Preparation and Reactions of Base-Free Bis(1,2,4-tri-*tert*-butylcyclopentadienyl)uranium Oxide, Cp'_2UO

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Reduction of the uranium metallocene $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UCl_2$ (**1**), Cp'_2UCl_2, in the presence of 2,2′-bipyridyl and sodium naphthalene gives the dark green metallocene complex $Cp'_2U(bipy)$ (**6**), which reacts with *p*-tolyl azide or pyridine-*N*-oxide to give $Cp'_2U{=}N(p\text{-tolyl})$ (**7**) or $Cp'_2U(O)(py)$ (**8**), respectively. The Lewis acid BPh_3 precipitates $Ph_3B(py)$ and gives the base-free oxo Cp'_2UO (**10**), which crystallizes from pentane. The oxometallocene **10** behaves as a nucleophile with Me_3SiX reagents, but it does not exhibit cycloaddition behavior with acetylenes, suggesting that the polar resonance structure $Cp'_2U^+{-}O^-$ dominates the double-bond resonance structure $Cp'_2U{=}O$.

Introduction

The U–O functional group is ubiquitous in uranium chemistry, as shown by the prevalence of binary oxides in the solid state and the uranyl ion UO_2^{2+} in solution, which illustrates the thermodynamic stability of the U–O bond.[1] Although the rate of ligand substitution on the uranyl ion is rapid in solution,[2,3] the rate of oxygen atom exchange in aqueous acid is very slow,[4] but it is rapid in basic solution.[5] The gas phase ions UO_x^{n+} have been generated in a mass spectrometer, and their reactions with hydrocarbons have been studied.[6–9] In addition to providing reactivity patterns, these gas phase studies yield useful thermodynamic bond disruption enthalpies for the U–O bonds, which lie in the range 120–190 kcal mol^{-1}.[6–9]

This paper describes the synthesis of base-free $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UO$ (**10**), Cp'_2UO, and some of its reactions with silyl- and alkylhalides. These reactions provide a molecular model for the heterogeneous reaction of solid U_3O_8 and chlorocarbons that results in complete destruction of the latter to CO_x and HCl.[10] This unusual and potentially useful reaction probably occurs at the surface U–O functional group, which implies that the U–O group in a well-defined molecular compound will provide molecular models for this reaction as well as information about the nature of the multiple U–O bond. A portion of this work has been previously communicated.[11]

Results and Discussion

Strategy. Our strategy is to use substituted cyclopentadienyl ligands that are more heavily substituted than the $1,3\text{-}(Me_3E)_2C_5H_3$ (E = C, Si) ligands, since these less substituted cyclopentadienyl ligands yield oxo-dimers of the type $(\eta^5\text{-}1,3\text{-}R_2C_5H_3)_4U_2(\mu\text{-}O)_2$ (R = $SiMe_3$, CMe_3), which have been prepared by two synthetic routes: the reaction of the corresponding dimethyl derivatives with water or the thermal oxidative elimination of dihydrogen from the corresponding dimeric hydroxides, eqs 1 and 2, respectively.[12–14] The oxide dimers give molecular ions in their mass spectra and they do not undergo intermolecular exchange in solution up to 130 °C, implying that dissociation to monomers does not occur. As a consequence, the reaction chemistry of the U–O functional group is nonexistent, although the cyclopentadienyl rings can be removed by proton sources, such as excess water. Clearly, preparation of a monomeric oxometallocene derivative of uranium is desirable, so the intrinsic reaction chemistry can be explored.

$$2(1,3\text{-}R_2C_5H_3)_2UMe_2 + 2H_2O \rightarrow (1,3\text{-}R_2C_5H_3)_4U_2(\mu\text{-}O)_2 + 4CH_4 \quad (1)$$

$$(1,3\text{-}R_2C_5H_3)_4U_2(\mu\text{-}OH)_2 \rightarrow (1,3\text{-}R_2C_5H_3)_4U_2(\mu\text{-}O)_2 + H_2 \quad (2)$$

Increasing the number of Me_3C groups on the cyclopentadienyl framework should increase the steric hindrance between the cyclopentadienyl groups in a hypo-

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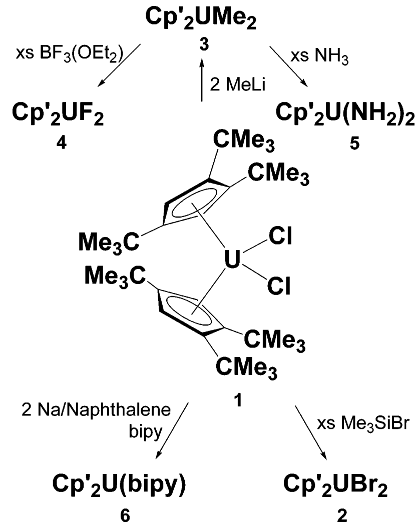
thetical oxo-dimer and perhaps yield monomers. This is a useful strategy for preparation of the monomeric cerium hydride [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2CeH$, abbreviated as Cp'_2CeH,[15] where Cp′ is used as the symbol for 1,2,4-$(Me_3C)_3C_5H_2$ in this paper, while the 1,3-$(Me_3C)_2C_5H_3$ ligand yields the dimeric hydride [η^5-1,3-$(Me_3C)_2C_5H_3]_4$-$Ce_2(\mu\text{-}H)_2$.[16] Accordingly, synthesis of Cp'_2UCl_2 (**1**), its conversion to the dimethyl derivative Cp'_2UMe_2 (**3**), and reaction of the latter with water is a synthetic objective. Although the dimethyl derivative Cp'_2UMe_2 (**3**) can be made, its reactions with water under various conditions are not clean. The reaction mixtures always contain large amounts of the free diene, $(Me_3C)_3C_5H_3$, and therefore water is not a useful reagent for synthesis of this oxometallocene derivative of uranium.

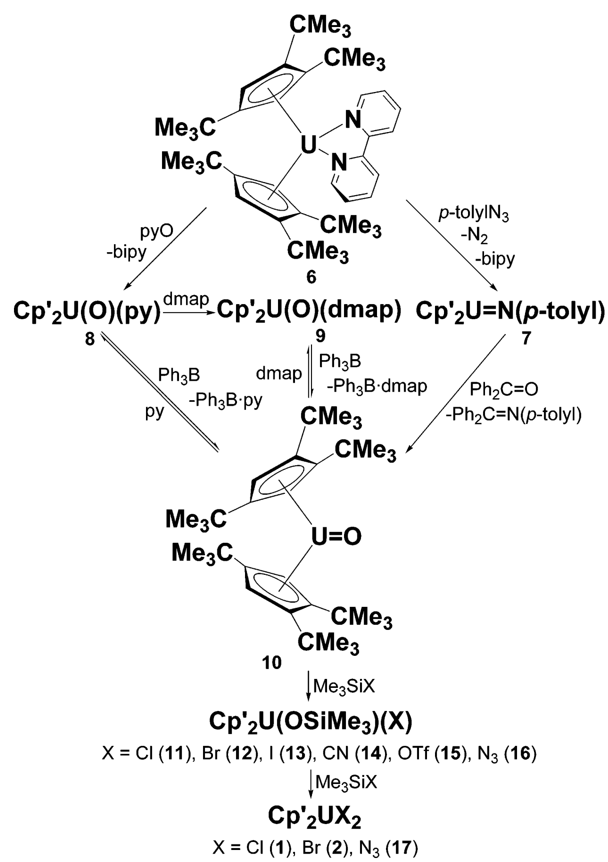
A new and successful strategy is derived from our synthesis of (η^5-$C_5Me_5)_2Ti(O)(py)$, which results from exposure of (η^5-$C_5Me_5)_2Ti(C_2H_4)$ to N_2O in pyridine.[17] Unfortunately, an analogous uranium complex, such as $Cp'_2U(C_2H_4)$, is unavailable, but the isolable bipyridyl derivative Cp′$_2$U(bipy) (**6**), described below, is a useful starting material. The literature contains two examples of generating the (η^5-$C_5Me_5)_2U$ fragment (and (η^5-$C_5Me_5)_2UCl_2$), by valence disproportionation of (η^5-$C_5Me_5)_2UCl$, which is trapped by acetylenes or organic azides.[18,19] In addition, the isolable benzene or toluene complexes [(η^5-$C_5Me_5)_2U]_2$(PhH) and {[(Me_3C)(3,5-$Me_2C_6H_3)]N_2U\}_2$(PhMe) function similarly.[20,21]

Cp'_2UX_2. The preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**), Cp'_2UCl_2, has been reported,[22] and a large-scale preparation (20−30 g) is given in the Experimental Section. The synthetic routes to the metallocenes described in this paper are shown in Schemes 1 and 2, and some of their physical properties are listed in Table 1. The halides and pseudohalide Cp'_2UX_2 (X = F (**4**), Cl (**1**), Br (**2**), N_3 (**17**)) are all red or orange-red in color, soluble in and readily crystallized from pentane, and give monomeric molecular ions in their EI mass spectra. The dibromide complex **2** is obtained from anion exchange between Me_3SiBr and Cp'_2UCl_2 (**1**), but the diiodide complex cannot be obtained pure by anion exchange between **1** and Me_3SiI, as a mixture of all three possible metallocenes is obtained. The dimethyl complex Cp'_2UMe_2 (**3**) is obtained from the reaction of Cp'_2UCl_2 (**1**) with MeLi in diethyl ether in good yield. Monitoring the reaction by ^1H NMR spectroscopy in Et_2O-d_{10} shows that some Cp′Li is formed, the amount increasing with time, showing that the Cp′ ligands are not substitutionally inert. Cp'_2UMe_2 (**3**) reacts with ammonia to yield the yellow diamide $Cp'_2U(NH_2)_2$ (**5**). Exposure of **3** to $BF_3(OEt_2)$ yields the difluoride Cp'_2UF_2 (**4**), a synthetic route also used to prepare (η^5-1,3-$R_2C_5H_3)_2UF_2$.[23]

Scheme 1



Scheme 2



The solid-state crystal structures of **1**, **3**, **4**, **5**, and **17** have been determined. Crystal data for all of the structures are shown in Table 2, and selected geometrical parameters are shown in Table 3. ORTEP diagrams for **4** and **17** are shown in Figures 1 and 2,

