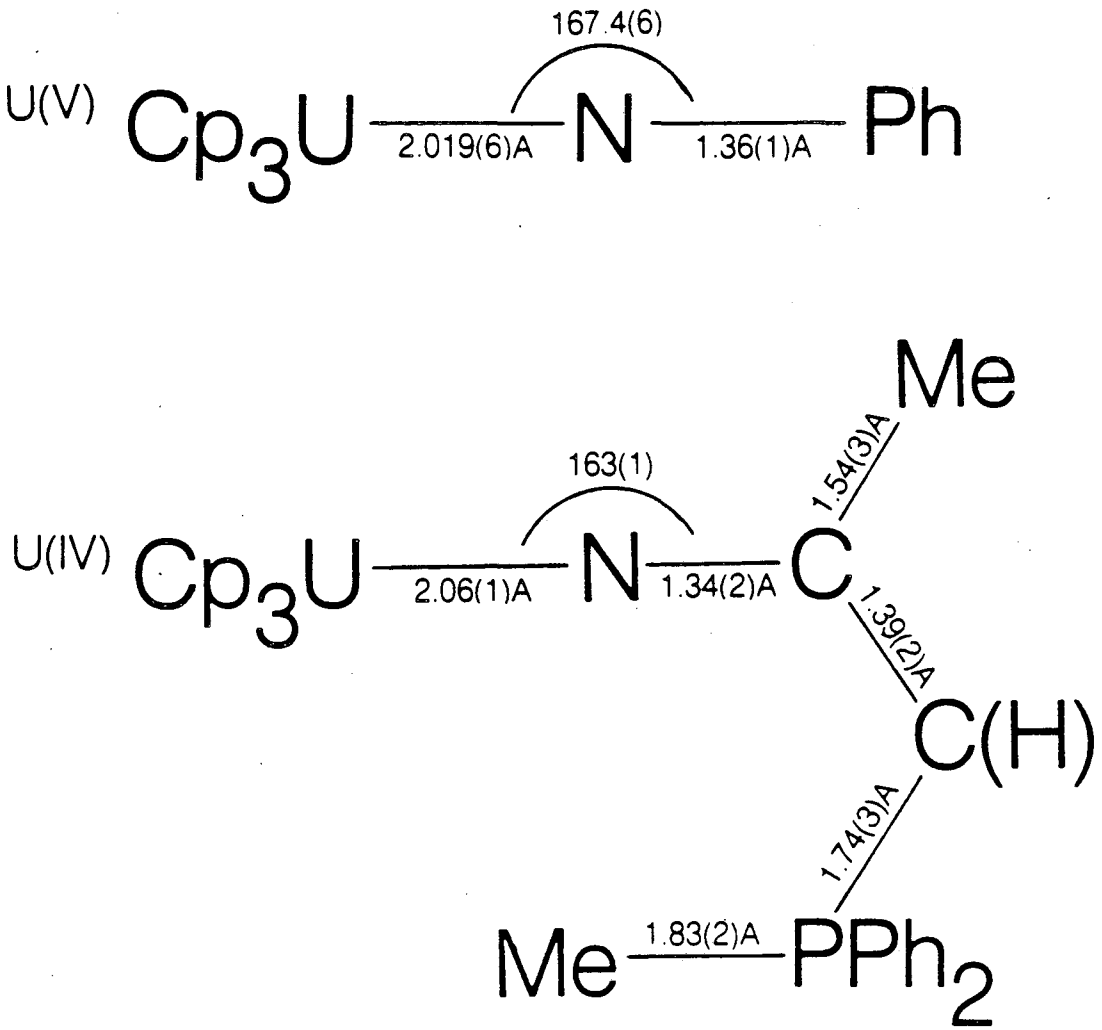


XBL 847-3151A

ORTEP Drawing of $(MeC_5H_4)_3U{=}NPh$

Figure 10

There is one other uranium compound in the literature for which claims have been made that uranium-nitrogen bond is multiple. Upon insertion of CH_3CN into what is advertised as a U-C multiple bond[54] in $(C_5H_5)_3UCHC(Me)PPh_3$, the compound $(C_5H_5)_3UNC(Me)CHP(Ph)_3$ can be isolated[55]. The compound has a U-N distance of 2.06(1)Å, and a U-N-C angle of 163(1)Å, strikingly similar to the geometry about the U(V) imido compound. The U-N multiple bond character in $(C_5H_5)_3UNC(Me)PPh_3$ is open to debate, as there are several ways to interpret the reported data. The most disturbing aspect of this compound is the oxidation state of the metal. No characterization of metal oxidation state was discussed, although the "^{1}H NMR linewidths are narrow". It is stated that "U(IV) is a very electron deficient ion" that will interact with lone pairs of electrons, and that "the U-X multiple bonds in $Cp_3U{=}NC(Me)P(Ph)_3$ also fulfill this role", from which a tetravalent metal center must be inferred. Magnetic susceptibility studies on this compound would be particularly helpful in understanding the nature of the U-N bond, clarifying the oxidation state and establishing the origin of the narrow NMR linewidths. Bond distances in the ylide group were found to be ambiguous in interpreting the directionality of the multiple bonding about the carbon bound to the nitrogen (Figure 11); if the N-C bond is best described as a double bond, based on the reported short N-C distance of 1.34(2)Å, then on valence bond arguments the U-N bond should be described as single. The involvement of nitrogen lone pairs in the bonding scheme is harder to describe unequivocally, but π-bonding in uranium compounds is not a



Imido Complexes of U(IV) and U(V)

XBL 8512-4984

Figure 11

new observation, putting this molecule in a class with the uranium dialkylamides.

The geometry about the U(V) imido ligand is similar to the majority of transition metal imido complexes. Near linearity of M-N-R angles in imido ligands is a recurring structural feature, and the interaction is formally described as a M-N triple bond, with two nitrogen lone pairs in addition to the sp hybrid orbital involved in bonding with the metal[56]. While there are a number of transition metal imido complexes containing bent imido ligands, two particularly important examples contain both linear and bent imido ligands. In cis-$Mo(NPh)_2(S_2CNEt_2)_2$,[57] one Mo-N-C is 169.4°, and the other 139.4°, while $OsO_2[NCMe_3]_2$, contains Os-N-C angles[58] of 178.9° and 155.1°. Surprisingly, the formal decrease in M-N bond order results in a bond length increase of only 0.035Å and 0.009Å, respectively. The small perturbation of bond length in these structures underscores the danger of using length to define bond order in the uranium compounds, as well as in all the other compounds. The bond length is, however, a good first approximation of bond order.

If the oxidation state ambiguities are set aside, the U(IV) and U(V) imido complexes are almost identical in geometry, suggesting a similar degree of multiple bond character between U and N. Whether solid state packing forces are responsible for the deviation from absolutely linear M-N-R angles, or there is some degree of lone pair character at nitrogen remains unclear. Chemically the nitrogen lone pair is inert to the acid $AlMe_3$. The trimethylsilylimido complexes do not react with D_2, CS_2, $OPPh_3$, or diphenylacetylene, but will react

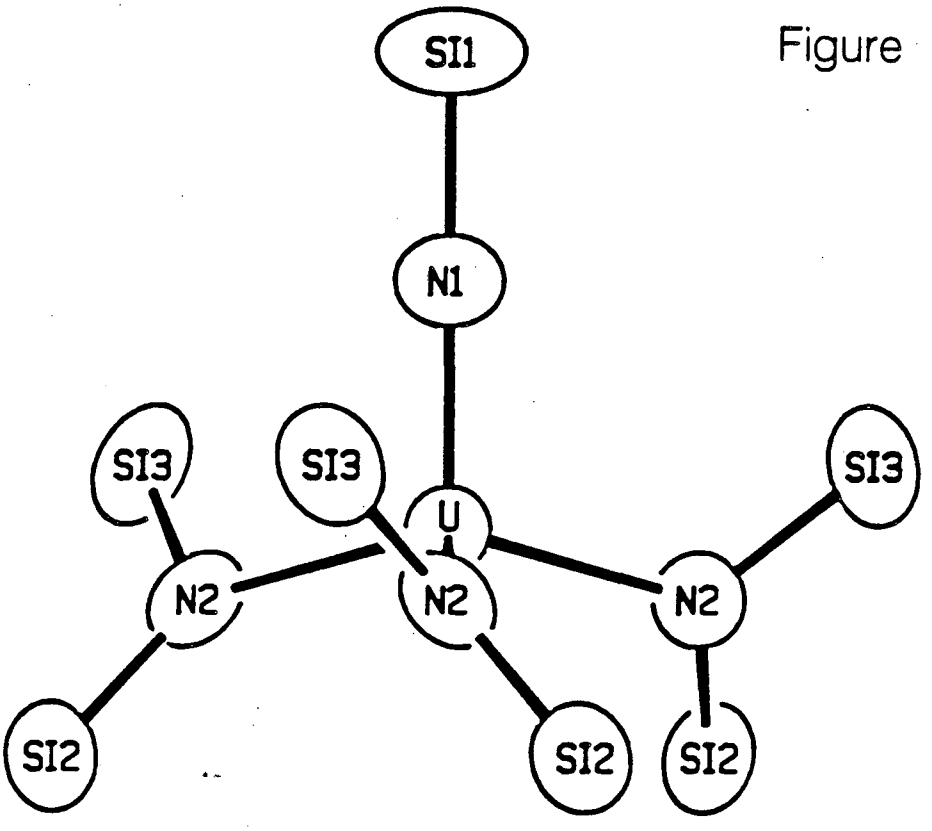
with CO or CNR to form U(IV) compounds. The reaction between $(RC_5H_4)_3UNSiMe_3$ and EtNC (R=H, Me) in diethyl ether or hexane was complete in 24 hours, forming a light green crystalline compound. The color is actually informative, as only amido or alkoxo complexes of Cp_3UX have thus far been reported as green and the alkyl derivatives are red. Integration of the ^1H NMR spectrum indicated a ratio of 1 ethyl group to 3 Cp's, and no trace of the $SiMe_3$ fragment remains; the IR spectrum contained a band at 2080 cm^{-1}. Upon air oxidation this band decreased in intensity and two new stretches were observed at 2220 and 2140 cm^{-1}. The elemental analysis indicated that there were $2N/Cp_3U$, thus the imido group cleaved at the N-Si bond. A formula consistent with the data is Cp_3U-N=C=NEt, although the analytical results were consistently low in %C. The mass spectrum of the MeC_5H_4 compound contained a parent ion at $[(MeC_5H_4)_3UNCNEt]_2$-MeC_5H_4 = 1009amu, but dimerization is inconsistent with the extreme hexane solubilities of the compounds, and the possibility of reaction in the mass spectrometer source must be considered. Evidence against this being the reaction product is obtained in the CO reaction, which if similar should yield Cp_3UNCO. Again, a green product was formed upon exposure of the imido complexes to an atmosphere of CO, but the product was insoluble in all solvents including CH_2Cl_2, the preferred solvent in isolating Cp_3UNCO[59]. The IR spectrum contains a band at 2060 cm^{-1}, significantly shifted from the observed stretch at 2180 for $(MeC_5H_4)_3UNCO$. Although an alternative reaction product is Cp_3UOCN, for which no IR data is available, the presumed oligiomeric solid state structure of $Cp_3U(NCO)$ suggests that U-NCO or U-OCN would

have identical solid state properties. The reaction of $Cp_3UNSiMe_3$ and 2,6 dimethylphenylisocyanide can be monitored by ^1H NMR spectroscopy in C_6D_6; there is no initial shift of the U(V) resonances upon addition of isocyanide, eliminating quantitative formation of a coordination complex as the initial step. Over a period of hours at 60°C, sets of resonances due to at least two different U(IV) compounds were observed; the final product appeared to precipitate. This reaction in hexane at room temperature deposited a 10-20% yield of crystalline material over a period of days, though this matter was not pursued.

The reaction of EtNC with the phenylimido complex gave an entirely different product. Upon addition of EtNC to an ether solution of $(MeC_5H_4)_3UNPh$, the color again lightened in 24 hours, but crystallization of the product from hexane yielded the light red amido complex $(MeC_5H_4)_3UNHPh$. The presence of the proton in this U(IV) compound was deduced from the parent ion in the mass spectrum ($(MeC_5H_4)_3UNHPh$ = 567amu) and the single proton resonance in the ^1H NMR spectrum at -158 ppm, typical of hydrogen attached to an atom directly bound to $Cp_3U(IV)$. The chemical shifts of this compound were identical to the U(IV) impurity that was so difficult to remove in the isolation of $(MeC_5H_4)_3U{=}NPh$. Repeated recrystallization of the U=NPh compound invariably showed that trace amounts of phenylamido complex continued to be present. It appears that the phenylimido complex is thermally unstable in solution, abstracting a proton from either the solvent or glassware. In the absence of solvent, $(MeC_5H_4)_3UNPh$ can be heated to 120°C (m.p.112°) for two hours and recovered unchanged.

Uranium (V), with only one 5f electron, is expected to have a simple uv-visible spectrum. Crystal field analysis of the optical transitions usually assumes that the ligands are point charges, a description not entirely appropriate for the Cp ligands. It was therefore of interest to see if uranium(V)imido complexes could be isolated with a coordination sphere containing only monodentate ligands, finally giving optical spectroscopists an ideal molecular U(V) system to study. Use of the bis-silylamide ligand system offered additional incentive for isolating these U(V) compounds; silylamide complexes of U(IV) have been structurally characterized, and these four coordinate molecules offer a less saturated metal coordination sphere with which to study the effects of metal oxidation state on M-L bond lengths. The relative ease of isolating the $(MeC_5H_4)_3UN{=}Ph$ compound inspired the intitial use of PhNNN, but the reaction product, $[(Me_3Si)_2N]_3U{=}NPh$, could never be isolated as crystalline material; trace quantities of crytalline material that would not redissolve in toluene were occasionally isolated. In contrast, the reaction between $[(Me_3Si)_2N]_3U$ and Me_3SiNNN in hexane yielded an imido complex that crystallized upon addition of the azide. The chemical shift of the $SiMe_3$ group is shifted 3 ppm from those of the Cp compounds, suggesting a change in either metal-ligand distance or a difference in imido geometry. The amido proton resonances are extremely broad in spite of the four bond separation from the metal, $\nu_{1/2}$= 60Hz, at -2.29ppm. The chemical ionization mass spectrum of this compound had a M+1 peak (806), while electron impact M.S. gave a M-1 peak. The solid state structure of this compound (Figure 12) is interesting as

Figure 12



ORTEP Drawing of $((Me_3Si)_2N)_3U{=}NSiMe_3$

The methyl groups have been omitted

XBL 8512-4990

the 180° U-N-Si angle contains no trace of the proported stereochemically active nitrogen lone pair in $(MeC_5H_4)_3UN{=}Ph$, and involvment of the imido nitrogen lone pairs with acceptor orbitals of either the uranium or silicon must be considered. The U-N (imide) distance, 1.90(3)Å, is by far the shortest to date, 0.12Å shorter than the distance in $(MeC_5H_4)_3U{=}NPh$, and begins to approach the U-O distances (ca. 1.78 Å) found in uranyl complexes. This bond length decrease is most easily rationalized as a product of the decreased metal coordination number, although from the PES data presented below, this contraction could also result from a relatively increased U-N electrostatic attraction, resulting from substitution of Cp by the less electron donating silylamide ligands. The U-N (amide) distance, 2.28(2)Å, is longer than the 2.237(9)Å U-N distance in $[(Me_3Si)_2N]_3U$-H[60], as well as in the six coordinate $[(Me_3Si)_2N]_2UCl_2(DME)$[61], U-N= 2.234(7)Å, yet it is 0.10Å shorter than in $[(Me_3Si)_2N]_3UMe$[62], U-N = 2.37(1)Å. The suprising variation in the U(IV) structures makes unequivocal interpretation of the U(IV)/U(V) distances from such a small data set impossible, although it is interesting to note that again the U(V) ion appears to have an "ionic radius" larger than that suggested by Shannon[3].

The imido complexes $[(Me_3Si)_2N]_3U{=}NSiMe_3$ and $(MeC_5H_4)_3U{=}NSiMe_3$ have been studied[63] by gas phase photoelectron spectroscopy, with the assigned ionization potentials listed in Table 4. From the data it is obvious that the silylamide ligand is less electron donating than the Cp ligands, with lower metal IE's in the Cp compounds. This observation is consistent with that in chapter two, where U(III)Cp

complexes had a more electrion rich metal center than the U(III)silylamide complex. In $[(Me_3Si)_2N]_3U{=}NSiMe_3$, the assignments of

Table 4 Assigned Ionizations (ev) for $R_3U{=}NSiMe_3$ compounds[63]

	$[(Me_3Si)_2N]_3U{=}NSiMe_3$	$(MeC_5H_4)_3U{=}NSiMe_3$
metal valence e^-	6.79	6.45
Np-π(imido)	7.76	under Cp's
Np-π(amido)	8.60	under Cp's
Cp		7.76, 8.60, 9.13

the amido and imido π-electron bands were based on relative signal intensity. A covalent bonding model in this complex would have us predict a higher IE for the imido π-electrons, as the shorter bond implies multiple bond character and a stabilization of the N π-electrons, while from a purely electrostatic analysis, the imido N dianion should more readily lose an electron resulting in a lowered IE. The data thus far conform to the ionic model.

Diazoalkanes are similar to organic azides in their propensity to eliminate N_2, and thus it seemed reasonable to expect that the reaction of R_2CNN with U(III) would yield the uranium carbene $U{=}CR_2$. Upon addition of $NNCPh_2$ to an ether solution $MeCp_3U$-thf, no obvious color change was observed, and there was no apparent evolution of N_2. The hexane solubility of the resultant compound indicated that a reaction had occured, and small yields (20%) of an exceedingly pyrophoric compound could be isolated by crystallization. The ^1H NMR spectrum of the compound revealed Cp chemical shifts and linewidths

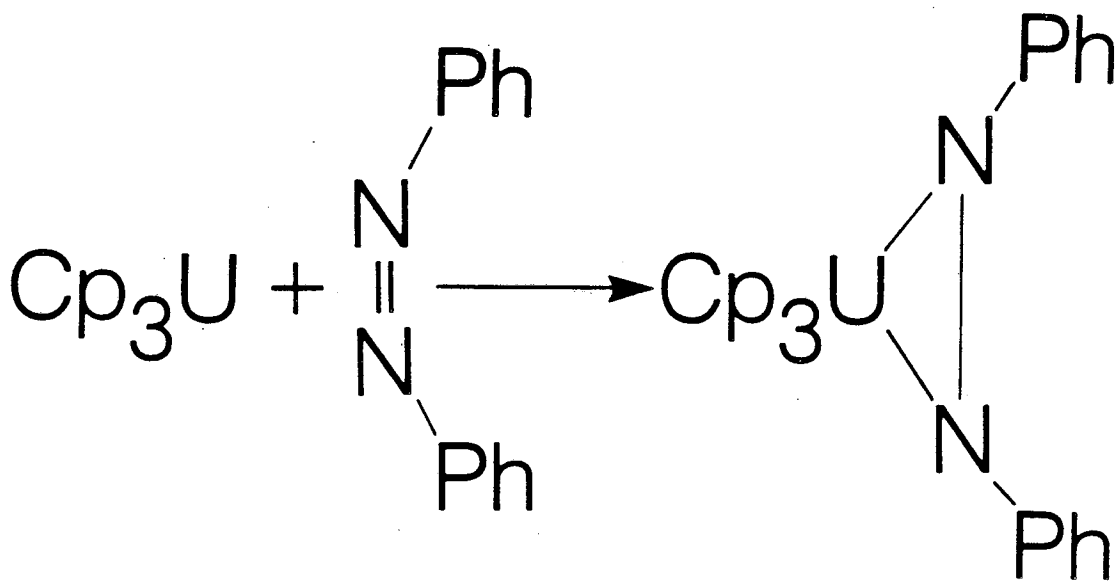
virtually identical to the U(V) imido complexes, as expected for a U(V) carbene compound, but the elemental analysis and mass spectrum both showed that the compound was instead an azine complex of uranium, $Cp_3U{=}N{-}N{=}CR_2$. The large number of broad resonances attributed to the phenyl protons in $Cp_3UNNCPh_2$ indicated a nonlinear U-N-N-C functionality (bent at either nitrogen) with a substantial interconversion barrier. Apparently initial coordination of the diazoalkane is favored at the terminal nitrogen, followed by rapid ligand reduction before the metal can approach the carbon atom. The formation of a nitrogen dianion rather than a carbon dianion can be rationalized with simple electronegativity arguments. The extreme air sensitivity of the compound (relative to $Cp_3U{=}NR$) can be attributed to the more exposed nitrogen dianion.

