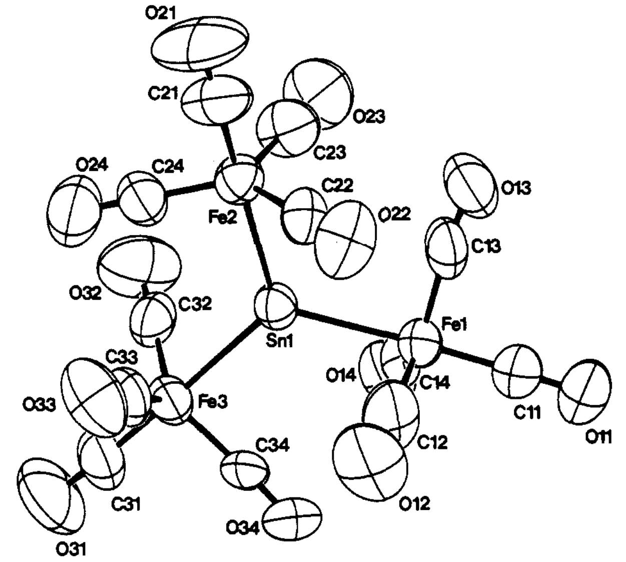

Figure 1. ORTEP diagram of one independent $[Sn\{Fe(CO)_4\}_3]^{2-}$ anion.

chloride or lead(II) acetate (eq 1; E = Sn, Pb), respectively, or upon exposure of $[Et_4N]_2[E\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ to pressures of CO gas (eq 2).[12,13]

$$2E^{2+} + 3[HFe(CO)_4]^- + 3OH^- \rightarrow E^0 + [E\{Fe(CO)_4\}_3]^{2-} + 3H_2O \quad (1)$$

$$[E\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]^{2-} + CO \rightarrow [E\{Fe(CO)_4\}_3]^{2-} + Fe(CO)_5 \quad (2)$$

X-ray analysis shows **1** and **2** to be isomorphous. The asymmetric unit consists of four disordered $[Et_4N]^+$ cations and two $[E\{Fe(CO)_4\}_3]^{2-}$ anions, with trigonal-planar main-group atoms coordinated to three essentially equivalent (noncrystallographically) trigonal-bipyramidal $[Fe(CO)_4]$ groups. The $[Sn\{Fe(CO)_4\}_3]^{2-}$ dianion is shown in Figure 1. The E atoms occupy axial positions on the metals. The mean deviation from planarity does not exceed 0.022 Å (Sn) or 0.020 Å (Pb) for either molecule in the asymmetric unit. The average E-Fe bond length, for both molecules in the asymmetric unit, is 2.548 (7) Å for Sn and 2.624 (4) Å for Pb. In comparison, the Pb-Fe(CO)$_4$ linkages in $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ have an average Pb-Fe distance of 2.655 (6) Å.[13] The Fe-C distances for **1** and **2** range from 1.67 (3) to 1.78 (3) Å and from 1.66 (3) to 1.88 (5) Å, respectively. No iron-iron bonds are observed for **1** or **2**.