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Table 1. Physical Properties of $Cp'_2U(X)(Y)$, $Cp' = 1,2,4\text{-}(CMe_3)_3C_5H_2$

compound	mp (°C)	^{1}H NMR (δ, 30 °C)[a]				
		$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	ring C*H*	other
Cp'_2UCl_2 (**1**)	192−194	9.8 (12)	9.8 (12)	−20.2 (7)	30.3 (110)	
Cp'_2UBr_2 (**2**)	205−206	12.2 (570)	12.2 (570)	−20.5 (40)	32.7 (850)	
Cp'_2UMe_2 (**3**)	143−144	3.3 (5)	3.3 (5)	−7.5 (8)	7.6 (25)	UCH_3, −98 (45)
Cp'_2UF_2 (**4**)	160−162	0.64 (10)	0.64 (10)	−7.9 (3)	8.6 (12)	
$Cp'_2U(NH_2)_2$ (**5**)	165−167	5.4 (4)	−1.9 (5)	−1.9 (5)	14.1 (46)	UNH_2, −34 (27)
$Cp'_2U(bipy)$ (**6**)	271−276	1.1 (4)	1.1 (4)	−8.8 (3)	1.4 (4)	bipyridyl 3-C*H*[b] 97.2 (12) 4-C*H*[b] −7.4 (d, *J* = 7.2 Hz) 5-C*H*[b] −57.9 (11) 6-C*H*[b] −99.4 (16)
$Cp'_2U[N(4\text{-}MeC_6H_4)]$ (**7**)	234−239	−6.1 (11)	−6.1 (11)	−22.5 (9)	22.2 (18)	N-tolyl *o*-C*H*[b] 29.4 (d, *J* = 7.2 Hz) *m*-C*H*[b] 24.7 (d, *J* = 7.2 Hz) *p*-CH_3 23.7 (5)
$Cp'_2U(O)(py)$ (**8**)	199−206	23.4 (19)	−9.0 (300)	−9.0 (300)	*c*	pyridine[c]
$Cp'_2U(O)(4\text{-}Me_2NC_6H_4N)$ (**9**)	202−209	26.3 (5)	0.61 (37)	−18.1 (34)	*c*	pyridine[d] $N(CH_3)_2$ −6.8 (17)
Cp'_2UO (**10**)	178−180 (dec)	27.0 (9)	−12.2 (25)	−35.1 (7)	98.7 (23) −90.5 (22)	
$Cp'_2U(OSiMe_3)(Cl)$ (**11**)	248−250	9.1 (66)	−5.2 (48)	−12.8 (50)	14.8 (165) −8.0 (232)	$SiCH_3$, 24.3 (31)
$Cp'_2U(OSiMe_3)(Br)$ (**12**)	271−273	10.9 (136)	−5.8 (94)	−13.1 (96)	15.8 (190) −15.9 (273)	$SiCH_3$, 27.3 (30)
$Cp'_2U(OSiMe_3)(I)$ (**13**)	288−290	12.4 (408)	−7.4 (261)	−11.9 (347)	8.0 (339) −17.2 (683)	$SiCH_3$, 31.2 (27)
$Cp'_2U(OSiMe_3)(CN)$ (**14**)	267−268	7.8 (280)	−6.5 (200)	−14.2 (220)	13.0 (346) 5.2 (404)	$SiCH_3$, 27.2 (91)
$Cp'_2U(OSiMe_3)(OTf)$ (**15**)	210−212	2.0 (3028)	2.0 (3028)	−12.8 (627)	*c*	$SiCH_3$, 31.5 (34)
$Cp'_2U(N_3)_2$ (**17**)	193−194 (dec)	5.9 (63)	5.9 (63)	−19.3 (9)	28.8 (831)	

[a] The chemical shifts are expressed in δ units with δ > 0 to downfield in C_6D_6 or C_7D_8 at 30 °C. The values in parentheses are the full widths at half-maximum (Hz). [b] The specific assignments are uncertain, although the chemical shift values are not. [c] These resonances are not observed at room temperature. [d] The ortho and meta resonances are not observed at room temperature.

and ORTEP diagrams for **1**, **3**, and **5** are in the Supporting Information since the stereochemistry of the latter three metallocenes is essentially identical to those shown in Figures 1 and 2. The orientation of the cyclopentadienyl rings in all five metallocenes is nearly eclipsed, with the Me_3C groups on each ring at the back of the wedge located as far from each other as possible. This orientation sets the disposition of the other four Me_3C groups such that two of them pointing toward the open wedge are nearly eclipsed. The two X groups are oriented on either side of the eclipsed Me_3C groups such that the molecule has idealized C_2 symmetry.

The geometrical parameters for the five structures are similar to each other, Table 3. The averaged U−C(Cp′) distances range from 2.75 to 2.85 Å, the Cp′(cent)−U−Cp′(cent) angles from 143° to 147°, and the X−U−X angles from 97° to 104° in $Cp'_2U(N_3)_2$ and $Cp'_2U(NH_2)_2$, respectively. The geometrical parameters for the other three metallocenes lie within these extreme values. The difference between the U−X distances in these metallocenes parallel the change in radius of the individual X groups.[24]

The ^{1}H NMR spectra at room temperature of the Cp'_2UX_2 metallocenes show the Me_3C groups in a 2:1 intensity ratio and, where located, a single Cp′ ring CH resonance, Table 1. This pattern is consistent with metallocenes that have idealized C_{2v} symmetry in solution. This implies that the Cp′ rings are fluxional, since the solid-state structures have idealized C_2 symmetry. Lowering the temperature of solutions in C_7D_8 results in decoalesence of the Me_3C resonance of area 2 so that at low temperature the Me_3C resonances appear as three equal intensity resonances, and the Cp′ ring CH resonances appear as a pair of resonances of equal intensity. A plot of δ vs T^{-1} for only the Me_3C resonances is shown for Cp'_2UF_2 (**4**) in Figure 3, which shows the temperature dependence of the chemical shifts from which a ring rotation barrier of approximately 12 kcal mol^{-1} is calculated at the coalescence temperature of 233 K. The barriers for some of the other metallocenes reported here are given in Table 4. The fluxional process that gives rise to site exchange in the Cp'_2UX_2 metallocenes is nearly identical for the series **1**, **4**, and **17**, suggesting that the physical process that gives rise to the barrier involves ring rotation of the Cp′ rings around their pseudo-C_5 axis. As the rings rotate about this axis, they pass through several conformations, each of which has a different free energy and symmetry, which are related by different energy barriers.[25,26] The largest barrier presumably involves a conformation in which the Me_3C groups at the back of the wedge pass through an eclipsed conformation. Since the Cp′(cent)−U−Cp′(cent) angles are essentially the same for **1**, **4**, and **17** (Table 3), it follows that the solution barriers should be nearly identical. The barriers in $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UX_2$ are about 3−4 kcal mol^{-1} larger than in $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2UX_2$ for a given X group.[23] The larger rotational barrier and the more open Cp′(cent)−U−Cp′(cent) angle by about 20° are consistent with the notion that the barrier is largely due to the steric hindrance

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Table 2. Selected Crystal Data and Data Collection Parameters for 1, 3, 4, 5, 7, 9, 14, and 17

	1	**3**	**4**	**5**
formula	$C_{34}H_{58}Cl_2U$	$C_{36}H_{64}U$	$C_{34}H_{58}F_2U$	$C_{34}H_{62}N_2U$
fw	775.77	734.90	742.83	736.91
space group	$Pca2_1$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a (Å)	16.154(1)	10.337(1)	10.219(1)	10.269(1)
b (Å)	10.340(1)	25.591(3)	17.012(2)	25.460(1)
c (Å)	20.513(1)	13.151(2)	19.282(2)	13.202(1)
α (deg)	90	90	90	90
β (deg)	90	90.017(2)	90	90.100(1)
γ (deg)	90	90	90	90
V (Å^3)	3426.4(3)	3479.1(7)	3351.9(6)	3451.7(2)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.504	1.403	1.472	1.418
μ(Mo Kα)$_{calc}$ (cm^{-1})	49.14	4.69	4.87	47.26
size (mm)	0.05 × 0.14 × 0.25	0.23 × 0.20 × 0.15	0.27 × 0.17 × 0.12	0.34 × 0.35 × 0.15
temp (K)	131(1)	120(2)	133(2)	161(1)
diffractometer	Bruker SMART CCD	SMART CCD	SMART CCD	Siemens SMART
scan type	ω (0.3 deg per frame)	ω (0.3 deg per frame)	ω (0.3 deg per frame)	ω (0.3 deg per frame)
2θ range (deg)	3.00 to 45.00	4.44 to 47.14	4.86 to 49.22	4.00 to 46.50
no. of reflns, collected	14 508	15 595	14 989	16 178
no. of unique reflns	3288 (R_{int} = 0.075)	5725 (R_{int} = 0.0743)	5534 (R_{int} = 0.0466)	6244 (R_{int} = 0.030)
no of obsd reflns	3765	4353	5089	4704
no of variables	333	355	353	334
abs corr (T_{max}, T_{min})	1.00, 0.60	0.54, 0.41	0.56, 0.35	0.95, 0.63
R	0.037	0.036	0.033	0.032
R_w	0.043	0.069	0.075	0.044
R_{all}	0.058	0.057	0.036	0.048
gof	1.21	0.91	1.03	1.60
max. Δ/σ in final cycle	0.00	0.001	0.013	0.00

	7	**9**	**14**	**17**
formula	$C_{41}H_{65}NU$	$C_{41}H_{68}N_2OU$	$C_{38}H_{67}NOSiU$	$C_{34}H_{58}N_6U$
fw	810.00	843.03	820.05	788.89
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
a (Å)	16.608(1)	10.773(1)	12.786(2)	16.481(2)
b (Å)	12.174(1)	12.037(2)	17.319(3)	11.292(2)
c (Å)	19.371(1)	16.180(2)	18.007(3)	19.268(3)
α (deg)	90	95.815(1)	90	90
β (deg)	108.357(1)	102.558(1)	90	90.216(2)
γ (deg)	90	101.994(1)	90	90
V (Å^3)	3717.23(8)	1979.56(4)	3987.3(11)	3586.2(8)
Z	4	2	4	4
D_{calc} (g/cm^3)	1.447	1.414	1.366	1.461
μ(Mo Kα)$_{calc}$ (cm^{-1})	43.95	41.32	4.13	4.56
size (mm)	0.20 × 0.16 × 0.13	0.10 × 0.19 × 0.25	0.28 × 0.27 × 0.03	0.18 × 0.11 × 0.08
temp (K)	164(1)	140(2)	128(2)	110(2)
diffractometer	Siemens SMART	Siemens SMART	Bruker SMART CCD	Bruker SMART CCD
scan type	ω (0.3 deg per frame)	ω (0.3 deg per frame)	ω (0.3 deg per frame)	ω (0.3 deg per frame)
2θ range (deg)	4.00 to 46.50	4.00 to 46.50	4.56 to 49.0	4.86 to 48.32
no. of reflns, collected	17110	11012	17738	15572
no. of unique reflns	6569 (R_{int} = 0.049)	6763 (R_{int} = 0.025)	6535 (R_{int} = 0.0453)	5873 (R_{int} = 0.0641)
no of obsd reflns	4164	5761	6007	4292
no of variables	388	406	400	388
abs corr (T_{max}, T_{min})	0.5, 0.40	0.9, 0.7	0.89, 0.39	0.71, 0.49
R	0.028	0.027	0.035	0.041
R_w	0.034	0.031	0.083	0.088
R_{all}	0.044	0.035	0.042	0.069
gof	1.10	1.04	1.035	1.010
max. Δ/σ in final cycle	0.00	0.013	0.001	0.001

Table 3. Selected Distances (Å) and Angles (deg)

	1	**3**	**4**	**5**	**7**	**9**	**14**	**17**
C(Cp′)···U (av)	2.78(5)	2.80(7)	2.76(3)	2.85(6)	2.80(5)	2.87(3)	2.79(2)	2.75(2)
C(Cp′)···U (range)	2.72(1)	2.727(8)	2.716(6)	2.756(6)	2.720(6)	2.841(4)	2.695(6)	2.714(7)
	2.84(1)	2.894(8)	2.806(6)	2.926(7)	2.912(6)	2.927(4)	2.980(7)	2.802(6)
Cp′(cent)···U (av)	2.50	2.53	2.48	2.55	2.53	2.61	2.51	2.48
Cp′(cent)−U−Cp′(cent)	145	147	144	146	143	142	140	143
U···X (av)	2.570(2)	2.37(3)	2.081(5)	2.193(5)	1.988(5)	U···O 1.860(3)	U···O 2.104(4)	2.219(6)
						U···N 2.535(4)	U···C 2.415(6)	2.244(6)
X−U−X (av) or X−U−Y (av)	98.1(8)	97.6(3)	99.8(2)	104.4(2)		88.7(1)	86.6(2)	97.1(2)

between the Me_3C groups at the back of the metallocene wedge and not directly due to the size of the X groups.[23]

