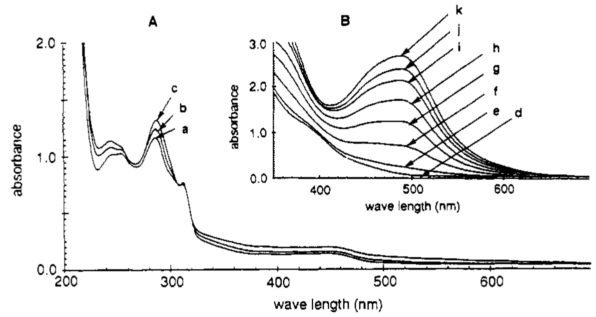

Figure 2. Electronic absorption spectra of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (5.50×10^{-5} mol/dm^3 (A) and 4.08×10^{-4} mol/dm^3 (B)) in CH_3CN in the presence of various concentrations of Bu_4NOH: 0 (a and d); 1.73 (b); 3.46 (c); 2.04 (e); 3.06 (f); 4.04 (g); 5.10 (h); 6.08 (i); 7.10 (j); 8.16 $\times 10^{-4}$ mol/dm^3 (k).

(trans to CO) distance, 2.10 (1) Å, is also close to the Ru–N2 (trans to NO_2) distance, 2.11 (1) Å. A distinct difference in electron-donor and/or -acceptor character of the carbonyl and nitro ligands of $[Ru(bpy)_2(CO)(NO_2)]^+$ was not observed from the comparison of bond lengths between Ru and bpy ligands.

Although two oxygen atoms of the nitro group of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ are disordered in the solid state, dissociation of NO_2^- from $[Ru(bpy)_2(CO)(NO_2)]^+$ may be neglected in a solution, since no ligand exchange between NO_2^- and $^{15}NO_2^-$ took place at all in the reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with 2 equiv of $Na^{15}NO_2$ in MeOH for 2 days.[7] The electronic absorption spectrum of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ showed no change between acidic (pH 1.0) and alkaline (pH 12.0) aqueous solutions. On the basis of smooth reactions of eqs 1 and 4 in H_2O, both the CO and NO_2^- of $[Ru(bpy)_2(CO)(NO_2)]^+$ are considered to be less reactive than the CO of $[Ru(bpy)_2(CO)_2]^{2+}$ and NO_2^- of $[Ru(bpy)_2Cl(NO_2)]$. It is well-known that basicity of OH^- is effectively enhanced in organic solvents compared with that in H_2O.[8] In fact, addition of a methanolic solution of Bu_4NOH (0.26 mol/dm^3) to a CH_3CN solution of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (0.055 mmol/dm^3) results in an increase in electronic absorption bands at 290 and 490 nm with an isosbestic point at 310 nm up to a certain concentration of OH^- (0.35 mmol/dm^3) (Figure 2), and neutralization of the resulting solution by aqueous $HClO_4$ (0.20 mol/dm^3) regenerated the electronic absorption spectrum of $[Ru(bpy)_2(CO)(NO_2)]^+$. However, an addition of a large excess of Bu_4NOH into a CH_3CN solution of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (0.102 mmol/dm^3) caused a decrease in the absorbance at the 490-nm band and an appearance of a new band at 585 nm, which remained even after neutralization by aqueous $HClO_4$. In accordance with these observations, a crude product obtained in the reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with 2 equiv of KOH in CH_3OH showed strong IR bands at 1650, 1378, and 1331 cm^{-1} assigned to $\nu(C{=}O)$ of a hydroxycarbonyl moiety,[9] $\nu_{as}(NO_2)$, and $\nu_s(NO_2)$, respectively, with a weak $\nu(C{\equiv}O)$ band at 1983 cm^{-1} due to a contamination of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ and neutralization of the product by aqueous HCl in MeOH regenerated $[Ru(bpy)_2(CO)(NO_2)]^+$. On the other hand, when $[Ru(bpy)_2(CO)(NO_2)]PF_6$ was allowed to react with 20 equiv of Bu_4NOH in MeOH, the reaction product exhibited only a strong band at 1574 cm^{-1} without any $\nu(NO_2)$ band. These observations suggest that $[Ru(bpy)_2(CO)(NO_2)]^+$ reversibly is converted into $[Ru(bpy)_2(C(O)OH)(NO_2)]$ in low OH^- concentrations in MeOH (eq 5),[10] while $[Ru(bpy)_2(CO)(NO_2)]^+$ decomposes in the presence of large excess of OH^- presumably by dissociation of NO_2^- from unstable $[Ru(bpy)_2(C(O)O)(NO_2)]^-$.