Organic azides and diazoalkanes are known to be thermally unstable, and thus it seemed advantageous to determine whether uranium imido complexes could be approached via alternative synthetic routes. Preliminary results of Berg indicated that Yb(II) could act either as a one electron reducing agent toward azobenzene (PhN=NPh) forming an azobenzene radical anion complex similar to known Ti or V complexes, or, if the addition stoichiometry was altered, forming a dimeric Yb complex with a bridging PhNNPh. If $(C_5Me_5)_2Yb$ could effectively coordinate each N, then it seemed reasonable to expect that Cp_3U would too, setting up possible cleavage of the N-N bond to form U(V) imido complexes. The few known examples of azoalkane complexes reacting with transition metal compounds (Co, Ir)[64] to yield imido species have required electronic activation of the azo species with electron

withdrawing CF_3 or $SiMe_3$ groups, but this electronic driving force could be attained using a low valent electropositive metal. When azobenzene and $(MeC_5H_4)_3U$-thf were added in the same reaction vessel, and hexane then added by syringe, a compound of apparent stoichiometry $(MeC_5H_4)_3U(PhNNPh)$ was isolated from hexane. The ^1H NMR linewidths are similar to the known U(V) Cp linewidths, suggesting that the compound is described as in Figure 13. The compound could never be isolated in a completely pure state, reminiscent of the problems encountered in isolating $(MeC_5H_4)_3UNPh$, and there appeared to be a small amount of $(MeC_5H_4)_3U{=}NPh$ in the NMR sample. When the reaction was redone to obtain additional product, an ether solution of PhNNPh was instead added to an ether solution of $(MeC_5H_4)_3U$-thf, immediately forming a light (U(IV)) red precipitate. Crystallization of the reaction product from ether gave a compound with a melting point range 165-170°C, and an NMR spectrum too complex to immediately analyze. Elemental analysis revealed a high percentage of N for any of the expected Cp_3UR products, but the mass spectrum seemed to solve the problem, containing a parent ion for $[(MeC_5H_4)_2U(PhNNPh)]_2$. The apparent loss of MeC_5H_4 accounted for the large amount of nitrogen present, although C and H were still higher than the expected value. The NMR spectrum contained twice as many peaks as expected for this compound, and thus it was concluded that a thf molecule was coordinating to one of the uranium atoms, destroying the symmetry and raising the amount of C and H. Structural characterization offered an alternative explanation. Single crystals from the reaction mixture were shown to be the bridging imido dimer $[(MeC_5H_4)_2U{=}NPh]_2$. The ^1H

U(V) Azobenzene Complex

Figure 13



XBL 8512-4981

NMR spectrum and elemental analysis were then consistent with a roughly 70/30 mixture of bridging PhNNPh and PhN dimers (Reaction 10), reminiscent of the reaction between Ti(III) and azobenzene[65], which forms an asymmetrically bridged dimer (Reaction 11). Yields of the uranium mixture were poor (5-10%)

10 $Cp_3U + PhN{=}NPh \longrightarrow (Cp_2UNPh)_2 + (Cp_2U)_2(\mu\text{-}PhNNPh)_2$.....

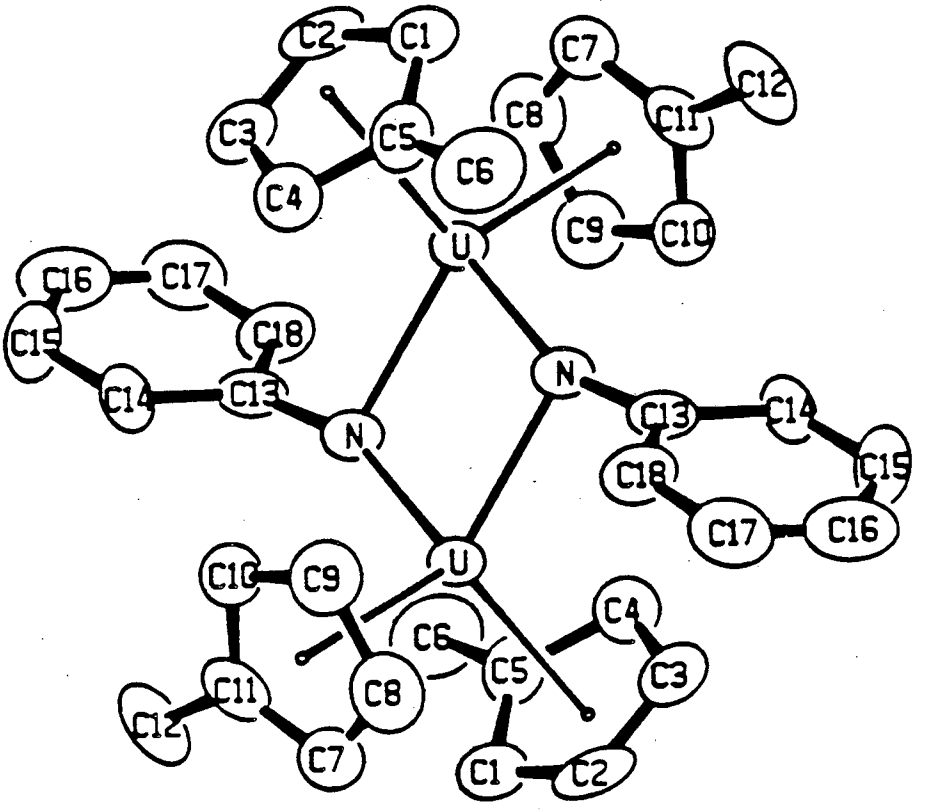
11 $CpTiCl_2 + PhN{=}NPh \longrightarrow (CpTiCl)_2(\mu\text{-}NPh)(\mu\text{-}PhNNPh) + CpTiCl_3$

via the azobenzene reaction, and separation of the two dimeric compounds appeared impossible by repeated crystallization, necessitating an alternate synthetic approach.

In Chapter one, the facile exchange of Cp ligands in coordinating solvents was noted. Given this information, and the apparent instability of the U(V) imido compounds, $(MeC_5H_4)_3U{=}NPh$ was allowed to react with $(MeC_5H_4)_3U$-thf in thf. After 24 hours, NMR analysis of the reaction mixture revealed that no starting material remained, the only two products being $(MeC_5H_4)_3UN(H)Ph$ and the desired dimer. No evidence for the formation of $(MeC_5H_4)_4U$ in this reaction mixture was observed. The identical reaction in benzene, as monitored by ^1H NMR, did not proceed similarly, instead forming a compound with one Cp resonance and broad linewidths (possibly $[(MeC_5H_4)_3U]_2NPh$). Attempted crystallization of the THF reaction product from hexane yielded a mixture identical to the initial product. In isolating the amido complex, it was virtually impossible to crystallize from ether, thus extraction of the mixture with ether, followed by cooling the

filtrate, yielded pure $[(MeC_5H_4)_2U{=}NPh]_2$. The oxidation state of the metal is clearly U(IV) judging from the NMR linewidths, and the compound has an informative mass spectrum, with parent ion M^+ = 974, M^+ -Cp = 895, M^+-2Cp = 816, M^+-3Cp = 737, M^+-4Cp = 658, and $M^+/2$ = 487amu. The structure of the complex (Figure 14) is particularly interesting, as the bridging imido ligands are unsymmetrically disposed, with inequivalent U-N distances of 2.156(8) and 2.315(8)Å. These are roughly as expected for U-N double and single bonds, and are consistent with the formulation of the U-N triple bond in $(MeC_5H_4)_3UNPh$ (U=N = 2.02(1)Å). The U-C (Cp) distances average 2.76(2)Å, similar to most other uranium Cp complexes, although the range of U-C distances (from 2.74-2.79Å) is greatly reduced. There is also a 2.86(1)Å close contact from the ipso carbon C(14) to the metal, similar to the close contacts found in numerous actinide-benzyl complexes (listed in Chapter 1, Table 1). The U-N-Ph angle, 157(1)° suggests hybridization about the nitrogen intermediate between sp and sp^2. No change in the ^1H NMR spectrum indicating formation of a monomeric coordination complex was noted when bipyridine was added to an NMR sample of the compound.

Dimeric bridging imido complexes are known to adopt two geometric forms, with either symmetric or asymmetric M-N bonds. The former is known for the the polymer[66] $[Cl_2TiNSiMe_3]_\infty$ and the zirconium[67] and titanium[68] complexes $[(Me_2N)_2M]_2(\mu\text{-t-BuN})_2$ while the latter is adopted by the uranium dimer and the molybdenum[69] and tungsten[68] compounds $[Me_2(t\text{-BuN})_2M]_2$. The difference in geometries has been described in molecular orbital language, where the localization of



ORTEP Drawing of $[(MeC_5H_4)_2U{=}NPh]_2$

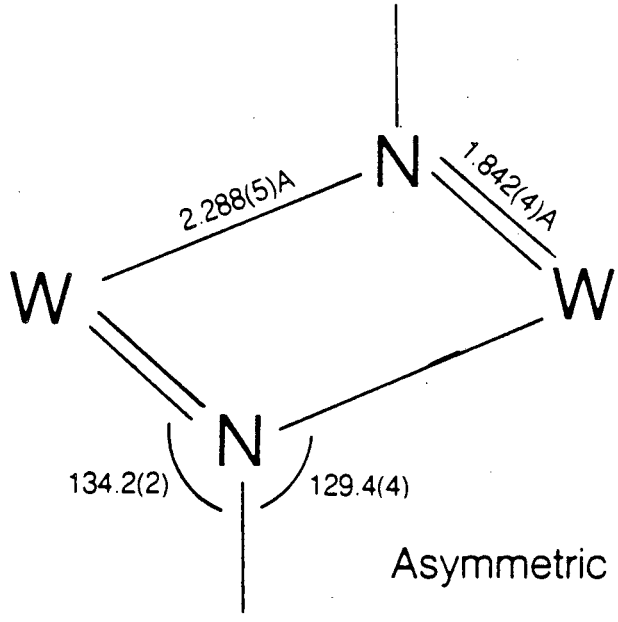
XBL 8512-4987

Figure 14

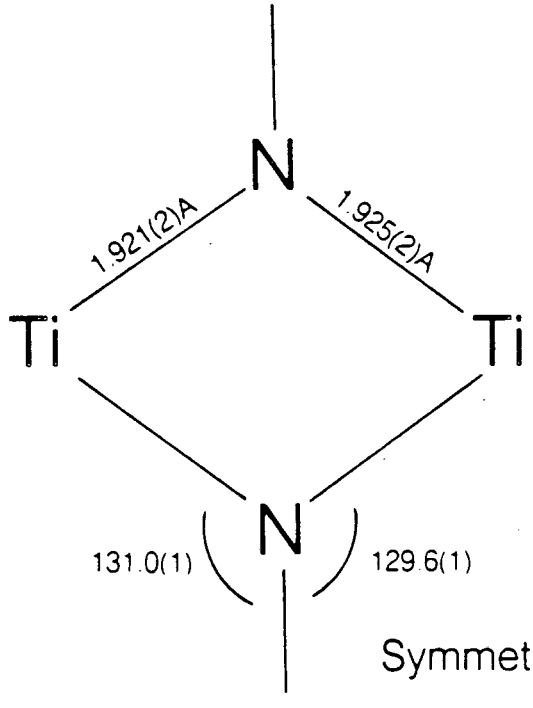
electron density in the M=NR double bond is the result of favourable π-overlap between the imido group and d or p orbitals on the metal, in contrast to the delocalized, or 'aromatic' nature of the bonding in the 'ionic' Group (IV) metal compounds. A comparison between the uranium and transition metal structures is shown in Figure 15. The uranium compound does not display the large disparity in M-N distances observed in the tungsten compound, but the 157° M-N-R angle and 0.15Å bond length difference is entirely consistent with a localized M-N multiple bond. Interpretation of bond distances or angles in organoactinide complexes is not developed to the same degree as transition metal compounds, and interpretation of an observed geometry by use of molecular orbitals is unwarranted at this time. There exist a large number of actinide complexes which contain unsymmetrically disposed bridging or unaccountably displaced terminal ligands, but there also exist examples with symmetric structures. There has never been a systematic study of the effect of small perturbations from the imido ligands on the resulting μ-imido complex geometry while maintaining a constant coordination sphere. There are a number of interesting synthetic alterations one could make in this system; substitution of Th for U, or P for N, could yield data that are helpful in interpreting the asymmetric bridge structure. One approach to the Th compound, reaction of $Cp_2ThMe_2(DMPE)$ with $PhNH_2$ in ether, gave no isolable product, but the experiment should be repeated with rigorously purified aniline.

Alternatively, substition of the phenyl group by one incapable of coordination to the metal center, should sufficiently alter the U-N-R

Transition Metal Bridging Imido Complexes



Asymmetric Bridge



Symmetric Bridge

XBL 8512-4998

Figure 15a

Bridging Imido Complexes of Uranium

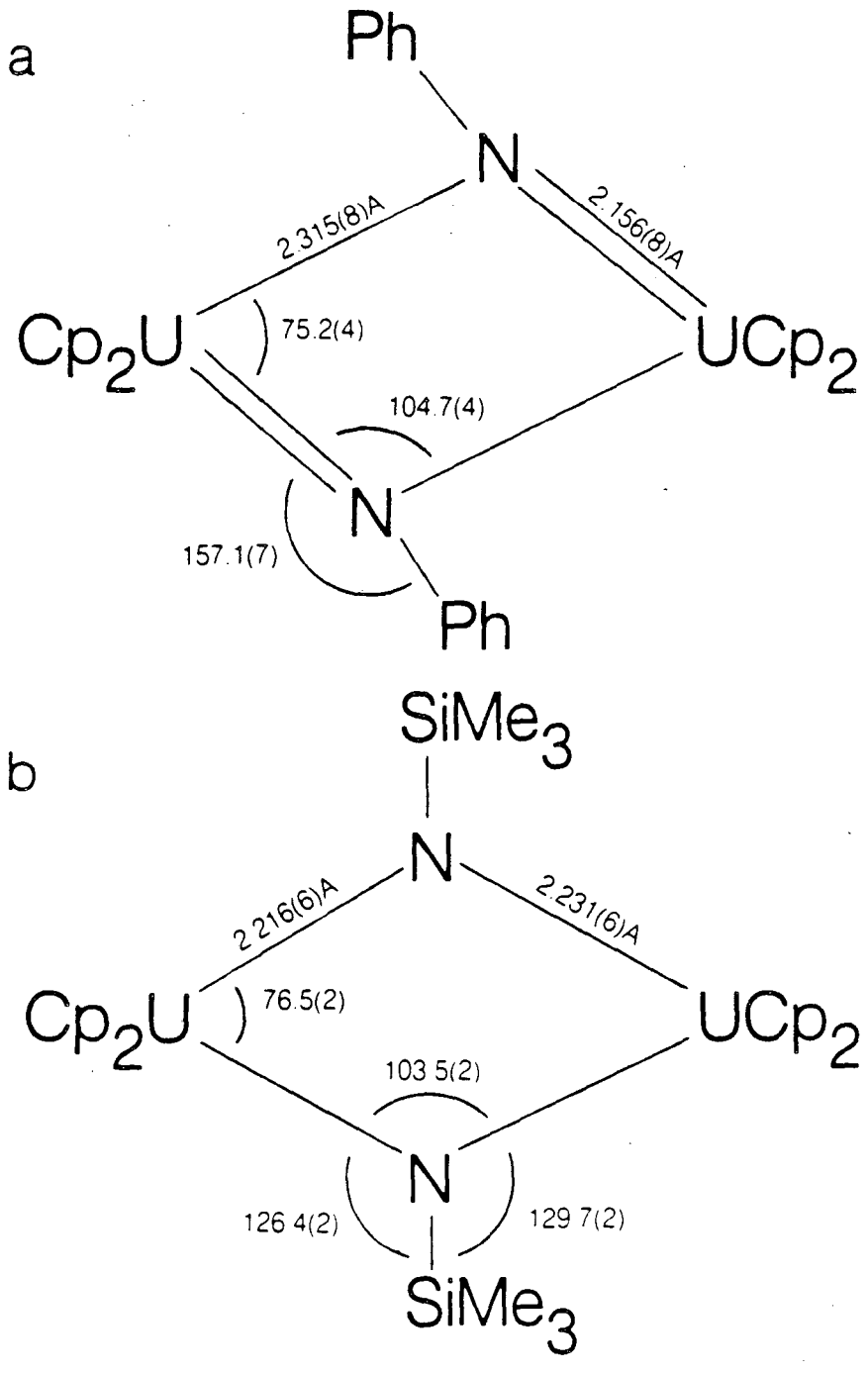
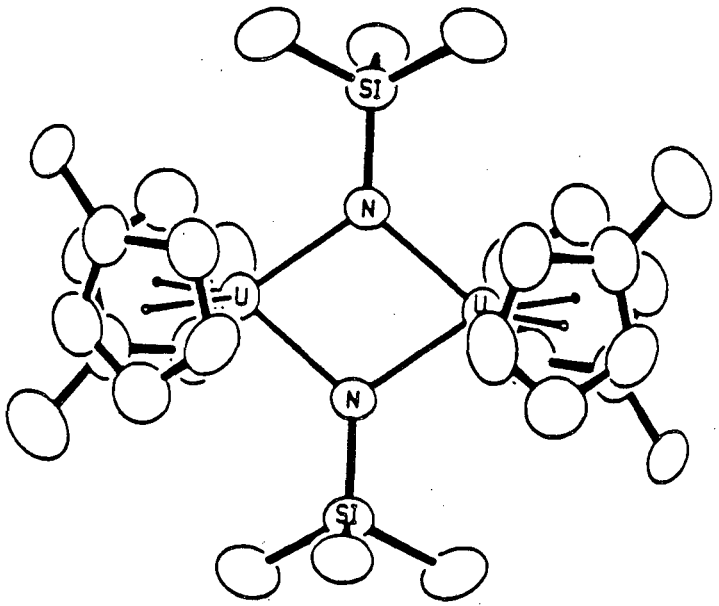