Cp′$_2$U(bipy). The bipyridyl complex Cp′$_2$U(bipy) (**6**) is prepared by the slow addition of 2 equiv of sodium naphthalene to a 1:1 mixture of Cp′$_2$UCl$_2$ (**1**) and 2,2′-bipyridyl in tetrahydrofuran, Scheme 1. The complex is soluble in toluene, from which it may be crystallized as large dark green crystals. The compound melts at

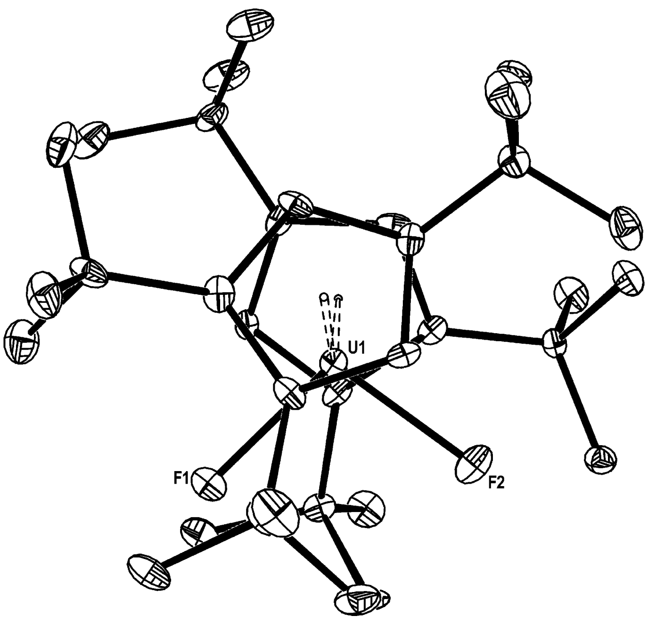

Figure 1. ORTEP drawing of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**) with 35% thermal ellipsoids.

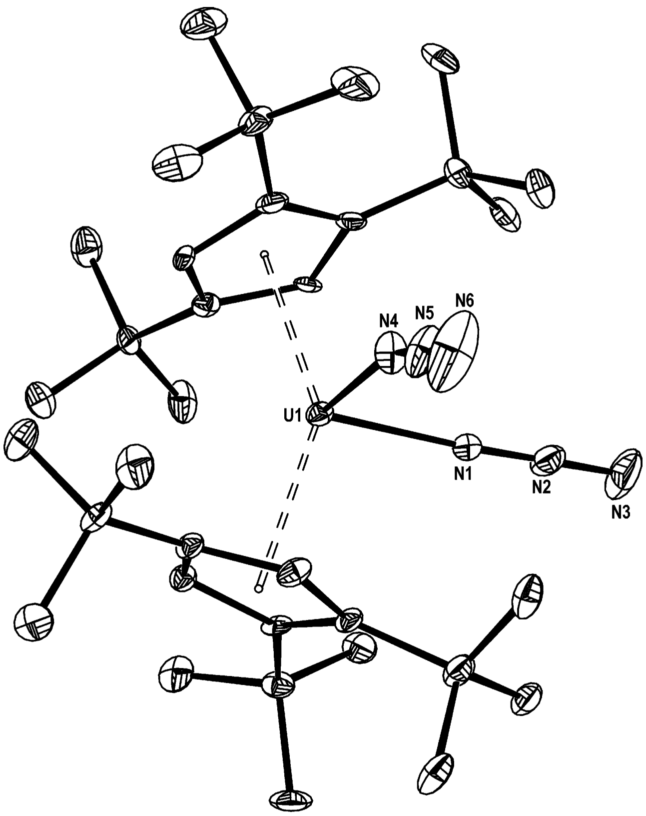

Figure 2. ORTEP drawing of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(N_3)_2$ (**17**) with 35% thermal ellipsoids.

271−276 °C and gives a molecular ion in its mass spectrum, and the ^{1}H NMR spectrum in C_6D_6 at 30 °C shows resonances for all ring and bipyridyl resonances, Table 1. The infrared spectrum shows strong absorptions at 935, 955, and 1495 cm^{-1}, features associated with the bipyridyl radical anion,[27,28] which implies that

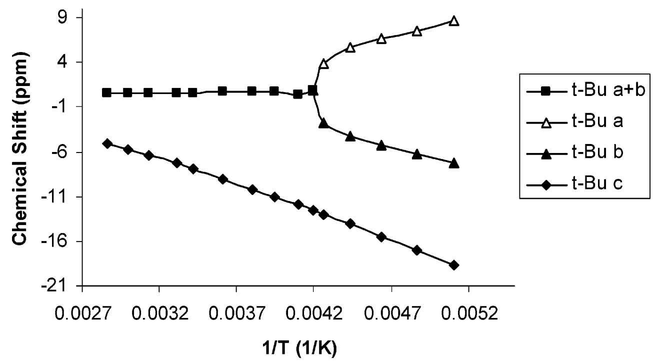

Figure 3. Plots of δ versus $1/T$ for [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**) in C_7D_8.

the complex is not a U(II) metallocene.[29] For the purpose of the present paper, however, the bipyridyl complex **6** is a useful starting material for the molecules described next.

Cp′₂U=N(*p*-tolyl). The bipyridyl complex Cp′$_2$U(bipy) (**6**) reacts with *p*-tolyl azide to give Cp′$_2$U=N(*p*-tolyl) (**7**) and N_2, Scheme 2. The imide **7** is soluble in pentane, from which it may be crystallized, gives a monomeric molecular ion in its mass spectrum, and is a monomer in the solid state as shown by the ORTEP diagram in Figure 4. The orientation of the Cp′ rings is such that the Me_3C groups at the back of the wedge avoid each other as much as possible, which results in an eclipsing interaction between a Me_3C group pointing toward the open wedge and the N-*p*-tolyl group. The eclipsing interaction results in a long U−C(3) distance, the carbon atom of the cyclopentadienyl ring to which the eclipsed Me_3C group is attached, of 2.912(6) Å. This distance is longer than the average U−C(Cp′) distance of 2.80(5) Å. The eclipsing interaction results in bending of the planar N-*p*-tolyl group toward the other Cp′ ring, so the U−N−C(35) angle is 172.3(5)°. Related distortions are apparent, as the [Cp′(C(18)−C(22))cent]−U−N and [Cp′(C(1)−C(5))cent]−U−N angles are 104° and 112°, respectively. The *p*-tolylimido ligand is planar and oriented so that the plane defined by the tolyl group is nearly a perpendicular bisector (83°) of the plane that contains the Cp′(cent)−U−Cp′(cent). The U−N distance of 1.988(5) Å is in the range found in (η^5-$C_5Me_5)_2$U[N-2,4,6-(*t*-Bu)$_3C_6H_2$] (1.95(1) Å),[30] (η^5-$C_5Me_5)_2$U(O)(N-2,6-*i*-$Pr_2C_6H_3$) (1.988(4) Å),[31] (η^5-$C_5Me_5)_2U(NPh)_2$ (1.952(7) Å),[32] (η^5-$C_5Me_5)_2$U[N-2,4,6-(*t*-Bu)$_3C_6H_2$][N−N=CPh_2] (1.987(5) Å),[33] and (η^5-$C_5Me_5)_2$Th[N-2,6-$Me_2C_6H_3$][thf] (2.045(8) Å).[34]

Cp′₂UO(py) and Cp′₂UO(dmap). Treatment of Cp′$_2$UCl$_2$ (**1**) with 2 equiv of potassium graphite in tetrahydrofuran, followed by addition of 2 equiv of pyridine-*N*-oxide, gives the cluster Cp′$_4U_6O_{13}$(bipy)$_2$.[22] In contrast, reaction of Cp′$_2$U(bipy) (**6**) with 1 equiv of pyridine-*N*-oxide in diethyl ether gives a red solution from which

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Table 4. Barriers to Me_3C Group Site Exchange in $Cp'_2U(X)(Y)^a$

	Cp'_2UCl_2 (**1**)	Cp'_2UF_2 (**4**)	$Cp'_2U(O)(py)$ (**8**)	$Cp'_2U(O)(dmap)$ (**9**)	$Cp'_2U(N_3)_2$ (**17**)
T_c	−40	−40	30	60	−33
$\Delta G^‡$	12	12	12	15	12

[a] The free energy of activation was determined by the temperature dependence in C_7D_8 of only the Me_3C groups and is expressed in units of kcal mol^{-1}, and T_c is in units of °C. When X = Y = Br (**2**) or Me (**3**), the resonance disappears at about −10 °C but does not reappear as two sharp resonances by −70 °C.

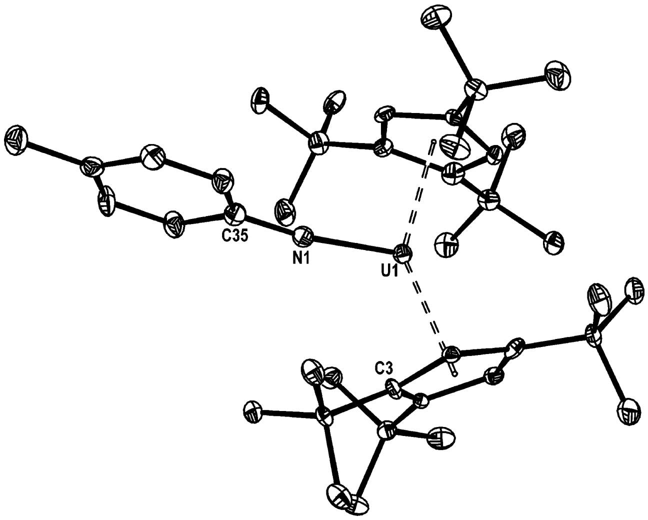

Figure 4. ORTEP drawing of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U{=}N(p\text{-tolyl})$ (**7**) with 35% thermal ellipsoids.