Discussion

Formally, the main-group atom can be considered as a 4+ ion bonded to three two-electron-donor $Fe(CO)_4^{2-}$ groups, resulting in an E atom with six electrons, less than a filled octet. This electron deficiency might be removed through localized multiple bonding as in the group IV complexes $[(\mu_3\text{-}E)\{(\eta^5\text{-}C_5H_4R)Mn(CO)_2\}_3]$ (E = Ge,[6] Sn,[7] Pb;[8] R = H, CH$_3$), where one localized main-group/manganese double bond is observed. On the other hand, the extra electrons necessary to complete the octet around the main-group atom may be obtained from delocalized multiple bonds as in the transition-metal complexes $[NH_4]_4[Ir_3N(SO_4)_6(H_2O)_3]$[16] $[(\mu_3\text{-}As)\{[Cr(CO)_5]_2[Mn(CO)_5]\}]$,[5] $[(\mu_3\text{-}As)\{[Cr_2(CO)_9][Mn(CO)_5]\}]$,[5] $[Na(THF)_2][Sb\{Cr(CO)_5\}_3]$,[5] and $Te\{MnCp(CO)_2\}_3$.[17] Several observations, however, suggest that **1** and **2** do not have multiple bonding. In both **1** and **2**, the E-Fe bond distances are equivalent and the angles around the central lead are nearly the same; thus, unquestionably no localized double bond is present. In **2**, the Pb-Fe bond lengths are shortened as compared to the Pb-Fe(CO)$_4$ distances in the electron-sufficient $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$; however, this shortening is not as dramatic as that seen for some of the other main-group-transition-metal compounds where multiple bonding is invoked.[7] The longer Pb-Fe$_2$(CO)$_8$ linkages (2.832 (4) and 2.823 (4) Å) in $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ are believed to result from the steric repulsions of the Fe(CO)$_4$ groups. This idea is supported by the shorter Pb-Fe$_2$(CO)$_8$ distances seen in $Pb[Fe_2(CO)_8]_2$ (2.606 (3) to 2.634 (5) Å). The Sn-Fe bond distances in **1** compare favorably with the average Sn-Fe single-bond distances in $Sn[Fe_2(CO)_8]_2$[18] (2.54 Å) and $Fe_3(CO)_9\{\mu_3\text{-}SnFe(CO)_2Cp\}_2$[19] (2.537 (4) Å). Since the symmetry of the Fe(CO)$_4$ group is C_{3v} with Sn(IV) or Pb(IV) occupying an axial site, the E atoms are not in the expected positions for maximizing multiple-bonding interactions. The equatorial positions on trigonal-bipyramidal Fe(CO)$_4$ would be preferred over the axial positions for the strongest π-interactions.[20] The E-Fe bond lengths in **1** and **2** may also be due to steric interactions of the Fe(CO)$_4$ groups; crowding is evident in molecular models of these compounds.

As with a number of other main-group/transition-metal carbonyl complexes, one notes that several of the Pb-Fe- and Sn-Fe-equatorial CO angles are slightly tilted toward the main-group atom ($\angle$E-Fe-C(eq) range: **1**, 80.5 (8)-89.0 (7)°; **2**, 81 (1)-90 (1)°), so the electron deficiency at tin or lead may be lessened by donation from the π-clouds of the CO groups.

It is interesting to note that the anions adopt the planar geometries described and not equally probable pyramidal structures containing one Fe-Fe bond and a lone pair of electrons on the main-group element. Such forms may be interconverting in solution. Investigations into the reactivity of **1** and **2** are continuing.

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Supplementary Material Available: For **1** and **2**, crystallographic details, complete tables of crystal, data collection, and refinement parameters, bond distances and angles, positional parameters, and anisotropic thermal parameters, and ORTEP diagrams of both anions (35 pages); structure factor tables (57 pages). Ordering information is given on any current masthead page.

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Uranium Alkoxide Chemistry. 3. *tert*-Butyl Isocyanide Adducts of Tris(2,6-di-*tert*-butylphenoxy)uranium(III)[1]

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We recently reported the preparation and characterization of the first uranium(III) phenoxide complex, $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$ (**1**).[2] This uranium(III) compound is unusual because its coordination number is 3[3,4] and because the sterically demanding

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(4) (a) The only other well-characterized UX$_3$ compounds, where X is a monodentate ligand, are $U[N(SiMe_3)_2]_3$[4b] and $U[CH(SiMe_3)_2]_3$.[4c] (b) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507. (c) Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. *Organometallics* **1989**, *8*, 855.

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phenoxide ligands impart remarkable kinetic stability to the coordinatively unsaturated uranium center. Previously, we noted that **1** reacts with the Lewis bases THF, EtCN, and Ph_3PO to form pseudotetrahedral adducts $LU(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$.[2] In this paper we describe the solution reactions of **1** with *tert*-butyl isocyanide, a sterically unencumbered ligand that forms both 1:1 and 1:2 adducts in solution with the related cerium(III) complex, $Ce(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$.[5] Sen and co-workers have isolated and structurally characterized the 1:2 complex $Ce(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(CN\text{-}t\text{-}Bu)_2$. The latter has a distorted-trigonal-bipyramidal structure, with one isonitrile in an axial site and the other in an equatorial site.[5]