$$[Ru(bpy)_2(CO)(NO_2)]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(C(O)OH)(NO_2)] \quad (5)$$

Related to the $Ru{-}NO_2^-$ bond cleavage of $[Ru(bpy)_2(CO)(NO_2)]^+$ in the presence of a large excess of OH^- in MeOH, treatment of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with an excess amount of gaseous HCl or aqueous HCl (10 N) in CH_3OH caused loss of NO_2^- ligand, and $[Ru(bpy)_2(CO)Cl]PF_6$ was selectively formed in a ca. 80% yield. On the basis of the fact that $[Ru(bpy)_2(CO)(NO_2)]PF_6$ undergoes no substitution reaction by either $Na^{15}NO_2$ or Et_4NCl in MeOH, the formation of $[Ru(bpy)_2(CO)Cl]^+$ in the reaction of $[Ru(bpy)_2(CO)(NO_2)]^+$ with HCl may result from fission of the $Ru{-}NO_2^-$ bond after protonation of NO_2^- of $[Ru(bpy)_2(CO)(NO_2)]^+$ in MeOH. The present study reveals that CO of $[Ru(bpy)_2(CO)(NO_2)]^+$ undergoes a reversible nucleophilic attack of OH^- to form $[Ru(bpy)_2(C(O)OH)(NO_2)]$. However, not only deprotonation of $[Ru(bpy)_2(C(O)OH)(NO_2)]$ but also protonation of $[Ru(bpy)_2(CO)(NO_2)]^+$ result in the cleavage of the $Ru{-}NO_2^-$ bond.

Acknowledgment. We thank Professor Yoshihiko Kushi and Professor Shie-Ming Peng for their advice on X-ray crystal analysis.

Supplementary Material Available: Tables of atomic parameters with averaged thermal parameters and anisotropic thermal parameters (3 pages); tables of observed and calculated structure factor data (9 pages). Ordering information is given on any current masthead page.

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[7] The IR spectrum of the reaction mixture was consistent with summation of those of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ and $Na^{15}NO_2$.

[8] (a) Shaik, S. S. *J. Org. Chem.* **1987**, *52*, 1563. (b) Sawyer, D. T.; Roberts, J. L., Jr. *Acc. Chem. Res.* **1988**, *22*, 469. (c) Fukuzumi, S.; Yorisue, T. *J. Am. Chem. Soc.* **1991**, *113*, 7764.

[9] $[Ru(bpy)_2(CO)(C(O)OH)]^+$ shows a $\nu(C{=}O)$ at 1578 cm^{-1}.[3]

[10] The occurrence of eq 5 may be supported also by a reversible reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with CH_3ONa in CH_3OH affording $Ru(bpy)_2(C(O)OCH_3)(NO_2)$ ($\nu(C{=}O)$ 1574 cm^{-1}).