Figure 15b

XBL 8512-5015

angle so as to have a measurable effect on the U-N bonding. Using the most successful synthetic approach to these compounds, $(MeC_5H_4)_3U$-thf was allowed to react with $(MeC_5H_4)_3U{=}NSiMe_3$. Crystallization from hexane produced two distinct crystalline forms; the major product contained no nitrogen, and exhibited an ion in the mass spectrum consistent with $(MeC_5H_4)_4U$. The minor product, which was separated by hand, contained a parent ion in the mass spectrum for the expected dimer; in contrast with the phenyl analog, this compound contained none of the obvious fragmentation patterns, showing only trace loss of one of the Cp rings. The unit cell of the compound was the same as that of the Ph derivative, though the volume was slightly larger. As shown in Figure 16, the compound contains nearly symmetric imido bridges between the metal centers, with U-N distances of 2.216(4)Å and 2.231(4)Å. These distances are in the range found for a large number of terminal dialkylamide complexes of U(IV), and close to the average of the two inequivalent U-N distances found in the bridging phenyl compound. Thus if the R groups are stabilizing the imido N by withdrawing electron density, Ph and $SiMe_3$ have comparable withdrawing capabilities. If the six bonding electrons available at nitrogen are all involved in bonding with the metal, then single, double and triple U-N bond lengths can be considered roughly 2.02Å, 2.16Å, and 2.31Å, respectively. The predominant 2.23Å terminal U-N bond lengths observed in terminal uranium dialkylamide complexes are then consistent with partial U-N double bond character, explaining the planar geometries at the nitrogen atom. The 3.493(1)Å U-U distance in the $SiMe_3$ derivative is increased relative to the 3.542(1)Å distance

ORTEP Drawing of $[(MeC_5H_4)_2UNSiMe_3]_2$



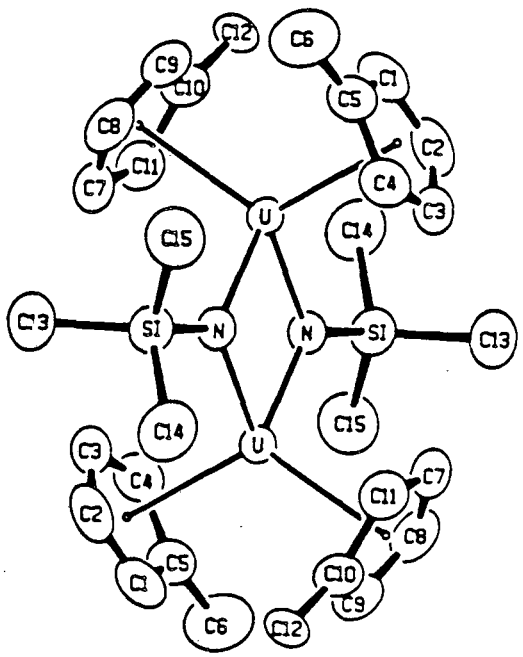


Figure 16

XBL 8512-5001

in the Ph compound, demonstrating that the observed asymmetry is not a result of repulsive interactions between the metal centers. Such a gross geometric perturbation from alteration of the imide ligand is unparalleled in d-metal chemistry.

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CHAPTER FOUR: EXPERIMENTAL DETAILS

General

The ^{1}H (89.5MHz), ^{13}C (22.5MHz), and ^{31}P (36.2MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer in deuterated benzene or toluene dried over NaK alloy. Solvent was used as an internal reference; in C_6D_6, δ = 128.0 (^{13}C) or 7.15 (^{1}H), and in C_7D_8, the methyl signals were used, δ = 20.4 (^{13}C), 2.09 (^{1}H). The ^{13}C data are reported with coupling constants when available, or multiciplities when partially decoupled. Spectra without J_{CH} were ^{1}H decoupled. The $^{31}P\{^{1}H\}$ spectra were referenced to external 85% H_3PO_4 (δ= 0.0). The thermocouple was calibrated with a methanol sample[1].

The IR spectra were recorded on a Perkin-Elmer 297 spectrometer; the CO spectra were calibrated with a polystyrene window. Magnetic susceptibility measurements were done as previously described[2]. Mass spectra were obtained with Atlas MS-12 and Consolidated 12-110 instruments from the U.C.Berkeley mass spectroscopy laboratory. Elemental analyses were obtained from the College of Chemistry Microanalytical Laboratories.

All work was conducted under inert atmosphere (Ar or N_2) using standard Schlenk techniques, or in an inert atmosphere glovebox. Melting points were measured in sealed capillaries and are uncorrected.

Unless the purchased UCl_4 completely dissolved in thf, it required treatment with $SOCl_2$ reflux for 7 days, followed by repeated

extraction of the finely ground solid with dry CH_2Cl_2 until the solution was colorless, and heating under vacuum (150°C, 8-10 hours, 1 mtorr). The UBr_4 was prepared according to literature procedures[3]. The $ThCl_4$ was always treated with $SOCl_2$ as above.

Cyclopentadienide anion was prepared from freshly cracked C_5H_6 monomer as either the Na or K salt in thf, or as the K salt in diethyl ether; the K reaction is slightly more exothermic. Methylcyclopentadiene is considerably less reactive than cyclopentadiene, and it's rate of reaction with K is convenient. Trimethylsilylcyclopentadiene was prepared from KC_5H_5 and $ClSiMe_3$ in diethyl ether; isolation by filtration and fractional distillation gave yields greater than 70-80%, and the entire procedure can be performed under rigorously H_2O and O_2 free conditions. Synthesis according to literature procedure[4] invaribly gave a product heavily contaminated with thf and water. $NaN(SiMe_3)_2$ was prepared according to the literature method[5], as was $MX_4(DMPE)_2$,[6] NNNPh[7], $SeP(n\text{-}bu)_3$,[8] and $TeP(n\text{-}bu)_3$.[9] Bis 1,2-dimethylphosphinoethane was prepared from the tetrachloride and MeMgCl[10]. Pyridine, SC_4H_8, and very wet $P(OMe)_3$ were dried over Na and distilled. S.Stults supplied the $NNCPh_2$, and R. Shinomoto, the $(MeBH_3)_4U$.

CHAPTER ONE

$(C_5H_5)_2UCl_2(DMPE)$

$UCl_4(DMPE)_2$ (1.25 g, 1.84 mmol) was dissolved in tetrahydrofuran (40 mL) and the solution was cooled to -70°C. NaC_5H_5 (4.0 mL 0.91 M. in thf, 3.7 mmol) was added dropwise by syringe, and the solution

color slowly changed from blue to green. The temperature was raised slowly to -45°C and held there for one hour, then warmed to room temperature. Toluene was added (10 mL), and the green solution was filtered. The volume was reduced under reduced pressure to ca. 13 mL, and the solution was cooled to -75°C. Green crystals, m.p 231-232°C, (0.82g, 76%) were collected and dried under vacuum. ^{1}H NMR (C_6D_6, 21°C): 12.89(10H), 4.79(12H), -0.99(4H). ^{13}C NMR (C_6D_6, 21°C): 290.03, 40.53, 32.81. Anal. Calcd. for $C_{16}H_{26}Cl_2P_2U$: C, 32.6; H, 4.45; Cl, 12.0; P, 10.5. Found: C, 32.9; H, 4.53; Cl, 12.8; P, 10.2. IR data (Nujol, KBr): 1280 m, 1140 w, 1013 s, 944 s, 930 s, 807 m, 790 s, 728 s, 696 s, 645 w cm^{-1}.

$(MeC_5H_4)_2UCl_2(DMPE)$

$UCl_4(DMPE)_2$ (0.75 g, 1.1 mmol was dissolved in thf (40 mL) and the solution cooled to -78°C. NaC_5H_4Me (2.18 mL 1.01 M in thf, 2.21 mmol) was added dropwise by syringe, and the color of the solution slowly turned brown. The solution was left at -70°C for 4 hours, then warmed to room temperature. The solvent was removed under vacuum, and the brown solid was extracted with a toluene/pentane mixture (5 mL/5 mL). The solution was filtered and cooled to -25°C, yielding dark green-brown crystals, m.p. 152°C. Yield was 0.32 g, 47%. ^{1}H NMR (C_7D_8, 28°C): 14.18(4H), 13.43(12H), 7.10(4H), -1.78(4H), -9.15(6H). ^{13}C NMR (C_7D_8, 25°C): 308.5, 260.7, 222.0, 37.55, 30.00, -17.60. Anal. Calcd. for $C_{18}H_{30}Cl_2P_2U$: C, 35.0; H, 4.90; P, 10.0; Cl, 11.5. Found: C, 35.3; H, 4.85; P, 9.90; Cl, 11.5. IR data (Nujol, CsI):

1288 w, 1236 w, 1139 w, 1045 w, 1073 w, 1025 m, 930 m, 890 w, 845 m, 777 m, 697 m, 645 m, 605 w, 444 m, 330 s, 238 s, 215 s cm^{-1}.

$(C_5H_5)_2UBr_2(DMPE)$

$UBr_4(DMPE)_2$ (3.60 g, 4.19 mmol) was dissolved in thf (100 mL) and the solution temperature lowered to -70°C. NaC_5H_5 (9.22 mL, 0.91 M in thf, 8.4 mmol) was added by syringe. The temperature of the solution was raised slowly to -50°C, where the color slowly changed to brown. After one hour at -50°C, the solution was raised to room temperature and the thf was removed under vacuum. The brown solid was extracted with toluene (20 mL), filtered, and cooled to -78°C. Brown needles (1.8 g, 63%), m.p. 230-232°C, were collected and dried under vacuum. ^1H NMR (C_7D_8, 23°C): 16.30(12H), 8.23(10H), -0.40(4H). ^{13}C NMR (C_7D_8, 25°C): 298.90, 48.34(broad, PCH_2), 39.17(d, J_{PC}=10.25 Hz). Anal. Calcd. for $C_{16}H_{26}Br_2P_2U$: C, 28.3; H, 3.86; P, 9.13; Br, 23.6. Found: C, 28.2; H, 3.70; P, 9.12; Br, 23.7. IR data (Nujol, CsI): 1413 m, 1282 m, 1147 w, 1069 w, 1014 s, 945 s, 929 s, 885 w, 864 w, 838 w, 795 w, 782 s, 731 s, 699 s, 645 m, 228 m cm^{-1}.

$(C_5H_5)_2UMe_2(DMPE)$

$(C_5H_5)_2UCl_2(DMPE)_2$ (1.20 g, 2.04 mmol) was dissolved in toluene (30 mL), and diethyl ether (150 mL) was added. The solution was cooled to -70°C, and MeLi (4.47 mL, 0.91 M in ether, 4.1 mmol) was added by syringe. The solution was warmed slowly to -55°C, where the color began turning red. After one hour at -55°C, the temperature was raised to -20°C, and the ether was removed by vacuum until the total

volume was 20 mL. Pentane (50 mL) was added, and the red solution was filtered and cooled to -78°C. Red crystals (0.39 g, 36%), m.p. 84-86°C(dec.), were collected and dried under vacuum. ^{1}H NMR (C_7D_8, -12°C): 99.18(6H), -7.99(12H), -17.87(4H), -29.34(10H). ^{13}C NMR could not be obtained due to apparent thermal instability. Anal. Calcd. for $C_{18}H_{32}P_2U$: C, 39.4; H, 5.88; P, 11.3. Found: C, 39.6; H, 5.54; P, 9.69. IR data, (Nujol, CsI): 1279 w, 1140 m, 1095 m, 1060 w, 1010 s, 944 s, 885 m, 840 w, 827 w, 775 s, 690 m, 640 m, 608 w, 470 m, 365 s, 214 s cm^{-1}. If MeMgCl was used as the alkylating agent, the reaction proceeded slowly at -20°C, and only the redistribution product Cp_3UMe could be isolated. With $AlMe_3$, a red solution immediately formed at -70°C, but the product decomposed above -30°C, giving an insoluble precipitate.

$(C_5H_5)_2U(CH_2SiMe_3)_2(DMPE)$

To $(C_5H_5)_2UCl_2(DMPE)$ (0.65 g, 1.1 mmol) dissolved in toluene/diethyl ether (25/350 mL) at -70°C was added by syringe $LiCH_2SiMe_3$ (2.01 mL, 1.1 M in hexanes, 2.2 mmol). After half of the addition the solution turned red and a precipitate was evident. The remaining Li reagent was added, and approximately three minutes later the solution cleared. The solution was kept at -70°C for two hours, then warmed to room temperature. The solvent was removed, and the red solid extracted with pentane (2 x 5 mL). Cooling the red filtrate yielded red crystals (0.16 g, 21%), m.p. 70-73°C(dec). ^{1}H NMR (C_7D_8, -80°C): 132.76(4H), 41.42(18H), -18.13(12H), -31.79(4H), -53.21(10H). Anal. Calcd. for $C_{24}H_{68}Si_2P_2U$: C, 41.6; H, 6.94; P, 8.96. Found: C,

41.5; H, 7.04; P, 6.45. IR data (Nujol, CsI): 1300 m, 1260 s, 1100 s, 1020 s, 940 m, 890 m, 862 m, 834 m, 798 s, 470 w, 395 s, 255 w cm^{-1}.

$(C_5H_5)U(CH_2SiMe_3)_3(DMPE)$

$UCl_4(DMPE)_2$ (0.97 g, 1.4 mmol) was dissolved in thf, and the temperature of the solution was lowered to -78°C. $LiCH_2SiMe_3$ (3.9 mL, 1.1 M in hexanes, 4.3 mmol) was added by syringe. The color immediately changed from blue to dark green. After stirring for one hour, NaC_5H_5 (1.51 mL, 0.91 M in thf, 1.4 mmol), was added by syringe. The solution was kept at -70°C for two hours, while the color slowly went red. The temperature was raised to -10°C, and the solvents were removed by vacuum. The red solid was extracted with a toluene/pentane mixture (10 mL/50 mL), but crystallization could not be induced at -78°C. The solution was then taken to dryness, and the red solid extracted with pentane (30 mL). Cooling to -60°C yielded red crystals (0.24g, 23%), m.p. 100-101°C. ^1H NMR (C_7D_8, -70°C): 85.22(4H), 58.44(9H), 56.31(9H), -15.16(6H), -19.88(4H), -23.03(3H), -37.83(18H), -43.74(6H), -76.32(3H). At higher temperatures, a number of peaks broaden into the baseline, and only three peaks can be observed at 45°C: 9.05(9H), -14.82(6H), -22.26(2H). No carbon spectrum could be obtained. Anal. Calcd. for $C_{23}H_{54}P_2Si_3U$: C, 39.0; H, 7.68; P 8.76. Found: C, 38.7; H, 7.41; P, 7.72. IR data, (Nujol/CsI): 1298 w, 1282 w, 1245 m, 1234 m, 1013 w, 939 m, 927 w, 898 w, 870 m, 850 s, 814 m, 783 m, 772 m, 747 w, 730 m, 720 m, 705 w, 670 w, 425 w, 335 w cm^{-1}.

$[(C_5H_5)_3U]_2DMPE$

To $UCl_4(DMPE)_2$ (1.69 g, 2.48 mmol) dissolved in thf (30 mL) at -70°C was added NaC_5H_5 (1.77 mL 1.4 M in thf, 2.5 mmol). After 30 minutes LiMe (8.19 mL 0.91 M in ether, 7.5 mmol) was added by syringe. The temperature was raised to -60°C, and the solution slowly turned red. After one hour, the temperature was raised to -20°C, and the thf removed by vacuum. Toluene (20 mL) and DMPE (1 mL, 6 mmol) were then added by syringe, and the cherry red solution was kept at room temperature for 14 hours, during which the solution darkened, and pressure increased in the flask. Pentane (10 mL) was added, the solution was filtered, and cooled (-20°C). After two days, red crystals (0.08 g, 19% based on Cp), m.p. >300°C, were collected and dried. The compound would not redissolve in hydrocarbon solvents. The ^1H NMR spectrum required 500 scans, and the S/N ration was such that the integrations are ±40%. ^1H NMR (C_6D_6, 30°C): -4.79(broad signal, $\nu_{1/2}$= 150 Hz, 7H), -16.90(5H), -13.07(.6H). The peak at -13.07 increased in relative intensity with time. IR data (Nujol, CsI): 1300 w, 1288 w, 1260 w, 1096 w, 1010 m, 938 m, 898 m, 770 s, 747 s, 728 w, 213 m cm^{-1}.

$(C_5H_5)_2ThCl_2(DMPE)$

$ThCl_4(DMPE)_2$ (0.87 g, 1.3 mmol) was dissolved in thf (50 mL) and the solution temperature lowered to -70°C. NaC_5H_5 (2.84 mL 0.91 M in thf, 2.6 mmol) was added dropwise by syringe. The temperature was held at -70°C for four hours, and then warmed to room temperature. The thf was removed by vacuum, and the white solid extracted with

toluene (2 x 10 mL). The filtrate was concentrated to ca. 7 mL, and cooled to -78°C. Clear crystals (0.42 g, 56%) were collected and dried, m.p. 253°C. Crystals suitable for X-ray analysis were obtained by recrystallizing from a toluene/ether (6 mL/4 mL) mixture at -20°C. ^{1}H NMR (C_6D_6, 21°C): 6.34 (s, 10H, below -12°C this splits into an apparent triplet J_{CP}= 0.55 Hz. The spectrum was recorded using 32K data for an 800 Hz sweep width), 1.16(m, 4H, the distance between the outermost peaks is 13.8 hz), 0.97(12H, t, J_{PH}=9.6 hz). ^{13}C NMR (C_6D_6, 21°C): 118.12, 26.58(t, J=11.85 Hz), 12.84 (t, J= 3.9 Hz). ^{31}P NMR (C_6D_6, 21°C, external H_3PO_4 reference): -19.76. Anal. Calcd. for $C_{16}H_{26}Cl_2P_2Th$: C, 33.0; H, 4.49; P, 10.6; Cl, 12.2. Found: C, 33.2; H, 4.64; P, 10.3; Cl, 12.0. IR data (Nujol/CsI): 1420 w, 1283 m, 1260 m, 1145 m, 1127 w, 1098 w, 1060 wm 1012 s, 945 s, 930 s, 869 w, 820 s, 780 s, 729 m, 698 s, 645 w, 605 w, 265 w, 228 s.

