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Bent and Linear Uranium(IV) Metallocenes with Terminal and Bridging Cyanide Ligands

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Treatment of $Cp^*_2UI_2$ with KCN in thf led to the formation of $Cp^*_2U(CN)_2$ (**2**), which further reacted with NR_4CN to give $[Cp^*_2U(CN)_3][NR_4]$ (R = Et, **3**; R = ${}^nBu$, **3′**) and $[Cp^*_2U(CN)_5][NR_4]_3$ (R = Et, **4**; R = ${}^nBu$, **4′**). While the triscyanide **3′** adopts the familiar bent sandwich configuration, the pentacyanide **4** is, after the $[Cp^*_2U(NCMe)_5]^{2+}$ cation, the second example of a linear metallocene resulting from complete saturation of the equatorial girdle. Compound **3′** was also obtained by oxidation of the trivalent compound $[Cp^*_2U(CN)_3][N^nBu_4]_2$; the rapid and reversible electron transfer between the U(III) and U(IV) complexes was revealed by ^1H NMR spectroscopy. The NMR spectra also revealed that **4** is partially dissociated in thf into **3**, providing the first example of an equilibrating couple of bent and linear metallocenes [$K = 4.24(4) \times 10^{-5}$ at 25 °C, $\Delta H = 199(6)$ kJ mol^{-1}, and $\Delta S = 586(20)$ J mol^{-1} K^{-1}]. The trinuclear compound $[Cp^*_2UCl_2(\mu\text{-}CN)]_2Mg(thf)_4$ (**1**) and the 2D polymeric complex $[Cp^*_2U(dmf)_3(\mu\text{-}NC)_2(AgI)_2]_n$ (**5**), which were obtained during initial attempts on the synthesis of **2**−**4** and uranium(V) derivatives, exhibit a bent and linear sandwich structure, respectively.

Introduction

The cyanide ion CN^- is certainly one of the most common ligands in coordination chemistry, a prominent position that is justified by its ability to strongly bind metal ions, in their different oxidation states, and to adopt several ligation modes, thus affording a rich variety of homo- and heteropolynuclear compounds with interesting structures and physicochemical properties.[1] By comparison with the great number and diversity of cyanide complexes of d transition metals, which attract much attention for their fundamental aspects and applications in various domains, from biology to materials science, such compounds of the f elements seem to have been neglected.[1] These were limited to a few trivalent lanthanide (Ln) and uranium complexes, that are $[Ln(CN)_3]_n$,[2] $[(C_5H_5)_2M(CN)]_n$ (M = U, Nd, Yb),[3] $[Cp^*_2Sm(\mu\text{-}CN)(CNR)]_3$ ($Cp^* = \eta\text{-}C_5Me_5$; R = ${}^tBu$, Cy),[4] and $[Cp^*_2Sm(\mu\text{-}CN)]_6$,[5] and a handful of uranium(IV) complexes, that are $UCl_3(CN)(NH_3)_4$,[6] $[(C_5H_4R)_3U(CN)]_n$ (R = H,[3,7] Me,[7] ${}^tBu$,[8a] Me_3Si[8b]), $(C_5H_2{}^tBu_3)_2U(OSiMe_3)(CN)$,[9] and $(C_5HMe_4)_3U(CN)_{0.6}(Cl)_{0.4}$.[10] Being convinced that there is no scientific reason for this situation, we were interested in developing the cyanide chemistry of uranium and the lanthanides, in particular because of the novel structures and reactions that could be expected from their high coordination numbers, with the possible contribution of the f orbitals. We recently reported on the neutral oligomeric uranium(III) and cerium(III) cyanido metallocenes $[Cp^*_2M(\mu\text{-}CN)]_n$ and their mononuclear anionic derivatives $[Cp^*_2M(CN)_3][N^nBu_4]_2$ (M = U, Ce),[11] which are the first polycyanides of a trivalent f element to have been crystallographically characterized, and the actinyl cyanides $[UO_2(CN)_5][NEt_4]_3$[12] and $[Cp^*UO_2(CN)_3][NEt_4]_2$,[13] the latter being the first cyclopentadienyl complex of uranyl. After

