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Synthesis and Properties of High-Valent Organouranium Complexes Containing Terminal Organoimido and Oxo Functional Groups. A New Class of Organo-f-Element Complexes

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Abstract: Monoimido derivatives of uranium(IV) have been prepared by both metathesis and direct protonation routes. The reaction of lithium anilide with $(\eta^5\text{-}C_5Me_5)_2UMeCl$ in the presence of tetramethylethylenediamine (TMED) results in the isolation of the salt $[Li(TMED)][\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ (**1**). Compound **1** crystallizes in the space group $P3_2$, with unit cell dimensions $a = 17.545(2)$ Å, $c = 9.407(2)$ Å, $V = 2507.8(7)$ Å^3, $Z = 3$. Metathesis reactions with potassium anilide salts similarly result in the formation of monoimido chloride anionic derivatives of U(IV); these can be converted to neutral base adducts by reaction with the appropriate Lewis base at room temperature. A more direct route to the formation of neutral organoimido species with sterically encumbered aryl substituents is the reaction of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ with 1 equiv H_2NAr (Ar = 2,6-diisopropylphenyl or 2,4,6-tri-*tert*-butylphenyl). The base-free 2,6-diisopropyl derivative is highly soluble in all solvents, and the product of this protonation is best isolated as a base adduct, $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)$ (**6**). The 2,4,6-tri-*tert*-butylphenylaniline product does not react further with tetrahydrofuran, however, and may be isolated as the base-free imido complex $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (**8**). Compound **8** crystallizes in the space group $Pmn2_1$, with unit cell dimensions $a = 13.450(5)$ Å, $b = 12.138(5)$ Å, $c = 10.510(3)$ Å, $V = 1715.9(10)$ Å^3, $Z = 2$. All of the organoimido compounds of uranium(IV) exhibit rich chemistry with two electron oxidative atom transfer reagents, providing an entirely new class of organouranium(VI) complexes containing terminal imido and oxo functional groups. Bis(imido) complexes such as $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)_2$ (**3**) can also be prepared by the unprecedented intramolecular reductive cleavage of 1,2-diphenylhydrazine at a uranium(IV) center. These complexes are in general surprisingly unreactive, but compound **3** will effect the unprecedented homolytic cleavage of dihydrogen to yield a bis(amide) derivative. The physical properties and chemical stability of these species suggests that significant uranium−imido and −oxo multiple bond character is present.

Introduction

The chemistry of early d-element complexes containing one or more multiply bonded functional groups, and in particular organoimido (M=NR) ligands, has proven to be of great interest to synthetic chemists in recent years.[1] These investigations have produced stable species incorporating a broad array of ancillary ligands, as well as homoleptic complexes for a number of metals. The ligand set most commonly employed in the isolation of organoimido complexes of the early transition metals, however, is the bent metallocene framework. Molecular species of the general formula $(\eta^5\text{-}C_5R_5)_2M({=}NR')$ (R = Me, H; R′ = alkyl, aryl) now exist for representative elements of the groups 4, 5, and 6.[2−4] The unique chemical, structural, and electronic properties exhibited by this class of complexes have given rise to a number of synthetic and theoretical investigations.[2−5] Molecular f-element complexes containing organoimido functional groups, in contrast, remain comparatively rare.[6] In particular, no direct f-element analogs of the bent metallocene complexes $(\eta^5\text{-}C_5R_5)_2M({=}NR')$ have been isolated where R′ is a simple alkyl or aryl substituent. While it is generally presumed that the $(\eta^5\text{-}C_5Me_5)_2An$ and $(\eta^5\text{-}C_5H_5)_2M$ frameworks yield roughly comparable steric environments around the metal center (given the inherent differences in ionic radius between actinide and comparable d-metal ions), extensive studies of the chemical[7] and electronic[8] properties of the $[(\eta^5\text{-}C_5Me_5)_2An]^{2+}$ (An = Th or U) framework have often revealed striking differences with respect to their early d-element analogs. This unique reactivity has been attributed to a number

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of factors, including the greater polarity of actinide–element bonds, enhanced coordinative flexibility of the 5f ions, and/or the potential for f-orbital involvement in bonding.[7] Regardless of the origin of this difference, it is reasonable to expect that actinide complexes of the general formula $(\eta^5\text{-}C_5Me_5)_2An({=}NR)$ (An = Th or U) will not exhibit the same physical properties as their d-element analogs, and in fact should show fundamentally different chemical behavior.

We recently reported that $(\eta^5\text{-}C_5Me_5)_2UMeCl$ and $(\eta^5\text{-}C_5Me_5)_2UMe_2$ react with anilide salts or 2,6-disubstituted anilines, respectively, to form arylimido complexes of uranium(IV) with the concomitant loss of methane.[6a,b] These compounds can be oxidized by organic azides[6b] or amine *N*-oxides[6a] to produce bis(pentamethylcyclopentadienyl)uranium(VI) complexes containing terminal bis(organoimido) or imidooxo functional groups. In this paper, we report in detail the syntheses and properties of a family of bis(pentamethylcyclopentadienyl)uranium(IV) arylimido complexes produced from both metathesis and protonation routes and discuss their two electron oxidation reactions with organic azides, amine *N*-oxides, and nitrous oxide. As part of this study, the solid state structures of the anionic arylimido species $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ (**1**) and the neutral terminal arylimido complex $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (**8**) have been determined. The latter compound represents the first f^2 analog of the known d^2 group 6 organoimido complexes of the general formula $(C_5H_4R)_2M({=}N^tBu)$ (M = Mo or W).[4] We also report here the preparation of complexes of the formula $(\eta^5\text{-}C_5Me_5)_2U(NPh)(NR)$ (R = C_6H_5 or 4-CH_3-C_6H_4) by the intramolecular reductive cleavage of the 1,2-diarylhydrazido(2−) ligand at a uranium(IV) metal center, as well as the reduction of complexes of the formula $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)(NR)$ (R = C_6H_5 or $Si(CH_3)_3$) to $(\eta^5\text{-}C_5Me_5)_2U(NHC_6H_5)(NHR)$ by the homolytic cleavage of dihydrogen. Both of these reaction types are unprecedented in the d-block elements.

Results

Schemes 1 and 2 summarize the reactions reported in this study.

Imido Complexes of Uranium(IV). One of the most common synthetic methodologies for the introduction of an amido functionality to a d-element is α-H abstraction from a primary amide by alkyl or amido ligands.[1] Despite this, the utility of this approach for the introduction of an imido group in f-element chemistry has not been demonstrated prior to these investigations. Metathesis routes prove most generally useful for the introduction of imido functional groups at uranium(IV). The room temperature reaction of $(\eta^5\text{-}C_5Me_5)_2UMeCl$[9] with 1 equiv of LiNHPh in THF/TMED results in the slow evolution of methane (ca. 15 min) and the formation the brown-orange salt $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NPh)Cl]$ (**1**). The reaction of $(\eta^5\text{-}C_5Me_5)_2UMeCl$ with $Li(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ in THF similarly results in the formation of $[Li(THF)_x][(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)Cl]$ ($x = 1-2$) in high yield, but the analogous reaction with $Li(NH\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ results in an intractable green solid, presumably due to reduction of the uranium metal center. Attempts to displace LiCl from these complexes with Lewis bases have not proven successful. The reaction of compound **1** in toluene with 1.5 equiv of pyridine gave no reaction even when heated to reflux for days. However, the reaction of $(\eta^5\text{-}C_5Me_5)_2UMeCl$ with 1 equiv of KNHAr (Ar = Ph, 2,4,6-$Me_3C_6H_2$, or 2,6-i-$Pr_2C_6H_3$) in THF provides in high yield the nonstoichiometric potassium salts $[K(THF)_x][(\eta^5\text{-}C_5Me_5)_2U(NAr)Cl]$ ($x = 2-3$). Dissolution of $[K(THF)_x][(\eta^5\text{-}C_5Me_5)_2U(NAr)Cl]$ in toluene followed by the slow addition of a slight excess of pyridine (ca. 1.5 equiv) at room temperature results in an immediate color change from red-orange to deep green, forming the neutral $(\eta^5\text{-}C_5Me_5)_2U(NAr)(py)$ (py = pyridine) in high yield (Scheme 1).

Aniline protonation routes have also been employed in producing the arylimido complexes; the utility of this reaction is dependent on the steric bulk of the aryl substituent, however. The room temperature reaction of 1 equiv of H_2NPh with $(\eta^5\text{-}C_5Me_5)_2UMe_2$ in diethyl ether affords an equimolar mixture of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ and $(\eta^5\text{-}C_5Me_5)_2U(NHPh)_2$. All attempts to further induce α-H abstraction from a primary amide by an amido ligand in these systems proved unsuccessful in our hands. Thus, in contrast to analogous group 4 complexes,[2] thermolyzing $(\eta^5\text{-}C_5Me_5)_2U(NHPh)_2$ in toluene in the presence of pyridine (110 °C) resulted in no observable reaction when monitored by ^1H NMR. The formation of imido complexes in protonation reactions can be promoted by the use of bulkier aryl substituents, however. The reaction of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ with 1 equiv of either 2,6-diisopropylaniline or 2,4,6-tri-*tert*-butylaniline in toluene at elevated temperatures produces the corresponding terminal imido compound $(\eta^5\text{-}C_5Me_5)_2U(NAr)$ (Ar = 2,6-i-$Pr_2C_6H_3$ or 2,4,6-t-$Bu_3C_6H_2$) in quantitative yield (^1H NMR) with the concomitant loss of 2 equiv of methane (Scheme 1). $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (**8**) is easily isolated as a sparingly soluble olive powder and does not form a base adduct with THF, whereas $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ is highly soluble in all solvents and is best isolated as the less soluble base adduct $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)$ (**6**).

Molecular Structures of $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ and $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$. Structural studies of early d-element metallocene imido complexes of the general formulas $(\eta^5\text{-}C_5R_5)_2M({=}NR)$ (M = V, Mo) and $(\eta^5\text{-}C_5R_5)_2M({=}NR)(L)$ (M = Zr, L = THF; and M = Ta, L = H) have been used in conjunction with other spectroscopic and theoretical techniques to investigate the bonding of the imido functional group.[2-4,10] To assess the coordination environment in related f-element complexes, the molecular structures of $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ (**1**) and $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (**8**) were determined.

A. $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ (1). Figure 1 presents the molecular structure of **1**, while Tables 1 and 2 summarize the crystal and structural data. The molecule is of the Cp_2ML_2 "bent metallocene" type with a normal centroid–U–centroid angle of 132.4° and an average U–C_{ring} distance of 2.77(2) Å (within the range found for other uranium(IV)–$C(\eta^5\text{-}C_5Me_5)$ complexes).[11] The U–Cl distance of 2.690(5) Å is slightly longer than that found in other tetravalent actinide metallocene-geometry complexes (e.g., U–Cl = 2.579(2) Å in $(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2UCl_2$).[12] The long U–Cl distance reflects competitive coordination by the four-coordinate lithium atom which bridges between Cl(1) and N(1). The Li(1)–N(1)

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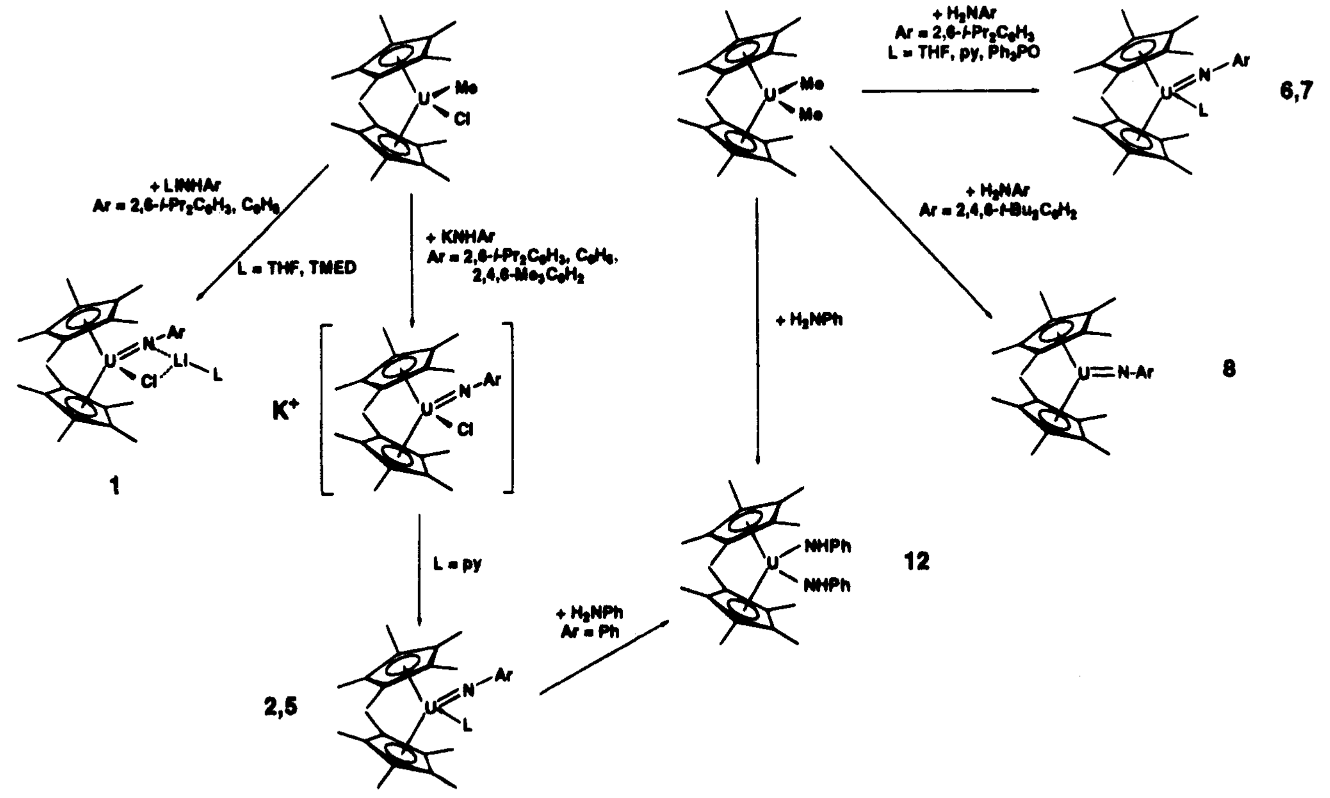
Scheme 1. Syntheses of U(IV) Organoimido Complexes