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Synthesis, Characterization, and X-ray Structure of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

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In continuing our studies of uranium in the trivalent oxidation state, we have discovered $UI_3(THF)_4$ to be a convenient precursor to U(III) coordination and organometallic complexes,[2] owing to its clean metathesis reactions with potassium and sodium salts of a variety of alkoxide, amide, cyclopentadienyl, and pentadienyl ligands. In contrast to the relatively clean products obtained by metathesis with dialkylamides,[2] treatment of $UI_3(THF)_4$ with 3 equiv of the potassium salt of 2,6-diisopropylaniline (NH_2Ar) yields intractable products. The nature of the products formed in these 3:1 reactions of potassium monoalkyl amides are still under investigation. We have determined, however, that the reaction of $UI_3(THF)_4$ with excess potassium 2,6-diisopropylanilide cleanly gives the brown crystalline title complex, as shown in eq 1.

$$UI_3(THF)_4 + {\geq}5KNHAr \rightarrow \{[K(THF)_2]_2[U(NHAr)_5]\}\cdot THF + 3KI \quad (1)$$

Lithium and sodium complex salts of the actinides are well-known; their formation pervades metathesis reactions of 4f- and 5f-element compounds.[3] Formation of "ate" complexes from

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[1] (a) California Institute of Technology. (b) Los Alamos.

[2] (a) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (b) Clark, D. L.; Watkin, J. G.; Sattelberger, A. P.; Schake, A. R.; Avens, L. R.; Burns, C. J. Manuscript in preparation.

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Table I. Crystallographic Data for $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

temp, °C	−70	chem formula	$UK_2O_5N_5C_{80}H_{130}$
space group	$P2_1/c$	fw	1558.19
a, Å	21.726 (7)	ρ_{calcd}, g cm^{-3}	1.289
b, Å	15.378 (6)	μ, cm^{-1}	20.68
c, Å	25.007 (8)	λ(Mo Kα radiation), Å	0.709 26
β, deg	106.07 (4)	min/max transm	0.86
V, Å^3	8028 (10)	$R(F_o)$	0.083
Z	4	$R_w(F_o)^a$	0.092

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$ where $w = 1/\sigma^2(F_o) = 4F_o^2/\{\sigma^2(I) + (pF_o^2)\}$.

potassium reagents is unusual, however,[4] and we have observed only neutral complex formation in other metathesis reactions of $UI_3(THF)_4$ with potassium salts.[2] We describe here the X-ray structure of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ and some of its physical properties.

Experimental Section

General Procedures and Techniques. The majority of starting materials and products are moisture- and oxygen-sensitive. All manipulations were therefore carried out under an inert atmosphere using standard Schlenk or glovebox techniques. Toluene, hexane, and tetrahydrofuran were distilled from NaK alloy under nitrogen. Toluene-d_8 and THF-d_8 were degassed, dried, and stored over NaK alloy. Potassium hydride was purchased from Aldrich as a 60% dispersion in mineral oil and vacuum-filtered on a coarse-porosity frit. The resulting solid was washed with hexane and dried in vacuo to yield a white, pyrophoric powder. 2,6-Diisopropylaniline (NH_2Ar) was obtained from Aldrich (90%) and distilled and stored under N_2 prior to use. Potassium 2,6-diisopropylanilide (KNHAr) was prepared by slow addition of a slight excess of 2,6-diisopropylaniline to a toluene suspension of KH and allowed to stir for 12 h. The gelatinous product was collected by vacuum filtration on a medium-porosity frit, washed with hexane until the washings were colorless, and dried in vacuo. $UI_3(THF)_4$ was prepared as previously reported.[2]

NMR spectra were recorded at 22 °C on a Bruker WM 300 or an IBM Instruments Corp. AM 250 spectrometer in dry and oxygen-free toluene-d_8 or THF-d_8. All ^1H NMR chemical shifts are reported in ppm (δ) relative to the ^1H impurity in toluene-d_8 set at 2.09 ppm or THF-d_8 set at 1.73 ppm. Infrared spectra were recorded on a Bio-Rad Digilab FTS 40 spectrophotometer as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer utilizing sealed tin capsules for sample delivery. Electronic absorption spectra were recorded on a Perkin-Elmer Lamba 9 UV-vis-NIR spectrophotometer, and extinction coefficients were measured from the baseline.