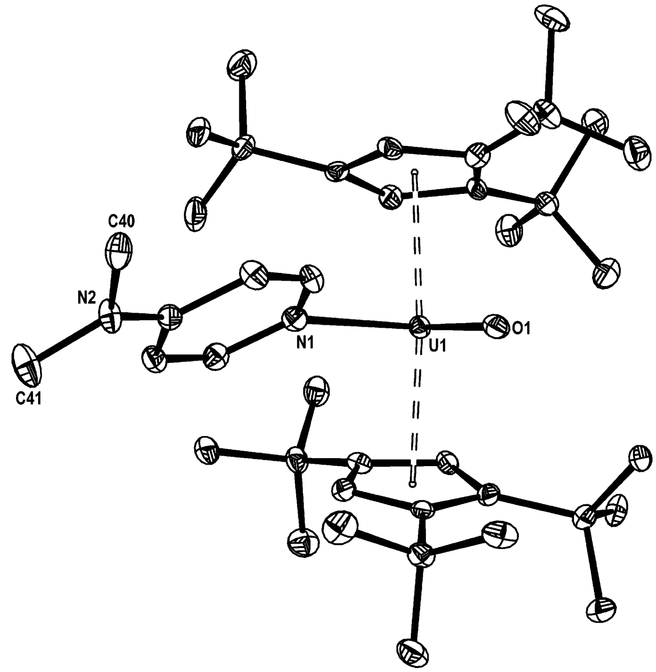

Figure 5. ORTEP drawing of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(O)(dmap)$ (**9**) with 35% thermal ellipsoids.

red crystals of $Cp'_2U(O)(py)$ (**8**) are isolated in 65% yield. The crystal structure of a related metallocene oxo adduct, $(\eta^5\text{-}C_5Me_5)_2U(O)[C(NMeCMe)_2]$, where $C(NMeCMe)_2$ is an N,N′-heterocyclic carbene ligand, has been reported recently.[35] This, along with $(\eta^5\text{-}C_5H_5)_2U(O)(thf)$,[36] are the only other terminal oxometallocene uranium(IV) derivatives of the general class $(\eta^5\text{-}C_5R_5)_2U(O)(L)$, where L is a neutral ligand, that have been reported. Ligand exchange in $Cp'_2U(O)(py)$ (**8**) occurs on the chemical time scale since addition of $4\text{-}Me_2NC_5H_4N$ (dmap) displaces pyridine in diethyl ether solution and the complex $Cp'_2U(O)(dmap)$ (**9**) may be crystallized as green-yellow blocks from that solution. An ORTEP of **9** is shown in Figure 5, crystal data are in Table 2, and selected geometrical parameters are listed in Table 3. The orientation of the Cp′ rings is nearly staggered, and the oxygen atom and the dmap ligand lie in the open wedge of the bent metallocene. The dmap ligand is nearly planar, the dihedral angle defined by intersection of the planar pyridine ring and the NMe_2 group is 15°, and the planar pyridine ring is twisted out of the plane defined by the UNO atoms. Thus, the molecule has no symmetry in the solid state. It is interesting to note that there is a short intermolecular contact between O(1) and C(40), a methyl group of the NMe_2 group on the dmap ligand, of 3.321(6) Å. The U(1)−N(1) distance of 2.535(4) Å is slightly shorter than the average U−N distance of 2.65 Å in $Cp_2U(triflate)_2(py)_2$[37] and $(\eta^5\text{-}MeC_5H_4)_3U(4\text{-}Me_2NC_5H_4N)$.[38] The U(1)−O(1) distance of 1.860(3) Å is significantly shorter than that found in $(\eta^5\text{-}C_5Me_5)_2U(O)[C(NMeCMe)_2]$ of 1.917(6) Å,[35] but slightly longer than that found in $(\eta^5\text{-}C_5Me_5)_2U(O)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ of 1.844(4) Å,[30] and identical to that found in $(\eta^5\text{-}C_5Me_5)_2U(O)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ of 1.859(6) Å.[31] The U−O distance is rather longer than that found in uranyl salts, which lies in the range 1.70−1.76 Å.[39] The infrared spectra of **8** and **9** show narrow, intense features at 760 and 765 cm^{-1}, respectively, that are assigned to the U−O stretching frequencies. Although this assignment is not supported by labeling studies, the values are comparable to those found in $(\eta^5\text{-}C_5Me_5)_2U(O)(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ of 751 cm^{-1} and $(\eta^5\text{-}C_5Me_5)_2U(O)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)$ of 753 cm^{-1},[31] which are supported by ^{18}O labeling studies.[30] In addition, the asymmetric U−O stretching frequency in matrix-isolated UO_2 is at 776 cm^{-1}.[40]

The ^1H NMR spectrum of $Cp'_2UO(py)$ (**8**) in C_7D_8 at 30 °C shows the Me_3C resonances as a 1:2 pattern, but the resonance of area 2 is very broad. The pyridine ring and Cp′ ring CH resonances are not observed, Table 1. Addition of free pyridine does not alter the appearance of the spectrum except that resonances due to free pyridine are observed. Heating the sample with added pyridine sharpens the two Me_3C resonances, and at temperatures greater than 60 °C three resonances appear at approximately 0, 5, and 10 ppm in an area ratio of 2:1:2 due to the pyridine ring CH's. A resonance due to the Cp′ ring CH cannot be assigned with

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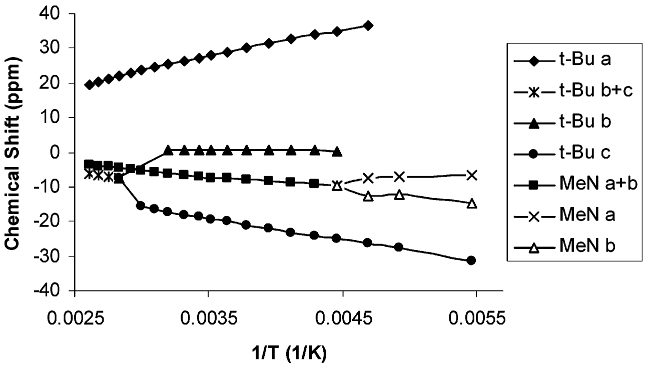

Figure 6. Plots of δ versus $1/T$ for $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U$(O)(dmap) (**9**) in C_7D_8.

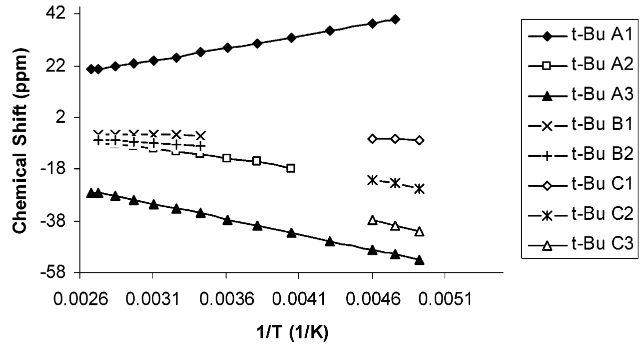

Figure 7. Plots of δ versus $1/T$ for $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U$(O) (**10**) in C_7D_8.

certainty. This change in line shape suggests that exchange between free and bound pyridine is slow at room temperature, but the individual pyridine ring resonances are not resolved, and at higher temperature, intermolecular exchange is rapid so that average chemical shifts are observed. As the temperature is decreased below 30 °C, the Me_3C groups decoalesce to a 1:1:1 pattern, but neither the pyridine nor Cp′ ring CH resonances are visible, presumably due to their line widths. Using the Me_3C resonances, the barrier to Me_3C site exchange is calculated to be 12 kcal mol^{-1}.

The ^{1}H NMR spectrum of Cp′$_2$UO(dmap) (**9**) provides more information about the dynamic processes that occur in solution. At 30 °C, the three chemically inequivalent Me_3C resonances of the Cp rings and the chemically equivalent Me_2N resonances of the dmap ligand are observed in the ^{1}H NMR spectrum in C_7D_8, Table 1. The Cp′ ring and pyridine ring CH resonances are not conclusively identified due to their line widths, as is the case in the pyridine complex **8**. At 30 °C, addition of free dmap to Cp′$_2$UO(dmap) (**9**) does not perturb the resonances due to the Me_3C and Me_2N groups. Increasing the temperature of this mixture to 60 °C results in coalescences of the Me_2N resonance of the free and coordinated dmap. Thus at 30 °C, intermolecular exchange is slow, but by 60 °C, it is rapid on the NMR time scale. A plot of the chemical shifts of the Me_3C and Me_2N resonances as a function of T^{-1}, in the absence of added dmap, is shown in Figure 6. It is clear that at 30 °C the three Me_3C resonances are inequivalent, as expected for a molecule of C_s symmetry; that is, the individual Cp′ rings are related by a time-averaged plane of symmetry, but a perpendicular plane of symmetry and a C_2 axis are absent. As the temperature is raised, two Me_3C resonances coalesce so that time-averaged C_{2v} symmetry is observed. As this process occurs near the temperature where intermolecular ligand exchange occurs, the physical process of ligand dissociation that generates a metallocene of averaged C_{2v} symmetry is sufficient to cause the coalescence and the barrier is about 15 kcal mol^{-1}, Table 4. The Me_2N resonances are chemically equivalent at 30 °C, implying that the planar pyridine ligand is free to rotate about the U−N bond in solution. As the temperature is lowered, the Me_2N resonance decoalesces and two distinct methyl resonances emerge, consistent with slowing and stopping rotation about the U−N bond. This assumes that the entire 4-$Me_2NC_5H_4N$ ligand rotates rather than just the Me_2N group since the pyridine ring resonances cannot be identified with certainty. The $\Delta G^{\ddagger}(T_c = -49\ °C)$ is 9.7 kcal mol^{-1} for the dmap rotational barrier.

Cp′$_2$UO. Although Cp′$_2$U(O)(py) (**8**) exchanges with dmap in solution, poorer donor ligands cannot compete with these nitrogen heterocycles. To investigate the intrinsic reactivity patterns of the U−O functional group, and to compare them with those of base-free imide **7**, a synthetic route to the base-free oxo compound is needed. This is accomplished by addition of BPh_3, which forms the insoluble BPh_3(py) complex and leaves the base-free oxo Cp′$_2$UO (**10**) in toluene solution, Scheme 2. Removal of toluene yields a brown-red solid that may be crystallized as brown-red microcrystals from pentane.[41] The Lewis acid−base reaction is reversible in solution, since addition of pyridine regenerates the complex **8** quantitatively. The base-free metallocene **10** gives a monomeric molecular ion in its mass spectrum, but the ^{1}H NMR spectrum is difficult to reconcile with a simple monomeric species in solution.

The ^{1}H NMR spectrum of the base-free oxo **10** consists of five resonances in either C_7D_8 or C_7H_{14} at 99.0, 27.1, −12.3, −35.1, and −90.8 ppm in area ratio 2:9:9:9:2 at 19 °C. The chemical shifts of the Me_3C resonances in **10** are qualitatively similar to those in the dmap complex **9** and imply that the two Cp′ rings are related only by a plane of symmetry in a molecule of idealized C_s symmetry. This requires that the Cp′ rings are not free to oscillate about their pseudo-C_5 axis in order to generate a time averaged C_2 axis, which is improbable given the barriers shown in Table 4. The variable-temperature ^{1}H NMR spectra show that the 19 °C spectrum in either solvent is deceptively simple. A plot of δ vs T^{-1} in C_7D_8 solvent of the Me_3C resonances is shown in Figure 7. As the temperature is increased, the total intensity of the three equal area Me_3C resonances at 27, −12, and −35 ppm, A set (A1, A2, and A3), decrease as two new resonances in a 1:2 ratio appear at −6.5 and −9.7 ppm, B set (B1 and B2). As the temperature is increased, the A:B ratio decreases, and at 100 °C the ratio is approximately 3:1. The relative intensity of the individual components within the A and B sets does not change with temperature, although their chemical shifts are temperature dependent. Cooling to 19 °C regenerates the original spectrum without loss in absolute intensity. The behavior on cooling is rather

(41) We have been unable to obtain single crystals of this material. Further physical studies including EXAFS are in progress. The EXAFS studies were essential in defining the molecular structure of other oxo metallocenes described in ref 13.

more complex. As the temperature is decreased from 19 °C to −40 °C, the middle resonance (A2) in the A set of resonances broadens and disappears into the baseline. On further cooling to −70 °C, three equal area resonances, C set (C1, C2, and C3), emerge from the baseline, but their common parentage is not the middle resonance (A2) of the A set; see Figure 7. In addition, the deshielded resonance (A1) in the A set broadens and disappears by −70 °C, while the upfield resonance (A3) is still visible. During the cooling process the absolute intensity of the A-set of resonances decreases by about 50%, but the new resonances that appear do not account for the "lost" intensity. On warming to 19 °C, the original spectrum is observed with the original absolute intensity.