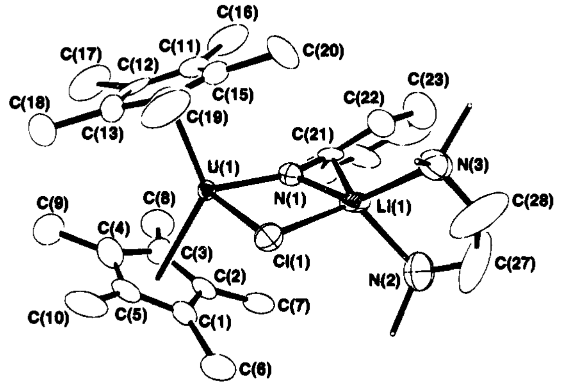


Figure 1. ORTEP drawing of [Li(TMED)][(η^5-C_5Me_5)$_2$U(NC_6H_5)Cl] (**1**) with the atomic numbering scheme (TMED methyl groups and hydrogen atoms omitted for clarity).

Table 1. Crystallographic Parameters for the Compounds [Li(TMED)][(η^5-C_5Me_5)$_2$U(NC_6H_5)Cl] (**1**) and (η^5-C_5Me_5)$_2$U-(N-2,4,6-*t*-$Bu_3C_6H_2$) (**8**)

	[Li(TMED)]-[(η^5-C_5Me_5)$_2$U-(NC_6H_5)Cl] **1**	(η^5-C_5Me_5)$_2$U-(N-2,4,6-*t*-$Bu_3C_6H_2$) **8**
empirical formula	$C_{32}H_{51}ClLiN_3U$	$C_{38}H_{59}NU$
space group	$P3_2$	$Pmn2_1$
temp (K)	173	173
a (Å)	17.545(2)	13.450(5)
b (Å)	17.545(2)	12.138(5)
c (Å)	9.407(2)	10.510(3)
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	90
V (Å^3)	2507.8(7)	1715.9(10)
Z	3	2
ϱ_{calc} (Mg/m^3)	1.506	1.486
radiation (λ (Å))	Mo Kα (0.71073)	Mo Kα (0.71073)
fw (g/mol)	758.2	767.9
μ (mm^{-1})	4.957	4.755
range	3–45	3–45
scan type	2θ–θ	2θ–θ
R^a (%)	5.22	3.55
R$_w$^{a} (%)	5.38	3.95

^{a} $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \sum\sqrt{w}|F_o - F_c|/\sum\sqrt{w}F_o$.

distance is 2.14(4) Å; an interaction also exists between the lithium ion and the *ipso* carbon of the phenyl ring (Li(1)–C(21) = 2.76(3) Å). The coordination of the lithium ion to the chloride and imido ligands accounts for the relatively small equatorial N(1)–U–Cl(1) angle of 89.3(4)°.[6a,b,11] The most important information may be obtained from an examination of the geometry of the arylimido ligand, however. The U–N(1) bond distance in compound **1** is 2.051(14) Å, which while long, does not fall outside the range of terminal U–N distances found in other structurally characterized complexes of uranium(V) and -(VI) containing organoimido functional groups (U(1)–N(1) range = 1.91(2)–2.07(2) Å).[6,13] Typical uranium(IV)–N "single" bond distances range from 2.250(4) Å in (η^5-C_5Me_5)$_2$U(NHC_6H_5)$_2$[14] to 2.29(1) Å in (η^5-C_5H_5)$_3$UN(C_6H_5)$_2$.[15] The U–N(1)–C(21) bond angle is (159.8(13)°). Although significantly bent from linear, this angle is still larger than that observed for actinide arylamide complexes.[16] The short U(1)–N(1) bond distance and large U–N(1)–C(21) bond angle may be interpreted as suggesting the polarization of lone pair electrons on the nitrogen toward the uranium center, or their

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Li(TMED)][(η^5-C_5Me_5)$_2$U(NC_6H_5)Cl] (**1**)

U(1)−Cl(1)	2.690(5)	U(1)−C(Cp*)avg	2.77(2)
U(1)−N(1)	2.051(14)	U(1)−Cent(1)	2.494
U(1)···Li(1)	3.19(4)	U(1)−Cent(2)	2.492
Li(1)−Cl(1)	2.44(3)	Li(1)−N(2)	2.10(3)
Li(1)−N(1)	2.14(4)	Li(1)−N(3)	2.26(5)
Li(1)−C(21)	2.76(3)		
N(1)−C(21)	1.40(2)		
N(2)−C(27)	1.48(4)	N(3)−C(28)	1.38(4)
N(2)−C(29)	1.49(3)	N(3)−C(31)	1.43(4)
N(2)−C(30)	1.46(4)	N(3)−C(32)	1.42(5)
C(27)−C(28)	1.28(6)		
Cl(1)−U(1)−N(1)	89.3(4)	Cent(2)−U(1)−Cl(1)	103.9
Cent(1)−U(1)−Cl(1)	104.2	Cent(2)−U(1)−N(1)	106.8
Cent(1)−U(1)−N(1)	111.2	Cent(1)−U(1)−Cent(2)	132.4
U(1)−Cl(1)−Li(1)	76.8(8)		
U(1)−N(1)−Li(1)	99.4(10)		
U(1)−N(1)−C(21)	159.8(13)		
Li(1)−N(1)−C(21)	100.4(15)		
Cl(1)−Li(1)−N(1)	94.4(14)	N(1)−Li(1)−N(2)	118.2(17)
Cl(1)−Li(1)−N(2)	113.7(14)	N(1)−Li(1)−N(3)	143.1(18)
Cl(1)−Li(1)−N(3)	100.9(12)	N(2)−Li(1)−N(3)	85.9(15)
Cl(1)−Li(1)−C(21)	124.3(15)	N(1)−Li(1)−C(21)	29.9(7)
		N(2)−Li(1)−C(21)	101.6(12)
		N(3)−Li(1)−C(21)	124.1(16)

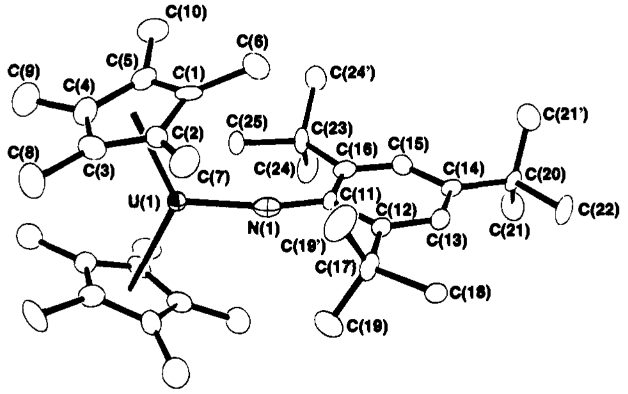

Figure 2. ORTEP drawing of (η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$) (**8**) with the atomic numbering scheme (hydrogen atoms omitted for clarity).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$) (**8**)

U(1)−N(1)	1.952(12)	U(1)−Cent	2.515
U(1)···C(25)	2.951(15)	U(1)−C(Cp*)avg	2.790(12)
C(11)−C(12)	1.46(2)	C(13)−C(14)	1.40(2)
C(11)−C(16)	1.42(2)	C(14)−C(15)	1.40(2)
C(12)−C(13)	1.39(2)	C(15)−C(16)	1.38(2)
C(12)−C(17)	1.56(3)	C(14)−C(20)	1.52(2)
C(17)−C(18)	1.56(3)	C(20)−C(21)	1.53(2)
C(17)−C(19)	1.53(2)	C(20)−C(22)	1.53(3)
C(16)−C(23)	1.57(2)		
C(23)−C(24)	1.53(2)		
C(23)−C(25)	1.55(2)		
N(1)−U(1)−Cent	112.2	Cent−U(1)−Cent′	133.8
U(1)−N(1)−C(11)	162.3(10)		
N(1)−C(11)−C(12)	120.6(12)	C(13)−C(14)−C(15)	114.6(12)
N(1)−C(11)−C(16)	122.3(12)	C(13)−C(14)−C(20)	122.6(13)
C(12)−C(11)−C(16)	117.1(12)	C(15)−C(14)−C(20)	122.9(13)
C(11)−C(12)−C(13)	118.9(12)	C(14)−C(15)−C(16)	125.0(14)
C(11)−C(12)−C(17)	120.3(13)	C(11)−C(16)−C(15)	119.9(13)
C(13)−C(12)−C(17)	120.9(13)	C(11)−C(16)−C(23)	126.4(13)
C(12)−C(13)−C(14)	124.6(13)	C(15)−C(16)−C(23)	113.8(13)
C(12)−C(17)−C(18)	109.9(15)	C(18)−C(17)−C(19)	106.6(10)
C(12)−C(17)−C(19)	109.3(10)	C(19)−C(17)−C(19′)	115.0(17)
C(14)−C(20)−C(21)	109.8(9)	C(21)−C(20)−C(22)	107.4(10)
C(14)−C(20)−C(22)	113.7(14)	C(21)−C(20)−C(21′)	108.6(14)
C(16)−C(23)−C(24)	109.4(10)	C(24)−C(23)−C(25)	105.9(10)
C(16)−C(23)−C(25)	116.8(12)	C(24)−C(23)−C(24′)	109.1(14)

involvement in multiple bonding to the uranium. The interaction of the imido group with the lithium counterion is responsible for only small perturbations to this picture (the slightly long U−N bond distance and the bending about the U−N−C_{ipso} angle).

B. (η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$) (8). Figure 2 presents the molecular structure of **8**, while Tables 1 and 3 summarize the crystal and structural data. On the basis of room temperature NMR data and the structural precedent provided by (η^5-C_5Me_5)$_2$V(=N-2,6-$Me_2C_6H_3$)[3c] and (η^5-C_5H_4Me)$_2$Mo(=N^{t}Bu),[4] compound **8** was expected to exhibit a nearly linear U−N−C_{ipso} linkage and approximate C_2 symmetry along the U(1)−N(1) bond. Unexpectedly, compound **8** displays considerable asymmetry in the conformation of the two ortho *tert*-butyl groups with respect to their orientation toward the uranium metal center. For one of the *tert*-butyl groups (centered on C(17)), a "normal" conformation is found such that the distance between the uranium atom and its methyl groups has been maximized as would be expected for such a bulky substituent. In contrast, the other *tert*-butyl group (centered on C(23)) has adopted the exact opposite conformation, with a unique methyl group, C(25), pointed directly toward the uranium metal center at a distance of 2.951(15) Å and a C(25)−U(1)−N(1) angle of 66.2(5)°. There is a growing number of structurally characterized examples of this unusual conformation in aryl oxide and aryl amide complexes of the early d-block and f-block elements.[17] A difference Fourier map of the low-temperature X-ray diffraction data of **8** revealed the location of most hydrogen atoms, but when attempts were made to refine their positions several were poorly behaved and failed to converge. The nature of this interaction is as of yet unclear. The U(1)−N(1)−C(11) bond angle is 162.3(10)°, with the aryl substituent canted toward this close C(25)−U(1) contact. We have observed no spectroscopic or chemical evidence in support of an agostic interaction,[18] however, and the C(16)−C(23)−C(25) angle of 116.8(12)° is significantly larger than the other comparable ortho Ar−C−CH_3 angles (Ar−C−CH_3 avg = 109.5(11)°) which implies a net repulsive interaction between the uranium metal center and the unique methyl group.[17b]

The singular feature of the solid state structure of **8** is the extremely short U(1)−N(1) bond length of 1.952(12) Å. The U(1)−N(1) bond length agrees well with other short U−N bond lengths in arylimido complexes of uranium(V) and -(VI)[19] when differences in ionic radii due to uranium oxidation state and