Experimental Section

General Information. Manipulations of air-sensitive solids and solutions were performed within the confines of a helium-filled Vacuum Atmospheres glovebox, equipped with a high-capacity (MO-40-2H) Dri-Train purification system. Compound **1** was prepared from $U[N(SiMe_3)_2]_3$[4] and 3 equiv of $HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ according to the published procedure.[2] *tert*-Butyl isocyanide was purchased from Aldrich, degassed with several freeze-pump-thaw cycles, and stored over activated 3-Å molecular sieves. Deuterated solvents were degassed with several freeze-pump-thaw cycles and then stored over sodium amalgam. Proton NMR spectra were obtained on an IBM AF-250 instrument. Chemical shifts are reported in ppm, referenced to the ^1H impurity in benzene-d_6 (δ 7.15) or the methyl ^1H impurity in toluene-d_8 (δ 2.09). Temperature calibration for the variable-temperature experiments was obtained with use of MeOH (195–295 K) or ethylene glycol (>295 K).[6] Room-temperature infrared spectra were obtained in hexane solution by using a 0.1 cm NaCl liquid cell or as Nujol mulls between KBr plates on a Digilab FTS-40 infrared spectrometer.

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(CN\text{-}t\text{-}Bu)$ (2). Compound **2** was prepared by adding 33 μL (2.92×10^{-4} mol) of *t*-BuNC to 250 mg (2.93×10^{-4} mol) of **1** dissolved in 30 mL of hexane. After being stirred for 0.5 h, the royal blue solution was evaporated to dryness in vacuo and a dark blue microcrystalline solid was isolated. Anal. Calcd for $C_{47}H_{72}NO_3U$: C, 60.24; H, 7.74; N, 1.49. Found: C, 59.99; H, 7.60; N, 1.40. IR (KBr, cm^{-1}): 2177 (m), 1581 (mw), 1405 (vs), 1352 (m), 1260 (m), 1231 (vs), 1194 (ms), 1127 (mw), 1119 (mw), 1101 (m), 882 (mw), 861 (vs), 819 (ms), 796 (w), 748 (s), 651 (s).

$U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(CN\text{-}t\text{-}Bu)_2$ (3). Compound **3** was prepared by adding a large excess ($\geq$10 equiv) of *t*-BuNC to 250 mg (2.93×10^{-4} mol) of **1** dissolved in 30 mL of hexane. Concentration of the dark blue-green solution to ca. 5 mL and cooling to −40 °C gave dark green **3**, which was isolated (ca. 40% yield) by filtration and brief drying in vacuo. **3** readily loses *t*-BuNC under dynamic vacuum; elemental analyses were not obtained. IR (KBr, cm^{-1}): 2163 (m), 1587 (mw), 1401 (vs), 1261 (m), 1235 (ms), 1195 (s), 1121 (ms), 1099 (m), 882 (w), 857 (s), 814 (s), 790 (mw), 748 (s), 724 (mw), 696 (w), 645 (ms), 539 (mw), 522 (w), 443 (mw).

NMR Titrations. Approximately 50 mg (5.9×10^{-5} mol) of **1** was dissolved in ca. 2 mL of benzene-d_6, and the solution was placed in a 5-mm NMR tube fitted with a septum cap. The purity of the sample was then verified by proton NMR. The tube was returned to the glovebox, and with a microliter syringe, a measured quantity of *t*-BuNC was introduced through the septum. Subsequent spectra were obtained in a similar manner.

Solution IR Experiments. All spectra were recorded relative to a reference spectrum of pure hexane. Approximately 50 mg (5.9×10^{-5} mol) of **1** was dissolved in 5 mL of hexane, and 3.5 μL (3.09×10^{-5} mol) of *t*-BuNC was added, yielding a royal blue solution. The latter was placed in the IR cell, and a spectrum was recorded. The cell was returned to the glovebox and 13.4 μL (2.36×10^{-4} mol) of *t*-BuNC was added, generating a dark blue-green solution. The IR spectrum of this solution was recorded.