Syntheses of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$. A 5.04-g (5.56-mmol) sample of royal blue $UI_3(THF)_4$ was placed in a 125-mL flask equipped with a magnetic stirbar. Approximately 50 mL of THF was added, and the solution was stirred until all of the solid dissolved. Potassium 2,6-diisopropylanilide (KNHAr, 7.30 g, 33.8 mmol) was added slowly to the $UI_3(THF)_4$ solution with stirring over a period of 10 min. The reaction proceeds smoothly with the immediate formation of a dark-brown solution along with the precipitation of some white and gray solids. After stirring for 24 h under inert atmosphere, the solution was vacuum-filtered through Celite on a medium-porosity frit. The Celite pad and frit were washed with THF until the filtrate was colorless. THF was then removed in vacuo from the combined filtrate to provide a brown microcrystalline product. The product was extracted into 100 mL of toluene and filtered through Celite on a medium-porosity frit and similarly washed. Toluene was then removed in vacuo to afford 5.04 g (3.23 mmol, 58% yield) of a brown microcrystalline solid. An analytical sample was recrystallized from THF/hexane. Anal. Calcd for $UK_2N_5O_5C_{80}H_{130}$: C, 61.67; H, 8.41; N, 4.49. Found: C, 62.45; H, 8.54; N, 4.56. ^1H NMR data (THF-d_8, 22 °C): δ 5.61 (10 H, C*H*Me$_2$), 4.78 (10 H, meta), 1.12 (5 H, para), −5.49 (60 H, CH*Me*$_2$). IR (cm^{-1}): 3272 (vw), 1400 (s), 1379 (s), 1357 (m), 1328 (s), 1253 (s, br), 1215 (m), 1169 (w), 1150 (m), 1138 (m), 1111 (m), 1054 (s), 1041 (m), 906 (s), 884 (s), 838 (s), 744 (s), 624 (w), 538 (m). UV-vis-NIR absorption spectrum in THF solution [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 239 (46 680), 290 (29 720), 320s (11 230), 623 (44), 661 (36), 688 (31), 750 (31), 888 (55), 1015 (40), 1047 (44), 1107 (81), 1145 (65), 1190 (59), 1307 (43), 1456 (45), 1557 (35).

Table II. Selected Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] for $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

atom	x	y	z	B, Å^2
U	0.25044 (5)	−0.0034 (1)	0.20019 (4)	2.40 (2)[a]
K(1)	0.0893 (3)	−0.2674 (5)	0.1616 (3)	4.3 (2)[a]
K(2)	0.3572 (3)	0.2328 (5)	0.1134 (3)	4.0 (2)[a]
N(1)	0.2900 (8)	−0.002 (2)	0.2975 (6)	2.7 (4)
N(2)	0.3548 (9)	0.014 (2)	0.1957 (8)	4.2 (5)
N(3)	0.242 (1)	−0.121 (1)	0.1370 (8)	2.7 (5)
N(4)	0.156 (1)	−0.044 (1)	0.2233 (8)	3.0 (5)
N(5)	0.213 (1)	0.122 (2)	0.156 (1)	5.0 (7)
O(1)	−0.006 (1)	−0.331 (2)	0.0751 (9)	6.9 (6)
O(2)	0.388 (1)	0.245 (2)	0.0195 (9)	6.9 (6)
O(3)	0.062 (1)	−0.394 (2)	0.2292 (8)	6.5 (6)
O(4)	0.402 (1)	0.401 (2)	0.1385 (9)	7.6 (7)
O(5)	0.297 (2)	0.528 (3)	0.397 (1)	17 (1)