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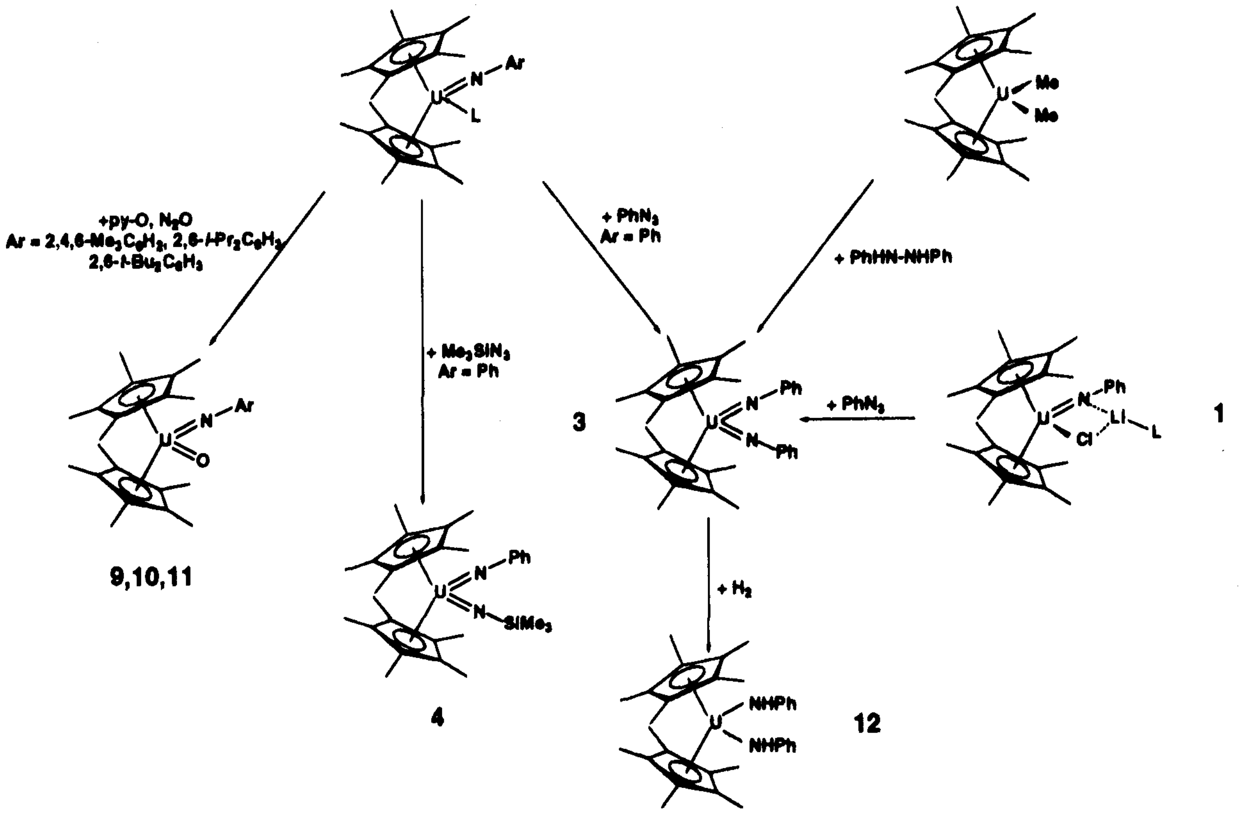
(16) (a) The U−N−C_{ipso} angles in (η^5-C_5Me_5)$_2$U(NHC_6H_5)$_2$ are 134.7(4)° and 149(3)°, respectively, unpublished result. (b) The U−N−C_{ipso} angles in {[K(THF)$_2$][U(NH-2,6-^{i}$Pr_2C_6H_3$)$_5$]}·THF range from 141(2)° to 156(2)°, see: Nelson, J. E.; Clark, D. L.; Burns, C. J.; Sattelberger. A. P. *Inorg. Chem.* **1992**, *31*, 1973.

(17) (a) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger. A. P.; Streib, W. E.; Van Der Sluys, W. G.; Watkin. J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811. (b) Fanwick, P. W.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73.

(18) The asymmetry in the conformation of the two ortho *tert*-butyl groups observed in the solid state structure of compound **8** could not be frozen out in low-temperature NMR studies (toluene-d_8). The insolubility of compound **8** precluded NMR studies below 235 K. (a) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (d) Rothwell. I. P. *Polyhedron* **1985**, *4*, 177 and references therein.

(19) (a) Other short U=NAr bond distances (Å): (η^5-MeC_5H_4)$_3$U(=NPh), 2.019 (6), ref 6f: [N($SiMe_3$)$_2$]$_3$U(=NPh)F, 1.979 (8), ref 6c; (η^5-C_5Me_5)$_2$U(=NPh)$_2$, 1.952 (7), ref 6b; (η^5-C_5Me_5)$_2$U(=N-2,6-^{i}$Pr_2C_6H_3$)(=O), 1.988 (4), ref 6a.

Scheme 2. Syntheses of U(VI) Complexes



coordination number are taken into account.[20] This may suggest a relatively high formal bond order where one pair or both pairs of nitrogen lone pairs are involved in bonding to the uranium atom.

Preparation and Reactivity of Organometallic Complexes of Uranium(VI) Containing Organoimido and Oxo Ligands. Two synthetic methodologies have been developed for the preparation of uranium(VI) complexes of the general formula $(\eta^5\text{-}C_5Me_5)_2U(=NR)(=E)$, where E = NR or O (Scheme 2). The most general route is two-electron oxidative atom transfer utilizing organic azides (N_3R) or oxygen transfer reagents (amine *N*-oxides or nitrous oxide). Oxidative atom transfer chemistry for the introduction of imido and oxo functional groups is well precedented in the d-elements.[1] This method has been successfully utilized with uranium(III) precursors for the preparation of terminal organoimido complexes of uranium(V).[6d-f] The uranium(IV) organoimido complexes (**1**, **2**, **5**, **6**, **8**) react readily at room temperature with two-electron atom transfer reagents to generate U(VI)−imido (**3**, **4**) and −oxo (**9**, **10**, **11**) complexes, respectively, in high yield (Scheme 2).[6a,b]

Another method which has proven useful in the synthesis of bis(imido) complexes is the reductive cleavage of 1,2-disubstituted hydrazines. The cleavage of azo and hydrazo compounds for the introduction of a *single* organoimido functional group finds precedent in d-element chemistry.[1,21] f-Element organometallic complexes have been shown to react with azobenzene and hydrazobenzene leading in some cases to NN bond cleavage; however, phenylimido functional groups are not observed products.[22] We have observed that $(\eta^5\text{-}C_5Me_5)_2UMe_2$ or $(\eta^5\text{-}C_5Me_5)_2UMeCl$ react with 1,2-diphenylhydrazine or 1-lithio-1,2-diphenylhydrazine, respectively, to produce $(\eta^5\text{-}C_5Me_5)_2U(NPh)_2$ (**3**) in high yield (Scheme 2).[6b] This is the first example, to our knowledge, of the reductive cleavage of an azo or hydrazo compound yielding *two* organoimido functional groups at a single metal center.

Either a unimolecular or a bimolecular pathway can be proposed for the generation of a bis(organoimido)uranium(VI) complex by the cleavage of a 1,2-disubstituted hydrazido(2−) ligand at a uranium(IV) center. Though it is tempting to invoke a unimolecular mechanism involving the intermediacy of an η^2-1,2-diphenylhydrazido(2−) species, bis(pentamethylcyclopentadienyl) f-element complexes containing bridging 1,2-diphenylhydrazido(2−) ligands are well precedented.[22] To more firmly establish how compound **3** arises the experiment was carried out with an asymmetrically substituted hydrazobenzene. When $(\eta^5\text{-}C_5Me_5)_2UMe_2$ is reacted with 1 equiv of $(4\text{-}MeC_6H_4)NHNH(C_6H_5)$ in benzene for 56 h only one product is observed, $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}4\text{-}MeC_6H_4)(NPh)$, formed in quantitative yield (eq 1).[23] This result indicates a unimolecular reaction involving the reductive cleavage of an η^2-1,2-diphenylhydrazido(2−) ligand at a single uranium(IV) metal center.

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[20] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

[21] For a recent example of the reduction of hydrazobenzene to yield a mono-phenylimido complex of zirconium, see: Zambrano, C. H.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1994**, *13*, 1174 and references therein.

[22] (a) Evans, W. J.; Kociok-Köhn, G.; Leong, V. S.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 3592. (b) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983. (c) Trifonov, A. A.; Bochkarev, M. N.; Schumann, H.; Loebel, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1149.

[23] In an NMR tube 0.015 g of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ was reacted at room temperature with 1 equiv of $(4\text{-}C_6H_4Me)NHNH(C_6H_5)$ in C_6D_6 with an internal standard of hexamethylbenzene. After 56 h a quantitative yield of $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}4\text{-}C_6H_4Me)(=NPh)$ was observed by ^1H NMR. No redistribution of organoimido ligands was observed for $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}4\text{-}C_6H_5Me)(=NPh)$ or $(\eta^5\text{-}C_5Me_5)_2U(=NPh)(=NSiMe_3)$ (**4**) over days in solution at room temperature. $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}4\text{-}C_6H_4Me)(=NPh)$: ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 9.26 (t, 2 H, J_{HH} = 8.05 Hz, meta), 9.14 (d, 2 H, J_{HH} = 8.05 Hz, meta), 7.67 (s, 3 H, $4\text{-}CH_3\text{-}C_6H_4$), 4.11 (s, 30 H, C_5Me_5), 3.02 (d, 2 H, J_{HH} = 8.05 Hz, ortho), 2.58 (d, 2 H, J_{HH} = 8.05 Hz, ortho), 0.93 (t, 1 H, J_{HH} = 8.05 Hz, para). ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C) δ 189.0 (C_{phenyl}), 182.2 (C_{phenyl}), 180.8 (C_{phenyl}), 156.2 ($C_{ipso/ring}$), 142.8 ($C_{ipso/ring}$), 136.3 (C_{phenyl}), 110.1 (C_{phenyl}), 107.9 (C_{phenyl}), 106.3 ($C_{ipso/ring}$), 8.8 ($4\text{-}Me\text{-}C_6H_4$), 7.7 ($C_5Me_5$). Anal. Calcd for $C_{33}H_{42}N_2U$: C, 56.24; H, 6.01; N, 3.97. Found: C, 56.31; H, 6.07; N, 3.74.

$$(\eta^5\text{-}C_5Me_5)_2UMe_2 + (4\text{-}MeC_6H_4)NHNH(Ph) \xrightarrow{-2MeH} (\eta^5\text{-}C_5Me_5)_2U(=N\text{-}4\text{-}C_6H_4Me)(=NPh) \quad (1)$$

Preliminary reactivity studies of the unsaturated functional groups have shown some interesting differences between the complexes of uranium(IV) and -(VI) as well as the d-element organoimido and oxo metallocene systems.[2-4,24-27] In contrast to the relatively reactive "$(\eta^5\text{-}C_5H_5)_2Zr(=NR)$" complex,[2] we have found no evidence for CH bond activation or alkyne cycloaddition chemistry in these systems, even in those systems which have the steric flexibility to coordinate additional Lewis bases (e.g. $(\eta^5\text{-}C_5Me_5)_2U(=N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$. As observed in the "$(\eta^5\text{-}C_5H_5)_2Zr(=NR)$" system, $(\eta^5\text{-}C_5Me_5)_2U(NPh)(py)$ (**2**) reacts slowly (ca. days) with aniline to produce $(\eta^5\text{-}C_5Me_5)_2U(NHPh)_2$ in quantitative yield. In contrast to the zirconium complex, however, this reaction is irreversible even in refluxing toluene in the presence of pyridine. The uranium(VI) complexes similarly display a dearth of reactivity. Neither the bis(imido) nor the imido–oxo complex reacts with alkenes, alkynes, or phosphines. $(\eta^5\text{-}C_5Me_5)_2U(NPh)_2$ (**3**) is unreactive toward aniline or ammonia, and rapidly decomposes in the presence of trace amounts of water. Most interesting is the reduction of $(\eta^5\text{-}C_5Me_5)_2U(NPh)(NR)$ (R = Ph (**3**), $SiMe_3$ (**4**)) by dihydrogen (Scheme 2). All of the uranium(VI) complexes react with dihydrogen, but only the bis(imido) complexes yield tractable products (the oxo complexes decompose upon reaction). Both **3** and **4** react slowly (ca. days) with 1 atm of dihyrogen to produce the uranium(IV) bisamide compounds $(\eta^5\text{-}C_5Me_5)_2U(NHPh)(NHR)$ (R = Ph (**12**), $SiMe_3$ (**13**)) in quantitative yield. Further characterization of these complexes will be described elsewhere.[14]

Discussion

Complexes of the d-transition metals with such terminal multiply-bonded functional groups as alkylidene ($M{=}CR_2$), alkylidyne ($M{\equiv}R$), imido ($M{=}NR$), nitrido ($M{\equiv}N$), and oxo ($M{=}O$) ligands form a very important class of molecules.[1] Not only are they the object of numerous theoretical investigations of metal–ligand multiple bonding, but they have also been shown to be important homogeneous catalysts for reactions such as polymerization, oxidation, and aziridination of organic substrates.