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(8) (a) Mehdoui, T. Thèse de Doctorat, Université Paris XI, 2005. Synthesis of $(C_5H_4{}^tBu)_3U(CN)$: A flask was charged with $(C_5H_4{}^tBu)_3U$ (105 mg, 0.147 mmol), and thf (10 mL) was condensed in at −78 °C. At room temperature, the color of the solution turned violet upon addition of ${}^tBuNC$ (150 μL, 1.32 mmol). After refluxing for 6 h, the green powder of $(C_5H_4{}^tBu)_3U(CN)$, which was deposited from the orange solution, was filtered off, washed with a mixture of thf (10 mL) and pentane (15 mL), and dried under vacuum (71.3 mg, 77%). The compound is insoluble at room temperature in pentane, toluene, THF, and pyridine, and the ^1H NMR spectrum could not be recorded. Anal. Calcd for $C_{28}H_{39}NU$: C, 53.58; H, 2.23; N, 6.26. Found: C, 53.30; H, 2.36; N, 6.32. IR (Nujol) for ν(CN): two thin and strong bands at 2115 and 2108 cm^{-1}. (b) Synthesis of $(C_5H_4SiMe_3)_3U(CN)$: A flask was charged with $[(C_5H_4SiMe_3)_3U][BPh_4]$ (1.8 g, 1.85 mmol) and N^nBu_4CN (500 mg, 1.76 mmol), and thf (50 mL) was condensed in at −78 °C. After warming to room temperature, the green suspension was stirred for 30 min; the green precipitate of $(C_5H_4SiMe_3)_3U(CN)$ was filtered off, washed three times with thf (50 mL), and dried under vacuum (1.2 g, 96%). The compound is insoluble in the usual organic solvents, preventing the NMR spectra from being recorded. Anal. Calcd for $C_{25}H_{39}NSi_3U$: C, 44.43; H, 5.81; N, 2.07. Found: C, 44.35; H, 5.68; N, 2.07. IR (Nujol) for ν(CN): two thin and strong bands at 2088 and 2078 cm^{-1}.

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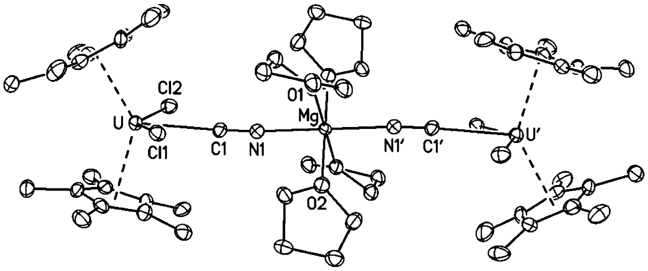

Figure 1. View of complex **1**. Hydrogen atoms have been omitted. Displacement parameters are drawn at the 30% probability level. Symmetry code: ′ = 1 − *x*, −*y*, 1 − *z*.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in [Cp*$_2$UCl$_2$(μ-CN)]$_2$Mg(thf)$_4$ (1)

U−C(1)	2.591(11)
U−Cl(1)	2.640(3)
U−Cl(2)	2.666(3)
⟨U−C(Cp*)⟩[a]	2.759(17)
U−Cp*1[a]	2.488
U−Cp*2[a]	2.479
Mg−N(1)	2.121(9)
Mg−O(1)	2.112(7)
Mg−O(2)	2.100(7)
C(1)−N(1)	1.143(13)
Cp*1−U−Cp*2[a]	135.3
C(1)−U−Cl(1)	71.9(3)
C(1)−U−Cl(2)	71.2(3)
U−C(1)−N(1)	175.1(10)
Mg−N(1)−C(1)	170.9(10)

[a] Cp* is the centroid of the cyclopentadienyl ring.