[a] Refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Structural Determination. Crystallographic data are summarized in Table I. Single crystals of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ were grown by layering a saturated THF solution with hexane and slowly cooling to −40 °C. Most crystals mounted for inspection fractured easily, and the compound appeared to lose solvent from the lattice at room temperature in the X-ray beam, necessitating low-temperature data collection. This resulted in some broadening of the Bragg reflections however, limiting the quality of the data acquired. A single crystal measuring 0.21- × 0.31- × 0.45-mm was mounted on a glass fiber and transferred directly to the cold stream of an Enraf-Nonius CAD4 automated diffractometer operating at −70 °C. Cell constants and the orientation matrix were determined from the setting angles of 25 reflections with $12° < 2\theta < 30°$. The data were collected by utilizing Mo Kα radiation. Examination of the systematic absences uniquely identified the space group as $P2_1/c$. A semiempirical absorption correction was applied to the data on the basis of the average relative intensity curve of azimuthal scans. The structure was solved by a combination of Patterson and difference Fourier methods.[5] The uranium and potassium atoms were refined anisotropically; all other atoms were refined with isotropic thermal parameters. The difference Fourier map revealed a THF of solvation present in the lattice. The positional and thermal parameters of this molecule were refined but tended to oscillate, leading to relatively large shifts in the final least-squares cycle. The Δ/σ values for all other atoms were less that 0.1 in the final refinement. Selected positional and equivalent thermal parameters are given in Table II.

Results and Discussion

In the solid state, $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ is monomeric, with five nitrogen atoms of the amide ligands coordinated to uranium in an approximately trigonal-bipyramidal geometry. An ORTEP drawing of the molecule is shown in Figure 1. The uranium atom lies within the plane formed by the equatorial amide nitrogen atoms to within 0.006 (1) Å. Each potassium cation interacts with the arene ring of one equatorial and one axial amide ligand, increasing the angle subtended by these ligands (N(2)–U–N(5) = 95.9 (9)°, N(3)–U–N(4) = 92.9 (7)°), as well as decreasing the angle formed by the axial ligands (N(2)–U–N(4) = 166.0 (7)°). In addition, each potassium is also coordinated by two tetrahydrofuran molecules.

The U–N bond distances (Table III) vary from 2.26 (3) to 2.38 (2) Å, with an average value of 2.34 Å. The trigonal-bipyramidal coordination geometry about the uranium center is similar to that

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(5) All calculations were performed on a MicroVax local area network utilizing Enraf-Nonius SDP software and all physical constants tabulated therein.

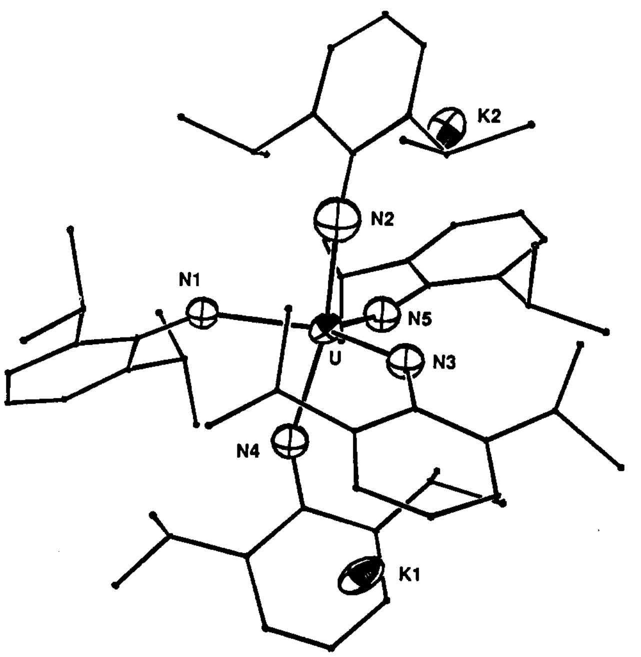

Figure 1. ORTEP drawing of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ emphasizing the trigonal-bipyramidal coordination geometry about uranium and showing selected atom labeling.

found in the U(IV) alkoxide complex $[Li(THF)_4][U(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]$,[6] which possesses an average U–O bond distance of 2.17 (2) Å. These uranium–ligand bond lengths are comparable when corrected for the 0.13–0.15-Å increase of ionic radius in U(III) with respect to U(IV).[7] The average of U–N bond length is also similar to that determined for $U[N(SiMe_3)_3]$ (2.320 (4) Å).[8] The U–N–C angles range from 141 (2) to 156 (2)°, with an average value of 149 (2)°. Although the protons on the primary amides were not located in the final difference Fourier map, the values of these angles preclude identification of these ligands as imido groups, which typically display near-linear U–N–C angles.[9]