Aside from complexes of the actinyl ions $(AnO_2)^{2+}$, there are very few examples of analogous compounds of the f-transition series.[6,28] Extension of studies beyond oxo complexes to isoelectronic imido and alkylidene analogs would dramatically increase our understanding of the nature of multiple bonding in the chemistry of the f-elements. There are a number of reasons why it would be valuable to have access to a broader base of information concerning actinide–ligand multiple bonding. The actinyl ions themselves are important species in many aqueous aerobic systems and merit further study in order to understand their electronic structure. Predicting the chemical stability of these functional groups is also of practical interest; while hydrolysis reactions are known to be important in some pH ranges,[29] little more than an empirical understanding exists of this behavior in aqueous media. Finally, one might expect some synthetic utility to arise from these functional groups bound to f-metal centers. Complexes of the actinides in general display a higher degree of ionic character in chemical bonding than their d-transition metal counterparts. This should result in significant metal–ligand charge separation. The highly basic ligands may be expected to be reactive toward aliphatic and unsaturated organic substrates, as has been observed in the chemistry of group 4 analogs.

The reasons for this paucity of actinyl analogs are apparent. The actinide ions are large, and therefore not easily sterically saturated. The small, highly-charged functional groups have a high propensity to bridge metal centers, and in the absence of other strong Lewis bases, these interactions can give rise to molecular aggregates by facile ligand transfer reactions between coordinatively unsaturated species. In order to be able to isolate more examples of this class of complexes, it is necessary to target molecules in which terminal multiply-bound functional groups are prevented from adopting bridging geometries by the steric bulk of the ancillary ligand set.

A major goal of the study of metal–ligand multiple bonding is to develop meaningful comparisons between the properties of actinide complexes and those of analogous d-element complexes, as well as correlate chemical reactivity patterns with molecular and electronic structure. The bis(pentamethylcyclopentadienyl)uranium framework[7] $[(\eta^5\text{-}C_5Me_5)_2U]^{2+}$, in addition to providing a sterically encumbered metal environment, represents one of the only series of organoactinides which contains a ligand array nearly identical to that of a well-characterized d-element system which supports metal–ligand multiple bonds.[6a,b] Thus, a detailed comparison of many chemical and physiochemical properties should be possible employing this ligand set.

The other requirement for successful isolation of new f-element oxo, imido, and alkylidene complexes is development of a general route for the introduction of these functional groups. Of previously investigated actinide organoimido complexes,[6] the organoimido functional group was introduced in nearly all cases by two-electron oxidation of the metal center and by organic azide. The application of this synthetic methodology is obviously limited to the preparation of pentavalent and hexavalent complexes, as only U^{3+} and U^{4+} precursors are available. We have sought alternative and more general methodologies to effect the syntheses of terminal organoimido actinide complexes. Specifically, we have investigated the utility of α-hydrogen abstraction reactions from a primary amide by alkyl or amido ligands, a synthetic strategy commonly used in d-transition metal chemistry.[1] This methodology has been used for the preparation of zirconocene imido complexes, $(\eta^5\text{-}C_5H_5)_2Zr(=NR)$, and thus allows a direct comparison between analogous d- and f-metal systems.

The addition of metal amides MNHAr (M = Li or K; Ar = C_6H_5 or $2,4,6\text{-}C_6H_2Me_3$) to a THF solution of $(\eta^5\text{-}C_5Me_5)_2$-

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[24] For complexes of the general formula $(\eta^5\text{-}C_5R_5)_2M(=O)$ (M = Ti, V), see: Smith, M. R., III; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.

[25] For complexes of the general formula $(\eta^5\text{-}C_5R_5)_2Zr(=O)$, see: (a) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (b) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. (c) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761. (d) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917. (e) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

[26] For complexes of the general formula $(\eta^5\text{-}RC_5H_4)_2M(=O)$ (M = Mo, W), see: (a) Green, M. L. H.; Lynch, A. H.; Swanwick, M. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1445. (b) Silavwe, N. D.; Chang, M. Y.; Tyler, D. R. *Inorg. Chem.* **1985**, *24*, 4219. (c) Henary, M.; Kaska, W. C.; Zink, J. I. *Inorg. Chem.* **1991**, *30*, 1674.

[27] For complexes of the general formula $(\eta^5\text{-}C_5Me_5)_2W(=O)$, see: (a) Parkin, G.; Bercaw, J. B. *Polyhedron* **1988**, *7*, 2053. (b) Parkin, G.; Bercaw, J. B. *J. Am. Chem. Soc.* **1989**, *111*, 391. (c) Parkin, G.; Bercaw, J. B. *Chem. Soc., Chem. Commun.* **1989**, 255.

[28] (a) Brown, D. R.; Denning, R. G.; Jones, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2601. (b) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853.

[29] Weigel, F. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; Chapter 5 and references therein.

UMeCl results in the facile room temperature elimination of methane and the formation the corresponding uranium(IV) arylimido salts of the general formula $[M(THF)_x][(\eta^5\text{-}C_5Me_5)_2U(NAr)Cl]$ ($x = 1-3$). Although the structure of **1** reveals that the imido group is stabilized by interaction with the lithium counterion, this interaction is not key in driving the reaction. The elimination of methane from uranium(IV) amide methyl complexes appears to be general even for bulkier arylimido ligands such as 2,6-diisopropylphenylimido where steric congestion about the actinide–metal center precludes the formation of a tight ion pair.[14] This is in contrast to the analogous zirconium systems, in which the room temperature addition of lithium amides to zirconocene methyl chlorides results only in the isolation of the methyl amide $(\eta^5\text{-}C_5H_5)_2ZrMe(NHR)$ (R = 4-$C_6H_4{}^tBu$ or ^tBu). Only upon thermolysis (≥85 °C) of the zirconocene methyl amide complexes, $(\eta^5\text{-}C_5H_5)_2ZrMe(NHR)$, is the extrusion of methane observed to generate the transient zirconocene imido species $(\eta^5\text{-}C_5H_5)_2Zr(=NR)$.[2] It is also unusual to note that while amine elimination from $(\eta^5\text{-}C_5H_5)_2Zr(NHR)_2$ has been demonstrated, the analogous process does not occur in the uranium system.

The substantial increase in temperature and reaction time required to synthesize the neutral uranium(IV) arylimido complexes $(\eta^5\text{-}C_5Me_5)_2U(NAr)$ (Ar = 2,6-*i*-$Pr_2C_6H_3$ and 2,4,6-*t*-$Bu_3C_6H_2$) by the direct protonation of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ with the corresponding anilines verses halide metathesis reactions suggests that the mechanism of formation of the neutral uranium(IV) arylimido complexes from $(\eta^5\text{-}C_5Me_5)_2UMe_2$ most likely involves initial coordination of the aniline to the uranium center followed by proton transfer from the coordinated aniline to the uranium-bound methyl group then loss of a second equivalent of methane by an α-hydrogen abstraction pathway. Similar reaction pathways have been suggested from mechanistic studies of the thermal reactions of $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ with amines.[2d] Consistent with the hypothesis of steric control, the bulk of the 2,6-diisopropyl- and 2,4,6-tri-*tert*-butyl-substituted arylamines precludes introduction of a second arylamide functional group, either by reaction with a second equivalent of aniline or in metathetical reactions of $(\eta^5\text{-}C_5Me_5)_2UCl_2$ with anilide salts.[14]

A study of the reactivity of bis(pentamethylcyclopentadienyl)-uranium(IV) arylimido complexes reveals that in the absence of steric barriers, the arylimido functional group is susceptible to protonation by excess aniline, even in the presence of another strong Lewis base. $(\eta^5\text{-}C_5Me_5)_2U(NPh)(py)$ (**2**) reacts over days with excess aniline to provide $(\eta^5\text{-}C_5Me_5)_2U(NHPh)_2$ (**12**) in quantitative yield as observed by ^1H NMR (Scheme 1). The 2 + 2 cycloaddition of alkynes as demonstrated by the analogous group 4 complexes is not observed in these systems, however. None of the bis(pentamethylcyclopentadienyl)uranium(IV) arylimido complexes reported herein cycloadd internal alkynes to form azametallacyclobutanes as is observed in zirconocene arylimido complexes.[2]

The most striking chemistry exhibited by these bis(pentamethylcyclopentadienyl)uranium(IV) arylimido complexes is their reaction with 2-electron oxidative atom transfer reagents such as organic azides, nitrous oxide, and amine *N*-oxides to provide complexes of the general formula $(\eta^5\text{-}C_5Me_5)_2U(=NAr)(=E)$ (Ar = C_6H_5, E = NC_6H_5 (**3**) or $NSiMe_3$ (**4**); Ar = 2,4,6-$Me_3C_6H_2$ (**9**), 2,6-*i*-$Pr_2C_6H_3$ (**10**), or 2,4,6-*t*-$Bu_3C_6H_2$ (**11**), E = O), Scheme 2 (Figure 3).[6a,b] No analogous d-element complexes exist, which raises significant questions regarding the electronic structure of these complexes regarding the participation of valence metal orbitals (5f, 6d, and 7p) in ligand to f-metal π-bonding. The assignment of the formal oxidation state of the uranium as +6 is supported by both the electronic spectroscopy (lacking any features attributable to metal-based transitions) and the NMR spectra of the complexes. The NMR spectra[6a,b] reveal that the observed chemical shifts lie significantly outside the normal diamagnetic region. The uranium is behaving as a temperature independent paramagnet, as has been observed for U(VI) in both $UO_2{}^{2+}$ and UF_6.[30]

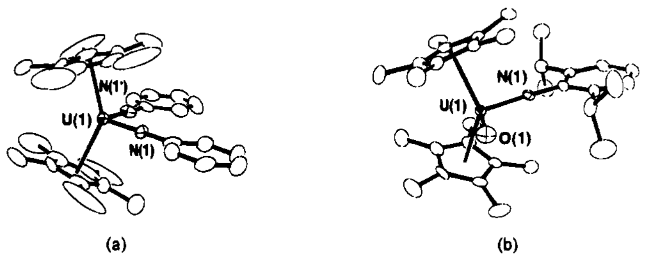

Figure 3. ORTEP drawings of $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)_2$ (a) and $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O)$ (b) from refs 6a and 6b.

None of the bis(organoimido)uranium(VI) complexes ($(\eta^5\text{-}C_5Me_5)_2U(NPh)(NR)$: R = Ph (**3**), 4-Me-$C_6H_4$, $SiMe_3$ (**4**)) exhibits any propensity to exchange organoimido ligands in solution.[23] In contrast, the single terminal oxo functional group is kinetically stabilized on the $(\eta^5\text{-}C_5Me_5)_2U^{VI}$ framework only by the use of bulky 2,6-alkylarylimido ligands ($(\eta^5\text{-}C_5Me_5)_2U(NAr)(O)$: Ar = 2,4,6-$Me_3C_6H_2$ (**9**), 2,6-*i*-$Pr_2C_6H_3$ (**10**), 2,4,6-*t*-$Bu_3C_6H_2$ (**11**).[6a] When either $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NPh)]$ (**1**) or $(\eta^5\text{-}C_5Me_5)_2U(NPh)(py)$ (**2**) is reacted with 1 equiv of pyridine *N*-oxide, an immediate color change to black-brown is observed along with the formation of a light brown precipitate, eq 2. Analysis of the soluble products by ^1H NMR reveals that

$$2\ (\eta^5\text{-}C_5Me_5)_2U(NPh)(py) + 2\ \text{py-O} \rightarrow (\eta^5\text{-}C_5Me_5)_2U(NPh)_2 + [C_5Me_5]_2 + \text{“}UO_2\text{”} \quad (2)$$

a mixture of $(\eta^5\text{-}C_5Me_5)_2U(NPh)_2$ (**3**) and $[C_5Me_5]_2$ is formed.[31] Thus, while the mechanism of this reaction is unclear, it seems likely that $(\eta^5\text{-}C_5Me_5)_2U(NPh)(O)$ is formed initially, and then undergoes bimolecular ligand exchange providing **3** as well as $[C_5Me_5]_2$ and an insoluble amorphous uranium oxide material. Attempts to trap other intermediates with Lewis bases have so far proved unsuccessful.

Transition metal complexes of the general formula $(\eta^5\text{-}C_5R_5)_2M(=E)$, where E = NR or O,[2,4,24-27] constitute a special class of imido/oxo derivatives. It has been postulated that these complexes must balance the donor ability of the imido/oxo functional groups with those of the cyclopentadienyl ligands. Group 6 analogs of this general formula[4,26,27] (M = Mo or W) appear to be 20-electron complexes if the imido or oxo ligands are considered to donote their full compliment of electrons (1σ, 2π) giving a M≡E bond order of 3. Similarly, the group 4 analogs ($(\eta^5\text{-}C_5H_5)_2Zr(=NR)(L)$) could be considered 20-electron complexes.[2a] The bonding in these species has been

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(30) (a) McGlynn, S. P.; Smith, J. K. *J. Mol. Spectrosc.* **1961**, *6*, 164. (b) Attempts to measure the magnetic moment of these complexes have been hampered by the small size of the expected paramagnetic moment with respect to the large applied molecular diamagnetic correction. While measurements clearly suggest temperature independent behavior with a small positive moment, the value is exceeded by the uncertainty of the measurement in experiments conducted to date.