Results and Discussion

A series of room-temperature ^1H NMR spectra showing the titration of **1** with *t*-BuNC are presented in Figure 1. Upon addition of 0.33 equiv (spectrum b) of *t*-BuNC, a singlet corresponding to the coordinated *t*-BuNC of $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(CN\text{-}t\text{-}Bu)$ (**2**) appears at δ −14.8. The phenoxide *t*-Bu signal of **2** is observed downfield of the phenoxide *t*-Bu signal of **1**. Isocyanide exchange between **1** and **2** occurs at a rate comparable to the NMR time scale at room temperature. The phenoxide *t*-Bu signals of both **1** and **2** are broadened relative to the phenoxide *t*-Bu resonance of pure **1**, but separate aromatic resonances for **1** and **2** are not resolved. The latter is a consequence of the fact that the chemical shift difference between the aromatic protons of **1** and **2** is small compared to the chemical shift difference between the phenoxide *t*-Bu signals of **1** and **2**. Increasing the concentration of *t*-BuNC causes the signals of **2** to increase in intensity at the expense of the signals due to **1**. For $\leq$1.0 equiv of added ligand, there is no significant change in the chemical shift of the coordinated *t*-BuNC resonance, indicating that the equilibrium (eq 1) lies heavily toward product. We estimate that the equilibrium constant for reaction 1 is $\geq 10^4$ M^{-1}.

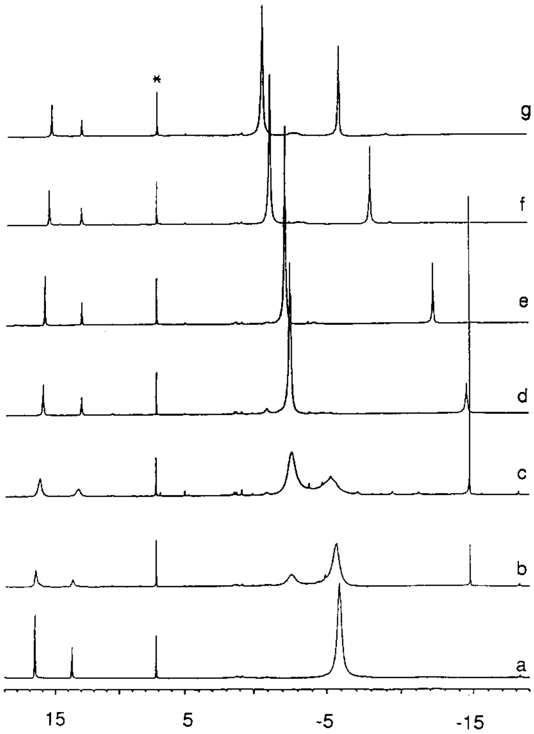

Figure 1. Room-temperature ^1H NMR spectra of 50 mg of **1** with (a) 0.00, (b) 0.33, (c) 0.66, (d) 1.05, (e) 1.25, (f) 1.98, and (g) 2.77 equiv of *t*-BuNC. The ^1H impurity of benzene-d_6 is marked by an asterisk.

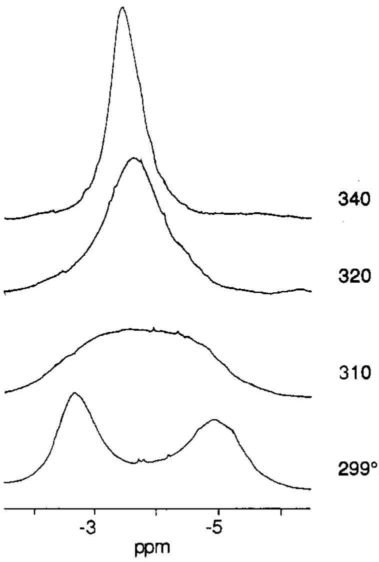

Figure 2. ^1H NMR spectra of the phenoxide *t*-Bu region of a 1:1 mixture of compounds **1** and **2** as a function of temperature.

$$\underset{\mathbf{1}}{U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3} + t\text{-}BuNC \rightleftarrows \underset{\mathbf{2}}{U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(CN\text{-}t\text{-}Bu)} \quad (1)$$