these compounds in the +3 and +6 oxidation states, we wish now to present the corresponding series of uranium(IV) cyanido metallocenes, which are the new precursor Cp*$_2$U(CN)$_2$ (**2**) and its anionic derivatives [Cp*$_2$U(CN)$_3$][NEt$_4$] (**3**) and [Cp*$_2$U(CN)$_5$][NEt$_4$]$_3$ (**4**).[14] While the triscyanido compound **3** adopts the familiar bent sandwich configuration, the pentacyanide **4** represents, with the recently reported [Cp*$_2$U(NCMe)$_5$]$^{2+}$ cation,[15] a novel class of linear metallocenes in the f-element series, resulting from complete saturation of the equatorial girdle; the partial dissociation of **4** into **3** provides the first example of an equilibrating couple of bent and linear metallocenes. We will also describe the X-ray crystal structures of the trinuclear compound [Cp*$_2$UCl$_2$(μ-CN)]$_2$Mg(thf)$_4$ (**1**) and a dmf solvate of the polymeric complex [Cp*$_2$U(dmf)$_3$(μ-NC)$_2$(AgI)$_2$]$_n$ (**5**), which were obtained during initial attempts at the synthesis of **2**−**4** and uranium(V) derivatives and which exhibit a bent and linear sandwich structure, respectively.

Results and Discussion

The Bent Metallocenes. Substitution of a chloride ligand by a cyanide ion was successful in the synthesis of UCl$_3$(CN)(NH$_3$)$_4$[6] and [(C$_5$H$_4$R)$_3$U(CN)]$_n$ (R = H,[3,7] Me[7]) from UCl$_4$ and (C$_5$H$_4$R)$_3$UCl, respectively. In contrast, reaction of Cp*$_2$UCl$_2$ and alkali metal cyanides in thf did not afford the desired cyanide derivative Cp*$_2$U(CN)$_2$ (**2**). In one experiment with NaCN, a few orange crystals were deposited and found by X-ray diffraction analysis to be the trinuclear compound [Cp*$_2$UCl$_2$(μ-CN)]$_2$Mg(thf)$_4$ (**1**). The latter obviously resulted from the presence of traces of MgCl$_2$ in the sample of Cp*$_2$UCl$_2$, which was prepared by treating UCl$_4$ with Cp*MgCl(thf).[16] A view of **1** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The centrosymmetric complex is built up of two Cp*$_2$UCl$_2$ units attached to a Mg(μ-NC)$_2$(thf)$_4$ fragment via the carbon atoms of the bridging cyanide ligands. The uranium atom is in the familiar bent sandwich configuration adopted by the Cp*$_2$UX$_2$L compounds, with the X and L ligands in the equatorial plane. The average U−C(Cp*) and U−Cl distances of 2.759(17) and 2.653(13) Å, respectively, are similar to those measured in Cp*$_2$UCl$_2$L [2.74(2) and 2.696(2) Å for L = pyrazole;[17] 2.773(1) and 2.69(5) Å for L = HNPPh$_3$],[18] where the L ligand is between the two Cl groups. These distances are also similar to those of 2.75(2) and 2.69(3) Å in the acetonitrile adduct Cp*$_2$UCl$_2$(NCMe), which exhibits an asymmetric arrangement of the Cl and MeCN ligands in the equatorial girdle.[19] The U−C(CN) distance of 2.591(11) Å can be compared with those of 2.508(7)−2.615(7) Å in the U(III,IV) mixed valence compound [{Cp*$_2$U}$_2$(μ-CN){(μ-CN)$_2$Na(thf)}$_2$]$_\infty$, the only other complex exhibiting f-element−CN−M bridges (M = main group or d transition metal).[11] The magnesium atom in **1** is surrounded by four oxygen and two nitrogen atoms in an octahedral arrangement quite identical to that found in [Cp*WMe$_3$(μ-NNH)]$_2$Mg(thf)$_4$[20] and [{PhB(CH$_2$P^{i}Pr$_2$)$_3$}Co(μ-N$_2$)]$_2$Mg(thf)$_4$;[21] in particular, the average Mg−O and the Mg−N distances of 2.106(6) and 2.121(9) Å, respectively, can be compared with those of 2.13(4) and 2.06(7) Å in the W$_2$Mg complex and those of 2.08(8) and 2.103(4) Å in the Co$_2$Mg complex. The Mg−N distance is also quite similar to that of 2.149(7) Å in *catena*-[MgL$_2$(H$_2$O)$_2$(μ-NC)Fe(CN)$_4$L]·H$_2$O (L = 1-methylimidazole).[22]