(31) An NMR tube was charged with 0.015 g of $(\eta^5\text{-}C_5Me_5)_2U(=NPh)(py)$ (**2**) and C_6Me_6 as an internal standard in C_6D_6. To the solution was added pyridine *N*-oxide (ca. 1 equiv) resulting in an immediate color change. The reaction monitored by ^1H NMR revealed within 30 min an equimolar mixture of $(\eta^5\text{-}C_5Me_5)_2U(=NPh)_2$ (**3**) and $[C_5Me_5]_2$ in quantitative yield. Compounds $(\eta^5\text{-}C_5Me_5)_2U(=NPh)_2$ (**3**) and $[C_5Me_5]_2$ were identified by their characteristic spectra, see 6b for **3** and Jutzi, P.; Kohl, F. (*J. Organomet. Chem.* **1979**, *164*, 141) for $[C_5Me_5]_2$.

investigated using molecular orbital calculations.[10,32] It has been proposed that these complexes may respond to electronic pressures in one of two ways: localization of one lone pair of electrons at the imido or oxo ligand (formation of a formal metal–ligand double bond), or donation of the second lone pair into a metal–cyclopentadienyl antibonding orbital. The first situation has been used to explain the low-energy M–O stretching frequencies in $(\eta^5\text{-}C_5H_5)_2M(=O)$[26a] (M = Mo, W) and $(\eta^5\text{-}C_5Me_5)_2W(=O)$[27a] and the high reactivity of the group 4 imido ligands.[2] The second explanation accounts for observations of distortions in cyclopentadienyl ring geometry in $(\eta^5\text{-}C_5Me_5)_2V(=N\text{-}2,6\text{-}C_6H_3Me_2)$[3c] and the observed ring-slip observed in the complex $(\eta^5\text{-}C_5H_4{}^iPr)(\eta^3\text{-}C_9H_7)Mo(=N^tBu)$.[4] Additionally, Bercaw and Parkin demonstrated ring slippage in $(\eta^5\text{-}C_5Me_5)_2W(=O)$ which reacts cleanly with peroxides (H_2O_2 or Me_3CO_2H) to provide $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$.[27a]

Actinide complexes of the formula $(\eta^5\text{-}C_5Me_5)_2An(=E)$ present an additional possibility, in that they possess empty f-orbitals of the appropriate symmetry to accept electron density from the imido or oxo group. The structure of **8** does not provide conclusive evidence either supporting or refuting metal–nitrogen multiple bonding. The steric bulk of the aryl group likely affects both the observed structure and the chemical behavior of the complex (the lack of reactivity of these complexes may simply be due to steric congestion).

The situation is further complicated in the case of the uranium(VI) bis(imido) and imido–oxo derivatives by the presence of two π-donor ligands in the equatorial plane of the bent metallocene fragment. A hypothetical d-element analog would be a 20-electron species even if both ligands were acting only as 4-electron donors. The additional electrons from the ligand lone pairs either must be localized on the imido or oxo ligands or else must be involved in a ligand-to-metal π-bonding interaction. In most f-element organometallic chemistry, calculations demonstrate that the empty d orbitals are primarily responsible for interactions with filled ligand orbitals, and that f-orbitals primarily house metal valence electrons.[33] Preliminary calculations have highlighted that there are no 6d orbitals of the appropriate symmetry to accept electrons from the in-plane π combination of the nitrogen 2p orbitals in the complex $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)_2$.[34] There are, however, 5f orbitals of the appropriate symmetry which appear to be instrumental in stabilizing these lone pairs. The involvement of 5f orbitals in actinide–ligand multiple bonding has precedent; 2p–5f interactions have been invoked in theoretical investigations of the uranyl ion[35] to explain the linear O–U–O geometry and the strength of the U–O bond. If this type of interaction is important in $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)_2$ and related species, π-bonding would manifest itself in both the spectroscopy and chemical reactivity of these species.

The nature of the uranium–nitrogen and uranium–oxygen bonding in these complexes was probed using vibrational spectroscopy. Unambiguous identification of the metal–nitrogen and metal–oxygen bond stretching frequencies was achieved through the use of isotopic labeling (^{15}N and ^{18}O) experiments. The evidence gathered from infrared spectra suggests that the U–N bond order in the imido groups is comparable to that observed in previously reported monoimido complexes of uranium(V) and uranium(VI). Of the few careful ^{15}N infrared studies on d-element organoimido complexes the phenylimido ligand has been investigated most extensively.[1,3c,36]

Table 4. Infrared Data for ^{14}N and ^{15}N Derivatives

complex	ν_{U-N} (cm^{-1})	ν_{N-C} (cm^{-1})
$[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(^{14}NC_6H_5)Cl]$ (**1**)	898	1274
$[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(^{15}NC_6H_5)Cl]$	888	1263
$(\eta^5\text{-}C_5Me_5)_2U(^{14}NC_6H_5)(py)$ (**2**)	917	1302
$(\eta^5\text{-}C_5Me_5)_2U(^{15}NC_6H_5)(py)$	905	1288
$(\eta^5\text{-}C_5Me_5)_2U(^{14}NC_6H_5)_2$ (**3**)	912, 907	1270, 1255
$(\eta^5\text{-}C_5Me_5)_2U(^{15}NC_6H_5)_2$	900, 895	1257, 1247

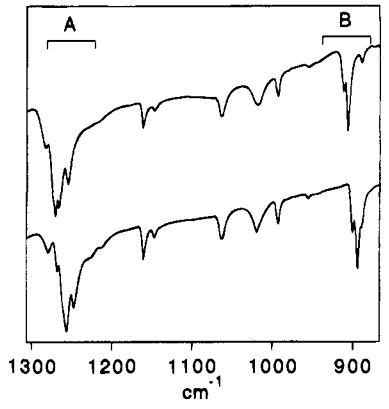

Figure 4. IR spectra of $(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)_2$ (top trace) and $(\eta^5\text{-}C_5Me_5)_2U(^{15}NC_6H_5)_2$ (bottom trace).

Preparations of $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NPh)]$ (**1**), $(\eta^5\text{-}C_5Me_5)_2U(NPh)(py)$ (**2**), and $(\eta^5\text{-}C_5Me_5)_2U(NPh)_2$ (**3**) were carried out with ^{15}N-labeled phenylimido ligands, and the infrared spectra were compared with those obtained for the ^{14}N phenylimido complexes (Table 4). In all cases bands in two distinct regions 1260–1275 and 900–930 cm^{-1} were observed to shift upon ^{15}N labeling (regions A and B, Figure 4). These shifts are attributed to mixtures of the $\nu_{N-C(phenyl)}$ and ν_{U-N} modes and correlate well with observed shifts in ^{15}N labeling studies on analogous d- and f-element phenylimido complexes.[37]

Also of great interest are the U–O stretching frequencies in the U(VI) oxo complexes reported in this study as well as the U(V) complexes reported previously.[6a] In the structure of $(Me_5C_5)_2U(NAr)(O)$[6a] (Ar = 2,6-i-$Pr_2C_6H_3$) the uranium–oxygen bond length is significantly longer (1.844(4) Å) than the U–O bond lengths typical for complexes of the uranyl ion $(UO_2)^{2+}$ (1.70–1.76 Å).[38] The longer U–O bond length in $(Me_5C_5)_2U(NAr)(O)$ likely reflects a reduced bond order relative to that suggested for the uranyl ion.[35] Preparations of $(\eta^5\text{-}C_5Me_5)_2U(NAr)(O)$ (Ar = 2,4,6-$Me_3C_6H_2$ (**9**), 2,6-i-$Pr_2C_6H_3$ (**10**), 2,4,6-t-$Bu_3C_6H_2$ (**11**) were carried out with (ca. 40% enriched) ^{18}O labeled oxo ligands, and the infrared spectra were compared with those obtained for the ^{16}O oxo complexes. In all cases within experimental error (2 cm^{-1}) a strong new band was observed at 715 cm^{-1} in the partially ^{18}O-labeled species, and

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(32) Jørgensen, K. A. *Inorg. Chem.* **1993**, *32*, 1521.

(33) Burns, C. J.; Bursten, B. E. *Comments Inorg. Chem.* **1989**, *9*, 61.

(34) Bursten, B. E. Private communication.

(35) (a) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656. (b) Wadt, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 6053.

(36) (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *Inorg. Chem.* **1982**, *21*, 978. (c) Goegen, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157. (d) Seng Tan, L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 1744. (e) Osborne, J. H.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3098.

(37) Infrared spectroscopic studies of $^{14}N/^{15}N$ labeled $(\eta^5\text{-}C_5Me_5)_2V(=NPh)$ reveal bands at 1330 and 934 cm^{-1} which shift to 1307 and 923 cm^{-1} upon ^{15}N labeling. These have been attributed to the N–C(phenyl) and V–N vibrations, respectively, see: Osborne, J. H.; Trogler, W. C. ref 36e. Similar studies on $(\eta^5\text{-}MeC_5H_4)_3U(=NPh)$ bands at 1271 and 909 cm^{-1} which shift to 1260 and 895 cm^{-1} upon ^{15}N labeling; Andersen, R. A. Private communication.

(38) (a) Burns, J. H. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hill: New York, 1986; Chapter 20. (b) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984; p 1265.

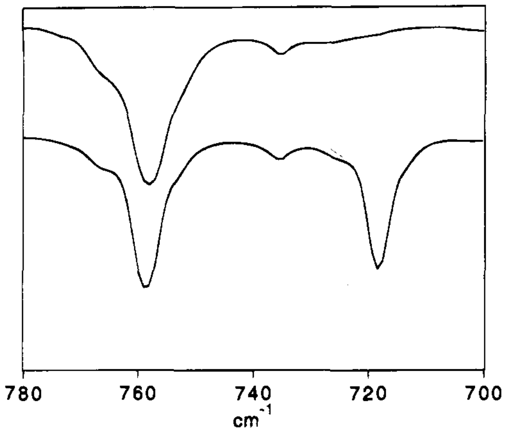

Figure 5. IR spectra of $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}Me_3C_6H_2)(O)$ (top trace) and $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,4,6\text{-}Me_3C_6H_2)(^{16/18}O)$ (40% ^{18}O, bottom trace).

the strong band appearing at 755 cm^{-1} in the ^{16}O oxo complex was observed to decrease in intensity (Figure 5).[39]

The reduced energy of the U−O vibrational mode with respect to those found in the uranyl ion (ν_s = 860 cm^{-1}, ν_{as} = 930 cm^{-1})[30a] clearly suggests that the overall U−O bond order is lower in complex **9** than in its linear dioxo analog. Based on an ionic model, Coulombic repulsion between the imido and oxo ligands would tend to weaken the U−E bond strength in a bent geometry. Matrix isolation studies of ThO_2 and UO_2, which display bent geometries, similarly possess lower M−O asymmetric frequencies (Th, ν_{as} = 735 cm^{-1}; U ν_{as} = 776 cm^{-1}).[40] It must also be noted,[1a] however, that imido ligands can be relatively strong π-bases (relative to the more electronegative oxo ligand), and will therefore compete more effectively for empty metal-based orbitals of the appropriate symmetry. This competition will result in a lower overall U−O bond order in the mixed ligand complexes.

The chemical stability of the species supports the hypothesis that f orbitals may be involved in stabilizing lone-pair electron density. Graphic evidence of this stability is provided by the observation of unimolecular cleavage of 1,2-disubstituted hydrazines in the synthesis of the bis(phenylimido)uranium(VI) complex. The substantial kinetic barrier to the *four*-electron cleavage of bound azo,[41] dioxygen,[42] nitroso,[43] ketone, and imine[44] ligands at a single metal center without assistance, despite a large thermodynamic driving force,[45] has been noted by many investigators. The failure of single d-block metal centers to undergo *four*-electron oxidative addition reactions of double bonded substrates has been attributed to a general symmetry-derived restriction on this reaction.[42,46] The fact that the f^2 $(\eta^5\text{-}C_5Me_5)_2U^{IV}$ fragment readily effects the *intra*molecular cleavage of the 1,2-diphenylhydrazido(2−) ligand to form the uranium(VI) bis(phenylimido) complex, where the analogous group 6 d^2 complex $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}PhNNPh)$ is stable,[41c] attests to the thermodynamic stability of uranium(VI) with multiply bonded functional groups and suggests the participation of f-element orbitals of the correct symmetry (5f or 7p) in the electron pair transfer from uranium(IV) to the 1,2-diphenylhydrazido(2−) ligand N−N σ^* orbital.[42]

Additional evidence of the stability of the hexavalent species is provided by examination of their reaction chemistry. Given the reactivity observed for group 4 organoimido complexes, it is not unreasonable to expect that the imido ligands in the uranium(VI) compounds would behave as potent nucleophiles (even assuming some degree of f-orbital stabilization of nitrogen lone pair electrons). No reaction is observed with traditional electrophiles such as methyl iodide, however. Similarly, the complexes are stable for prolonged periods in hydrocarbon solvents (in the absence of air and water), and there is no evidence of C−H activation of aliphatic or aromatic substrates. While the complexes react with potent Brønsted acids such as water, they exhibit no reaction with ammonia. Attempts to induce functional group transfer reactivity also proved unsuccessful. It was expected that the unusual *cis* disposition of the imido (or imido and oxo) functional groups in these species could lead to olefin addition reactions similar to those obtained with reducible d^0 transition metal complexes.[47] Complexes **3**, **4**, **9**, **10**, and **11** do not react with either ethylene or 3-hexyne, however.