In many structurally characterized "ate" complexes,[3,4] the alkali-metal cation does not interact with the anion but is complexed by neutral oxygen or nitrogen donor atoms ligands. In other members of this class, the alkali-metal cation coordinates to a halide ligand or to the heteroatom of the amide or alkoxide functional group. A striking feature of the solid-state structure of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ is that the potassium counterions interact with the aryl rings of the amido ligands, rather than the nitrogen atoms. Each potassium cation displays close contacts with all six carbons of one aryl ring (η^6-coordination) and four carbon atoms of a second ring (η^4-coordination). The potassium–carbon distances range from 3.06 (3) to 3.38 (3) Å, with an average value of 3.22 (3) Å. All other potassium–carbon contact distances are longer than 3.5 Å (the mean distance of the potassium ions from the aryl planes is 2.915 (7) Å). These η^6–π interactions are rare in alkali-metal arene complexes.[10] The average K–C distance of 3.22 Å can be compared to the average η^6-arene K–C distances found in $K[Al_7O_6Me_{16}]\cdot C_6H_6$ (3.33 Å),[11] $K[AlMe_3NO_3]\cdot C_6H_6$ (3.38 Å),[12] and $[K(db\text{-}18\text{-}c\text{-}6)][Al_2Me_6Cl]\cdot 2C_6H_6$ (3.39 Å).[13]

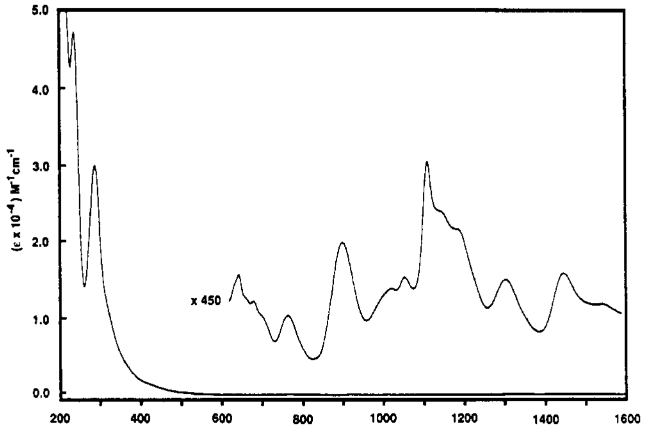

Figure 2. UV–vis–NIR absorption spectrum of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ in THF solution at 25 °C.

$\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ is exceedingly air- and moisture-sensitive. It is soluble in THF and very soluble in toluene, yielding solutions which range in color from pale yellow to dark brown, depending on concentration. The room-temperature ^1H NMR spectrum in toluene-d_8 shows only broad resonances consistent with THF involved in a dynamic exchange process between free and coordinated THF. In trivalent uranium chemistry, we typically observe coordinated THF resonances at high field. For example, in $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(THF)$, the resonances for the coordinated THF appear at δ −18.4 and −44.6.[14] Cooling the toluene-d_8 sample to 225 K yields an extremely complex spectrum, presumably due to the low symmetry associated with tight ion-pairing in the hydrocarbon solvent. In contrast, the spectrum of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ obtained in THF-d_8 displays resonances consistent with a single type of aryl group, indicating a fluxional process which equilibrates axial and equatorial ligands. Upon cooling, the anilide ligand resonances coalesce into the baseline at ca. 180 K.