An interpretation of the high-temperature ^{1}H NMR spectrum is that a dimer−monomer equilibrium exists in solution and the monomer concentration increases with temperature. The 2:1 pattern of the Me_3C resonances suggests the monomer has C_{2v} symmetry, as in the high-temperature spectra of the pyridine complexes **8** and **9**. Unfortunately, aromatic and aliphatic hydrocarbon solvents are the only ones that are compatible with the base-free oxometallocene **10**, so using solvents of different dielectric constant is not possible, and this postulate cannot be tested. The low-temperature behavior is more difficult to interpret since the intensity changes show that not all of the resonances are observed. A postulate is that the dimer is largely present at room temperature and below, and the dimer has averaged C_{2h} symmetry as in $[\eta^5\text{-}1,3\text{-}(Me_3E)_2C_5H_3]_4U_2(O)_2$ (E = C, Si).[12−14] Cooling slows Cp′ ring rotation and some of the Me_3C resonances disappear. Unfortunately, single crystals of the base-free metallocene **10** cannot be grown, which would be the ultimate test of this proposition. EXAFS studies have been used to solve a related structural dilemma, and such a study is contemplated for Cp'_2UO.[13]

Reactions of 10. The oxo **10** reacts with excess Me_3SiCl rapidly to give $Cp'_2U(OSiMe_3)(Cl)$ (**11**) cleanly at room temperature in a mixing experiment in C_6D_6 in an NMR tube. The reaction does not proceed further unless heated. Heating at 65 °C slowly yields Cp'_2UCl_2 (**1**) and $(Me_3Si)_2O$; $t_{1/2}$ is about 30 h at this temperature. The $Cp'_2U(OSiMe_3)(Cl)$ (**11**) is prepared on a synthetic scale in two ways: reaction of $Cp'_2UO(py)$ (**8**) and Me_3SiCl in toluene followed by crystallization from pentane, or reaction of Cp'_2UCl_2 (**1**) with 1 equiv of $LiOSiMe_3$ in diethyl ether followed by crystallization from pentane. Synthesis and characterization details for this and the other metallocenes described in this section are given in the Experimental Section, and some physical properties are listed in Table 1. In mixing experiments monitored by ^{1}H NMR spectroscopy, excess Me_3SiX reacts rapidly and cleanly to yield $Cp'_2U(OSiMe_3)(X)$ (X = Br (**12**), I (**13**), CN (**14**), OTf (**15**)). In the case of X = Br, some Cp'_2UBr_2 (**2**) and $(Me_3Si)_2O$ are formed, but the rate is very slow; even at 65 °C, $t_{1/2}$ is about 70 h. In the case of X = I, OTf, or CN, no resonances due to Cp'_2UX_2 are detected when the solutions are kept at 65 °C for up to 3 days. In contrast, excess Me_3SiN_3 reacts with **10** instantaneously to give $Cp'_2U(N_3)_2$ (**17**) and $(Me_3Si)_2O$; no resonances attributable to $Cp'_2U(OSiMe_3)(N_3)$ (**16**) are detected. However, upon addition of 1 equiv of Me_3SiN_3 to Cp'_2UO (**10**) on a synthetic scale, the ^{1}H NMR spectrum of the crude products shows resonances due to $Cp'_2U(N_3)_2$ (**17**), unreacted Cp'_2UO (**10**), and three new resonances attributable to $Cp'_2U(OSiMe_3)(N_3)$ (**16**). The latter resonances disappear on addition of more Me_3SiN_3. On a synthetic scale, the method of choice is addition of excess Me_3SiX to $Cp'_2U(O)(py)$ in toluene followed by crystallization from pentane. The ^{1}H NMR spectra of these compounds show the Me_3C resonances as a 1:1:1 pattern (except for the diazide) consistent with a molecule of C_s symmetry. The infrared spectrum of **14** shows a CN absorption at 2040 cm^{-1}, which may be compared to a value of 2110 cm^{-1} found in $(\eta^5\text{-}C_5H_5)_3U(CN)$.[42] The infrared spectrum of **17** shows two N_3 absorptions at 2100 and 2080 cm^{-1}, close to that found in $[(ArO)_3tacn]U(N_3)$ ($[(ArO)_3tacn]^{3-}$ = [1,4,7-tris(3,5-di-*tert*-butyl-2-oxybenzyl)-1,4,7-triazacyclononane]$^{3-}$) of 2080 cm^{-1}.[43]

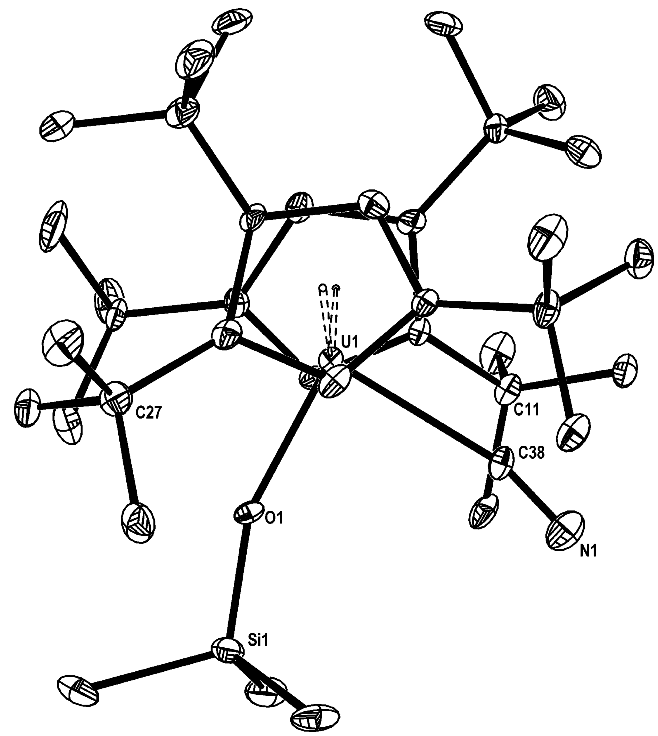

Figure 8. ORTEP drawing of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(OSiMe_3)(CN)$ (**14**) with 35% thermal ellipsoids.

An ORTEP diagram of the solid-state structure of **14** is shown in Figure 8. The orientation of the rings is rather different from those observed for the molecules shown in Figures 1 and 2. The rings are nearly staggered, and the Me_3C groups at the back of the wedge are avoiding each other as much as possible. However, the other four Me_3C groups are oriented to the left and right side of the open wedge, while the $OSiMe_3$ and CN groups occupy sites in the wedge. The U−O−$SiMe_3$ and U−C−N angles are not linear; U−O−Si is 160.6(3)° and U−C−N is 164.5(7)°. A nonlinear U−O−Si angle is common, while a U−C−N angle is not. Perhaps a reason for the bending can be traced to the $OSiMe_3$ group avoiding the methyl groups on C(27), while the CN group is avoiding those on C(11).

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Silicon tetrafluoride reacts instantaneously, as does $BF_3(OEt_2)$, with Cp′$_2$UO (**10**) in C_6D_6 to give resonances due to Cp′$_2$UF$_2$ (**4**) in the ^{1}H NMR spectrum. The conversion is quantitative, but the fate of the nonmetal fragment is unknown. The difluoride Cp′$_2$UF$_2$ (**4**) is also formed from the oxo **10** and Me_3SiCF_3. The binary silicon halides SiX_4 (X = Cl, Br, I) give resonances attributable to Cp′$_2$U(OSiX$_3$)(X) since their ^{1}H NMR spectra show three equal area resonances for the Me_3C groups, which over time evolve into the spectra of Cp′$_2$UX$_2$ (X = Cl (**1**), Br (**2**)). In the case of the iodide, the end point is a mixture that may contain Cp′$_2$UI$_2$, but this deduction is uncertain since the diiodide complex has not been prepared in pure form.

In contrast to the alkylsilyl halides, aryl and alkyl halides do not react cleanly with Cp′$_2$UO (**10**). Fluorobenzene does not react with **10**, and the reactions of chloro- and bromobenzene are not clean. Chlorobenzene reacts rapidly in C_6D_6 as the resonances due to Cp′$_2$UO (**10**) disappear and nine new paramagnetic resonances in approximately equal relative intensity (see Experimental Section for details) along with resonances due to Cp′H appear in an approximate area ratio of 2:1. The intensity ratio does not change when the sample is heated to 65 °C for 1 day, and resonances due to Cp′$_2$UCl$_2$ (**1**) are not observed. Repeating the experiment with C_6D_5Cl gives the same results, showing that the nine resonances are due to nine Me_3C groups, which implies that a mixture of compounds are formed. Bromobenzene behaves similarly, but the chemical shifts of the nine resonances are different, implying that a halide or halides are attached to uranium. *tert*-Butyl chloride reacts with Cp′$_2$UO (**10**) in C_6D_6 to generate a ^{1}H NMR spectrum that contains nine resonances whose chemical shifts and relative intensities are identical to those observed in the reaction of PhCl, and resonances due to Cp′H and isobutene. Repeating the experiment with $(CD_3)_3CCl$ yields the same result and no Cp′D is observed, implying that the source of H(D) is not the alkyl chloride.

The oxo **10** reacts rapidly with AgF to give Cp′$_2$UF$_2$ (**4**) as the only paramagnetic compound observed in the ^{1}H NMR spectrum along with the dimer Cp′$_2$. Silver chloride also reacts rapidly with the oxo **10**, as resonances due to Cp′$_2$UO (**10**) disappear from the ^{1}H NMR spectrum and nine resonances with chemical shift and intensity ratios identical to those in the PhCl reaction appear along with resonances due to Cp′$_2$. Adding more AgCl results in the disappearance of the nine resonances, while the resonances for Cp′$_2$ increase in intensity. Silver bromide behaves similarly, and the chemical shifts and relative intensity of the nine resonances are identical to those formed in reaction of PhBr.

A mixture of Cp′$_2$UO (**10**) with Cp′$_2$UF$_2$ (**4**) gives a ^{1}H NMR spectrum that contains only the resonances of the individual starting compounds. However, mixing Cp′$_2$UO (**10**) and Cp′$_2$UCl$_2$ (**1**) in C_6D_6 gives resonances due to Cp′$_2$, Cp′$_2$UCl,[44] and nine resonances whose chemical shifts and relative intensity are identical to those in the reaction of PhCl or AgCl with Cp′$_2$UO (**10**). No change is observed over time or upon heating.

In summary, Me_3SiX reacts with Cp′$_2$UO (**10**) cleanly to give addition products, which, in some cases, react further to give the metathesis products. This implies that the Cp′$_2$UO (**10**) is an excellent nucleophile. The other reactions described are more complex, but a pattern is apparent. It seems reasonable to postulate that halide atom transfer occurs and the resulting Cp′$_2$U(O)(X) metallocene decomposes by losing Cp′$_2$ or Cp′H fragments. Since these reactions are not clean, they are not studied further.