Since the Cl$^-$ ligand of Cp*$_2$UCl$_2$ could not be replaced with CN$^-$, the iodide and triflate counterparts Cp*$_2$UI$_2$ and Cp*$_2$U(OTf)$_2$ were considered as precursors;[15] the much greater lability of I$^-$ and OTf$^-$ versus Cl$^-$ was clearly evidenced by the distinct behavior of the precursors Cp*$_2$UX$_2$, which, in acetonitrile, are transformed into the neutral Cp*$_2$UCl$_2$(NCMe)[19] or dicationic [Cp*$_2$U(NCMe)$_5$][X]$_2$ (X = I, OTf) compounds.[15] Reaction of Cp*$_2$UI$_2$ with 2 equiv of KCN in thf at 20 °C readily afforded a red solution and an off-white precipitate of KI; after filtration and evaporation, the red powder of Cp*$_2$U(CN)$_2$ (**2**) was isolated in 85% yield (eq 1).

$$\mathrm{Cp^*{}_2UI_2} + 2\ \mathrm{KCN} \xrightarrow{\mathrm{thf}} \underset{(\mathbf{2})}{\mathrm{Cp^*{}_2U(CN)_2}} + 2\ \mathrm{KI} \qquad (1)$$

Treatment of Cp*$_2$UI$_2$ with NEt$_4$CN in place of KCN also gave **2**, which was converted into the anionic triscyanide derivative [Cp*$_2$U(CN)$_3$][NEt$_4$] (**3**) upon addition of a third equivalent of the tetraalkylammonium salt (eq 2). Complex **3**, which is much more soluble than **2** in polar organic solvents, was easily extracted in thf from the insoluble NEt$_4$I precipitate and was isolated as a brown powder in 83% yield. Changing

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NEt_4CN with N^nBu_4CN in its reaction with $Cp^*_2UI_2$ also led to the formation of the anionic triscyanide complex, but the

$$Cp^*_2UI_2 + 3\,NR_4CN \xrightarrow{thf} \underset{R = Et\ (\mathbf{3}),\ R = {}^nBu\ (\mathbf{3'})}{[Cp^*_2U(CN)_3][NR_4]} + 2\,NR_4I \quad (2)$$

latter could not be separated from the released salt N^nBu_4I because of their similar solubility in thf. However, dark orange crystals of $[Cp^*_2U(CN)_3][N^nBu_4]\cdot1.5thf$ (**3′**·1.5thf) suitable for X-ray diffraction were formed by slow diffusion of diethyl ether into a thf solution of $Cp^*_2UI_2$ and N^nBu_4CN.

The successive syntheses of **2** and **3** from $Cp^*_2UI_2$ parallel those of the uranium(III) cyanide metallocenes $[Cp^*_2U(\mu\text{-}CN)]_n$ and $[Cp^*_2U(CN)_3][N^nBu_4]_2$ from $Cp^*_2UI(py)$.[11] Complex **3′** was also readily formed by oxidation of $[Cp^*_2U(CN)_3][N^nBu_4]_2$ with 0.5 equiv of I_2 in thf, and the uranium(III) compound was in turn obtained by potassium amalgam reduction of **2**, followed by addition of N^nBu_4CN. The ^1H NMR spectra of solutions containing mixtures of the $[Cp^*_2U(CN)_3]^-$ and $[Cp^*_2U(CN)_3]^{2-}$ anions exhibited single averaged resonances corresponding to the Cp* ligands, revealing rapid and reversible electron transfer between the U(III) and U(IV) centers (eq 3). Similar behavior of the redox systems $(C_5H_4R)_3UX/[(C_5H_4R)_3UX]^-$ (R = H, ^tBu, $SiMe_3$; X = H, Cl, BH_4, Me) was previously noted.[23]