$(C_5H_5)_2ThMe_2(DMPE)$

$(C_5H_5)_2ThCl_2(DMPE)$ (0.66g, 1.1 mmol) was dissolved in diethyl ether/toluene (200/20 mL) and the solution cooled (-78°C). LiMe (2.49 mL 0.91 M in ether, 2.3 mmol) was added by syringe. Over a three hour period the solution was warmed to -10°C, and the solvent was removed by vacuum. The white solid was extracted twice with a toluene/pentane mixture (5mL /20 mL), and the combined filtrates cooled to -78°C. Clear crystals (0.29 g, 49%), m.p. 139°C(dec), were collected and dried. The crystals appeared to eliminate a gas upon heating at 124-128°C. ^{1}H NMR (C_6D_6, 21°C): 6.15(10H, s), 1.03(4H, m), 0.80(12H, t, J=1.47 Hz), -0.11(6H, s). At lower temperatures the peak at -0.11

split into a triplet due to coupling with the phosphine ligand, with J_{PH}=4.8 Hz. ^{31}P NMR (C_6D_6, 21°C): -37.69, but at low temperatures the peak split into a multiplet. Anal. Calcd. for $C_{18}H_{32}P_2Th$: C, 39.9; H, 5.90; P, 11.44. Found: C, 39.5; H, 5.73; P, 10.00. IR data (Nujol/CsI):1419 w, 1295 m, 1279 m, 1140 m, 1090 s, 1060 w, 1010 s, 937 s, 925 w, 827 w, 775 s, 690 s, 640 w, 500 m, 465 w, 360 s, 217 s cm^{-1}.

$(C_5H_5)_2Th(CH_2C_6H_5)_2$(DMPE)

$(C_5H_5)_2ThCl_2$(DMPE) (1.15 g, 1.97 mmol) was dissolved in a mixture of ether and toluene (300 mL/30 mL), and the solution cooled to -70°C. Benzyl lithium (4.92 mL 0.80 M in toluene, 3.5 mmol) was added dropwise by syringe. The solution was stirred for 2 hours, and then warmed slowly to -10°C. The solvent was removed by vacuum, the yellow solid was extracted twice with a pentane/toluene mixture (10 mL/10 mL), and the filtrate was cooled to -78°C. Yellow crystals (0.52 g, 38%), m.p. 150-151°C(dec), were collected and dried under reduced pressure. ^1H NMR (C_7D_8, 20°C): 6.74, 7.19 (10H, broad multiplets), 5.89 (10H, s), 1.43 (4H, s), 1.20 (4H, m), 0.81 (12H, broad peak). Anal. Calcd. for $C_{30}H_{40}P_2Th$: C, 51.9; H, 5.80; P, 8.92. Found: C, 51.6; H, 5.83; P, 7.98. IR data (Nujol, CsI): 1587 s, 1560 w, 1282 w, 1260 w, 1205 s, 1013 m, 995 w, 972 w, 962 w, 918 s, 860 m, 830 w, 810 m, 790 s, 783 m, 775 s, 740 s, 694 m, 544 w, 512 w, 308 w cm^{-1}.

$(C_5H_5)Th(CH_2SiMe_3)_3(DMPE)$

To $ThCl_4(DMPE)_2$ (1.14 g, 1.69 mmol) dissolved in thf (150 mL) at -70°C was added by syringe NaC_5H_5 (1.7 mL 0.91 M in thf, 1.6 mmol); after 30 minutes, $LiCH_2SiMe_3$ (4.64 mL 1.1 M in hexane, 5.1 mmol) was added. The solution slowly turned opaque as LiCl precipitated. After two hours, the solution temperature was raised to room temperature, and the solvent removed by vacuum. The residue was extracted with hexane (40, 30 mL), filtered, and cooled (-70°C) yielded feathery white crystals (0.42g, 52%), m.p. 117-119°C(dec). Upon melting gas evolution was observed, and the color of the sample turned orange. This decomposition product melted reversibly when cooled to room temperature and placed back in the melting point apparatus. ^1H NMR (C_6D_6, 26°C): 6.44(5H, s), 1.08(4H, m), 0.83(12H, t), 0.31(27H, s), -0.45(6H, s). At low temperatures, the Cp resonance splits into two peaks of varying relative areas. At -66°C, there are peaks at 6.66 and 6.26 ppm with roughly 1:1 intensities. Raising the temperature relatively increases the intestity of the peak at 6.66 ppm. Anal. Calcd. for $C_{23}H_{54}P_2Si_3Th$: C, 39.0; H, 7.58; P, 8.63. Found: C, 39.0; H, 7.17; P, 6.33. IR data (Nujol, CsI): 1298 w, 1245 m, 1234 s, 1011 m, 940 m, 900 w, 850 s, 813 w, 777 s, 720 s, 669 m, 427 w, 374 w, 355 w cm^{-1}.

Attempted preparation of $(C_5H_5)_2Th(CH_2SiMe_3)_2(DMPE)$

To $Cp_2ThCl_2(DMPE)$ (0.81 g, 1.4 mmol) dissolved in ether/toluene (200/25 mL) was added by syringe $LiCH_2SiMe_3$ (2.35 mL, 1.1 M in hexane, 2.6 mmol). The solution was kept at -70°C for two hours, then warmed

slowly (four hours) to room temperature. All solvent was removed, and the white solid was extracted with pentane (3x 20 mL). Cooling the filtrate yielded clear needles (0.21 g), of compound identified as $(C_5H_5)Th(CH_2SiMe)_3(DMPE)$ by ^1H NMR spectroscopy.

Reaction of $(C_5H_5)_2UCl_2(DMPE)$ with $NaN(SiMe_3)_2$

To $Cp_2UCl_2(DMPE)$ (0.46 g, 0.78 mmol) dissolved in toluene (30 mL) was added by syringe $NaN(SiMe_3)_2$ (6.2 mL 0.26 M in toluene, 1.6 mmol). After the first equivalent was added, the solution turned red; addition of the second equivalent caused no further color change. The solution was stirred for one hour, and then kept at room temperature for three hours. Removal of the solvent left a red solid which was extracted with toluene/pentane (10/30 mL) and again with toluene (10 mL). Cooling the combined filtrate yielded tan crystals (0.12 g, 32%) of Cp_3UCl (by IR, ^1H NMR). The remaining supernatent was taken to dryness and shown by ^1H NMR to be a mixture of traces of Cp_3UCl and the previously reported bis(silylamide) uranium metallacycle[14].

Reaction of Cp_3UCl with $UCl_4(DMPE)_2$

A solution of $UCl_4(DMPE)_2$ (1.10 g, 1.62 mmol) and Cp_3UCl (0.79g, 1.7 mmol) was refluxed in toluene (30 mL) for three days. Removal of the solvent left a mixture which was shown by ^1H NMR spectroscopy to contain starting materials and <u>ca.</u> 1% $Cp_2UCl_2(DMPE)$.

$(MeC_5H_4)_3UCl$

To UCl_4 (4.00 g, 10.5 mmol) dissolved in thf (80 mL) was added by syringe $Na(MeC_5H_4)$ (31.3 mL 1.01 M in thf, 31.6 mmol). Instantly the solution color turned red. After three hours, the thf was removed by vacuum, and the red solid extracted with toluene/pentane (5x, 10/10 mL). Cooling the red filtrate (-80°C) yielded light red needles (3.2g, 65%), m.p. 207-210°C. ^1H NMR (C_7D_8, 25°C): 11.86(2H), -0.44(3H), -19.79(2H). ^{13}C NMR (C_7D_8, 25°C): 267.49, 231.79, 226.40, -12.20. Mass spectrum: M^+= 468, Cp_3U^+= 433, Cp_2UCl^+= 403, $CpUCl^+$= 338 amu. IR data (Nujol, CsI): 1490 w, 1345 w, 1260 w, 1070 w, 1047 w, 1028 s, 932 m, 840 m, 785 s, 720 w, 696 w, 609 m, 345 m, 240 s cm^{-1}.

$(MeC_5H_4)_3UAlH_4$

To Cp_3UCl (0.45 g, 0.96 mmol) dissolved in thf at -70°C was added $LiAlH_4$ (35 mg, 0.92 mmol). The solution color immediately turned grey; after stirring at -70°C for one hour, the solution was warmed to room temperature, and was stirred for 24 hours. The solvent was removed under reduced pressure, leaving a green-red solid which was insoluble in toluene. THF (10 mL) was added, the green solution was filtered and cooled (-20°C), yielding green crystals (0.12g) which desolvated when exposed to vacuum. Anal. Calcd. for $C_{15}H_{19}AlU$: C, 39.8; H, 4.12; Al, 5.81. Found: C, 40.9; H, 4.19; Al, 6.2. IR data (Nujol, CsI): 1300w, 1259s, 1080s, br, 1040s, br, 1013s, br, 791s, 750m, 720w, 390w cm^{-1}. Substitution of $LiAlD_4$ gives the following IR: 1300w, 1280w, 1260w, 1070m, 1025s, 918w, 873m, 770s, br, 600m, 534w, 305w, 230w cm^{-1}.

$(MeBH_3)_4U(DMPE)$

To $U(MeBH_3)_4$ (0.24 g, 0.68 mmol) dissolved in pentane (20 mL) was added by syringe DMPE (0.11 mL, 0.66 mmol). Immediately a green precipitate formed, leaving a colorless solution. Hexane was removed by vacuum, and the green solid was dissolved in toluene (10 mL). The toluene was filtered, concentrated to ca. 3 mL, and cooled (-20°C). Green diamonds (0.16 g, 48%), m.p. 131-132°C(dec), were collected and washed with ether. ^1H NMR (C_7D_8, -54°C): 429.10(3H), 57.46(3H), -7.79(6H), -14.86(2H), -15.41(3H), -30.87(3H). Anal. Calcd. for $C_{10}H_{40}B_4P_2U$: C, 23.9; H, 8.01; P, 12.3. Found: C, 23.4; H, 8.25; P, 9.99. IR data (Nujol, CsI): 2950 m, 1415 w, 1300 m, 1285 m, 1220 s, 1075 s, 940 s, 925 s, 890 m, 865 m, 830 m, 795 m, 735 m, 705 m, 645 m, 439 w, 264 s cm^{-1}.

$[(Me_3Si)_2N]_3U$

To $[(Me_3Si)_2N]_3UCl$ (16.5 g, 21.9 mmol) suspended in hexanes (100 mL) was added t-butyllithium (15.1 mL 1.45 M in hexane, 21.9 mmol). Instantly the color darkened. After 24 hours, the deep red solution was filtered, concentrated (ca. 40 mL) and cooled (-80°C). Red needles were collected and recrystallized from hexane to remove traces (ca. 5% each) of tris silylamide uranium hydride[14] and silylamide metallacycle[14], identified by ^1H NMR. Final yield was 11.5 g, 73%.

$(MeC_5H_4)_3UCMe_3$

$(MeC_5H_4)_3UCl$ (2.83 g, 5.55 mmol) was dissolved in toluene (50 mL), and t-butyllithium (3.83 mL 1.45 M in hexane, 5.60 mmol) was

added by syringe. The solution turned dark green immediately. After one hour, the solvent was removed by vacuum, the dark green solid dissolved in ether (55 mL), and the solution was filtered and cooled (-80°C). Green needles (1.87 g, 63%), m.p. 220-226°C(dec), were collected and dried by vacuum. ^{1}H NMR (C_7D_8, 28°C): 10.07(2H), -6.17(2H), -9.27(3H), -19.31(3H). ^{13}C NMR (C_7D_8, 28°C): 259.01(d), 231.65(s), 228.98(d), -42.89(q), -176.94(q). Anal. Calcd. for $C_{22}H_{30}U$: C, 49.6; H, 5.67. Found: C, 48.9; H, 5.79. IR data (Nujol, CsI): 1260 w, 1086 w, 1040 m, 845 m, 814 m, 773 s, 720 m, 400 w, 330 w cm^{-1}.

$(MeC_5H_4)_3UCOCMe_3$

$(MeC_5H_4)_3UCMe_3$ (1.9 g, 3.6 mmol) was dissolved in hexane (30 mL), and the solution was placed under one atomsphere of carbon monoxide for six hours, during which the color gradually changed from green to red, and some precipitate formed. Filtration of the solution, followed by cooling (-80°C), yielded a red semicrystalline solid (0.22 g, 11%), m.p. 72-76°C. ^{1}H NMR (C_7D_8, 31°C): 6.97(2H), -6.72(2H), -7.09(3H), -13.96(3H). ^{13}C NMR (C_6D_6, 31°C): 185.10(d), 181.52(d), 163.77(s), 22.20(q), -33.01(q). The acyl carbon was not observed. Anal. Calcd. for $C_{23}H_{30}OU$: C, 49.3; H, 5.39. Found: C, 49.2; H, 5.44. IR data (Nujol, CsI): 1490 m, 1305 w, 1258 w, 1237 w, 1222 w, 1068 w, 1045 m, 1030 m, 970 w, 927 m, 885 w, 843 m, 762 s, 718 m, 600 m, 389 m, 330 m, 229 m cm^{-1}. The compound did not react with D_2 (75 psi, in toluene).

$(MeC_5H_4)_3UF$

(A) $(MeC_5H_4)_3U$-thf (1.49 g, 2.72 mmol) was dissolved in toluene (20 mL). The reaction vessel was exposed to a vacuum, then the flask was connected to a metal vacuum line and a PF_3 atmosphere line. The flask was opened to the PF_3 atmosphere, and the color immediately changed from brown to green. After four hours, the contents of the flask were taken to dryness, and the green solid extracted with toluene (20 mL). The green solution was filtered, concentrated to ca. 15 mL, and cooled to -20°C, yielding light green crystals (0.26 g, 19%), m.p. 198-202°C.

(B) $(MeC_5H_4)_3UCMe_3$ (0.71 g, 1.33 mmol) was dissolved in toluene (25 mL), and the solution exposed to an atmosphere of PF_3 as in (A) above. The solution was stirred for 20 hours, and then taken to dryness. Extraction with toluene (25 mL), followed by concentration to 20 mL, and cooling to -20°C yielded a green compound (0.12 g, 18%) identical to that formed in (A) above. ^1H NMR (C_6D_6, 27°C): 5.61(2H), -2.11(3H), -19.25(3H). ^{13}C NMR (C_6D_6, 27°C): 221.38(d), 173.78(d), 151.41(s), -6.87(q). Anal. Calcd. for $C_{18}H_{21}FU$: C, 43.7; H, 4.28. Found: C, 43.8; H, 4.38. IR data (Nujol, CsI): 1061 w, 1045 w, 1028 m, 973 w, 930 w, 890 w, 840 m, 770 s, 720 m, 610 w, 467 s, 344 m, 236 m cm^{-1}. By comparison with the IR spectrum of $(MeC_5H_4)_3UCl$, the band at 467 cm^{-1} can be assigned to the U-F stretch.

CHAPTER TWO

$(MeC_5H_4)_3U \cdot OC_4H_8$

Sodium naphthalide was prepared by stirring $C_{10}H_8$ (0.98 g, 7.68 mmol) in thf (20mL) in the presence of a large excess of Na slices for 20 hours. The dark green solution was then transfered by cannula into a 500 mL round-bottomed flask containing UCl_4 (2.90 g, 7.67 mmol) dissolved in thf (50 mL). An instant purple suspension developed. The mixture was allowed to stir for 8 hours, and then $NaMeC_5H_4$ (18.26 mL 1.26 M in thf, 23.0 mmol) was added by syringe. Upon addition of approximately half the NaCp, the solution color turned brown. After complete addition of the Cp anion, the brown solution was allowed to stirr for 6 hours, then the thf was removed under reduced pressure. The flask was then almost completely immersed in a hot water bath (50-60°C) for 1.5 hours under dynamic vacuum, to remove naphthalene. Diethyl ether (150 mL) was added, and after approximately 40 minutes, the brown solution was filtered, and concentrated to 120 mL. Cooling the solution to -80°C yielded brown needles (2.1 g, 50%), m.p. 136-140°C. An additional 10-20% can be recovered by concentrating the supernatent to ca. 40 mL, and again cooling to -80°C. ^1H NMR (C_6D_6, 27.5°C): -11.62(6H), -13.99(4H), -14.39(6H), -15.61(9H), -31.06(4H). The second and fifth resonances shift toward the diamagnetic region of the spectrum upon addition of thf. ^{13}C NMR (C_6D_6, 28°C): 286.01(d, J_{CH}=161.2), 275.13(d, J_{CH}=161.2), 256.89(s), -5.49(t), -84.17(br), -90.61(q). Anal. Calcd. for $C_{22}H_{29}OU$: C, 48.3; H, 5.33. Found: C, 47.9; H, 5.31. IR data (Nujol, CsI): 1651 w, br, 1596 w, br, 1508 w, 1260 m, 1234 w, 1210 w, 1170 w, 1032 s, 1015 s, 971 w, 954 w, 927 m,

848 w, 822 s, 779 s, 758 s, 721 s, 628 w, 615 m, 480 m, 400 w, 322 m cm^{-1}. The unit cell is orthorhombic; a = 16.64(3)Å, b = 9.06(1)Å, c = 13.36(2)Å.

$(MeC_5H_4)_3U \cdot N(CH_2CH_2)_3CH$

In a Schlenk flask was placed $(MeC_5H_4)_3U$-thf (1.00 g, 1.80 mmol) and quinuclidine (0.50 g, 4.3 mmol). Toluene (10 mL) was added, and the solution stirred for ten minutes. The solvent was removed by vacuum, and the brown solid extracted with a hexane/toluene mixture (50 mL/10 mL) at 55°C. Cooling the filtrate to -25°C yielded dark red needles (0.25 g, 23%), m.p. 159-162°C(dec). ^1H NMR (C_6D_6, 28°C): -10.14(6H), -10.78(6H), -11.09(6H), -14.27(9H), -14.64(6), -28.64(6). The resonances due to the quinuclidine ligand are the second, third, and sixth. ^{13}C NMR (C_6D_6, 32°C): 277.21(d, J=162.7 Hz), 273.28(d, J=162.7 Hz), 249.15(s), 13.94(q, J=140.7 Hz), -17.93(t, J=131.1 Hz), -83.87(q, J=124.6 Hz), -122.62(br). Anal. Calcd. for $C_{25}H_{34}NU$: C 51.2, H 5.84, N 2.39. Found: C 50.6, H 5.73, N 2.29. IR data (Nujol, CsI): 1656(br) m, 1345 w, 1308 m, 1270 w, 1235 w, 1196 m, 1114 w, 1042 s, 1035 m, 1028 m, 1012 w, 992 m, 973 m, 926 m, 893 w, 854 w, 822 m, 812 m, 780 w, 750 s, 530 w, 510 s, 475 w, 408 m, 322 m, 310 m, 215 s cm^{-1}.

$(MeC_5H_4)_3U \cdot py$

To $(MeC_5H_4)_3U$-thf dissolved in toluene (25 mL), was added by syringe pyridine (0.50 mL, 6.3 mmol). The solution color instantly changed from brown to green. The solution was filtered, and the filtrate was concentrated to 15 mL. Cooling (-20°C) yielded dark

green (black) needles. The supernatent was decanted and the crystals washed twice with hexane (5 mL). Drying by vacuum yielded 0.62 g (62%) of product, m.p. 126-129°C(dec). ^{1}H NMR (C_6D_6, 27°C): 8.47(1H, triplet, J=7.69 Hz), -5.12(2H), -10.10(6H), -14.25(9H), -17.06(6H), -19.02(2H). The pyridine peaks (2:2:1) exchange rapidly with added pyridine. ^{13}C NMR (C_6D_6, 32°C): 290.25(d, J=162.7), 279.52(d, J=162.7), 258.26(s), 126.24, 69.96, -83.21(q, J=123.6). One signal from the pyridine ligand that could not be located; it could be buried under the solvent signal, or if it is the carbon adjacent to the nitrogen, it could be too broad, as the width at half height of the peak at 69.96 ppm is 100 Hz. Anal. Calcd. for $C_{23}H_{26}NU$: C, 49.8; H, 4.73; N, 2.53. Found: C, 49.7; H, 4.55; N, 2.32. IR data (Nujol, CsI): 1685 w, 1650 w, 1593 m, 1573 w, 1565 w, 1295 w, 1236 w, 1212 m, 1167 w, 1150 w, 1058 m, 1040 m, 1028 m, 1000 m, 970 w, 927 w, 820 s, 765 w, 745 s, 697 s, 614 m, 479 w, 420 w, 320 s, 210 s cm^{-1}.