The room-temperature electronic absorption spectrum of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ recorded in THF solution from 1600 to 200 nm is shown in Figure 2. The absorption spectrum shows a manifold of weak (ϵ = 30–80 $M^{-1}\ cm^{-1}$) absorption bands in the near IR region, and three intense (ϵ = 11 000–47 000 $M^{-1}\ cm^{-1}$) absorption bands in the ultraviolet region. The position and weak intensity of the absorption features between 1600 and 600 nm are consistent with Laporte-forbidden f → f transitions of the uranium(III) center. The band maxima show a striking similarity to other U(III) inorganic (e.g., $UI_3(THF)_4$)[15] and organometallic (e.g., Cp_3UOEt_2)[16] complexes, as well as the U(III) aquo ion stabilized in perchloric acid.[17] Thus the f → f bands in the spectrum of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}$ serves as an electronic "fingerprint" for trivalent uranium, in support of its assignment as a pentacoordinate U(III) amido complex anion. A shoulder at 320 nm (ϵ = 11 230 $M^{-1}\ cm^{-1}$) is difficult to see in Figure 2 but becomes obvious upon spectrum expansion. This band is tentatively assigned as an f → d transition. The intensities of the bands at 290 nm (ϵ = 29 700 $M^{-1}\ cm^{-1}$) and 239 nm (ϵ = 46 700 $M^{-1}\ cm^{-1}$) are indicative of fully-allowed charge-transfer excitations. With five arene chromophores in the complex, the 239-nm absorption feature is assigned to the arene $\pi \rightarrow \pi^*$

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Table III. Selected Bond Distances (Å) and Angles (deg) for $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

U–N(1)	2.35 (1)	U–N(2)	2.32 (2)
U–N(3)	2.38 (2)	U–N(4)	2.37 (2)
U–N(5)	2.26 (3)		
K(1)–O(1)	2.72 (2)	K(1)–O(3)	2.72 (2)
K(2)–O(2)	2.62 (2)	K(2)–O(4)	2.78 (3)
K(1)–C(31)	3.38 (3)	K(1)–C(32)	3.15 (3)
K(1)–C(33)	3.06 (3)	K(1)–C(34)	3.24 (3)
K(1)–C(41)	3.14 (3)	K(1)–C(42)	3.06 (3)
K(1)–C(43)	3.11 (3)	K(1)–C(44)	3.24 (3)
K(1)–C(45)	3.30 (3)	K(1)–C(46)	3.34 (3)
K(2)–C(21)	3.29 (3)	K(2)–C(24)	3.30 (3)
K(2)–C(25)	3.09 (3)	K(2)–C(26)	3.11 (3)
K(2)–C(51)	3.26 (3)	K(2)–C(52)	3.38 (3)
K(2)–C(53)	3.34 (3)	K(2)–C(54)	3.21 (3)
K(2)–C(55)	3.15 (2)	K(2)–C(56)	3.22 (3)
N(1)–U–N(2)	88.1 (6)	N(1)–U–N(3)	129.4 (9)
N(1)–U–N(4)	80.9 (6)	N(1)–U–N(5)	118.3 (9)
N(2)–U–N(3)	87.2 (8)	N(2)–U–N(4)	166.0 (7)
N(2)–U–N(5)	95.9 (9)	N(3)–U–N(4)	92.9 (7)
N(3)–U–N(5)	112.3 (8)	N(4)–U–N(5)	97.1 (9)
U–N(1)–C(11)	148 (1)	U–N(2)–C(21)	156 (2)
U–N(3)–C(31)	141 (2)	U–N(4)–C(41)	152 (2)
U–N(5)–C(51)	149 (2)		

(benzenoid B-band) transition in the anilide ligand. The 290-nm band is assigned to a nitrogen-to-uranium ligand-to-metal charge-transfer (LMCT) excitation.

The infrared spectrum (4000–450 cm^{-1}) shows a weak, broad feature at 3300 cm^{-1}, which we assign as the N–H stretch. A strong band at 1583 cm^{-1} is assigned to the C=C aromatic stretch, and the vibrations at 744 and 684 cm^{-1} are consistent with C–H out of plane bending modes expected for a 1,2,3-trisubstituted arene ring. In addition, infrared absorption bands indicative of coordinated (1041, 884, 838 cm^{-1}) and nonligated (1054, 906 cm^{-1}) THF are observed.[18]

In summary, $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$ has been prepared by metathesis of $UI_3(THF)_4$ with potassium 2,6-diisopropylanilide in THF and structurally characterized. It is our expectation that complexes of the type $\{[K(THF)_2]_2[U(NH\text{-}Ar)_5]\}$ will be useful precursors for further explorations of low- and high-valent uranium chemistry.