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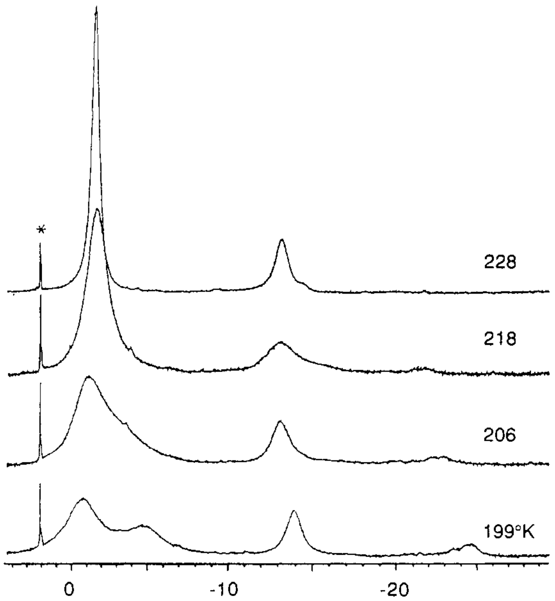

Figure 3. Variable-temperature ^{1}H NMR spectra of a solution in which 2 equiv of *t*-BuNC was added to compound **1**. The ^{1}H impurity of toluene-d_8 is marked by an asterisk.

The temperature dependence of the phenoxide *t*-Bu signals in a sample containing approximately a 1:1 mixture of compounds **1** and **2** is shown in Figure 2. Below 310 K, two phenoxide *t*-Bu resonances are observed. The aromatic resonances of the individual species can be resolved below 263 K. Above the 310 K coalescence temperature only one broad phenoxide *t*-Bu resonance is observed. Calculation of ΔG^* for the exchange process described by eq 1 yields a value of 13.7(5) kcal mol^{-1}.[7]

After the addition of 1.0 equiv of *t*-BuNC (spectra d–g in Figure 1), the isonitrile resonance shifts in a time-averaged fashion, indicative of exchange of free and coordinated *t*-BuNC at a rate faster than the NMR time scale. The phenoxide *t*-Bu signal of **2** also shifts in a time-averaged fashion, indicative of exchange between **2** and a new species, which we assign as the bis-adduct U(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$(CN-*t*-Bu)$_2$ (**3**). Thus, when greater than 1 equiv of *t*-BuNC is added, a new equilibrium is established (eq 2), whose equilibrium constant is small (ca. 0.1), but for which both k_1 and k_{-1} are fast compared to the NMR time scale.

$$\underset{\mathbf{2}}{\mathrm{U(O\text{-}2,6\text{-}}t\text{-}\mathrm{Bu_2C_6H_3)_3(CN\text{-}}t\text{-}\mathrm{Bu)}} + t\text{-}\mathrm{BuNC} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{3}}{\mathrm{U(O\text{-}2,6\text{-}}t\text{-}\mathrm{Bu_2C_6H_3)_3(CN\text{-}}t\text{-}\mathrm{Bu)_2}} \quad (2)$$

Figure 3 shows the variable-temperature behavior of a solution in which the ratio of *t*-BuNC to **1** is ca. 2:1. Below ca. 206 K, two phenoxide *t*-Bu resonances are observed. The signals at δ −0.9 and −5.0 are due to **3** are **2**, respectively. There are also two *t*-BuNC signals: one is the coordinated *t*-BuNC ligand resonance of **2** (δ −24.5) and the other is the isonitrile resonance of compound **3** (δ −13.9). A resonance corresponding to free *t*-BuNC is not observed in these spectra. Variable-temperature experiments in which a large excess of *t*-BuNC was added to **1** demonstrate that the signal of free *t*-BuNC is broad and obscured by the phenoxide *t*-Bu resonance of compound **3**. At high concentrations of *t*-BuNC, the equilibrium described by eq 2 is shifted toward **3**, and only the phenoxide *t*-Bu resonance of **3** is observed at 200 K.