$(MeC_5H_4)_3U \cdot NC_5H_4NMe_2$

To a mixture of $(MeC_5H_4)_3U$-thf/NaCl (1.39 g, 1.78 mmol U) and p-dimethylaminopyridine (0.30 g, 2.5 mmol) was added ether (30 mL). After 30 minutes, the deep red solution was filtered, concentrated (ca. 20 mL), and cooled (-20°C). Dark red crystals (0.24 g, 22%), m.p. 158-160°C(dec), were collected and dried. ^{1}H NMR (C_6D_6, 27°C): -4.12(10H, broad group of resonances, $\nu_{1/2}$= 200 Hz), -9.87(6H), -12.95(9H), -17.14(6H). Anal. Calcd. for $C_{25}H_{31}N_2U$: C, 50.3; H, 5.23; N, 4.69. Found: C, 50.7; H, 5.39; N, 5.15. IR data (Nujol, CsI):

1610 s, 1477 m, 1058 w, 1042 w, 1030 w, 998 s, 813 m, 750 s, 611 w, 542 w, 482 w cm^{-1}.

Attempted synthesis of $(MeC_5H_4)_3U \cdot NC_5H_4CN$

To a mixture of $(MeC_5H_4)_3U$-thf/NaCl (1.39 g, 1.78 mmol U) and p-cyanopyridine was added ether (50 mL). The solution color was purple at first then it slowly went green. After two hours, the solution was filtered, and the solid was extracted with ether (20 mL). Cooling the combined filtrates gave no solid material. The ether was removed, and the IR spectrum recorded. IR data (Nujol, CsI): 1600m, 1560w, 1405w, 1258s, 1093s, 1020s, 930w, 860w, 800s, 720w, 628m, 530w, 492w, 393m, 330w, 230w cm^{-1}. Free ligand contains bands at 2240, 1975 cm^{-1}. Nothing further was done with this material.

$(MeC_5H_4)_3U \cdot SC_4H_8$

To $(MeC_5H_4)_3U$-thf (0.88 g, 1.6 mmol) dissolved in toluene (10 mL) was added tetrahydrothiophene (0.15 mL, 1.7 mmol). The solution was stirred for five minutes with no observable color change. The toluene was removed by vacuum over a period of ten minutes. Diethyl ether (20 mL) was added by syringe, the red solution was filtered and the filtrate was concentrated to ca. 10 mL. Cooling (-20°C) overnight yielded large needles. The solution was decanted, and the crystals were washed with hexane (5 mL). Drying by vacuum yielded 0.28 g of product (31%), m.p. 98-101°C(dec). ^1H NMR (C_7D_8, 51°C): -16.00(9H), -13.44(6H), -10.21(6H), -13.99(4H), -12.67(4H). At room temperature the spectrum consisted of only four lines, with the second and fourth

resonace superimposed. The coordinated thiophene peaks rapidly exchange with added thiophene. ^{13}C NMR (C_6D_6, 25°C): 232.8, 224.1, 210.2, 15.8. The thiophene signals were not located. Anal. Calcd. for $C_{22}H_{29}SU$: C, 46.9; H, 5.19; S, 5.69. Found: C, 47.0; H, 5.16; S, 5.10. IR data (Nujol, CsI): 1300 w, 1251 w, 1230 w, 1208 w, 1192 w, 1166 w, 1128 w, 1038 m, 1026 s, 955 m, 921 m, 872 m, 847 m, 819 s, 750 s, 665 m, 608 m, 521 w, 328 s, 215 s cm^{-1}.

$(MeC_5H_4)_3U \cdot PMe_3$

To UCl_4 (1.0 g, 2.7 mmol) dissolved in thf (20 mL) was added $NaC_{10}H_8$, and $NaMeC_5H_4$ as described for the preparation of $(MeC_5H_4)_3U$-thf. After removal of the naphthalene, pentane (50 mL) was added, and then PMe_3 (1 mL., 6 mmol) was added by syringe. The mixture was stirred for one hour, and the red solution was filtered. Cooling to -20°C yielded 0.27 g (18%) red needles, m.p. 228-232°C(dec). ^1H NMR (C_6D_6, 31°C): -21.68(3H), -21.18(3H), -13.55(2H), -12.68(2H). The second resonance exchanges with added phosphine. ^{13}C NMR (C_6D_6, 31°C): 306.73, 291.34, 270.43, -96.70. Anal. Calcd. for $C_{21}H_{30}PU$: C, 45.7; H, 5.48; P, 5.62. Found: C, 45.5; H, 5.52; P, 4.66. IR data (Nujol, CsI): 1670 w, 1650 w, 1420 s, 1303 m, 1284 s, 1260 w, 1235 m, 1033 s, 945 s, 865 w, 816 s, 767 s, 740 s, 719 s, 660 w, 635 w, 605 m, 330 s, 210 s cm^{-1}.

$(MeC_5H_4)_3U \cdot P(OCH_2)_3CEt$

A solution of $P(OCH_2)_3CEt$ (0.50 g, 3.1 mmol) in diethyl ether (20 mL) was added by cannula to a solution of $(MeC_5H_4)_3U$-thf (1.27 g, 2.29

mmol) in ether (20 mL). Immediately a red precipitate formed, leaving the ether solution lightly colored. The ether was removed by vacuum, and the dark red solid was extracted twice with hot toluene (20 mL at 50°C). Cooling to -20°C yielded red crystals (0.64 g, 44%), m.p.>300°C. ^{1}H NMR (C_6D_6, 28°C): -3.92(2H, t, J=7.8 Hz), -5.78(3H, q), -8.03(6H), -10.73(6H), -17.86(6H), -21.11(9H). ^{13}C NMR (C_6D_6, 28.5°C):297.63, 274.49, 258.71, 29.96, 23.73, 17.40, .42, -83.67. Anal. Calcd. for $C_{24}H_{32}O_3PU$: C, 45.2; H, 5.06; P, 4.86. Found: C, 45.2; H, 5.08; P, 4.73. IR data (Nujol, CsI): 1348 w, 1234 w, 1188 w, 1149 m, 1033 s, 968 w, 952 s, 936 s, 847 m, 820 m, 766 s, 750 s, 640 s, 609 w, 530 m, 495 w, 420 w, 408 w, 370 m, 351 m, 330 m, 223 m cm^{-1}.

$(MeC_5H_4)_3U \cdot P(OMe)_3$

To $(MeC_5H_4)_3U$-thf (0.70 g, 1.3 mmol) dissolved in ether (20 mL) was added by syringe trimethylphosphite (0.20 mL, 1.6 mmol). The solution color immediately went from red to burgundy. After 5 minutes, the ether was removed, and the red solid dissolved in hexanes (20 mL). The solution was filtered and cooled (-20°C) to yield red plates (0.40 g, 52%), m.p. 104-106°C. ^{1}H NMR (C_6D_6, 34°C): -9.27(3H), -12.44(2H), -15.06(2H), -18.79(3H). ^{13}C NMR (C_6D_6, 35°C): 297.29, 282.23, 264.14, -81.27. No phosphite signal was located. Anal. Calcd. for $C_{21}H_{30}O_3PU$: C, 42.1; H, 5.04; P, 5.16. Found: C, 42.5; H, 4.99; P, 5.36. IR data (Nujol, CsI): 1300 w, 1260 w, 1234 w, 1170 m, 1056 m, 1020 s, 927 w, 847 w, 820 m, 745 s, 610 m, 518 m, 423 w, 380 m, 330 m, 220 m cm^{-1}.

$(MeC_5H_4)_3U \cdot PEt_3$

To $(MeC_5H_4)_3U$-thf (0.70 g, 1.3 mmol) dissolved in diethyl ether (20 mL) was added by syringe triethylphosphine (0.20 mL, 1.7 mmol), and the solution color turned slightly cherry red. After five minutes, the ether was removed by vacuum, and the red solid extracted with hexane (35 mL). Cooling (-80°C) yielded red plates (0.26 g, 34%), m.p. 106-108°C. ^1H NMR (C_7D_8, 24°C): -10.70(9H, t, J= 7.2Hz), -11.34(6H), -13.57(6H), -18.25(6H, q), -21.10(9H). ^{13}C NMR (C_7D_8, 34°C): 289.83, 284.43, 260.75, -22.32, -86.64. The $P-CH_2$ carbon was not located. Anal. Calcd. for $C_{24}H_{36}PU$: C, 48.6; H, 6.11; P, 5.22. Found: C, 48.5; H, 6.08; P, 3.52. IR data (CsI, Nujol): 1420 w, 1260 w, 1235 w, 1034 s, 980 w, 925 m, 846 m, 818 s, 740 s, 719 m, 670 m, 608 m, 417 w, 323 m, 218 m cm^{-1}.

$(MeC_5H_4)_3U \cdot CNEt$

To $(MeC_5H_4)_3U$-thf (0.69 g, 1.2 mmol) dissolved in diethyl ether (15 mL) was added by syringe ethylisocyanide (0.17 mL, 2.3 mmol). The ether was removed by vacuum after five minutes, leaving a red solid. Hexane (30 mL) was added, and the red solution was filtered and cooled to -20°C, yielding red needles (0.18 g, 28%), m.p. 59-60°C. ^1H NMR (C_6D_6, 34°C): -8.13(6H), -8.50(3H), -15.60(9H), -18.64(6H), -59.28(2H). ^{13}C NMR (C_6D_6, 29°C): 330.04(s), 279.96(d), 278.47(d), 94.54(br), -26.53(q), -105.76. Anal. Calcd. for $C_{21}H_{26}NU$: C, 47.6; H, 4.94; N, 2.64. Found: C, 47.3; H, 4.90; N, 2.16. IR data (Nujol, CsI): 2155 s, 1338 m, 1090 w, 1028 m, 925 w, 847 w, 823 m, 765 s, 740 s, 610 w, 328 m, 215 w cm^{-1}.

$(MeC_5H_4)_3U[CN2,6\text{-}Me_2C_6H_4]_2$

Addition of 2,6-dimethylphenylisocyanide (0.48 g, 3.3 mmol) to an ether solution of $(MeC_5H_4)_3U$-thf (0.64 g, 1.1 mmol) gave an immediate color change to blue. The solvent was removed under reduced pressure, and the blue solid extracted with hexane (30 mL). Cooling the filtrate (-20°C) afforded blue plates (0.49 g, 20%), m.p. 101-103°C. Anal. Calcd. for $C_{36}H_{40}N_2U$: C, 58.6;, H, 5.33; N, 3.80. Found: C, 57.8; H, 6.43; N, 3.40. ^1H NMR (C_6D_6, 31°C): -9.20(6H), -15.94(9H), -17.00(6H), -10.00(12H), .85(t, 4H), 13.89(d, 2H). ^{13}C NMR (C_6D_6, 31°C): 274.0, 253.6, 241.5, 213.9, 153.8, 71.8, 26.4, 17.1, -76.7. IR data (Nujol, CsI): 2095s, 2065s, 1177m, 1078w, 1060w, 1040w, 1025m, 973w, 925w, 843w, 811m, 767s, 759s, 745s, 715m, 505m, 465m, 386w, 322w, 270w cm^{-1}.

$(MeC_5H_4)_3U(CN2,6\text{-}Me_2C_6H_4)$

To a solution of $(MeC_5H_4)_3U$-thf (0.64 g, 1.1 mmol) in dietyl ether was added a solution of 2,6-dimethylphenylisocyanide (0.15 g, 1.1 mmol) in ether (20 mL). Immediately a dark blue-violet color was observed. The ether was removed under reduced pressure, and the solid dissolved in hexane (30 mL). Filtering and cooling (-20°C) the filtrate gave red needles (0.42g, 63%), m.p.73-76°C. Anal. Calcd. for $C_{27}H_{33}NU$: C, 53.5; H, 4.96; N, 2.31. Found: C, 53.2; H, 6.23; N, 1.97. IR data (Nujol, CsI): 2060s, 1165m, 1027m, 923w, 843w, 812m, 765s, 745s, 715m, 605m, 476m, 387w, 325m, 262 w cm^{-1}. The uncomplexed isocyanide ligand has a CN stretch at 2110 cm^{-1}.

$(MeC_5H_4)_3U\cdot NCEt$

$(MeC_5H_4)_3U$-thf (0.72 g, 1.3 mmol) was dissolved in diethyl ether (20 mL), and proprionitrile (0.10 mL, 2.5 mmol) was added by syringe. After five minutes the solvent was removed by vacuum. The red-black solid was not soluable in hexane, though it dissolved in ether (20 mL). The red ether solution was filtered, concentrated to ca. 5 mL, and cooled to -20°C, yielding dark red needles (0.44 g, 63%), m.p. 69-71°C. ^1H NMR (C_6D_6, 32°C): -5.98(6H), -8.14(3H), -13.21(9H), -20.32(6H), -39.00(2H). ^{13}C NMR (C_6D_6, 30°C): 289.99(d), 279.99(d), 255.85(s), -71.70(q). The base signals could not be located with certainty. Anal. Calcd. for $C_{21}H_{26}NU$: C, 47.6; H, 4.94; N, 2.64. Found: C, 47.4; H, 5.40; N, 2.63. IR data (Nujol, CsI): 2242 m, 1408 w, 1304 w, 1258 w, 1232 w, 1067 w, 1040 w, 1025 m, 970 w, 924 m,845 w, 820 m, 765 s, 737 s, 608 m, 326 m, 210 s cm^{-1}.

$(MeC_5H_4)_3U\cdot(Me)_2PCH_2P(Me)_2$

$(MeC_5H_4)_3U$-thf (0.26 g, 0.47 mmol) was dissolved in toluene (10 mL), and bis-dimethylphosphinomethane (0.20 mL, 1.2 mmol was added by syringe. After two minutes, the solvent was removed, and the red solid was extracted with hexane (20 mL). The solution was filtrated, and the filtrate was concentrated to 10 mL. Cooling to -20°C yielded red crystals (0.18 g, 63%), m.p. 76-78°C. A second crop (0.03 g, 10%) was obtained by concentrating the supernatent to 2 mL, and cooling to -20°C. ^1H NMR (C_7D_8, 60°C): -8.77(12H), -10.90(6H), -11.34(6H), -13.30(2H), -17.09(9H). ^{13}C NMR (C_7D_8, 29.5°C): 307.46, 293.55, 271 35, -97.79. The resonances due to the phosphine ligand could not be

found. Anal. Calcd. for $C_{23}H_{35}P_2U$: C, 45.2; H, 5.77; P, 10.1. Found: C, 44.8; H, 6.00; P, 10.2. IR data (Nujol, CsI): 1294 w, 1280 w, 1260 w, 1085 w, 1033 m, 971 w, 942 m, 904 m, 828 m, 744 s, 722 m, 608 w, 470 w, 328 w cm^{-1}.

$(MeC_5H_4)_3U \cdot OPPh_3$

To $(MeC_5H_4)_3U$-thf (0.71 g, 1.3 mmol) dissolved in ether (30 mL) was added $OPPh_3$ (0.17 g, 0.61 mmol) dissolved in ether (25 mL). Slowly a red precipitate formed. The mixture was stirred for 2.5 hours, and the solvent was then removed by vacuum. The brown solid was extracted with toluene (50, 30 mL), and the combined filtrates were cooled (-20°C), yielding red crystals (0.24 g, 52% based on OPR_3), m.p. 238-238.5°C. The compound shows a parent ion in the mass spectrum, M^+ = 753. ^1H NMR (C_6D_6, 32°C): 5.58(3H), 4.90(6H), -2.60(6H), -11.42(9H), -12.35(6H), -15.01(6H). The compound is not sufficiently soluble for a ^{13}C NMR spectrum. Anal. Calcd. for $C_{36}H_{36}OPU$: C, 57.4; H, 4.81; P, 4.11. Found: C, 57.8; H, 4.73; P, 3.48. IR data (Nujol, CsI): 1585 w, 1435 s, 1310 w, 1185 w, 1150 s, 1120 s, 1088 s, 1070 w, 1043 w, 1031 m, 1022 w, 996 w, 992 w, 942 w, 847 m, 821 m, 813 m, 765 m, 750 s, 725 s, 690 s, 610 m, 544 s, 520 w, 478 m, 445 w, 412 w, 324 m, 308 w, 294 w, 210 m cm^{-1}.

$(C_5H_5)_3U \cdot py$

Naphthalene (1.66 g, 13.0 mmol) was stirred over Na for 18 hours in thf (30 mL). The green solution was added by cannula to a 500 mL round bottom flask containing UCl_4 (4.86 g, 12.8 mmol) dissolved in

thf (60 mL). A purple precipitate formed immediately. After eight hours NaC_5H_5 (33.1 mL 1.16 M in thf, 38.4 mmol), was added by syringe, turning the solution dark brown, and producing a brown precipitate. This mixture was stirred for six hours, then the thf was removed by vacuum. The brown solid was heated (55°C) with a hot water bath for one hour under dynamic vacuum to remove naphtahlene. Toluene (350 mL) and pyridine (2.0 mL, 25 mmol) were added, causing the brown solution to turn green. This mixture was heated (55°C) for six hours, filtered while hot, and and the filtrate was cooled to -20°C. Green needles (3.2 g, 48%), m.p. 248-254°C(dec), were collected and dried in vacuum. A second crop can be obtained by concentrating the supernatent and again cooling to -20°C. This compound is the preferred starting material for $(C_5H_5)_3U{=}NR$ compounds. The supernatent from the first crystallization can be taken to dryness, pumped on at 60°C to remove residual naphthalene, and the residue allowed to react with NNNR reagents, as if it were pure, giving good yields of $(C_5H_5)_3UNR$ products. ^1H NMR (C_7D_8, 31°C): 7.71(1H, t, J=7.9), -4.85(2H), -15.39(15H), -18.54(2H). The solution was not sufficiently soluble for a ^{13}C NMR spectrum. Anal. Calcd. for $C_{20}H_{20}NU$: C, 46.9; H, 3.93; N, 2.73. Found: C, 46.9; H, 4.06; N, 2.94. IR data (Nujol, CsI): 1620 w, 1592 m, 1480 m, 1346 s, 1374 s, 1365 w, 1353 w, 1228 w, 1209 m, 1051 w, 1117 w, 1060 m, 1037 w, 1005 m, 783 s, 755 s, 697 s, 515 m, 470 w, 418 w, 205 m cm^{-1}.