Steric factors are not entirely responsible for the lack of observed reactivity. The uranium(VI) oxo complexes **9**, **10**, and **11** do not react with trimethylphosphine to yield the uranium(IV) monoimido species. We have successfully prepared the anticipated product of the reaction of phosphine with **10**, however, by direct reaction of the monoimido THF adduct with phosphine oxide (eq 3). The stability of the phosphine

$$(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF) + O{=}PMe_3 \rightarrow (\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(O{=}PMe_3) \quad (3)$$

oxide adduct clearly demonstrates that the transition state required for oxo abstraction from the uranium(VI) compounds is accessible, and that steric congestion is not the origin of the kinetic barrier to interconversion of **7** and **10**.

One reaction which proceeds cleanly is the reduction of the bis(imido) derivatives **3** and **4** with dihydrogen to yield the bis(amide) analogs (Scheme 2). Although the reaction proceeds slowly at room temperature ($t_{1/2}$ > 12 h), only the expected bis(amide) complexes $(\eta^5\text{-}C_5Me_5)_2U(NHC_6H_5)_2$ and $(\eta^5\text{-}C_5Me_5)_2U(NHC_6H_5)(NHSiMe_3)$ are formed. Reaction of the imido−oxo complexes with dihydrogen yields intractable

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[39] For the uranium(V) oxo compound $(\eta^5\text{-}C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2C_6H_3)({=}O)$, ref 6a, a strong new band was observed at 733 cm^{-1} and a strong band at 775 cm^{-1} was observed to decrease upon ^{18}O labeling (ca. 79% enriched) of the oxo ligand. Arney, D. S. J.; Burns, C. J. Unpublished results.

[40] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1986.

[41] For references regarding the existence of separate RNNR and $(NR)_2$ complexes, see: (a) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063. (b) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (c) Nakamura, A.; Aotake, M.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3456. (d) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2709.

[42] For references regarding the existence of separate O_2 and $(O)_2$ complexes, see: Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091.

[43] A striking example of the noninterconvertability of ONPh and (O)(NPh) complexes of molybdenum has been noted, see: (a) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 2597. (b) Maata, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

[44] A rare example of an apparent intramolecular *four*-electron oxidative addition of ketones, imines, and cumulenes at a tungsten(II) metal center has been studied in detail, see: (a) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (b) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213.

[45] Brown and Mayer, ref 42, have succinctly demonstrated the substantial kinetic barrier needed to overcome the tremendous thermodynamic driving force for O−O bond cleavage in d-metal peroxo complexes. While $(HBpz_3)ReO(OCH_2CH_2O)$ ($HBpz_3$ = hydridotris(1-pyrazolyl)borato) decomposes thermally to produce $(HBpz_3)ReO_3$ and ethylene, the thermodynamically more favorable *four*-electron cleavage of dioygen in $(HBpz_3)ReO(O_2)$ to form $(HBpz_3)ReO_3$ does not occur even under forcing conditions.

[46] For further discussion relating to analogous olefin, azo, nitroso, dioxygen, and ketone transition-metal complexes, see: (a) Lee, D. G.; Moylan, C. R.; Hayashi, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3003. (b) Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632.

[47] (a) Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981. (b) Criegee, R. *Justus Liebigs Ann. Chem.* **1936**, *522*, 75. (c) Kolb, H. C.; Andersson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 1278.

products; presumably the initially formed amide—hydroxide complexes react further (e.g. by intra- or intermolecular deprotonation of the hydroxide) and decompose. This type of homolytic cleavage of dihydrogen by a bis(imido) complex (or isoelectronic analog) has no precedent in d-metal chemistry; we are currently examining the mechanistic details of this reaction.[14]

Conclusion

It has been demonstrated that α-hydrogen abstraction from a primary amide by alkyl ligands is a convenient general route for the preparation of uranium(IV) arylimido derivatives. In the presence of the sterically encumbering bis(pentamethylcyclopentadienyl) framework, these complexes display terminal organoimido ligands. The amide ligands may be introduced by either metathesis routes (employing $(\eta^5\text{-}C_5Me_5)_2UMeCl$ as a reagent) or direct protonation reactions of primary amines with $(\eta^5\text{-}C_5Me_5)_2UMe_2$. The slower reaction rate in the latter preparations suggests that precoordination of the amine is the limiting factor in formation of the imido product. The steric bulk of the aryl group has a substantial effect on the stability of the product. In reactions employing aniline, the phenylimido product can only be isolated as a base adduct (with neutral Lewis bases or chloride anion as the stabilizing base). Direct reaction of aniline with $(\eta^5\text{-}C_5Me_5)_2UMe_2$ yields only the bis(amide) product. Bulkier 2,6-dialkyl-substituted arylamines can give rise to either base adducts or base-free arylimido products, depending on the reaction conditions.

These species are surprisingly unreactive in comparison to their group 4 analogs and show no evidence of reaction with saturated or unsaturated hydrocarbon substrates. They will react with a variety of two-electron oxidants, however, to yield novel bis(imido) and imido—oxo complexes. The uranium(VI) complexes are exceptionally stable in the absence of oxygen and moisture. One indication of the electronically stabilizing influence of the imido and oxo ligands on the high-valent metal center may be found in the unusual reactivity of $(\eta^5\text{-}C_5Me_5)_2UMe_2$ with *N,N'*-diarylhydrazines. The product of this reaction is not the expected η^2-hydrazido derivative, but rather the uranium(VI) bis(imido) complex, formed by intramolecular two-electron cleavage of the N—N bond. The unusual stability of these derivatives (both in their formation and in subsequent reactions) may be viewed as an indication of a substantial degree of ligand—metal π-bonding, perhaps involving the uranium 5f orbitals.

Experimental Section

General. All experiments were performed under an argon atmosphere using standard Schlenk techniques[48] or under helium in a Vacuum Atmospheres HE-553-2 drybox with a MO-40-2 Dri-Train at room temperature (unless otherwise indicated). Solvents were purified under N_2 by standard techniques[49] and transferred to the drybox without exposure to the air. The "cold" solvents used to wash isolated solid products were typically cooled to −35 °C before use. NMR solvents were degassed and passed down a short column (5−6 cm) of activated alumina prior to use.

Starting Materials. Uranium(IV) chloride was prepared by literature methods.[50] The compounds $(\eta^5\text{-}C_5Me_5)_2UCl_2$, $(\eta^5\text{-}C_5Me_5)_2U(Cl)CH_3$, and $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$ were prepared as described by Marks.[9b] Tetramethylethylenediamine (TMED) was diluted from sodium/benzophenone before use. Aniline 2,4,6-trimethylaniline, and 2,6-diisopropylaniline were obtained from Aldrich and vacuum distilled before use. 2,4,6-Tri-*tert*-butylaniline and *N,N'*-diphenylhydrazine were obtained from Aldrich and used as received. 1-(*p*-Tolyl)-2-phenylhydrazine was prepared from *p*-toluidene (Aldrich Chemical Co., Inc.) and nitrosobenzene (Aldrich Chemical Co., Inc.) in an analogous procedure to the preparation of azobenzene.[51] The azo compound was reduced with ammonium sulfide to 1-(*p*-tolyl)-2-phenylhydrazine[52] and recrystallized from dry pentane three times before use. Trimethylsilyl azide was obtained from Huber-Pfalzgraf and vacuum distilled then stored over 4Å sieves. Phenyl azide (20% in hexanes) was obtained from Huber-Pfalzgraf and used as received. Pyridine *N*-oxide was obtained from Aldrich and sublimed through 4Å sieves under dynamic vacuum (10^{-4} Torr) before use. Nitrous oxide, N_2O, was purchased from Trigas and passed through a double trap with glass beads at −78 °C before use.

Ligand Preparations. The lithium anilide salts LiNHPh and $Li^{15}NHPh$ were prepared by a method similar to that found in the literature.[53] $LiN(C_6H_5)\text{-}NH(C_6H_5)$ was made by the slow addition of *n*-butyllithium to an equimolar hexane solution of 1,2-diphenylhydrazine. The mixture was allowed to stir overnight, and the lithium salt was isolated by filtration. A near quantitative yield was obtained after washing with hexane and drying *in vacuo*. KNHAr (Ar = C_6H_5, 2,4,6-$Me_3C_6H_2$) salts were prepared by a method analogous to the literature preparation of $KNH(2,6\text{-}i\text{-}Pr_2C_6H_3)$.[16b] $N_2{}^{15}NC_6H_5$ was prepared as described in the literature.[54] $N_2{}^{18}O$ was prepared by the controlled thermal decomposition of NH_4NO_3 (79% ^{18}O, Icon Services, Inc.); H_2O was removed from the product by passing the gas through a double trap with 3 mm glass beads at −78 °C.

Physical Measurements. ^1H (300 or 250 MHz) NMR spectra were recorded at probe temperature on Bruker WM 300 or AF 250 spectrometers in C_6D_6, THF-d_8, or toluene-d_8. ^{13}C (50.25 or 62.9 MHz) NMR spectra were recorded at probe temperature on Bruker AM 200 or Bruker WM 300 spectrometers in C_6D_6. Chemical shifts were referenced to *protio* solvent impurities (δ 7.15 (C_6D_6), 1.73 (THF-d_8), 2.09 (toluene-d_8)) and solvent ^{13}C resonances (δ 128.0 (C_6D_6)) and are reported in ppm downfield of Me_4Si. Resonances associated with solvents of crystallization are not reported. Infrared spectra were obtained as Nujol mulls between KBr plates on a Bio-Rad Digilab FTS 40 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer utilizing sealed aluminum capsules for delivery. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrophotometer, and extinction coefficients were measured from the baseline.

Preparations. $[Li(TMED)][(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)Cl]$ (1). LiNHPh (0.234 g, 2.36 mmol) was added as a solid to a rapidly stirred maroon solution of $(\eta^5\text{-}C_5Me_5)_2U(Cl)CH_3$ (1.20 g, 2.15 mmol) in 50 mL of diethyl ether. The solution immediately became red-brown, and vigorous gas evolution was observed. After 1 h, tetramethylethylenediamine (0.300 g, 2.59 mmol) was added dropwise to the stirred red-brown solution with no observed change in color. The solution was stirred for an additional 12 h, and the solvent was removed under reduced pressure to yield a red-orange powder. The powder was dissolved in toluene (40 mL) and filtered through Celite, and the toluene was removed from the filtrate *in vacuo*. The resulting red-orange powder was washed with minimal cold hexane and dried *in vacuo*; yield 1.26 g (1.66 mmol) or 77%. Analytically pure samples were obtained by recrystallization from toluene/diethyl ether at −35 °C. Spectroscopic and analytical data are reported in ref 6b.

$(\eta^5\text{-}C_5Me_5)_2U(NC_6H_5)(py)$ (2). Solid $KNH(C_6H_5)$ (0.074 g, 0.565 mmol) was added to a rapidly stirred maroon solution of $(\eta^5\text{-}C_5Me_5)_2U(Cl)CH_3$ (0.300 g, 0.537 mmol) in 20 mL of THF. The solution immediately became red-brown, and vigorous gas evolution was observed. The solution was stirred for 18 h, after which time the solvent was removed under reduced pressure to afford a red-orange powder. The powder was dissolved in toluene (30 mL), and pyridine (0.069 g, 0.864 mmol) was added dropwise to the stirred red-orange solution.

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The solution became deep green with the concomitant precipitation of KCl. The solution was stirred 1 h then filtered through Celite and the toluene removed from the filtrate *in vacuo* to afford the product as a dark green powder. This product was washed with minimal cold hexane and dried *in vacuo*; yield 0.287 g (0.423 mmol) or 79%. Analytically pure samples were obtained by recrystallization from toluene/hexane at −35 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 32.41 (d, J_{HH} = 7.32 Hz, 2 H, C$_o$, NPh), 31.28 (t, J_{HH} = 7.32 Hz, 2 H, C$_m$, NPh), 12.71 (t, J_{HH} = 7.32 Hz, 1 H, C$_p$, NPh), 6.14 (t, J_{HH} = 7.32 Hz, 1 H, C$_p$, py), −2.22 (s, $\nu_{1/2}$ = 15 Hz, 30 H, C$_5$*Me*$_5$), −9.81 (s, $\nu_{1/2}$ = 60 Hz, 2 H, C$_m$, py), (C$_o$, py not observed). IR (Nujol mull, cm^{-1}): 1596 (s), 1578 (vs), 1567 (wsh), 1554 (m), 1501 (msh), 1486 (sbr), 1442 (vs), 1395 (w), 1366 (wsh), 1353 (w), 1302 (vsbr, ν C−N), 1286 (msh), 1272 (m), 1262 (m), 1236 (w), 1211 (s), 1166 (s), 1156 (m), 1147 (w), 1077 (sbr), 1063 (s), 1037 (s), 1022 (m), 1009 (s), 988 (vs), 917 (vs, ν U−N), 884 (m), 871 (s), 834 (mbr), 819 (m), 801 (w), 753 (vs), 705 (s), 691 (vs), 636 (m), 626 (w). Anal. Calcd for C$_{31}$H$_{40}$N$_2$U: C, 54.86; H, 5.94; N, 4.13. Found: C, 54.63; H, 5.94; N, 3.88.