Figure 4 shows a portion of the infrared spectra, i.e., the C≡N stretching region, of solutions in which (a) 0.5 equiv of *t*-BuNC was added to **1** and (b) 4.5 equiv of *t*-BuNC was added to **1**. When less than 1.0 equiv of *t*-BuNC is present in solution, only one C≡N stretch is observed, i.e., that corresponding to compound **2**. The frequency of 2175 cm^{-1} is higher than that observed for unligated *t*-BuNC, indicating that the isonitrile is acting primarily as a σ-donor.[8] When greater than 1.0 equiv of the isonitrile is present in solution, three C≡N stretches are observed, corresponding to a mixture of **2** (2175 cm^{-1}), **3** (2163 cm^{-1}), and free *t*-BuNC (2131 cm^{-1}). Nujol mull IR spectra of isolated solids **2** and **3** show only one C≡N stretch at 2177 and 2163 cm^{-1}, respectively.

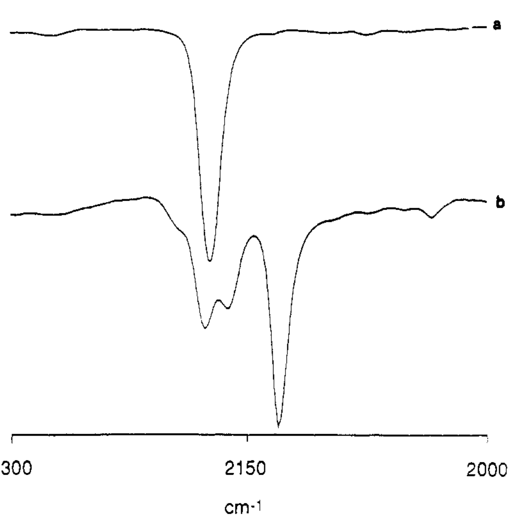

Figure 4. IR spectra between 2000 and 2300 cm^{-1} where (a) 0.5 equiv of *t*-BuNC was added to compound **1** and (b) 4.5 equiv of *t*-BuNC was added to compound **1** in hexane.

The solution and solid-state spectroscopic data suggest that **3** is a trigonal bipyramid with three equatorial phenoxide ligands and two axial isocyanide ligands. This ligand arrangement is slightly different than that observed in Sen and co-workers' Ce(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$(CN-*t*-Bu)$_2$ (vide supra).[5] The reason for this structural difference is not obvious since the ionic radii of U(III) and Ce(III) are very similar.[10] Attempts to obtain X-ray quality crystals of **3** have not been successful. We note that Brennan has isolated both Cp$_3$U(CN-2,6-Me$_2$C$_6$H$_4$) and Cp′$_3$U(CN-2,6-Me$_2$C$_6$H$_4$)$_2$ (Cp′ = MeC$_5$H$_4$) from the reactions of Cp′$_3$U(THF) with 2,6-dimethylphenyl isocyanide. The room-temperature ^{1}H NMR spectrum of his bis adduct shows only one type of isocyanide ligand, consistent with a trigonal-bipyramidal geometry and axial ligation of the isocyanides.[9,11]

Summary. The coordinatively unsaturated uranium(III) complex U(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$ is capable of binding one or two *t*-BuNC ligands in solution. The equilibrium constant for binding the first isonitrile ligand is estimated at $\geq 10^4$ M^{-1}, based on the negligible shift in the *t*-BuNC resonance at *t*-BuNC:**1** ratios $\leq$ 1. At room temperature, isonitrile exchange between the base-free complex and the 1:1 adduct occurs at a rate close to the NMR time scale. The 1:1 adduct, U(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$(CN-*t*-Bu), rapidly exchanges with free *t*-BuNC in solution. This exhange occurs primarily via U(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_3$(CN-*t*-Bu)$_2$, which can be detected at temperatures below ca. 206 K.

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(7) $\Delta G^* = aT[9.972 + \log(T/\delta\nu)]$, where $a = 4.575 \times 10^{-3}$ kcal/mol, $T = 310$ K, and $\delta\nu = 574$ Hz. See: Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 96.

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(11) The structurally characterized examples of Cp$_3$UL$_2$ complexes are all trigonal bipyramidal with the three η^5-C$_5$H$_5$ ligands occupying the equatorial vertices of the TBP. See: Marks, T. J.; Streitwieser, A., Jr. In *The Chemistry of the Actinide Elements*; Katz, J. J., Morss, L. R., Seaborg, G. T., Eds.; Chapman and Hall: New York, 1986; Vol. 2, Chapter 22, and references therein.