$(C_5H_5)_3U \cdot PMe_3$

To UCl_4 (1.0 g, 2.7 mmol) dissolved in thf (20 mL) was added by cannula $NaC_{10}H_8$ (0.34 g $C_{10}H_8$ dissolved in 20 mL thf over Na for 24 hours). After one day, NaC_5H_5 (15.0 mL 1.40 M in thf, 21.0 mmol) was added by syringe, and the brown mixture was stirred for 24 hours. The solvent was removed by vacuum, toluene (40 mL) was added, and trimethylphosphine (1 mL, 6 mmol) was added by syringe. After stirring for one hour, the red solution was filtered, concentrated to 20 mL, and cooled (-20°C). Dark red needles (0.62 g, 46%), m.p. 283-288°C(dec), were collected and washed with pentane. ^1H NMR (C_7D_8, 28°C): -16.28(15H), -22.06(9H). ^{13}C NMR (C_7D_8, 28°C): 294.94(d). The phosphine carbon signal could not be located. Anal. Calcd. for $C_{18}H_{24}PU$: C, 42.4; H, 4.75; P, 6.08. Found: C, 42.0; H, 4.67; P, 5.78. IR data (Nujol, CsI): 1730 w, 1625 w, 1418 w, 1305 w, 1288 m, 1260 m, 1090 w, 1010 s, 950 s, 790 w, 770 s, 755 s, 720 m, 662 w, 470 w, 397 w, 213 s cm^{-1}.

$(C_5H_5)_3U \cdot Me_2PCH_2PMe_2$

Crude $(C_5H_5)_3U$-thf was prepared by reducing UCl_4 with sodium naphthalene and $(C_5H_5)Na$ as in the preparation of $(MeC_5H_4)_3U$-thf. To impure $(C_5H_5)_3U$-thf (1.1 g, 1.4 mmol) was added $Me_2PCH_2PMe_2$ (0.50 mL, 3.0 mmol). Toluene (20 mL) was then added, and the red solution was filtered and cooled (-80°C). Black needles (0.08 g, 10%), m.p. >240°C, were isolated and washed with hexane. ^1H NMR (C_7D_8, 31°C): -12.06(12H), -16.14(15H), -17.89(2H). ^{13}C NMR (C_7D_8, 31°C): only the Cp resonance at 293.33(d) could be observed. Anal. Calcd. for

$C_{20}H_{29}P_2U$: C, 42.2; H, 5.13; P, 10.9. Found: C, 42.7; H, 5.40; P, 8.4. IR data (Nujol, CsI): 1292 m, 1281 m, 1250 w, 1149 w, 1090 w, 1009 s, 941 m, 900 m, 773 s, 747 s, 725 m, 693 w, 210 s cm^{-1}.

$(C_5H_5)_3U \cdot CNEt$

To a crude mixture of $(C_5H_5)_3U$-thf/NaCl (0.91 g, 1.2 mmol U) suspended in toluene (30 mL) was added ethylisocyanide (0.20 mL, 2.9 mmol). Instantly the solution color turned from red to burgundy. After stirring for six hours, the solution was taken to dryness, and the red solid was extracted with toluene (50 mL). Filtration of the extract followed by cooling, yielded red crystals (0.22 g, 36%), which appeared to begin to melt at 156-158°C, but then resolidified and remained a solid up to 300°C. A second crop was isolated by decanting the toluene, concentrating the liquor to ca. 20 mL. Cooling (-80°C) yielded an additional 0.26 g (42%). ^1H NMR (C_6D_6, 36°C): -8.88(3H), -14.07(15H), -55.27(2H). ^{13}C NMR (C_6D_6, 36°C): 277.35(d). The ligand resonances were not observed. Anal. Calcd. for $C_{18}H_{20}NU$: C, 44.3; H, 4.13; N, 2.87. Found: C, 44.0; H, 4.36; N, 2.60. IR data (CsI, Nujol): 2170 m, 2160 m, 1720 w br, 1620 w br, 1346 m, 1260 m, 1090 m, 1050 w, 1008 s, 792 s, 765 s, 740 s, 495 m, 468 w, 400 w, 344 w, 210 s cm^{-1}.

$(Me_3SiC_5H_4)_3UCl$

To UCl_4 (4.50 g, 11.8 mmol) dissolved in thf (50 mL) was added by syringe $KC_5H_4SiMe_3$ (46.2 mL 0.77 M in diethyl ether, 36 mmol). The color of the solution immediately turned red, and a precipitate

formed. After six hours, the solvent was removed, and the red solid was extracted with hot hexane (150, 50 mL, 55°C). The combined hexane filtrates were cooled (-80°C), yielding red needles (7.4 g, 91%), m.p. 101-102°C. ^{1}H NMR (C_7D_8, 21°C): 16.41(2H), -5.68(9H), -17.20(2H). ^{13}C NMR (C_7D_8, 21°C): 278.23, 250.33, 228.05, -4.97. Anal. Calcd. for $C_{24}H_{39}ClSi_3U$: C, 42.1; H, 5.97; Cl, 5.17. Found: C, 41.6; H, 5.78; Cl, 5.05. IR data (Nujol, CsI): 1685 w br, 1595 w br, 1404 w, 1309 m, 1247 s, 1195 w, 1175 s, 1079 w, 1040 s, 901 s, 875 w, 839 s, 797 s, 754 s, 720 w, 687 m, 633 m, 620 w, 416 s, 330 m, 323 w, 308 w, 262 w, 253 w, 242 m cm^{-1}.

Alkylations of $(Me_3SiC_5H_4)_3UCl$

Synthesis of $(Me_3SiC_5H_4)_3UR$, where R= benzyl, neopentyl was accomplished by low temperature (-70°C) addition of the alkyl lithium reagent to hexane solutions of the chloride, followed by filtering and cooling the red extracts at -80°C. ^{1}H NMR analysis indicated no restriction of Cp ring rotation, nor any significant thermal instability, and thus rigorous characterization was not pursued.

$(Me_3SiC_5H_4)_3ThCl$

To $ThCl_4$ (1.86 g, 4.97 mmol) suspended in thf (40 mL) at -60°C was added by syringe $KC_5H_4SiMe_3$ (19.4 mL 0.77 M in ether, 15 mmol). The temperature of the solution was allowed to warm to room temperature in 30 minutes, and then the reaction stirred for five hours. The solvent was removed, and the white solid was extracted with a toluene/pentane mixture (30/5 mL, 2X). The combined filtrates

were taken to dryness, leaving a white solid (0.84 g, 25%), m.p.140-142°C. ^{1}H NMR (C_7D_8, 21°C): 6.39(4H), 0.35(9H). At -90°C, the C-H resonances are split into two equal intensity peaks at 6.28 and 6.04 ppm. ^{13}C NMR (C_7D_8, 21°C): 130.56, 127.41 (between the solvent signals), 121.63, 0.54. IR data (Nujol, CsI): 1758 w br, 1674 w br, 1590 w br, 1405 m, 1364 m, 1308 m, 1246 s, 1192 w, 1174 s, 1067 m, 1040 s, 1017 w, 900 s, 854 m, 830 s, 792 s, 755 s, 724 w, 687 m, 635 m, 624 m, 416 m, 333 m, 307 m, 260 m, 243 m cm^{-1}.

$(Me_3SiC_5H_4)_3ThC_{10}H_8$ (?)

To $(Me_3SiC_5H_4)_3ThCl$ (1.23 g, 1.81 mmol) dissolved in thf (30 mL) at -60°C was added sodium naphthalene (0.24 g C_8H_{10}, 2.3 mmol over excess Na in 20 mL thf). The solution color immediately turned purple, and slowly went orange upon warming to room temperature. The solvent was removed under reduced pressure, and the red-violet solid was extracted with hexane (15 mL). Cooling the filtrate gave light red crystals (0.12 g, 9%). IR data (Nujol, CsI): 1595w, 1510w, 1268m, 1260m, 1250m, 1175w, 1150w, 1110w, 957w, 905m, 835m, 782s, 754w, 618m, 472m, 420w, 420w cm^{-1}. The ^{1}H NMR spectrum contained a large number of peaks in the aromatic portion of the spectrum, as well as thf resonances. If the red solution was left standing, it turned purple, the resonance attributable to the Cp ligand became two well defined multiplets, and the peaks due to naphthalene (?) shifted upfield. Addition of CCl_4 to this purple solution results in a yellow solution but apparently no formation of $CHCl_3$ (by addition of excess $CHCl_3$).

$(Me_3SiC_5H_4)_3U$

A. To $(Me_3SiC_5H_4)_3UCl$ (0.46 g, 0.67 mmol) dissolved in toluene (5 mL) was added by syringe sodium amalgam (1 mL, 1% Na, 2 mmol). The solution color slowly changed from red to green. After 4 hours at room temperature, the toluene was removed by vacuum, and the green solid was dissolved in pentane (5 mL). Filtering the pentane and cooling to -80°C yielded green crystals (0.22 g, 51%), m.p. 76-76.5°C.

B. To $(Me_3SiC_5H_4)_3UCl$ (7.60 g, 11.1 mmol suspended in hexane (100 mL) was added t-butyllithium (7.70 mL, 1.45 M in hexane, 11.2 mmol). The red mixture immediately began to turn dark green. After 8 hours, the solution was taken to dryness, the solid was extracted with hexane (150 mL), and the dark green solution was filtered. The filtrate can be taken to dryness, and the green oil will usually solidify in a few minutes to a few hours. The solid has the same IR and ^1H NMR spectra as the crystals isolated in method A. Yields are roughly 90%. ^1H NMR (C_6D_6, 28°C): -19.21(2H), -18.69(9H), 9.20(2H). ^{13}C NMR (C_6D_6, 28°C): 360.90, 331.97, 314.46, -59.94. Anal. Calcd. for $C_{24}H_{39}Si_3U$: C, 44.4; H, 6.05. Found: C, 43.9; H, 5.78. IR data (Nujol, CsI): 1310 w, 1260 w, 1248 s, 1175 s, 1090 w, 973 w, 950 w, 902 s, 835 s, 783 m, 766 s, 752 m, 723 m, 690 m, 627 m, 620 m, 565 w, 470 w, 420 s, 326 m, 312 m cm^{-1}.

$(Me_3SiC_5H_4)_3U \cdot CNEt$

To $(Me_3SiC_5H_4)_3U$ (1.15 g, 1.77 mmol) dissolved in hexane (30 mL) was added by syringe ethylisocyanide (0.13 mL, 1.9 mmol). The color immediately changed from green to burgundy. The solution was stirred

for five minutes, filtered, and cooled (-20°C). Red plates (0.36 g, 28%), m.p. 112-115°C, were collected and dried under vacuum. ^{1}H NMR (C_7D_8, 25°C): -1.10(6H), -6.30(27H), -8.77(3H), -18.94(6H), -61.68(2H). ^{13}C NMR (C_6D_6, 34°C): 327.78, 275.30, 273.94, -25.54. The base signals were not observed. Anal. Calcd. for $C_{27}H_{44}NSi_3U$: C, 46.0; H, 6.29; N, 1.99. Found: C, 45.9; H, 6.31; N, 1.93. IR data (Nujol, CsI): 2178 s, 2159 s, 1405 w, 1371 m, 1365 m, 1345 m, 1311 w, 1246 s, 1149 w, 1177 s, 1138 w, 1095 w, 1062 w, 1040 s, 902 s, 835 s, 765 s, 761 s, 690 m, 640 m, 625 m, 427 m, 322 m cm^{-1}.

$(Me_3SiC_5H_4)_3U \cdot NCEt$

To $(Me_3SiC_5H_4)_3U$ (0.71 g, 1.1 mmol) dissolved in hexane (20 mL) was added by syringe propionitrile (0.15 mL, 2.2 mmol), and the green solution immediately turned red. The solution was filtered, and the filtrate was cooled (-20°C). Red crystals (0.36 g, 47%), m.p. 132-134°C, were collected and dried. ^{1}H NMR (C_6D_6, 34°C): 0.18(6H), -6.04(27H), -9.43(3H), -18.68(6H), -46.40(2H). ^{13}C NMR (C_6D_6, 34°C): 322.7(s), 276.2(d), 275.2(d), 71.8(s), 69.9(t), -24.2(q), -94.2(q). Anal. Calcd. for $C_{27}H_{44}NSi_3U$: C, 46.0; H, 6.29; N, 1.99. Found: C, 46.0; H, 6.25; N, 1.97. IR data (Nujol, CsI): 2248 m, 1410 w, 1305 m, 1240 s, 1172 s, 1034 s, 970 w, 898 s, 830 s, 783 w, 762 s, 747 s, 718 w, 681 m, 632 m, 618 m, 420 s, 318 s cm^{-1}. The unit cell is triclinic; a = 24.042(6)Å, b = 24.430(5)Å, c = 11.309(5)Å, α = 88.90(3)°, β = 103.02(3)°, γ = 92.37(2)°.

$(Me_3SiC_5H_4)_3U \cdot py$

To $(Me_3SiC_5H_4)_3U$ (0.30 g, 0.46 mmol) dissolved in hexane (15 mL) was added by syringe pyridine (0.080 mL, 0.99 mmol). Immediately the solution turned red, and a red precipitate formed. The flask was taken to dryness, and the red solid was extracted twice with ether (20, 25 mL). The ether was filtered, and cooled (-20°C), yielding large black (red) blocks (0.12 g, 36%), m.p. 146°C(dec). ^1H NMR (C_6D_6, 35°C): 6.41(1H), -2.94(6H), -4.62(27H), -4.96(2H), -18.66(6H), -19.84(2H). ^{13}C NMR (C_6D_6, 34°C): 327.83(s), 280.20(d), 276.79(d), -20.91(q). The pyridine peaks were not located. Anal. Calcd. for $C_{29}H_{44}NSi_3U$: C, 47.8; H, 6.04; N, 1.92. Found: C, 47.5; H, 6.05; N, 1.63. IR data (Nujol, CsI): 1596 m, 1482 w, 1435 w, 1385 s, 1360 w, 1310 w, 1246 s, 1213 m, 1174 s, 1062 w, 1035 s, 998 w, 902 s, 830 s, 788 w, 765 s, 758 s, 747 s, 720 w, 700 m, 682 w, 636 m, 630 m, 580 w, 421 m, 318 m, 208 m cm^{-1}.

$(Me_3SiC_5H_4)_3U \cdot PMe_3$

To $(Me_3SiC_5H_4)_3U$ (2.96 g, 4.56 mmol) dissolved in hexane (60 mL) was added by syringe trimethylphosphine (1.5 mL, 14 mmol). The solution color immediately turned red. The solution was filtered, and the filtrate was concentrated to ca. 25 mL, and cooled (-80°C). A brick red solid, m.p. 72-76°C (0.42 g, 13%), was isolated and dried under vacuum. ^1H NMR (C_7D_8, 27.5°C): -5.25(27H), - 8.93(6H), -12.79(6H), -20.62(9H). ^{13}C NMR (C_6D_6, 31°C): 355.40(s), 300.20(d), 291.23(d), -23.26(q). The phosphine carbon signal was not located. Anal. Calcd. for $C_{27}H_{48}PSi_3U$: C, 44.7; H, 6.62. Found: C, 44.4; H,

6.82. IR data (Nujol, CsI): 1420 w, 1364 m, 1282 w, 1244 s, 1170 m, 1038 m, 1020 w, 950 w, 901 m, 832 s, 785 w, 755 s, 720 w, 687 w, 635 w, 621 w, 470 w, 425 w, 260 w cm^{-1}.

RELATIVE BASICITY

The toluene used for solvent was refluxed over Na for days in a greasless flask, vacuum transferred, and stored in a drybox over Na/K at all times. Traces of moisture react with trivalent uranium complexes, liberating excess ligand, making it far more difficult to establish relative concentrations in solution.

After the samples were sealed with a virgin septum wrapped with teflon tape, they were placed in the probe previously warmed to 50°C, and the temperature was allowed to equilibrate for roughly 20-30 minutes. An easy way to determine whether thermal equilibrium has been achieved is to moniter the observed chemical shifts as a function of time. Chemical shifts of paramagnetic compounds have a temperature dependence[15] (for one of the hydrides in $(CH_3BH_3)_4U(DMPE)$, the shift changed 1ppm/°C), and so if the observed shifts are continuously monitored, thermal equilibrium is established when there is no longer a shift in the resonances. This assumes that any chemical equilibrium is established relatively fast; with such labile ligands, this seems resonable. Approximately 5-10 minutes after equilibrium was established, the final spectrum was recorded. The temperatures measured were usually 50, 25, 0, -25, -50, and -70°C. In practice, it is not always possible to stabilize the probe exactly at the desired temperature. Measurments can be recorded to within 1°C of the desired

temperature, but a correction of the effect of this temperature change on the observed chemical shift must be made. A plot of chemical shift vs. 1/T can be made and the desired temperature interpolated, or the temperature behavior of the individual shift can quickly be determined by comparing the next highest and lowest temperatures, calculating the effect one degree would have, and adjusting appropriately.

The relative concentrations of species in solution was obtained in one of two ways. First, for all ligands except quinuclidine, exchange between free and coordinated ligands is rapid on an NMR timescale, giving only time averaged signals for both ligands and the Cp resonances. The relative concentration of paramagnetic species in solution was obtained by calculating the relative contribution of the individual Cp chemical shifts to that observed:

$$\delta_{obs} = \delta_a(\chi) + \delta_b(1-\chi)$$

Here δ_a and δ_b are known from previous experiments, δ_{obs} is the observed Cp chemical shift, and χ is the desired mole fraction. If B is added to Cp_3UA, then from (a) not only are [U-A] and [U-B] obtained but also [A], the concentration of uncoordinated A, must be equal to [U-B]. The only quantity remaining unknown is [B]. This is obtained by integration of the spectrum, and normalizing the intensity with respect to the number of protons contributing to the signal.

For example, if the initial [U-A] is set equal to 100, the total B added is 1.2B: 1A (by integration), and it is found that now 20 U

are U-B and 80 U are U-A (by Cp chemical shifts), then [U-B]= 20, and [A] must equal 20, [U-A]= 80, [B]= total B- [U-B]= 100 and

$$K_{eq} = \frac{[U\text{-}B][A]}{[U\text{-}A][B]} = \frac{[20][20]}{[80][100]}$$

CHAPTER THREE

$[(MeC_5H_4)_3U]_2OCNC_6H_5$

To $(MeC_5H_4)_3U$-py (0.60 g, 1.1 mmol) dissolved in toluene (10 mL) was added by syringe phenylisocyanate (0.25 mL, 1.1 mmol). Immediately a red precipitate formed as the solution color changed from green to light red. After five minutes, the solvent was removed by vacuum, and the red solid dissolved in toluene (10 mL). Hexane (20 mL) was added to the solution which was then cooled (-20°C). Red crystals (0.26 g, 40%), m.p. >300°C, were collected and dried. Addition of C_6H_5NCO to an NMR tube containing $(MeC_5H_4)_3U$-thf in C_6D_6 showed that this was the only product formed in the reaction. ^1H NMR (C_7D_8, 29°C): -3.14(9H), -21.73(9H), 12.55(6H), 4.39(6H), -7.86(6H), -18.62(6H), -24.92(2H,d J=7), 3.06(2H,m), 6.40(1H, t). ^{13}C NMR (C_7D_8, 32°C): 220.08(d), 219.17(d), 167.73(d), 156.22(d), 209.81(s), 195.83(s), -26.83(q), -51.22(q), 65.31, 118.64, 123.12, 139.97. Anal. Calcd. for $C_{43}H_{47}NOU_2$: C, 48.3; H, 4.43; N, 1.31. Found: C, 47.8; H, 4.37; N, 1.33. IR data (Nujol, CsI): 1592 m, 1576 w, 1310 w, 1260 s, 1169 w, 1158 w, 1138 w, 1070 w, 1049 w, 1037 m, 975 w, 930 w, 850 m, 773 s, 739 s, 725 w, 698 m, 607 w, 549 m, 372 m, 330 w, 235 m cm^{-1}.