(η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)$_2$ (3). (a) From [Li(TMED)][(η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)Cl] (1). A 20% hexane solution of N$_3$C$_6$H$_5$ (0.393 g, 0.661 mmol) was added dropwise to a rapidly stirred room temperature orange-red solution of [Li(TMED)][(η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)Cl] (**1**, 0.500 g, 0.659 mmol) in 60 mL of diethyl ether. The solution became dark black-brown, and the gentle evolution of gas was observed over a period of 20 min. The solution was stirred at room temperature for 12 h, after which time the solvent was removed under reduced pressure yielding a dark black-green powder. The solid was dissolved in toluene (40 mL) and filtered through Celite, and the toluene was removed from the filtrate *in vacuo*. The resulting black-green microcrystalline solid was washed with minimal cold hexane and dried *in vacuo*; yield 0.370 g (0.536 mmol) or 81%. **(b) From (η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)(py) (2).** A 20% hexane solution of N$_3$C$_6$H$_5$ (0.263 g, 0.442 mmol) was added dropwise to a rapidly stirred room temperature orange-red solution of (η^5-C$_5$Me$_5$)$_2$U(NPh)(py) (**2**, 0.300 g, 0.442 mmol) in 60 mL of diethyl ether. The solution became dark black-brown with the vigorous evolution of N$_2$ over a period of 1 min. The solution was stirred at room temperature for 12 h after which time the solvent was removed in vacuo yielding dark black-green microcrystals which were filtered off, washed with minimal cold hexane, and dried in vacuo; yield 0.266 g (0.385 mmol) or 87%. **(c) From (η^5-C$_5$Me$_5$)$_2$U(CH$_3$)Cl.** A solution of LiN(C$_6$H$_5$)−NH(C$_6$H$_5$) (0.068 g, 0.358 mmol) in 5 mL of diethyl ether was added dropwise to a rapidly stirred maroon solution of (η^5-C$_5$Me$_5$)$_2$U(Cl)CH$_3$ (0.200 g, 0.358 mmol) in 15 mL diethyl ether. The solution immediately became black-brown, and vigorous gas evolution was observed over 1 min. The solution was stirred at room temperature for 12 h, after which time the solvent was removed under reduced pressure to yield a dark black-green powder. The product was isolated as in procedure (a); yield (0.200 g (0.290 mmol) or 81%. **(d) From (η^5-C$_5$Me$_5$)$_2$U(CH$_3$)$_2$.** To (η^5-C$_5$Me$_5$)$_2$U(CH$_3$)$_2$ (0.015 g, 0.028 mmol) in 1 mL of C$_6$D$_6$ was added NH(C$_6$H$_5$)−NH(C$_6$H$_5$) (0.005 g, 0.027 mmol) and C$_6$Me$_6$ (0.005 g, 0.031 mmol) as an internal standard. The solution was allowed to react for 68 h, during which time the color became black-brown. Yield of **3** exceeded 98% as determined by ^{1}H NMR. Analytically pure samples of **3** were obtained by recrystallization from toluene/diethyl ether at −35 °C. UV/vis (ϵ, M^{-1} cm^{-1}): 228, (31100); 249 (16100); 256 (13500); 273 (29100); 389 (15800); 439 (14200) nm. ^{1}H, ^{13}C, IR, and analytical data are reported in ref 6b.

(η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)(NSi(CH$_3$)$_3$) (4). Neat N$_3$Si(CH$_3$)$_3$ (0.136 g, 1.19 mmol) was added dropwise to a rapidly stirred orange-red solution of [Li(TMED)][(η^5-C$_5$Me$_5$)$_2$U(NPh)Cl] (**1**, 0.300 g, 0.396 mmol) in 20 mL of diethyl ether at room temperature. The solution became dark black-brown over a period of 3−4 h. The reaction was stirred at room temperature for 56 h, after which the solvent was removed under reduced pressure to yield a dark black powder. The product was extracted into 40 mL of hexamethyldisiloxane and stirred 1 h. The extract was filtered through Celite, and the hexamethyldisiloxane was removed from the filtrate *in vacuo* to afford the product as a microcrystalline, black-green solid. The product was further washed with minimal cold hexamethyldisiloxane and dried *in vacuo*; yield 0.196 g (0.286 mmol) or 72%. Analytically pure samples were obtained by recrystallization from hexamethyldisiloxane at −35 °C. ^{1}H NMR (250 MHz, C$_6$D$_6$, 25 °C): δ 9.28 (t, 2 H, J_{HH} = 7.70 Hz, meta), 4.28 (s, 30 H, C$_5$*Me*$_5$), 2.49 (d, 2 H, J_{HH} = 7.70 Hz, ortho), 0.519 (s, 9 H, Si*Me*$_3$), 0.171 (t, 1 H, J_{HH} = 7.70 Hz, para). ^{13}C NMR (50.25 MHz, C$_6$D$_6$, 25 °C): δ 183.1 (C$_{phenyl}$), 145.4 (C$_{ipso}$/C$_{ring}$), 137.9 (C$_{phenyl}$), 107.9 (C$_{phenyl}$), 105.1 (C$_{ipso}$/C$_{ring}$), 17.2 (Si*Me*$_3$), 8.4 (*C*$_5$Me$_5$). IR (Nujol mull, cm^{-1}): 1575 (w), 1571 (m), 1558 (w), 1534 (vw), 1496 (wsh), 1480 (msh), 1438 (msh), 1424 (m), 1384 (m), 1344 (wsh), 1316 (w), 1284 (w), 1267 (s), 1263 (s), 1252 (m), 1238 (s), 1215 (w), 1159 (w), 1149 (vw), 1062 (m), 1017 (m), 991 (m), 966 (vs), 958 (vs), 905 (s), 889 (w), 833 (vs), 804 (wsh), 756 (s), 747 (m), 687 (s), 672 (w), 615 (w), 526 (m). UV/vis (ϵ, M^{-1} cm^{-1}): 220 (7330); 262 (6970); 347 (3000); 408 (5100); 435 (4100) nm. Anal. Calcd for C$_{29}$H$_{44}$N$_2$SiU: C, 50.72; H, 6.46; N, 4.08. Found: C, 50.16; H, 6.36; N, 3.83.

(η^5-C$_5$Me$_5$)$_2$U(N-2,4,6-Me$_3$C$_6$H$_2$)(py) (5). Solid KNH(2,4,6-Me$_3$C$_6$H$_2$) (0.097 g, 0.564 mmol) and (η^5-C$_5$Me$_5$)$_2$U(Cl)CH$_3$ (0.300 g, 0.537 mmol) were reacted as described for the preparation of (η^5-C$_5$Me$_5$)$_2$U(NC$_6$H$_5$)(py) (**2**). Yield of **5** as a dark green powder was 0.329 g (0.456 mmol) or 85%. Analytically pure samples were obtained by recrystallization from toluene/hexane at −35 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 49.87 (s, $\nu_{1/2}$ = 50 Hz, 3 H, C$_6$H$_2$*Me*$_3$), 41.38 (s, $\nu_{1/2}$ = 35 Hz, 1 H, meta), 32.80 (s, $\nu_{1/2}$ = 35 Hz, 1 H, meta), 28.14 (s, $\nu_{1/2}$ = 15 Hz, 3 H, C$_6$H$_2$*Me*$_3$), 4.60 (s, $\nu_{1/2}$ = 35 Hz, 1 H, py), −1.15 (s, $\nu_{1/2}$ = 15 Hz, 30 H, C$_5$*Me*$_5$), −2.29 (s, $\nu_{1/2}$ = 45 Hz, 3 H, C$_6$H$_2$*Me*$_3$), −11.88 (s, $\nu_{1/2}$ = 35 Hz, 2 H, py), −18.28 (s, $\nu_{1/2}$ = 50 Hz, 2 H, py). IR (Nujol mull, cm^{-1}): 1605 (w), 1599 (m), 1485 (m), 1460 (s), 1455 (s), 1442 (vs), 1411 (s), 1366 (m), 1318 (vw), 1295 (s), 1257 (vs), 1214 (m), 1165 (m), 1152 (w), 1068 (w), 1037 (m), 1020 (wbr), 1004 (w), 957 (m), 946 (wsh), 886 (vs), 857 (s), 802 (w), 751 (m), 742 (w), 704 (vs), 624 (w), 596 (w), 546 (m). Anal. Calcd for C$_{34}$H$_{46}$N$_2$U: C, 56.66; H, 6.43; N, 3.87. Found: C, 56.55; H, 6.29; N, 3.68.

(η^5-C$_5$Me$_5$)$_2$U(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(THF) (6). Neat 2,6-diisopropylaniline (0.329 g, 1.85 mmol) was added dropwise to an orange solution of (η^5-C$_5$Me$_5$)$_2$U(CH$_3$)$_2$ (1.00 g, 1.85 mmol) and THF (0.200, 2.79 mmol) in 40 mL of toluene at room temperature, and the mixture was transferred to a Teflon-sealed ampule. The solution was heated to 85 °C and stirred for 56 h, during which time the color became dark red-brown. The solvent was removed under reduced pressure to yield a dark red-brown powder. The product was washed with minimal cold pentane and dried *in vacuo*; yield 1.200 g (1.59 mmol) or 86%. Analytically pure samples were obtained by recrystallization from toluene at −35 °C. Spectroscopic and analytical data are reported in ref 6a.

(η^5-C$_5$Me$_5$)$_2$U(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(OPMe$_3$) (7). Trimethylphosphine oxide (0.030 g, 0.331 mmol) was added to a stirred brown-red solution of (η^5-C$_5$Me$_5$)$_2$U(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(THF) (**6**, 0.250 g, 0.331 mmol) in 10 mL of toluene at room temperature. The solution was stirred for 18 h, during which time the color of the solution became light orange-brown with the formation of a dark precipitate. The solid was isolated by filtration, washed with two 5-mL portions of diethyl ether, and dried *in vacuo* to yield a light orange-brown powder, yield 0.212 g (0.273 mmol) or 83%. Analytically pure samples were obtained by recrystallization from toluene/THF at −35 °C. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 42.29 (s, $\nu_{1/2}$ = 80 Hz, 1 H, C*H*Me$_2$), 42.79 (s, $\nu_{1/2}$ = 15 Hz, 1 H, meta), 42.08 (s, $\nu_{1/2}$ = 15 Hz, 1 H, meta), 35.42 (s, $\nu_{1/2}$ = 80 Hz, 1 H, C*H*Me$_2$), 19.45 (t, J_{HH} = 9.77 Hz, 1 H, para), 8.74 (s, $\nu_{1/2}$ = 15 Hz, 6 H, CH*Me*$_2$), 7.86 (s, $\nu_{1/2}$ = 15 Hz, 6 H, CH*Me*$_2$), −3.07 (s. $\nu_{1/2}$ = 15 Hz, 30 H, C$_5$*Me*$_5$), −18.20 (d, J_{PH} = 14.64 Hz, 9 H, OP*Me*$_3$). IR (Nujol mull, cm^{-1}): 1579 (m), 1496 (w), 1410 (vs), 1367 (wsh), 1357 (w), 1321 (vs), 1310 (s), 1297 (m), 1263 (vs). 1142 (m), 1122 (vs), 1113 (ssh), 1100 (s), 1050 (w), 1038 (m), 945 (s), 915 (vs), 859 (m), 803 (w), 796 (w), 745 (s), 936 (m), 715 (w), 697 (w), 596 (m).

(η^5-C$_5$Me$_5$)$_2$U(N-2,4,6-*t*-Bu$_3$C$_6$H$_2$) (8). 2,4,6-Tri-*tert*-butylaniline (0.484 g, 1.86 mmol) and (η^5-C$_5$Me$_5$)$_2$U(CH$_3$)$_2$ (1.00 g, 1.85 mmol) were dissolved in 40 mL of toluene at room temperature, yielding an orange solution. This solution was transferred to a Teflon-sealed ampule and heated to 85 °C. The mixture was stirred for 56 h, during which time the color became dark black. The solvent was removed under reduced pressure to yield a dark black-brown powder. The solid was washed with minimal room temperature hexane and dried *in vacuo*; yield 1.38 g (1.79 mmol) or 97%. Analytically pure samples were obtained by recrystallization from hot benzene. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 42.30 (s, $\nu_{1/2}$ = 80 Hz, 2 H, meta), 12.64 (s, $\nu_{1/2}$ = 80 Hz, 9 H, ^{t}Bu$_{para}$), −3.90 (s, $\nu_{1/2}$ = 100 Hz, 30 H, C$_5$*Me*$_5$), −9.36 (s, $\nu_{1/2}$

= 80 Hz, 18 H, ^{t}Bu$_{ortho}$). IR (Nujol mull, cm^{-1}): 1595 (w), 1454 (vs), 1448 (sh), 1436 (sh), 1404 (vs), 1359 (s), 1355 (s), 1349 (m), 1329 (w), 1267 (vs), 1237 (vs), 1207 (s), 1185 (m), 1176 (m), 1148 (w), 1119 (m), 1079 (brw), 1062 (brw), 1020 (m), 945 (w), 937 (m), 929 (m), 924 (s), 885 (s), 877 (vs), 801 (w), 777 (s), 767 (m), 757 (w), 728 (m), 694 (w), 654 (m), 643 (w), 622 (w), 562 (w), 482 (w), 443 (w). Anal. Calcd for $C_{38}H_{59}NU$: C, 59.44; H, 7.74; N, 1.82. Found: 59.44; H, 7.66; N, 1.66.