Addition of pyridine-*N*-oxide to Cp′$_2$UO (**10**) in C_6D_6 results in rapid disappearance of the resonances due to Cp′$_2$UO (**10**) and formation of resonances due to Cp′$_2$ in quantitative yield. It seems reasonable to suggest that the initial reaction is oxygen atom transfer generating "Cp′$_2$U(O)$_2$", which eliminates Cp′$_2$ and forms "UO_2". A similar reaction occurs when the oxo **10** is mixed with either Ph_3PS or Ph_3PSe, where the uranium-containing products are therefore "U(O)(E)" (E = S, Se).

As mentioned above, the oxo **10** forms isolable adducts with pyridine and 4-(dimethylamino)pyridine. These two adducts, **8** and **9**, along with those formed with Ph_3PO and Ph_2CO, are the only adducts that are stable in C_6D_6 solution. When the oxo **10** is exposed to other Lewis bases, such as ethers (diethyl ether or tetrahydrofuran), amines ($Me_{(3-x)}H_xN$, $x = 0-3$), or azomethines, decomposition occurs with formation of Cp′H. The decomposition rates vary from minutes to hours to days, but the final organic product is always Cp′H. No reaction is observed between the oxo **10** and dihydrogen, ethylene, and acetylenes RC≡CR (R = Me, Ph, Me_3Si). When the acetylene is RC≡CH, hydrogen atom transfer is observed, and Cp′H is the final product.

Reactions of 7. In contrast to the rich reaction chemistry of Cp′$_2$UO (**10**), the reactions of the base-free imide Cp′$_2$U=N(*p*-tolyl) (**7**) are meager. The imide **7** does not form adducts with ethers or pyridines. It does not react with Me_3SiX reagents except Me_3SiN_3, which gives Cp′$_2$U(N$_3$)$_2$ (**17**) in poor yield (20%). It does react with SiF_4 or $BF_3(OEt_2)$, giving Cp′$_2$UF$_2$ (**4**) in quantitative yield. Thus, the imido metallocene **7** is a poorer nucleophile than the oxo metallocene **10**. This result might be due to steric or electronic effects of the *p*-tolyl group. Experiments designed to test this proposition are underway.

Although the imide **7** does not react with Ph_3PE (E = O, S, Se), it reacts rapidly and quantitatively with pyridine-*N*-oxide to give Cp′$_2$. The cyclopentadienyl ring coupling product has been previously observed in the reaction of (η^5-C$_5$Me$_5$)$_2$U(NPh)(py) with pyridine-*N*-oxide, which gives a mixture of (η^5-C$_5$Me$_5$)$_2$U(NPh)$_2$, (C$_5$Me$_5$)$_2$, and "UO_2".[30] More surprising, however, is the reaction with Ph_2CO, which yields Cp′$_2$UO (**10**) and Ph$_2$C=N(*p*-tolyl) rapidly and cleanly in C_6D_6, Scheme 2. This reaction is important since it directly addresses the question of the bond enthalpy of the uranium oxo and imido bonds in these metallocenes. Information on this question is available from the heat of formation of ketones and azomethines, which suggests that the C=O bond is stronger than the C=NR bond by about 30 kcal mol^{-1}.[45,46] This difference implies that the U=O bond is stronger than the U=N(*p*-tolyl) bond by at least

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30 kcal mol^{-1}. The ability of benzophenone to act as an oxygen-atom transfer reagent has been observed previously.[47,48]

Conclusions

The bipyridyl complex Cp'_2U(bipy) (**6**) is a useful starting material for the oxo-metallocene and *p*-tolylimidometallocene. The base-free oxo Cp'_2UO (**10**) reacts with Me_3SiX reagents to yield addition products $Cp'_2U(OSiMe_3)(X)$ and in some cases substitution products, Cp'_2UX_2, as do $(\eta^5\text{-}C_5Me_5)_2Zr(O)(py)$[49] and $(\eta^5\text{-}C_5Me_5)_2Ti(S)(py)$.[50] The oxo Cp'_2UO (**10**) does not react with dipolar molecules such as acetylenes, RC≡CR, in contrast to $(\eta^5\text{-}C_5Me_5)_2Ti(O)(py)$.[51] The nucleophilic behavior is consistent with the view that the uranium−oxygen bond is better represented by the polar valence-bond resonance structure $U^+{-}O^-$, rather than the double-bond resonance structure U═O. Although the U═O bond enthalpy is unknown, the exchange reaction between Cp'_2U═N(*p*-tolyl) (**7**) and Ph_2CO indicates that U═O is at least 30 kcal mol^{-1} stronger than U═N(*p*-tolyl). Experiments that address the fundamental question about the nature of the multiple bonds in these uranium compounds are underway.

Experimental Section

General Procedures. All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and glovebox techniques. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Me_3SiX (X = Cl, Br, I, CN, OTf, N_3) were distilled under nitrogen before using. 2,2′-Bipyridyl (bipy), pyridine-*N*-oxide, Ph_3B, 4-dimethyaminopyridine (dmap), and $LiOSiMe_3$ were sublimed before using. $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Mg$[22] and $p\text{-}CH_3C_6H_4N_3$[52] were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained as Nujol mulls. ^1H NMR spectra were recorded on Bruker AVB-400, AVQ-400, and AV-300 spectrometers. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents, which are internal standards, for proton chemical shifts. Melting points were measured on a Thomas-Hoover melting point apparatus in sealed capillaries and are uncorrected. Electron impact mass spectra were recorded by the mass spectroscopy laboratory, and elemental analyses were performed by the analytical laboratories, both at the University of California, Berkeley.

Isomerization of $(Me_3C)_3C_5H_3$. To an NMR tube charged with $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Mg$ (30 mg) and C_6D_6 (0.5 mL) was added one drop of degassed H_2O. Two sets of resonances due to the kinetic and thermodynamic isomers were observed by ^1H NMR spectroscopy in an approximate area ratio of 2:1 at 20 °C. Kinetic isomer, ^1H NMR (C_6D_6): δ 6.45 (s, 1H, C*H*), 3.09 (s, 2H, CH_2), 1.37 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 1.16 (s, 9H, C(CH_3)$_3$). Thermodynamic isomer, ^1H NMR (C_6D_6): δ 6.42 (s, 1H, C*H*), 5.95 (s, 1H, C*H*), 2.95 (s, 1H, C*H*), 1.26 (s, 9H, C(CH_3)$_3$), 1.18 (s, 9H, C(CH_3)$_3$), 1.08 (s, 9H, C(CH_3)$_3$). This sample was heated at 65 °C and monitored periodically by ^1H NMR spectroscopy; after 28 h the conversion to the thermodynamic isomer was complete.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UCl_2$ (1). To a toluene (300 mL) suspension of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2Mg$ (25.0 g, 51 mmol) and UCl_4 (19.0 g, 50 mmol) was added freshly distilled pyridine (50 mL) dried with sodium. After the solution was heated at reflux for 1 day with stirring, the solvent was removed. The red residue was extracted with pentane (150 mL × 3) and filtered. The volume of the filtrate was reduced to 200 mL and cooled to −20 °C. Two crops of dark red crystals were collected by filtration. Yield: 26.4 g (68%). EI-MS [M$^+$], *m/z* (calcd, found): 774(100, 100), 775 (39, 38), 776 (71, 71), 777 (26, 25), 778 (15, 13), 779 (5, 4). Anal. Calcd for $C_{34}H_{58}Cl_2U$: C, 52.7; H, 7.55. Found: C, 52.6; H, 7.55.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UBr_2$ (2). Me_3SiBr (0.22 mL, 1.68 mmol) was added to a pentane (20 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UCl_2$ (**1**; 0.65 g, 0.84 mmol) with stirring at room temperature. After the mixture was stirred for 12 h at room temperature, the volatile components were removed. The resulting dark red solid was redissolved in pentane (20 mL), and the above procedure was repeated twice more. The dark red residue was extracted with pentane (15 mL × 2) and filtered. The volume of the filtrate was reduced to 5 mL, and cooling to −20 °C yielded red crystals, which were isolated by filtration. Yield: 0.62 g (85%). EI-MS [M$^+$], *m/z* (calcd, found): 862 (50, 48), 863 (19, 20), 864 (100, 100), 865 (38, 32), 866 (54, 52), 867 (19, 18), 868 (3, 3). Anal. Calcd for $C_{34}H_{58}Br_2U$: C, 47.2; H, 6.76. Found: C, 46.9; H, 6.85.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (3). A diethyl ether (11.6 mL) solution of MeLi (0.67 M in diethyl ether; 7.8 mmol) was slowly added to a diethyl ether (100 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UCl_2$ (**1**; 3.0 g, 3.9 mmol) with stirring at room temperature. After the solution was stirred for 1 h at room temperature, the solvent was removed. The red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding red crystals, which were isolated by filtration. Yield: 2.4 g (85%). EI-MS [M$^+$ − 15]: *m/z* 719. Anal. Calcd for $C_{36}H_{64}U$: C, 58.8; H, 8.78. Found: C, 59.0; H, 8.98.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UF_2$ (4). $BF_3{\cdot}OEt_2$ (1.0 mL, 7.9 mmol) was added to a pentane (50 mL) solution of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (**3**; 2.0 g, 2.72 mmol) with stirring at room temperature. After the solution was stirred at room temperature overnight, the solvent was removed. The orange-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 15 mL and cooled to −20 °C, yielding orange-red crystals, which were isolated by filtration. Yield: 1.4 g (70%). EI-MS [M$^+$], *m/z* (calcd, found): 742 (100, 100), 743 (37, 40), 744 (7, 10). Anal. Calcd for $C_{34}H_{58}F_2U$: C, 55.0; H, 7.87. Found: C, 54.7; H, 7.96.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U(NH_2)_2$ (5). In a 250 mL flask, $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2UMe_2$ (**3**; 1.0 g, 1.36 mmol) was dissolved in toluene (30 mL). The headspace of the flask was evacuated and replaced with 1 atm of NH_3 (dried over sodium metal at −35 °C). After the solution was stirred for 4 h at room temperature, the solvent was removed. The yellow residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding yellow crystals, which were isolated by filtration. Yield: 0.74 g (74%). EI-MS [M$^+$], *m/z* (calcd, found): 736 (100, 100), 737 (39, 40), 738 (8, 5). Anal. Calcd for $C_{34}H_{62}N_2U$: C, 55.4; H, 8.48; N, 3.80. Found: C, 55.8; H, 8.13; N, 3.68.