$(C_5H_5)_3UNSiMe_3$

To $(C_5H_5)_3U$-py (1.00 g, 1.95 mmol) suspended in toluene was added by syringe trimethylsilylazide (0.22 mL, 2.0 mmol). Gas evolution was immediate, and the color changed from green to red. The mixture was stirred for 12 hours, and the toluene was removed by vacuum. Hexane (40 mL) was added, and the red solution was filtered, concentrated to 35 mL, and cooled (-80°C), yielding dark red sheets (0.59 g, 58%), m.p. 207-208°(sublimes). ^1H NMR (C_6D_6, 32°C): -6.47(15H), 6.96(9H). ^{13}C NMR (C_6D_6, 32°C): 108.10(d), 72.27(q). Anal. Calcd. for $C_{18}H_{24}NSiU$: C, 41.4; H, 4.65; N, 2.69. Found: C, 41.5; H, 4.80, N, 2.56. Mass spectrum: M^+ = 520. IR data (Nujol, CsI): 1259 w, 1235 m, 984 s, 833 m, 800 w, 775 s, 745 w, 720 w, 578 w, 521 w, 470 w, 350 w, 225 w cm^{-1}.

$(MeC_5H_4)_3UNSiMe_3$

To $(MeC_5H_4)_3U$-thf (0.79 g, 1.4 mmol) dissolved in ether (20 mL) was added by syringe trimethylsilylazide (0.20 mL, 1.4 mmol). Gas evolution was immediately observed, though the color of the solution stayed dark red. The solution was stirred for 12 hours, and the ether removed by vacuum. The red solid was dissolved in hexane (30 mL), and the solution filtered and cooled (-80°C). Red crystals (0.26 g, 32%), m.p. 132-140°C, were collected and dried. ^1H NMR (C_6D_6, 36°C): 6.72(3H), 3.03(3H), -1.96(2H), -10.43(2H). ^{13}C NMR (C_6D_6, 36°C): 120.97, 100.91, 73.26, -2.28. Anal. Calcd. for $C_{21}H_{30}NSiU$: C, 44.8; H, 5.38; N, 2.49. Found: C, 45.2; H, 5.39; N, 2.30. Mass spectrum:

M^+ = 562. IR data (Nujol, CsI): 1238 m, 1035 w, 979 s, 830 m, 763 m, 745 w, 720 w cm^{-1}.

$(MeC_5H_4)_3UNPh$

To $(MeC_5H_4)_3U$-thf (1.40 g, 2.53 mmol) dissolved in ether (30 mL) was added by syringe phenylazide (0.30 g, 2.5 mmol). The color of the solution turned violet, and gas was evolved. After two hours at room temperature, the solvent was removed and the red solid was extracted twice with hexane (50 mL), filtered, and the filtrate was cooled to -20°C. Red needles (0.44 g, 30%), m.p. 108-110°C, were collected and dried. Repeated recrystallizations were necessary to remove a U(IV) impurity. Final yield was 0.22 g (15%). ^1H NMR (C_6D_6, 32°C): 3.67(9H), -3.39(6H), -10.83(6H), 18.51(2H), -2.40, (2H), 4.10(1H). ^{13}C NMR (C_6D_6, 32°C): Cp peaks were observed at 118.2, 99.3, 82.0, and -3.9 ppm (by comparison with $(MeC_5H_4)_3UNSiMe_3$. Only three of the four phenyl resonances could be located at 122.7, 97.56, and 108.4. Anal. Calcd. for $C_{24}H_{26}NU$: C, 50.9; H, 4.63; N, 2.47. Found: 1) C, 50.0; H, 4.72; N, 2.13. 2) C, 50.3; H, 4.81; N, 2.01. Mass spectrum: M^+ = 566. IR data (Nujol, CsI): 1580 w, 1571 w, 1555 w, 1259 s, 1157 w, 1149 w, 10621 w, 1045 w, 1030 w, 1018 w, 990 w, 970 w, 925 w, 904 m, 890 w, 860 w, 845 m, 777 s, 757 s, 720 m, 689 m, 600 w, 531 w, 330 m, 230 m cm^{-1}.

$(MeC_5H_4)_3UNCNEt(?)$

To $(MeC_5H_4)_3UNSiMe_3$ (0.80 g, 1.45 mmol) dissolved in ether (30 mL) was added by syringe ethylisocyanide (0.10 mL, 1.4 mmol). The

solution was kept at room temperature for four days, during which time the color went light green. Removal of the solvent, followed by extraction with hexane (30 mL), filtering the green solution which was concentrated to ca. 20 mL, and cooling (-80°C) gave green plates (0.28g, 35%), m.p. 76-80°C. Anal. Calcd. for $C_{21}H_{26}N_2U$: C, 46.3; H, 4.81; N, 5.14. Found: C, 43.7; H, 5.02; N, 4.67. ^1H NMR (C_6D_6, 31°C): 10.99(6H), -2.17(9H), -18.80(6H), -8.53(t, 3H), -9.62(q, 2H). ^{13}C NMR (C_6D_6, 31°C): 247.1, 211.1, 202.0, 8.38, 1.29, -13.33. IR data (Nujol, CsI): 2085s, 1494w, 1330m, 1258m, 1070w, 1048m, 1028m, 990m, 932m, 835m, 810m, 773s, 606m, 580w, 410w, br, 343m, 257m, 240 m cm^{-1}.

$(C_5H_5)_3UNCNEt(?)$

To $(C_5H_5)_3UNSiMe_3$ (0.70 g, 1.4 mmol) dissolved in ether (30 mL) was added by syringe ethylisocyanide (0.10 mL, 1.4 mmol). The solution was kept at room temperature for four days, during which time the color went light green. The solvent was removed under reduced pressure, and the green solid was extracted with ether (40 mL). Cooling the filtered green solution (-80°C) gave green needles (0.35 g, 51%), m.p. 174-179°C. Anal. Calcd. for $C_{18}H_{20}N_2U$: C, 43.0; H, 4.01; N, 5.57. Found: C, 43.7; H, 4.28; N, 4.95. ^1H NMR (C_6D_6, 31°C): -3.54(15H), 6.94(under solvent), -7.76(2H). IR data (Nujol, CsI): 2120m, 2085s, 1260m, 1080w, 1010w, 918m, 778s, 720w, 663w, 618m, 310w, br, 302w, 225m cm^{-1}.

$(MeC_5H_4)_3UNH(Ph)$

To $(MeC_5H_4)_3UNPh$ (0.91g, 1.6 mmol) dissolved in ether (20 mL) was added by syringe ethylisocyanide (0.11 mL, 1.6 mmol). The solution was allowed to stirr for 24 hours, as the color turned to a lighter red. The solvent was removed by vacuum, and the red solid was extracted with hexane (50 mL). Filtration of the red solution, followed by concentration (25 mL), and cooling, yielded red crystals (0.38 g, 42%), m.p. 120-122°C. ^1H NMR (C_6D_6, 31°C): 4.13(9H), -1.03(6H), -1.92(1H, t), -3.04(2H), -18.16(6H), -32.81(2H), -158.1(1H). ^{13}C NMR (C_6D_6, 31°C): 217.02, 204.01, 191.87, 124.96, 116.46, 97.01, -13.71. Mass spectrum: M^+= 567. Anal. Calcd. for $C_{23}H_{27}NU$: C 50.8, H 4.79, N 2.46. Found: C 50.7, H 4.63, N 2.01. IR data (Nujol, CsI): 1585 s, 1570 w, 1480 s, 1375 m, 1349 m, 1255 s, 1212 w, 1170 m, 1158 w, 1147 w, 1065 m, 1045 w, 1033 w, 1027 m, 989 m, 928 m, 890 w, 859 m, 840 s, 804 m, 775 s, 748 s, 688 s, 618 w, 611 w, 605 w, 588 s, 547 w, 494 m, 462 m, 344 m, 327 w, 255 m, 236 s, 204 s cm^{-1}.

$[(MeC_5H_4)_2UNPh]_2$

A mixture of $(MeC_5H_4)_3U$-THF (0.51 g, 0.93 mmol) and $(MeC_5H_4)_3UNPh$ (0.52 g, 0.92 mmol) was dissolved in thf (20 mL). After stirring for 24 hours, the solvent was removed, and an NMR analysis revealed that the reaction produced two products, the dimer and $(MeC_5H_4)_3UNH(Ph)$. Extraction of the red mixture with hexane (100 mL) followed by cooling (-80°C) yielded red crystalline material that was identical to the pre-crystallization mixture. The red material was taken into ether (25 mL), and the red solution was cooled (-20°C), yielding a red

microcrystalline solid (0.17 g, 38%), m.p. 167-170°C. ^{1}H NMR (C_6D_6, 31°C): 3.16(4H), -1.32(4H), -10.55(6H), -4.46(2H), -57.99(2H), -5.89(1H, t). ^{13}C NMR (C_6D_6, 31°C): 214.88(d), 207.33(s), 203.5(d), 156.09(d), 130.08, 86.70(d), -38.53(q). Mass spectrum: M^+= 974, M-Cp^+= 895, M-2Cp^+= 816, M-3Cp^+= 737, M-4Cp^+= 658, M/2$^+$= 487. Anal. Calcd. for $C_{36}H_{38}N_2U_2$: C, 44.4; H, 3.92; N, 2.87. Found: C, 44.0; H, 3.84; N, 2.42. IR data (CsI, Nujol): 1590 w, 1575 m, 1550 w, 1260 s, 1163 w, 1148 w, 1068 w, 1030 m, 1017 w, 990 w, 970 w, 925 w, 865 m, 820 m, 750 s, 613 m, 600 s, 538 m, 498 m, 383 m, 330 m, 235 m cm^{-1}.

$[(MeC_5H_4)_2UNSiMe_3]_2$

A mixture of $(MeC_5H_4)_3U$-THF (0.50 g, 0.91 mmol) and $(MeC_5H_4)_3UNSiMe_3$ (0.50 g, 0.92 mmol) was dissolved in thf (20 mL). After stirring for 24 hours, the solvent was removed,and the red solid extracted with ether (20 mL). Cooling the red filtrate yielded two crystalline forms, thin plates and polyfaceted crystals. The plates were shown by mass spectrum to be the desired product, M^+ = 983, $[M-Cp]^+$= 859 amu. The other product had a mass spectrum consistent with the formulation $(MeC_5H_4)_4U$, although it appeared impossible to completely separate crystals of this product from the imido dimer.

$[(Me_3Si)_2N]_3UNSiMe_3$

To $[(Me_3Si)_2N]_3U$ (1.12 g, 1.54 mmol) dissolved in hexane (25 mL) was added by cannula a solution of trimethylsilylazide (0.18g, 1.6 mmol) in ether (10 mL). The solution turned red-green, and gas evolution was observed. After stirring for 30 minutes, the solution

was filtered, and concentrated to ca. 5 mL. Cooling (-20°C) produced red blocks (0.32 g, 26%), m.p. 119-120°C. Decanting the supernatent, reducing the volume to ca. 1 mL, and again cooling to -20°C yielded a second crop (0.21 g, 17%). ^{1}H NMR (C_6D_6, 28°C): 9.84(9H), -2.29(54H). ^{13}C NMR (C_6D_6, 32°C): -1.45, -16.43. Anal. Calcd. for $C_{21}H_{63}N_4Si_7U$: C, 31.3; H, 7.87; N, 6.95. Found: C, 29.4; H, 7.98; N, 6.15. The compound shows an $[M+1]^+$= 806 peak in the CI mass spectrum, and $[M-1]^+$= 804 for EI. IR data (Nujol, CsI): 1245 s, 981 s, 900 s, 830 s, 766 s, 690 m, 652 w, 600 s, 388 s, 277 w, 254 w cm^{-1}.

$[(MeC_5H_4)_3U]_2CS_2$

To $(MeC_5H_4)_3U$-thf (0.55 g, 0.99 mmol) dissolved in ether (20 mL, 0°C), was added by syringe carbon disulfide (0.050 mL, 1.1 mmol dissolved in 10 mL of ether. After half a minute a microcrystalline precipitate formed. The solution was stirred at room temperature for 30 minutes, the ether was removed by vacuum, leaving a red solid. Toluene (10 mL) was added, and the solution was saturated by the addition of hexane (5 mL). Filtering the solution, followed by cooling (-20°C) yielded dark red needles (0.31 g, 56%), m.p. 235-240°C(dec). ^{1}H NMR (C_6D_6, 21°C): 2.40(2H), 0.19(3H), -1.75(2H), -10.01(2H), -19.19(3H), -22.02(2H). The compound was not sufficiently soluble to observe the ^{13}C NMR spectrum. Anal. Calcd. for $C_{37}H_{42}S_2U$: C, 43.3; H, 4.12; S, 6.24. Found: C, 43.4; H, 4.15; S, 6.05. IR data (Nujol, CsI): 1240 w, 1230 m, 978 m, 926 w, 865 w, 848 w, 835 w, 780 s, 762 s, 721 m, 340 m, 220 m cm^{-1}.

$[(Me_3SiC_5H_4)_3U]_2CS_2$

To $(Me_3SiC_5H_4)_3U$ (4.4 g, 6.7 mmol) dissolved in hexane (45 mL) at -70°C was added carbon disulfide (0.35 mL, 7.5 mmol). The color immediately changed to red, and a precipitate formed. The mixture was stirred for one hour, then warmed to room temperature. The hexane supernatent was decanted and cooled (-20°C) to yield red needles (0.26 g). The remaining precipitate was dissolved in toluene (20 mL), filtered, the volume was reduced to 18 mL. Cooling yielded an identical compound (1.2 g, total yield 30%), m.p.154-154.5°C. ^1H NMR (C_6D_6, 33°C): 1.33(9H), -12.69(9H), 5.22(2H), 4.09(2H), -5.39(2H), -19.24(2H). The peaks at 4.09 and -19.24 have $\nu_{1/2}$= 75 Hz, but no limiting slow exchange spectrum was observed to -80°C. ^{13}C NMR (C_6D_6, 32°C): 266.75(d), 260.30(d), 196.77(d), 161.72(d), 5.10(q), -18.48(q). Anal. Calcd. for $C_{19}H_{78}S_2Si_6U_2$: C, 42.8; H, 5.71; S, 4.66. Found: C, 42.8; H, 5.85; S, 4.65. IR data (Nujol, CsI): 1309 w, 1247 w, 1172 m, 1040 m, 995 w, 900 m, 835 s, 809 w, 786 m, 769 w, 753 m, 721 w, 690 w, 645 m, 620 w, 475 w, 420 s, 318 m, 230 w cm^{-1}. The unit cell is triclinic; a = 15.380(5)Å, b = 11.742(5)Å, c = 9.154(5)Å, α = 110.94(4)°, β = 101.83(3)°, γ = 79.59(3)°. This appears to be the only isolable product from the reaction; when a dilute solution of $(Me_3SiC_5H_4)_3U$ was added over 30 min. to a hexane solution containing 10 equivalents of CS_2 at -70°C, only the dimer was isolated.

$[(MeC_5H_4)_3UOCPh_2]_2$

A: To $(MeC_5H_4)_3U$-thf (0.54 g, 0.99 mmol) and benzophenone (0.18 g, 0.99 mmol) was added toluene (10 mL). The solution immediately

turned bright red. After 10 minutes, the toluene was removed, and the red semi-solid was extracted with ether (20 mL). The red solution was filtered, and a red crystalline material began forming. After half an hour the ether was just slightly colored. The ether was removed, and the red solid dissolved in toluene (15 mL). The red solution was saturated with hexanes (15 mL) and cooled (-20°C). Red crystals (0.26 g, 40%), m.p. 131-132°C, were collected and dried.

B: Benzophenone (0.18 g, 0.99 mmol) was dissolved in ether (30 mL) and stirred over Na slices for 24 hours. The blue solution was then added by cannula to a flask containing $(MeC_5H_4)_3UCl$ (0.51 g, 1.0 mmol) partially dissolved in ether (20 mL). The solution color immediately turned deep red. After 30 minutes, the solution was filtered, and the red solution was concentrated (15 mL), and cooled (-20°C). Red crystals (0.26 g, 40%), m.p. 150-151°C, were collected and dried. This material was found to be a slightly purer version of A. The ^1H NMR spectrum was too complex for accurate assignment, with clusters of peaks aroung the principal Cp resonances, and no clear assignments for the benzophenone group. There are two inequivalent $CH_3C_5H_4$ signals, with 1:1 areas. ^1H NMR (C_7D_8, 34°C): -.28(3H), -4.07(3H), -11.84(2H), -12.11(2H), -16.46(2H), -17.18(2H), 8.84(1H, m), 8.36 (1H, m), 6.56(1H, br), 5.78(.5H, br), .63(1H, m), -3.64(1H), -3.93(1H). No ^{13}C NMR was attempted. Anal. Calcd. for $C_{31}H_{21}OU$: C, 56.6; H, 4.75. Found: C, 56.8; H, 4.93. IR data (Nujol, CsI): 1650 w, 1598 w, 1562 m, 1317 m, 1301 m, 1248 m, 1200 m, 1150 m, 1122 s, 1084 w, 1067 w, 1048 m, 1030 m br, 997 s, 948 w, 935 m, 920 w, 908 w, 898 w, 850 m, 820 w, 803 w, 777 s, 765 s, 727 m, 695 m, 654 w, 643 m,

628 w, 612 w, 604 w, 535 w, 517 m, 485 m, 453 w, 383 m, 330 m, 240 m cm^{-1}. The solubility behaviour the same when di-p-methylbenzophenone was used, and the reaction of $(Me_3SiC_5H_4)_3U$ with benzophenone gave a product too soluble in hexane to isolate. Benzaldehyde appears to be too acidic to form the simple reduced species, with ring cleavage rapid relative to electron transfer; insoluble precipitates form upon addition of PhCHO to solutions of $(RC_5H_4)_3U$, R=Me, $SiMe_3$.

Reaction of $(MeC_5H_4)_3U$-thf with NO

To $(MeC_5H_4)_3U$-thf (0.91 g, 1.7 mmol) dissolved in toluene (20 mL) was added ca. 60 mL NO (2.7 mmol). An immediate precipitate formed, and the color of the solution went to a lighter brown. After 5 min., the solvent was removed, and the solid was extracted with toluene (50 mL). Cooling this red solution gave no crystalline material; the solvent was removed, and the IR spectrum of the solid recorded: 1602m, 1258s, 1090s, 1020s, 930w, 913w, 790s, 605m, 530m, 390m, 328w, 225m cm^{-1}.