(η^5-C_5Me_5)$_2$U(N-2,4,6-$Me_3C_6H_2$)(O) (9). Pyridine *N*-oxide (0.040 g, 0.416 mmol) was added to a rapidly stirred dark green solution of (η^5-C_5Me_5)$_2$U(N-2,4,6-$Me_3C_6H_2$)(py) (**5**, 0.300 g, 0.416 mmol) in 20 mL of toluene at room temperature. The solution immediately became dark black-brown. The reaction was stirred at room temperature for 12 h, after which the solvent was removed under reduced pressure to yield a dark black microcrystalline solid. The product was washed with minimal cold pentane and dried *in vacuo*; yield 0.238 g (0.362 mmol) or 87%. Analytically pure samples were obtained by recrystallization from hexane at −35 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 9.41 (s, 3 H, C*H*$_3$), 9.19 (s, 1 H, meta), 9.05 (s, 1 H, meta), 8.71 (s, 3 H, C*H*$_3$), 7.79 (s, 3 H, CH_3), 4.29 (s, 30 H, C_5*Me*$_5$). ^{13}C NMR (50.25 MHz, C_6D_6, 25 °C): δ 180.3 (C_{phenyl}), 166.5 (C_{phenyl}), 144.5 (C_{ipso}), 137.0 ($C_{phenyl/ring}$), 99.4 ($C_{phenyl/ring}$), 96.1 ($C_{phenyl/ring}$), 7.8 (C_5*Me*$_5$), 6.0 (*C*H$_3$), 5.1 (*C*H$_3$), 4.3 (*C*H$_3$). IR (Nujol mull, cm^{-1}): 1601 (s), 1484 (mbr), 1456 (sbr), 1423 (m), 1293 (w), 1232 (s), 1158 (w), 1147 (vw), 1075 (wbr), 1033 (brw), 1017 (mbr), 956 (m), 868 (w), 852 (s), 800 (w), 757 (vs, ν U−O). UV/vis (ϵ, M^{-1} cm^{-1}): 219 (22500); 270 (18000); 321 (10100); 409 (14400); 460 (12300); 550 (4920) nm. Anal. Calcd for $C_{29}H_{41}NOU$: C, 52.96; H, 6.28; N, 2.13. Found: C, 52.96; H, 6.27; N, 2.06.

(η-C_5Me_5)$_2$U(N-2,6-*i*-$Pr_2C_6H_3$)(O) (10). Pyridine *N*-oxide (0.068 g, 0.720 mmol) was added as a solid to a rapidly stirred room temperature red-green solution of (η^5-C_5Me_5)$_2$U(N-2,6-*i*-$Pr_2C_6H_2$)(THF) (**6**, 0.536 g, 0.710 mmol) in 20 mL of toluene. The solution became dark-brown over a period of 1 h. After being stirred at room temperature for an additional 18 h, the solvent was removed under reduced pressure to yield a dark black powder. The product was dissolved in 20 mL of hexane, and the solution was filtered through Celite. Following removal of the hexane under reduced pressure, the black powder was dissolved in 30 mL of hexamethyldisiloxane and refiltered. The hexamethyldisiloxane was removed from the filtrate *in vacuo* yielding 0.330 g (0.472 mmol, 66%) of black-green microcrystalline product suitable for further reactions. Analytically pure samples were obtained by recrystallization from hexamethyldisiloxane at −35 °C. UV/vis (ϵ, M^{-1} cm^{-1}): 198 (17800); 217 (20600); 263 (15000); 329 (7800); 415 (12000); 468 (8950) nm. ^{1}H, ^{13}C, IR, and analytical data are reported in ref 6a.

(η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$)(O) (11). A 100-mL flask was charged with (η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$) (**8**, 0.300 g, 0.391 mmol) and 30 mL of toluene. The dark red-green solution was degassed by successive freeze−pump−thaw cycles, and 1 atm of N_2O was introduced over the solution. The color of the solution immediately became dark black-brown. After the mixture was stirred at room temperature for an additional 3 h, the solvent was removed under reduced pressure to afford the product as a black powder. The product was washed with minimal cold hexane and dried *in vacuo*; yield 0.300 g (0.383 mmol, 98%). The black powder was suitable for further reactions. Analytically pure samples were obtained by recrystallization from toluene at −35 °C. ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ 10.01 (s, 1 H, meta), 9.91 (s, 1 H, meta), 4.73 (s, 30 H, C_5*Me*$_5$), 3.06 (s, 9 H, ^{t}Bu), 2.79 (s, 9 H, ^{t}Bu), 1.27 (s, 9 H, ^{t}Bu). ^{13}C NMR (50.25 MHz, C_6D_6, 25 °C): δ 210.5 (C_{phenyl}), 204.6 (C_{phenyl}), 172.3 (C_{phenyl}), 136.5 ($C_{phenyl/ring}$), 99.0 ($C_{phenyl/ring}$), 96.1 ($C_{phenyl/ring}$), 92.5 ($C_{phenyl/ring}$), 43.2, 42.8. and 39.7 (C*Me*$_3$), 25.6, 22.5, and 21.9 (*C*Me$_3$), 8.2 (C_5*Me*$_5$). IR (Nujol mull): 1597 (w), 1492 (vs), 1445 (ssh), 1425 (msh), 1395 (wsh), 1365 (m), 1361 (m), 1306 (brw), 1271 (w), 1253 (msh), 1247 (m), 1222 (m), 1200 (m), 1194 (msh), 1169 (vw), 1155 (vw), 1120 (m), 1063 (brw), 1018 (m), 972 (w), 948 (wbr), 922 (w), 883 (s), 860 (m), 805 (w). 774 (m), 755 (vs, ν U−O), 648 (m). UV/vis (ϵ, M^{-1} cm^{-1}): 217 (20400); 271 (11200); 360 (7950); 427 (12500); 501 (6820) nm. Anal. Calcd for $C_{38}H_{59}NOU$: C, 58.22; H, 7.59; N, 1.79. Found: C, 58.59; H, 7.20; N, 1.69.

(η^5-C_5Me_5)$_2$U(NHC_6H_5)$_2$ (12). A 50-mL flask was charged with (η^5-C_5Me_5)$_2$U(NC_6H_5)$_2$ (**3**, 0.200 g, 0.289 mmol) and 20 mL of toluene. The dark black-brown solution was degassed by successive freeze−pump−thaw cycles, and 1 atm of H_2 was introduced over the solution. The solution was stirred for 56 h, during which time the color became light orange-red. The solvent was removed under reduced pressure to yield a red-orange waxy solid. This product was dissolved in minimal hexane and cooled to −35 °C to yield the product formed as red blocks. The product was isolated and dried *in vacuo*; yield 0.116 g (0.168 mmol) or 58%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 5.91 (s, $\nu_{1/2}$ = 15 Hz, 30 H, C_5*Me*$_5$), 0.06 (t, J_{HH} = 7.60 Hz, 4 H, meta), −2.39 (t, J_{HH} = 7.60 Hz, 2 H, para), −27.80 (d, J_{HH} = 7.60 Hz, 4 H, ortho), −132.15 (s, 2 H, N*H*). IR (Nujol mull): 1596 (sbr), 1575 (m), 1500 (s), 1486 (s), 1453 (vs), 1377 (s), 1367 (msh), 1359 (m), 1351 (msh), 1315 (w), 1263 (msh), 1250 (sbr), 1209 (w), 1174 (m), 1171 (m), 1155 (w), 1142 (w), 1068 (sbr), 1025 (m), 992 (m), 969 (w), 955 (mbr), 947 (wsh), 876 (m), 843 (sbr), 823 (ssh), 800 (m), 745 (vs), 691 (s). Anal. Calcd for $C_{32}H_{42}N_2U$: C, 55.49; H, 6.11; N, 3.96. Found: C, 55.43; H, 6.01; N, 3.96.

(η^5-C_5Me_5)$_2$U(NHC_6H_5)(NHSi(CH_3)$_3$) (13). (η^5-C_5Me_5)$_2$U(NC_6H_5)-(NSi(CH_3)$_3$) (**4**, 0.200 g, 0.292 mmol) was reacted with 1 atm of H_2 as described for the preparation of (η^5-C_5Me_5)$_2$U(NHC_6H_5)$_2$ (**12**). Yield of **13** as red-orange crystals was 0.106 g (0.155 mmol) or 53%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 5.32 ($\nu_{1/2}$ = 15 Hz, 30 H, C_5*Me*$_5$), −1.78 (t, J_{HH} = 7.60 Hz, 2 H, meta), −3.30 (t, J_{HH} = 7.60 Hz, 1 H, para), −7.34 (s, 9 H, Si*Me*$_3$), −32.16 (s, 2 H, ortho), −124.50 (s, 1 H, N*H*), −142.24 (s, 1 H, N*H*). IR (Nujol mull, cm^{-1}): 3305 (w), 3268 (w), 1595 (vs), 1578 (m), 1487 (vs), 1447 (ssh), 1404 (msh), 1350 (m), 1318 (w), 1258 (vs), 1246 (ssh), 1207 (m), 1174 (m), 1150 (w), 1067 (m), 1020 (s), 995 (m), 965 (w), 949 (w), 860 (vs), 844 (s), 816 (m), 800 (m), 749 (s), 691 (s), 671 (m), 620 (w). Anal. Calcd for $C_{29}H_{46}N_2SiU$: C, 50.57; H, 6.73; N, 4.06. Found: C, 50.40; H, 6.72; N, 3.93.

Structural Determinations. (a) [Li(TMED)][(η^5-C_5Me_5)$_2$U-(NC_6H_5)Cl] (1). Dark brown columns of **1** were obtained by slow cooling of a toluene solution to −35 °C. A suitable crystal was isolated, mounted on a glass fiber using silcone grease, and transferred to the goniostat of a Siemens R3m/V diffractometer cooled to −100 °C for data collection. Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range 15 < 2θ < 25°. Final cell parameters are given Table 1, as are other crystallographic data. Data were collected utilizing the θ−2θ scan mode at a variable scan rate of 1.5 to 14.65 deg/min in ω. A total of 6640 (h,±k,±l) were collected. The systematic absences uniquely determined the space group as $P3_2$; this choice was verified by satisfactory solution and refinement of the structure. The structure was solved by direct methods and refined via standard least-squares and difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to the structure factor calculation in idealized positions without refinement (C−H fixed at 0.95 Å). The final residuals for 342 variables refined against 4140 unique reflections were R = 0.0522 and R_w = 0.0746. The highest peak in the final difference Fourier map had a height of 2.73 e/Å^3 and was associated with the uranium atom. All calculations were performed using the SHELTX PLUS software package licensed by Siemens Analytical X-Ray Corp. Selected bond distances and angles are given in Table 2.

(b) (η^5-C_5Me_5)$_2$U(N-2,4,6-*t*-$Bu_3C_6H_2$) (8). Dark brown plates of **8** were obtained by room temperature crystallization of a concentrated benzene solution. A suitable crystal was isolated, mounted on a glass fiber using silcone grease, and transferred to the goniostat of a Siemens R3m/V diffractometer cooled to −100 °C for data collection. Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range 15 < 2θ < 25°. Final cell parameters are given Table 1, as are other crystallographic data. Data were collected utilizing θ−2θ scan mode, at a variable scan rate of 1.5 to 14.65 deg/min in ω. A total of 2966 (±h,−k,l) were collected. The systematic absences uniquely determined the space group as $Pmn2_1$; this choice was verified by satisfactory solution and refinement of the structure. The structure was solved by direct methods and refined via standard least-squares and difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to the structure factor calculation in idealized positions without refinement (C−H fixed at 0.95 Å). The final residuals for 342 variables refined against 1580 unique reflections were $R = 0.0355$ and $R_w = 0.0447$. The highest peak in the final difference Fourier map had a height of 2.22 e/Å^3 and was associated with the uranium atom. All calculation were performed using the SHELTX PLUS software package licensed by Siemens Analytical X-Ray Corp. Selected bond distances and angles are given in Table 3.

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Supporting Information Available: Tables of final atomic coordinates and isotropic displacement information, including hydrogen atom locations, anisotropic displacement parameters, complete bond lengths, and bond angles for compounds **1** and **8**, full atomic numbering scheme for **1** and unit cell packing diagrams for **1** and **8** (21 pages); listing of structure factors for **1** and **8** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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