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Supplementary Material Available: Tables of crystallographic data, fractional coordinates, bond distances, bond angles, and anisotropic thermal parameters and figures of atomic numbering schemes for uranium and potassium coordination environments (13 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Technetium Complexes of Tripodal Oxygen Donor Ligands

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Recently, complexes containing the $Re^{VII}O_3^+$ moiety and the monoanionic, tridentate oxygen donor ligand $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$ (Figure 1, R is methyl or ethyl) have been synthesized.[1] There is current interest in rhenium and technetium $M^{VII}O_3^+$ complexes because of their scarceness[1-5] and the ability of $Tc^{VII}O_3^+$ complexes to oxidize olefins to diolates.[3-5] Details of the characterization and synthesis of the only reported technetium complex of this ligand, $[((\eta^5\text{-}C_5H_5)Co(P(OMe)_2{=}O)_3)TcO_3]$, are scant.[1] Because of these reasons, and the ability to alter the solubility properties of $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$ and its resulting metal complexes,[6] we have prepared several new, high oxidation state technetium complexes of $[(\eta^5\text{-}C_5H_5)Co(P(OR)_2{=}O)_3]^-$, where R is ethyl or butyl. The known complex (R is methyl) has been prepared here for comparison.

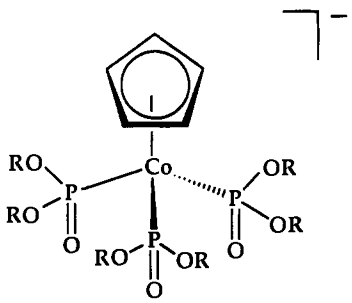

Figure 1. Ligand (L_{OR}) used in this study (R is methyl, ethyl, and butyl).

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 292 keV, $t_{1/2}$ = 2.12 × 10^5 years). All experiments have been done in laboratories approved for low-level radioactive materials following precautions detailed elsewhere.[7]

Ammonium pertechnetate was obtained as a gift from Du Pont/Biomedical Products. Solvents and reagents were used as received unless otherwise indicated. Methylene chloride was distilled over calcium hydride. Tetrahydrofuran was distilled over sodium metal and benzophenone. Pentane and octane were washed with sulfuric acid/nitric acid and water and were distilled over calcium chloride. The ligands, sodium (cyclopentadienyl)tris(diethyl phosphito)cobaltate, $Na(L_{OEt})$,[8] sodium (cyclopentadienyl)tris(dimethylphosphito)cobaltate, $Na(L_{OMe})$,[8] and sodium (cyclopentadienyl)tris(dibutylphosphito)cobaltate, $Na(L_{OBu})$,[9] were prepared by published procedures. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fast atom bombardment mass spectra (FABMS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun that produced a beam of 6–8-keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. Infrared spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer. NMR spectra were run on a Varian XL 300-MHz instrument SEP-PAK C_{18} cartridges were obtained from Waters Associates.

Preparation of ((Cyclopentadienyl)tris(diethyl phosphito)cobaltato)oxodichlorotechnetium(V), $[(L_{OEt})TcOCl_2]$. To 0.45 mL of a 0.22 M aqueous solution of $(NH_4)[TcO_4]$ (0.1 mmol) were added 1 mL of methanol, $Na(L_{OEt})$ (73.41 mg, 0.13 mmol), and 1 mL of concentrated HCl. The orange solution was refluxed for 2.5 h, during which time it became yellow-green, and a yellow-green solid precipitated. The mixture was stored at −20 °C overnight and was filtered onto a fritted glass funnel. A yellow-green solid was collected (40.12 mg), washed with water, and dried overnight in vacuo. A second crop precipitated from

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