$(MeC_5H_4)_3U(Co_4(CO)_9)$

To $(MeC_5H_4)_3U$-thf (0.42 g, 0.76 mmol) and $Co_2(CO)_8$ (0.26g, 0.77 mmol) was added diethyl ether (30 mL). The red solution was stirred for two hours, and filtered. Cooling the filtrate gave red crystals (0.12g, 16%), m.p. > 300°C. ^1H NMR (C_6D_6, 27°C): 5.27(2H), -1.53(2H), -10.57(3H). Anal. Calcd. for $C_{27}H_{21}Co_4O_9U$: C, 33.6; H, 2.19; Co, 24.7. Found: C, 34.0; H, 1.72; Co, 19.6. IR data (Nujol, CsI):

2080m, 2060m, 2050m, 2015s, 1980m, 1864m, 858w, 780m, 720m, 585m, 537m, 510m, 430m cm^{-1}.

$(C_5H_5)_3U(Co_4(CO)_9)$

To $(C_5H_5)_3U\cdot py$ (1.1 g, 2.2 mmol) and $Co_2(CO)_8$ (0.40 g, 1.2 mmol) was added toluene (30 mL). An instant red color was observed, and a precipitate formed in roughly two minutes. After 25 minutes, the mixture was taken to dryness, and the red solid was extracted with toluene (30, 25, 25 mL). Cooling the combined filtrates (-80°C) gave a small amount of brown solid (ca. 0.10g), m.p.>300 C. IR data (Nujol, CsI): 2025m, 1975w, 1872s, br, 1600w, 1155w, 1065m, 1013m, 800s, 752m, 720m, 700m, 625m, 558s, 510w, 250m cm^{-1}. The solution was decanted, concentrated to ca. 20mL, and cooled (-20°C), giving 0.15 g red crystals, which were recrystallized with diethyl ether (70 mL). ^1H NMR (C_6D_6, 31°C): -3.33. Anal. Calcd. for $C_{24}H_{15}Co_4O_9U$: C, 31.21; H, 1.63. Found: C, 37.14; H, 2.88. IR data (Nujol, CsI): 2020s, br, 1950s, br, 1880s, br, 1810m, 1260m, 1150w, 1090m, br, 1010s, 817s, 790s, 720w, 585s, 590s, 510s, 273s, 433s, 410m, 358w, 238m cm^{-1}.

$[(MeC_5H_4)_3U]_2O$

To $(MeC_5H_4)_3U$-thf (0.91 g, 1.7 mmol) dissolved in ether (20 mL) at -20°C was added slowly by syringe N_2O (18.6 mL, 1.66 mmol). The surface of the bubbles of N_2O was immediately coated with a light green precipitate. The mixture was stirred for 30 minutes, while the deep red color slowly faded. The solvent was removed, and the green solid extracted with toluene (100 mL, 55°C). Cooling (-20°C), yielded

light green microcrystalline needles (0.16 g, 20%), m.p. > 320°C. No ^{1}H NMR spectrum could be observed due to insolubility. Mass spectrum: M^+ = 966. Anal. Calcd. for $C_{39}H_{42}OU_2$: C, 44.7; H, 4.38. Found: C, 45.8; H, 4.42. IR data (Nujol, CsI): 1300 w, 1259 w, 1148 m, 1033 m, 848 s, 798 m, 788 m, 763 s, 720 m, 626 m, 610 s, 597 s, 324 m, 230 m cm^{-1}.

$[(MeC_5H_4)_3U]_2S$

A To a suspension of triphenylphosphinesulfide (0.51 g, 1.7 mmol) in ether (10 mL) was added by cannula $(MeC_5H_4)_3U$-thf (0.91 g, 1.7 mmol) in ether (20 mL). Immediately a red precipitate formed. The mixture was stirred for one hour, then the ether was removed by vacuum. The red solid was dissolved in toluene (25 mL), the solution was filtered, and cooled (-20°C). Dark red needles (0.16 g, 9.4%), m.p. 274.5-275.5°C, were collected and dried.

B $(CH_3C_5H_4)_3U$-thf (1.0 g, 1.8 mmol) was dissolved in ether (50 mL), and the Schlenk was evacuated until the ether refluxed. An atmosphere of carbonyl sulfide was then introduced, and an immediate precipitate formed. The mixture was stirred for ten minutes, and then taken to dryness. Extraction of the red solid with a toluene/hexane mixture (20 mL/10 mL, 15 mL/5 mL, 15 mL/5 mL), and cooling the combined filtrate yielded the same crystals (m.p., IR, ^{1}H NMR) as the phosphine sulfide reaction. ^{1}H NMR (C_6D_6, 32°C): -8.88(2H), -9.09(3H), -13.41(2H). ^{13}C NMR (C_6D_6, 34°C): 203.82, 201.09, 199.73, -34.05. Anal. Calcd. for $C_{36}H_{42}SU_2$: C, 44.0; H, 4.31; S, 3.26. Found: C, 44.4; H, 4.41; S, 3.10. IR data (Nujol, CsI): 1240 w, 1170 w, 1047

w, 1035 m, 973 w, 930 w, 888 w, 847 m, 795 w, 768 s, 727 m, 693 w, 604 m, 470 w, 358 s, 330 w, 236 s cm^{-1}. The reaction between $SPPh_3$ and $(Me_3SiC_5H_4)_3U$ or $((Me_3Si)_2N)_3U$ proceeds similiarly, but the extreme hexane solubilities of the uranium containing products resulted only in recovery of ca. 0.5 equivalents of $SPPh_3$.

$[(MeC_5H_4)_3U]_2Se$

To $(MeC_5H_4)_3U$-thf (1.4 g, 2.6 mmol) dissolved in toluene (40 mL) was added tri-n-butylphosphine selenide (0.77 g, 2.7 mmol) dissolved in toluene (10 mL). The solution color immediately turned cherry red, and a red precipitate formed. The mixture was stirred for one hour, and the toluene solution filtered. The red precipitate was dissolved in toluene (7 mL), the filtrates were combined, and cooled (-20°C), yielding red needles (0.25 g, 18%), m.p. 240-241°C. The supernatent liquid was concentrated to 20 mL, and again cooled (-20°C), yielding a second crop (0.27g, 20%). ^1H NMR (C_6D_6, 31°C): -8.31(3H), -8.69(2H), -14.50(2H). ^{13}C NMR (C_6D_6, 32°C): 214.6, 207.6, 205.9, -33.34. Anal. Calcd. for $C_{36}H_{42}SeU_2$: C, 42.0; H, 4.11. Found: C, 41.3; H, 3.90. The mass spectrum has a parent ion M^+= 1030. IR data (Nujol, CsI): 1980(w, br), 1490 w, 1240 w, 1045 w, 1035 m, 975 w, 928 w, 888 w, 845 m, 770 s, 725 m, 693 w, 605 m, 590 w, 470 w, 327 m, 238 m, 216 s cm^{-1}.

$[(MeC_5H_4)_3U]_2Te$

To $(MeC_5H_4)_3U$-thf (1.02 g, 1.84 mmol) dissolved in ether (30 mL) was added by cannulae tri-n-butylphosphine telluride (0.27g, 0.88 mmol) dissolved in ether (20 mL). An instant precipitate formed, and

the solution color turned dark green. The mixture was stirred for one hour, and the solvent was removed by vacuum. The solid was extracted with toluene (30 mL), the filtrate was concentrated to 10 mL, and cooled (-20°C). Dark green bars (0.28g, 28%), m.p. 200-200.5°C, were collected and dried by vacuum. ^{1}H NMR (C_6D_6, 31°C): -8.03(3H), -9.73(2H), -11.83(3H). ^{13}C NMR (C_6D_6, 32°C): 236.0(s), 227.5(d, J =167.1Hz), 217.2(d, J=167.1), -36.39(q, J= 126.0). The mass spectrum shows a parent ion M^+= 1080. Anal. Calcd. for $C_{36}H_{42}TeU_2$: C, 40.1; H, 3.93; Te, 11.83. Found: C, 42.1; H, 4.03; Te, 10.4. IR data (Nujol, CsI): 1970 w br, 1941 w, 1240 w, 1023 s, 972 w, 930 w, 845 s, 770 s, 725 s, 692 m, 603 m, 467 m, 330 s, 240 s cm^{-1}.

Reaction of $(Me_3SiC_5H_4)_3U$ with N_2O

To $(Me_3SiC_5H_4)_3U$ (1.68 g, 2.59 mmol) dissolved in hexane was added by syringe N_2O (60 mL, 2.7 mmol). The solution color immediately turned light red, and after a few minutes a precipitate started to form. The solution was stirred at room temperature for three hours, and the hexane was removed under reduced pressure. Extraction with hexane (40 mL), filtering the red solution and cooling (-80°C) yielded red diamonds (A) (0.32g, 32%), m.p. 267-270°C. ^{1}H NMR (C_6D_6, 31°C): 5.17(9H), -18.06(2H), -32.72(2H). ^{13}C NMR (C_6D_6, 31°C): 159.7, 86.4, 78.2, -2.82. IR data (Nujol, CsI): 1401w, 1375m, 1353w, 1308w, 1245s, 1174s, 1045s, 1095w, 1040s, 900s, 830s, 770s, 750s, 688m, 656s, 629s, 575m, 420m, 328m, 310m, 247m, 218w cm^{-1}. The unit cell is triclinic; a= 12.27A, b=22.69A, c= 12.66A, α= 93.83°, β= 110.99°, γ= 90.20°. The remaining light red precipitate was insoluble

in ether or toluene, but did dissolve in toluene upon addition of bipyridine. Recrystallization of the (A) from diethyl ether gave red needles, m.p. 65-70°C. The ^{1}H NMR spectrum was dependent on the length of time it took to get the sample tube in the probe. The sample appeared homogeneous, but contained peaks due to (A) and $(Me_3SiC_5H_4)_4U$, as well as peaks at 13.14, 1.93, and a number of small peaks at -12 to -21ppm. After 24 hours, the peaks due to this compound were gone, and the predominant compound in solution was (A). There was not sufficient amount of $(Me_3SiC_5H_4)_4U$ in solution to account for 50% of the starting material. IR data (Nujol, CsI): 1400m, 1360w, 1308m, 1250s, 1177s, 1095m, 1034s, 900s, 834s, 775s, 750m, 718w, 687m, 650s, 625s, 575m, 418s, 325s, 310m, 245m, 220m cm^{-1}. The unit cell is hexagonal; a= 24.98, b= 24.98, c= 17.01.

$(Me_3SiC_5H_4)_4U$

To $(Me_3SiC_5H_4)_3U$ (1.11 g, 1.71 mmol) dissolved in hexane (30 mL) at -70°C was added by syringe house oxygen (19 mL, 0.86 mmol). Immediately the solution turned red and a precipitate formed. After stirring for one hour, the mixture was warmed to room temperature and the red solution was filtered. The remaining precipitate was extracted with hexane (15 mL). Cooling the combined filtrates (-20°C) yielded red blocks (0.12g, 18% based on U/2), m.p. 174-176°C. ^{1}H NMR (C_6D_6, 31°C): -1.95(9H), -10.40(2H), -22.19(2H). ^{13}C NMR (C_6D_6, 31°C): 220.73(s), 187.62(d), 155.50(d), -22.19(q). The mass spectrum has a peak at $[M-15]^+$= 771. Anal. Calcd. for $C_{32}H_{52}Si_4U$: C, 48.4; H, 6.66. Found: C, 48.8; H, 6.68. IR data (Nujol CsI): 3870 br, 2240

br, 1415 w, 1399 m, 1371 s, 1309 m, 1245 s, 1181 s, 1075 m, 1036 s, 970 w, 894 s, 872 w, 825 s, 793 m, 767 s, 747 s, 681 m, 632 s, 614 m, 570 w, 413 s, 331 w, 316 s, 301 m, 262 w, 238 w cm^{-1}.

$(C_8H_8)U(C_5H_4SiMe_3)_2$

To $(Me_3SiC_5H_4)_3U$ (1.33 g, 2.05 mmol) dissolved in hexane (15 mL) was added C_8H_8 (0.22 g, 2.1 mmol) dissolved in hexane (10 mL). The reaction was stirred for four hours, during which time the solution color turned red and a dark precipitate formed. Filtration of the hexane, followed by extraction of the solid with hexane (15 mL), and cooling the combined filtrates (-20°C) yielded dark green crystals (0.26 g, 41%), m.p. 140-145°C. ^1H NMR (C_6D_6, 34°C): 22.97(4H), -11.29(4H), -14.63(18H), -37.18(8H). ^{13}C NMR (C_6D_6, 28°C): 271.6(d, J =168.5Hz), 248.7(d, J=165.6), 233.0(d, J=159.7), -28.8(q, J=119.0). Mass spectrum: M^+=616, $[M-C_8H_8]^+$= 512, $[M-Cp]^+$= 479, Cp+1= 138, 123(?), $C_8H_8^+$= 104, and $Si(CH_3)_3^+$= 73. Anal. Calcd. for $C_{24}H_{34}Si_2U$: C, 46.7; H, 5.56. Found: C, 46.5; H, 5.82. IR data (Nujol, CsI): 1245 s, 1175 m, 1045 m, 898 w, 885 w, 863 w, 850 w, 830 s, 785 s, 745 w, 722 s, 685 w, 627 m, 620 m, 412 m, 336 m cm^{-1}.

$(C_5H_5)_3UNNCPh_2$

To $(C_5H_5)_3U$-py (1.19 g, 2.32 mmol) suspended in toluene (30 mL) was added by cannula diphenyldiazomethane (0.45 g, 2.3 mmol) in toluene (10 mL). The solution color immediately turned red, and a pink precipitate was observed. The mixture was stirred for 25 minutes, and the solvent was removed. Extraction with ether (40 mL)

left behind the pink precipitate. The ether filtrate was taken to dryness, the red solid was extracted with hexane (120 mL), and the hexane solution was cooled (-80°C). Dark red crystals (0.26g, 18%), m.p. 150-154°C, were collected and dried. ^{1}H NMR (C_6D_6, 32°C): -7.00(15H), and broad resonances at 10.55, 9.02, and 5.08. ^{13}C NMR (C_6D_6, 32°C): the Cp resonance was found at 119.45. Mass spectrum: M^+= 613. Anal. Calcd. for $C_{28}H_{25}N_2U$: C, 53.6; H, 4.02; N, 4.46. Found: C, 53.4; H, 4.09; N, 4.39. IR data (Nujol, CsI): 1595 w, 1565 w, 1487 w, 1315 w, 1259 w, 1185 w, 1178 w, 1156 w, 1146 w, 1080 w, 1058 m, 1008 m, 935 m, 913 w, 804 m, 774 s, 699 m, 688 m, 643 w, 629 w, 616 w, 605 w, 495 w, 456 w, 320 w, 228 m cm^{-1}.

$(MeC_5H_4)_3UNNCPh_2$

To $(MeC_5H_4)_3U$-thf (0.98g, 1.8 mmol) dissolved in ether (25 mL) was added diphenyldiazomethane (0.37g, 1.9 mmol) dissolved in ether (20 mL). The solution color appears orange-red. After 5 minutes, the ether was removed by vacuum, leaving a red oil. Ether and hexane (20/50 mL) were added, and the red solution was filtered, concentrated to ca. 40 mL total volume, and cooled (-80°C). A red solid, m.p. 100-104°C (0.28g, 23%), was isolated and dried under reduced pressure. ^{1}H NMR (C_6D_6, 32°C): 5.85(3H, $\nu_{1/2}$= 28Hz), -6.05(2H, $\nu_{1/2}$= 80Hz), -10.21(2H, $\nu_{1/2}$= 60Hz). The phenyl protons were at 10.23, 8.52, and 5.13 ppm. ^{13}C NMR (C_6D_6, 32°C): 139.12, 110.90, -4.75. The phenyl carbons looked as if they were under the solvent signal. Mass spectrum: M^+= 670. Anal. Calcd. for $C_{31}H_{31}N_2U$: C, 55.6; H, 4.66; N, 4.18. Found: C, 55.3; H, 4.73; N, 4.00. IR data (Nujol, CsI): 1591

m, 1486 m, 1420 m, 1311 w, 1305 w, 1247 w, 1188 w, 1178 w, 1168 w, 1154 w, 1081 w, 1058 m, 1045 m, 1030 m, 1020 m, 947 m, 905 w, 884 w, 859 w, 840 m, 781 s, 762 s, 692 s, 678 m, 640 m, 498 w, 466 m, 343 m, 325 m, 242 s cm^{-1}.

Reaction of $(MeC_5H_4)_3U$-thf with NNC_5H_4

To $(MeC_5H_4)_3U$-thf (0.60 g, 1.1 mmol) dissloved in toluene (10 mL) was added diazocyclopentadiene (0.10 g, 1.1 mmol) dissolved in hexane (10 mL). After three hours, the solvent was removed, and the red solid extracted with diethyl ether (20 mL). The solution was filtered and cooled (-80°C), giving red microcrystals. ^1H NMR (C_6D_6, 32°C): -0.42, -2.8, -5.8, -12.4, -13.4, -14.1, -14.6, -15.6. This was not pursued further.

Reaction of $(MeSiC_5H_4)_3U$ with NNC_5H_4

To $(MeSiC_5H_4)_3U$ (1.7 g, 2.5 mmol) dissolved in hexane (20 mL) was added diazocyclopentadiene (0.24 g, 2.6 mmol). Immediately the solution turned red, and a trace of precipitate formed. The solution was left at room temperature for three hours, filtered, and cooled (-5°C), to yield $(MeSiC_5H_4)_4U$ (0.08g, 10%, assuming complete redistribution). A second product (needles) was obtained by further cooling the hexane solution to -80°C.

Reaction of $(MeC_5H_4)_3U$-thf with BPY

To $(MeC_5H_4)_3U$-thf (0.79 g, 1.4 mmol) dissloved in diethyl ether (20 mL) was added bipyridine (0.19 g, 1.5 mmol) dissolved in ether (10

mL) (added in two portions, with five minutes in between). An immediate green color appeared, and precipitate started forming after the first half equivalent of BPY was added. After five minutes, the ether was removed, and a metallic dark green solid was extracted with toluene (40, 30 mL). Cooling the toluene filtrate (-20°C) gave black (green) polyhedral crystals (0.18g), m.p. 248-249°C. The reaction, as monitored by ^{1}H NMR spectroscopy in C_6D_6, gave two products suggesting a ligand redistribution process is involved. ^{1}H NMR (32°C, C_6D_6): 22.90(10), 14.71(31), 12.55(d, 8), 7.54(t, 8), 4.16(11), 2.05(10), 0.27(6), -0.15(d, 8), -1.93(10), -12.28(9), -14.45(12), -26.90(11), -28.99(8), -79.77(12). The splitting pattern and the extreme shift of the last peak is reminiscent of the bridging phenyl imido compound. The mass spectrum contains peaks at 677, 652, 624, 538, and 475 amu. Anal. Calcd for $C_{26}H_{27}N_2U$: C, 51.56; H, 4.62; N, 4.49. Found: C, 47.92; H, 4.22; N, 7.43. IR data (Nujol, CsI): 1555m, 1495s, 1280s, 1240s, 1040s, 910s, 925m, 763m, 727s, 624m, 600m, 535w, 458w, 430w, 408w, 348w, 322w, 228w cm^{-1}. A broad absorption appears to preclude analysis of the spectrum at >1600cm^{-1}. The unit cell is orthrombic; a=16.77, b=11.96, c=12.93.

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