Preparation of $[\eta^5\text{-}1,2,4\text{-}(Me_3C)_3C_5H_2]_2U$(bipy) (6). A green THF solution of sodium naphthalene, which was prepared from naphthalene (3.3 g, 25.8 mmol) and sodium metal (1.0 g, 43.5 mmol) in THF (200 mL) with stirring overnight at

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room temperature, was slowly added to a THF (100 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**; 10 g, 12.9 mmol) and 2,2′-bipyridyl (bipy; 2.1 g, 13.5 mmol) with stirring at room temperature. After the green solution was stirred for 12 h, solvent was removed. The dark green residue was extracted with toluene (100 mL × 3) and filtered. The volume of the filtrate was reduced to 100 mL and cooled to −20 °C. Two crops of dark green crystals were collected by filtration. Yield: 7.2 g (65%). EI-MS [M$^+$], *m/z* (calcd, found): 860 (100, 100), 861 (51, 57), 862 (13, 16), 863 (2, 3). Anal. Calcd for $C_{44}H_{66}N_2U$: C, 61.4; H, 7.73; N, 3.25. Found: C, 61.2; H, 7.82; N, 3.28.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (7). A hexane (1.9 mL) solution of *p*-$CH_3C_6H_4N_3$ (1.2 M in hexane; 2.3 mmol) was added to a hexane (100 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(bipy) (**6**; 2.0 g, 2.3 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from green to dark brown. After the solution was stirred for 2 h at room temperature, solvent was removed and the dark brown solid was exposed to vacuum overnight at 50 °C in a water bath. The residue was extracted with pentane (25 mL × 2) and filtered. The volume of the dark brown solution was reduced to 20 mL and cooled to −20 °C, yielding dark brown crystals, which were isolated by filtration. Yield: 1.5 g (80%). EI-MS [M$^+$], *m/z* (calcd, found): 809 (100, 100), 810 (47, 58), 811 (12, 14), 812 (2, 2). Anal. Calcd for $C_{41}H_{65}NU$: C, 60.8; H, 8.09; N, 1.73. Found: C, 61.1; H, 8.40; N, 1.84.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(py) (8). To a diethyl ether (30 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$-(bipy) (**6**; 2.0 g, 2.3 mmol) was slowly added a diethyl ether (20 mL) solution of pyridine-*N*-oxide (0.22 g, 2.3 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from green to red. After the solution was stirred for 2 h at room temperature, solvent was removed and the red solid was exposed to vacuum overnight at 50 °C in a water bath. The residue was extracted with diethyl ether (25 mL × 2) and filtered. The volume of filtrate was reduced to 10 mL and cooled to −20 °C, yielding red crystals, which were isolated by filtration. Yield: 1.2 g (65%). IR: ν UO, 760(s) cm^{-1}. Anal. Calcd for $C_{39}H_{63}NOU$: C, 58.6; H, 7.94; N, 1.75. Found: C, 58.6; H, 8.29; N, 1.92.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(dmap) (9). A diethyl ether (20 mL) solution of 4-(dimethylamino)pyridine (dmap; 0.18 g, 1.48 mmol) was added to a diethyl ether (30 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(py) (**8**; 1.1 g, 1.38 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from red to yellow-green. After the solution was stirred for 2 h at room temperature, solvent was removed. The yellow-green residue was extracted with diethyl ether (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding yellow-green crystals, which were isolated by filtration. Yield: 0.75 g (65%). IR: ν UO, 765(s) cm^{-1}. Anal. Calcd for $C_{41}H_{68}N_2OU$: C, 58.4; H, 8.13; N, 3.32. Found: C, 58.6; H, 8.52; N, 3.39.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10). Method A. To a toluene (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$-(O)(py) (**8**; 1.6 g, 2.0 mmol) was added a toluene (10 mL) solution of Ph_3B (0.49 g, 2.0 mmol) with stirring at room temperature. During the course of the reaction, the color of the solution changed from red to brown-red and a precipitate (Ph_3B·py) appeared. After the solution was stirred for 2 h at room temperature, solvent was removed. The brown-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding brown-red microcrystals, which were isolated by filtration. Yield: 1.2 g (83%). EI-MS [M$^+$], *m/z* (calcd, found): 720 (100, 100), 721 (39, 34), 722 (7, 6). Anal. Calcd for $C_{34}H_{58}OU$: C, 56.6; H, 8.11. Found: C, 56.6; H, 7.95. This compound cannot be prepared in THF or diethyl ether solution, since in these solvents the diene, $(Me_3C)_3C_5H_3$ results.

Method B. NMR Scale. Ph_3B (5 mg, 0.02 mmol) was added to an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)-(dmap) (**9**; 17 mg, 0.02 mmol) and C_6D_6 (0.5 mL). The color of the solution immediately changed from yellow-green to brown-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Method C. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (**7**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added benzophenone (3.6 mg, 0.02 mmol). The color of the solution immediately changed from dark brown to brown-red. The ^{1}H NMR spectrum contained resonances consistent with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**) and Ph_2C=N-*p*-$C_6H_4CH_3$ (^{1}H NMR (C_6D_6): δ 7.97 (m, 2H, aryl *H*), 7.12 (m, 3H, aryl *H*), 6.98 (m, 2H, aryl *H*), 6.89 (m, 3H, aryl *H*), 6.77 (m, 4H, aryl *H*), 1.97 (s, 3H, C*H*$_3$)) (100% conversion). **10** cannot be isolated on a synthetic scale by this method, since in the presence of Ph_2C=N-*p*-$C_6H_4CH_3$ the diene $(Me_3C)_3C_5H_3$ slowly results.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Pyridine. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added a drop of pyridine. The color of the solution immediately changed from brown-red to red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(py) (**8**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with dmap. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added 4-(dimethylamino)pyridine (dmap; 2.5 mg, 0.02 mmol). The color of the solution immediately changed from brown-red to yellow-green, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(dmap) (**9**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)$(Cl) (11). Method A. Me_3SiCl (2.0 mL, 15.7 mmol) was added to a toluene (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(py) (**8**; 1.2 g, 1.5 mmol) with stirring at room temperature. After the solution was stirred overnight at room temperature, solvent was removed. The orange-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding orange-red crystals, which were isolated by filtration. Yield: 1.1 g (88%). EI-MS [M$^+$], *m/z* (calcd, found): 828 (100, 100), 829 (47, 50), 830 (46, 49), 831 (18, 20); the parent ion is [M − 15]$^+$. Anal. Calcd for $C_{37}H_{67}ClOSiU$: C, 53.6; H, 8.15. Found: C, 53.2; H, 8.37.

Method B. To a diethyl ether (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**; 2.0 g, 2.6 mmol) was added a diethyl ether (10 mL) solution of Me_3SiOLi (0.25 g, 2.6 mmol) with stirring at room temperature. After the solution was stirred at room temperature for one week, solvent was removed. The orange-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding orange-red microcrystals, which were identified as **11** by ^{1}H NMR spectroscopy. Yield: 1.6 g (75%). Solvent has a large effect on this reaction; the conversion is very low (below 10%) even at 65 °C for 3 days in THF or toluene solution.

Method C. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL), an excess of Me_3SiCl was added. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)$(Cl) (**11**) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 day, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**) was 35% complete, and after 3 days, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**) was complete.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)$(Br) (12). Method A. This compound was prepared as red crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$(O)(py) (**8**; 1.2 g, 1.5 mmol) and Me_3SiBr (2.0 mL, 15 mmol) in toluene (20 mL) by procedures similar to those used in the synthesis of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(Cl)$ (**11**). Yield: 1.1 g (85%). EI-MS [M+], *m/z* (calcd, found): 872 (89, 90), 873 (42, 40), 874 (100, 100), 875 (44, 40), 876 (13, 15); the parent ion is $[M - 15]^+$. Anal. Calcd for $C_{37}H_{67}BrOSiU$: C, 50.9; H, 7.74. Found: C, 50.7; H, 7.80.

Method B. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of Me_3SiBr. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(Br)$ (**12**) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 day, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UBr_2$ (**2**) was 15% complete, and after 10 days, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UBr_2$ (**2**) was complete.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(I)$ (13). Method A. This compound was prepared as red crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(py)$ (**8**; 1.2 g, 1.5 mmol) and Me_3SiI (2.0 mL, 14 mmol) in toluene (20 mL) by procedures similar to those used in the synthesis of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(Cl)$ (**11**). Yield: 1.2 g (87%). EI-MS [M+], *m/z* (calcd, found): 920 (100, 100), 921 (47, 35); the parent ion is $[M - 15]^+$. Anal. Calcd for $C_{37}H_{67}IOSiU$: C, 48.2; H, 7.34. Found: C, 48.0; H, 7.31.

Method B. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of Me_3SiI. The color of the solution immediately changed from brown-red to red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(I)$ (**13**) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(CN)$ (14). Method A. This compound was prepared as red crystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(py)$ (**8**; 1.2 g, 1.5 mmol) and Me_3SiCN (2.0 mL, 15 mmol) in toluene (20 mL) by procedures similar to those used in the synthesis of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(Cl)$ (**11**). Yield: 1.1 g (89%). IR: ν UCN, 2040(s) cm^{-1}. EI-MS [M+], *m/z* (calcd, found): 819 (100, 100), 820 (49, 50), 821 (15, 15), 822 (2, 2); the parent ion is $[M - CN]^+$. Anal. Calcd for $C_{38}H_{67}NOSiU$: C, 55.6; H, 8.24; N, 1.71. Found: C, 55.4; H, 8.12; N, 2.01.

Method B. NMR Scale. An excess of Me_3SiCN was added to an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL). The color of the solution immediately changed from brown-red to red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(CN)$ (**14**) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(OTf)$ (15). Method A. This compound was prepared as orange-red microcrystals from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$-(O)(py) (**8**; 1.2 g, 1.5 mmol) and Me_3SiOTf (2.0 mL, 11 mmol) in toluene (20 mL) by using the procedures similar to those used in the synthesis of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(Cl)$ (**11**). Yield: 1.2 g (86%). EI-MS: *m/z* 927 $[M^+ - CH_3]$. Anal. Calcd for $C_{38}H_{67}F_3O_4SSiU$: C, 48.4; H, 7.16. Found: C, 48.2; H, 7.24.

Method B. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of Me_3SiOTf. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(OTf)$ (**15**) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Preparation of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(N_3)_2$ (17). Method A. Me_3SiN_3 (2.0 mL, 15 mmol) was added to a toluene (20 mL) solution of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(py)$ (**8**; 1.2 g, 1.5 mmol) with stirring at room temperature. After the solution was stirred overnight at room temperature, solvent was removed. The orange-red residue was extracted with pentane (25 mL × 2) and filtered. The volume of the filtrate was reduced to 10 mL and cooled to −20 °C, yielding orange-red crystals, which were isolated by filtration. Yield: 1.0 g (85%). IR: ν UN_3, 2100, 2080 cm^{-1}. EI-MS [M+], *m/z* (calcd, found): 788 (100, 100), 789 (41, 45), 790 (8, 10). Anal. Calcd for $C_{34}H_{58}N_6U$: C, 51.7; H, 7.41; N, 10.7. Found: C, 51.7; H, 7.32; N, 10.7.

Method B. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of Me_3SiN_3. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(N_3)_2$ (**17**) were observed by ^{1}H NMR spectroscopy (100% conversion). Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**) or [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(py)$ (**8**) with 1 equiv of Me_3SiN_3 gave resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(N_3)_2$ (**17**) and resonances attributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiMe_3)(N_3)$ (**16**; ^{1}H NMR (C_6D_6): δ 18.6 (9H, $(CH_3)_3Si$), 5.6 (18H, $(CH_3)_3C$), −4.6 (18H, $(CH_3)_3C$), −11.7 (18H, $(CH_3)_3C$); the protons of the rings were not observed).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Pyridine-*N*-oxide. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added pyridine-*N*-oxide (2.0 mg, 0.02 mmol). The color of the solution immediately changed from brown-red to black, and resonances due to 2,3,5-$(Me_3C)_3C_5H_2)_2$[53] (^{1}H NMR (C_6D_6): δ 6.48 (4H, CH), 1.38 (36H, $(CH_3)_3C$), 1.01 (18H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy (100% conversion). (2,3,5-$(Me_3C)_3C_5H_2)_2$ can be isolated in 70% yield (0.33 g) from the reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 0.72 g, 1.0 mmol) and pyridine-*N*-oxide (0.10 g, 1 mmol) in pentane solution.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Ph_3PE (E = S, Se). NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added Ph_3PE (E = S, Se) (6 mg, 0.02 mmol). The color of the solution immediately changed from brown-red to black, and resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with SiF_4 or $BF_3(OEt_2)$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of SiF_4 or $BF_3(OEt_2)$. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Me_3SiCF_3. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of Me_3SiCF_3. The color of the solution immediately changed from brown-red to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**; 60% conversion) and resonances due to other unidentified uranium containing compounds were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with $SiCl_4$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of $SiCl_4$. The color of the solution immediately changed from brown-red to orange-red, and resonances at-

(53) Sitzmann, H.; Wolmershäuser, G. *Chem. Ber.* **1994**, *127*, 1335.

tributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiCl_3)(Cl)$ (^{1}H NMR (C_6D_6): δ 14.6 (18 H, $(CH_3)_3C$), −5.1 (18H, $(CH_3)_3C$), −14.8 (18H, $(CH_3)_3C$; the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 day, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**) was 30% complete, and after 4 days, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**) was complete.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with $SiBr_4$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of $SiBr_4$. The color of the solution immediately changed from brown-red to orange-red, and resonances attributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiBr_3)(Br)$ (^{1}H NMR (C_6D_6): δ 15.6 (18H, $(CH_3)_3C$), −4.7 (18H, $(CH_3)_3C$), −14.8 (18H, $(CH_3)_3C$; the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was maintained at 65 °C and monitored periodically by ^{1}H NMR spectroscopy. After 1 day, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UBr_2$ (**2**) was 20% complete, and after 10 days, conversion to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UBr_2$ (**2**) was complete.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with SiI_4. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of SiI_4. The color of the solution immediately changed from brown-red to orange-red, and resonances attributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(OSiI_3)(I)$ (^{1}H NMR (C_6D_6): δ 15.4 (18H, $(CH_3)_3C$), −3.3 (18H, $(CH_3)_3C$), −14.5 (18H, $(CH_3)_3C$); the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with C_6H_5Cl or C_6D_5Cl. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of C_6H_5Cl or C_6D_5Cl. The color of the solution immediately changed from brown-red to brown, and resonances due to $(Me_3C)_3C_5H_3$ and nine new resonances (^{1}H NMR (C_6D_6): δ 26.6 (9H, $(CH_3)_3C$), 23.4 (9H, $(CH_3)_3C$), 12.9 (9H, $(CH_3)_3C$), 1.6 (9H, $(CH_3)_3C$), −20.4 (9H, $(CH_3)_3C$), −25.5 (9H, $(CH_3)_3C$), −26.0 (9H, $(CH_3)_3C$), −28.0 (9H, $(CH_3)_3C$), −33.5 (9H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with C_6H_5Br. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of C_6H_5Br. The color of the solution immediately changed from brown-red to brown, and resonances due to $(Me_3C)_3C_5H_3$ and nine new resonances (^{1}H NMR (C_6D_6): δ 28.2 (9H, $(CH_3)_3C$), 22.5 (9H, $(CH_3)_3C$), 16.7 (9H, $(CH_3)_3C$), 4.3 (9H, $(CH_3)_3C$), −19.9 (9H, $(CH_3)_3C$), −27.8 (9H, $(CH_3)_3C$), −28.6 (9H, $(CH_3)_3C$), −29.6 (9H, $(CH_3)_3C$), −33.0 (9H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Me_3CCl or $(CD_3)_3CCl$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of Me_3CCl or $(CD_3)_3CCl$. The color of the solution immediately changed from brown-red to brown, and resonances due to $(Me_3C)_3C_5H_3$, $Me_2C{=}CH_2$ (^{1}H NMR (C_6D_6): δ 4.74 (s, 2H, CH_2), 1.58 (s, 6H, CH_3)),[54] and new nine resonances (^{1}H NMR (C_6D_6): δ 26.6 (9H, $(CH_3)_3C$), 23.4 (9H, $(CH_3)_3C$), 12.9 (9H, $(CH_3)_3C$), 1.6 (9H, $(CH_3)_3C$), −20.4 (9H, $(CH_3)_3C$), −25.5 (9H, $(CH_3)_3C$), −26.0 (9H, $(CH_3)_3C$), −28.0 (9H, $(CH_3)_3C$), −33.5 (9H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy. After 1 day at 65 °C or 10 days at room temperature, the nine resonances disappeared, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (**1**) were observed (30% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with AgF. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of AgF. The color of the solution immediately changed from brown-red to orange-red, and resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ along with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with AgCl. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of AgCl. The color of the solution immediately changed from brown-red to brown, and resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ and new nine resonances (^{1}H NMR (C_6D_6): δ 26.6 (9H, $(CH_3)_3C$), 23.4 (9H, $(CH_3)_3C$), 12.9 (9H, $(CH_3)_3C$), 1.6 (9H, $(CH_3)_3C$), −20.4 (9H, $(CH_3)_3C$), −25.5 (9H, $(CH_3)_3C$), −26.0 (9H, $(CH_3)_3C$), −28.0 (9H, $(CH_3)_3C$), −33.5 (9H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy. After 1 day at 65 °C or 10 days at room temperature, the nine resonances disappeared, and only resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ were observed (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with AgBr. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of AgBr was added. The color of the solution immediately changed from brown-red to brown, and resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ and new nine resonances (^{1}H NMR (C_6D_6): δ 28.2 (9H, $(CH_3)_3C$), 22.5 (9H, $(CH_3)_3C$), 16.7 (9H, $(CH_3)_3C$), 4.3 (9H, $(CH_3)_3C$), −19.9 (9H, $(CH_3)_3C$), −27.8 (9H, $(CH_3)_3C$), −28.6 (9H, $(CH_3)_3C$), −29.6 (9H, $(CH_3)_3C$), −33.0 (9H, $(CH_3)_3C$)) were observed by ^{1}H NMR spectroscopy. This NMR sample was monitored periodically by ^{1}H NMR spectroscopy. After 1 day at 65 °C or 10 days at room temperature, the nine resonances disappeared, and only resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ were observed (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (4). NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$-UF_2 (**4**; 15 mg, 0.02 mmol). The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl_2$ (1). NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2$-UCl_2 (**1**; 15 mg, 0.02 mmol). The color of the solution immediately changed from brown-red to black. Resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UCl$ (^{1}H NMR (C_6D_6): δ −7.8 (36H, $v_{1/2}$ = 45 Hz, $(CH_3)_3C$), −24.9 (18H, $v_{1/2}$ = 45 Hz, $(CH_3)_3C$); protons of the rings were not observed),[44] (2,3,5-$(Me_3C)_3C_5H_2)_2$, and new nine resonances (^{1}H NMR (C_6D_6): δ 26.6 (9H, $(CH_3)_3C$), 23.4 (9H, $(CH_3)_3C$), 12.9 (9H, $(CH_3)_3C$), 1.6 (9H, $(CH_3)_3C$), −20.4 (9H, $(CH_3)_3C$), −25.5 (9H, $(CH_3)_3C$), −26.0 (9H, $(CH_3)_3C$), −28.0 (9H, $(CH_3)_3C$), −33.5 (9H, $(CH_3)_3C$)) were observed in the ^{1}H NMR spectrum. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Ph_3PO. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added Ph_3PO (6 mg, 0.02 mmol). The color of the solution

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immediately changed from brown-red to brown, and resonances attributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(OPPh_3)$ (^{1}H NMR (C_6D_6): δ 8.8 (36H, $(CH_3)_3C$), 5.4 (18H, $(CH_3)_3C$); the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). This compound was not isolated on a synthetic scale, since it is poorly soluble in nonpolar solvents, and it decomposes to $(Me_3C)_3C_5H_3$ in polar solvents.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Ph_2CO. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added Ph_2CO (4 mg, 0.02 mmol). The color of the solution immediately changed from brown-red to brown, and resonances attributable to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(O)(OCPh_2)$ (^{1}H NMR (C_6D_6): δ 26.2 (18H, $(CH_3)_3C$), −8.0 (36H, $(CH_3)_3C$); the protons of the rings were not observed) were observed by ^{1}H NMR spectroscopy (100% conversion). When the sample was heated at 65 °C and monitored periodically by ^{1}H NMR spectroscopy, decomposition to $(Me_3C)_3C_5H_3$ and other unidentified uranium containing compounds was observed.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with Amines or PhC≡CH. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of amine (NH_3, $MeNH_2$, Me_2NH, Me_3N) or PhC≡CH. The color of the solution immediately changed from brown-red to brown, and resonances due to $(Me_3C)_3C_5H_3$ and resonances due to other unidentified uranium-containing compounds were observed.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (10) with C_6H_5F, RC≡CR (R = Me, Ph, Me_3Si), H_2 or C_2H_4. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UO$ (**10**; 15 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of C_6H_5F, RC≡CR (R = Me, Ph, Me_3Si), H_2, or C_2H_4. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (7) with Me_3SiX (X = Cl, Br, I), Ph_3PE (E = O, S, Se), Diethyl Ether, Tetrahydrofuran, Pyridines, 4-$Me_2NC_5H_4N$, or PhCl. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (**7**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of Me_3SiX (X = Cl, Br, I), Ph_3PE (E = O, S, Se), diethyl ether, tetrahydrofuran, pyridines, 4-$Me_2NC_5H_4N$, or PhCl. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (7) with Pyridine-*N*-Oxide. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (**7**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added pyridine-*N*-oxide (2 mg, 0.02 mmol). The color of the solution immediately changed from dark brown to black, and resonances due to (2,3,5-$(Me_3C)_3C_5H_2)_2$ were observed by ^{1}H NMR spectroscopy (100% conversion).

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (7) with Me_3SiN_3. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (**7**; 16 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added an excess of Me_3SiN_3. Resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U(N_3)_2$ (**17**; 20% conversion) along with other unidentified uranium-containing compounds were observed by ^{1}H NMR spectroscopy. The sample was monitored periodically by ^{1}H NMR spectroscopy, and the spectrum did not show any change when heated at 65 °C for 3 days.

Reaction of [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(p-tolyl) (7) with SiF_4 or $BF_3(OEt_2)$. NMR Scale. To an NMR tube charged with [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2U$=N(*p*-tolyl) (**7**; 15 mg) and C_6D_6 (0.5 mL) was added an excess of SiF_4 or $BF_3(OEt_2)$. The color of the solution immediately changed from dark brown to orange-red, and resonances due to [η^5-1,2,4-$(Me_3C)_3C_5H_2]_2UF_2$ (**4**) were observed by ^{1}H NMR spectroscopy (100% conversion).

Crystallographic data were deposited with the Cambridge Crystallographic Data Centre; copies of the data (CCDC 262849-262856) can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Supporting Information Available: Crystallographic data, labeling diagrams, tables giving atomic positions and anisotropic thermal parameters, bond distances and angles, and least-squares planes for each structure. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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