$$[Cp^*_2U(CN)_3]^- \underset{-e}{\overset{+e}{\rightleftharpoons}} [Cp^*_2U(CN)_3]^{2-} \quad (3)$$

Complexes **2** and **3** were characterized by their elemental analyses (C, H, N). The ^1H NMR spectrum of **2** in pyridine exhibits a single peak corresponding to the Cp* ligands at δ 8.13, a value characteristic of neutral $Cp^*_2UX_2$ complexes with a bent sandwich geometry for which the Cp* resonance is visible in the δ 5−18 region;[16] this signal is shifted at δ 6.75 on the spectrum of **3** in thf. The infrared spectra show strong absorption bands assigned to the ν(CN) stretching frequencies at 2134 cm^{-1} for **2** and 2053 and 2188 cm^{-1} for **3**. These values can be compared with those found in the uranium(IV) compounds $UCl_3(CN)(NH_3)_4$ (2120 cm^{-1}),[6] $[(C_5H_4R)_3U(CN)]_n$ (in the range 2088−2116 cm^{-1} for R = H, Me, ^tBu, Me_3Si),[3,7,8] and $(C_5H_2{}^tBu_3)_2U(OSiMe_3)(CN)$ (2040 cm^{-1})[9] and also in the uranyl complexes $[UO_2(CN)_5]^{3-}$ (2180 and 2190 cm^{-1})[12] and $[Cp^*UO_2(CN)_3]^{2-}$ (2069 and 2090 cm^{-1})[13] and the uranium(III) complexes $[(C_5H_5)_2U(CN)]_n$ (2112 cm^{-1})[3] and $[Cp^*_2U(CN)_3]^{2-}$ (2060 and 2091 cm^{-1}).[11]

The classical bent sandwich crystal structure of the anion of **3′** (Figure 2, Table 2) is very similar to that of its U(III) analogue, the average U−C(Cp*) and U−C(CN) distances [2.727(15) and 2.520(16) Å, respectively] being smaller by about 0.1 Å, in agreement with the variation in the radii of the U^{4+} and U^{3+} ions.[24] The U−C(CN) bond lengths in **3′**, which average 2.52(1) Å, are larger than those in the two other crystallographically characterized uranium(IV) cyanide complexes, $(C_5H_2{}^tBu_3)_2U(OSiMe_3)(CN)$ [2.415(6) Å][9] and $(C_5HMe_4)_3U(CN)_{0.6}(Cl)_{0.4}$ [2.31(4) Å],[10] reflecting the higher coordination number and negative charge of the anionic compound.

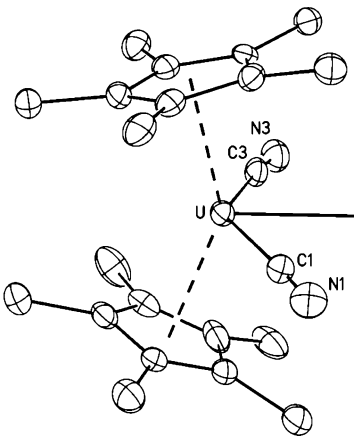

Figure 2. View of the anion of **3′**. Hydrogen atoms have been omitted. Displacement parameters are drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[Cp^*_2U(CN)_3][N^nBu_4]$ (3′)

U−C(1)	2.504(7)
U−C(2)	2.541(6)
U−C(3)	2.515(7)
⟨U−C(Cp*)⟩[a]	2.727(15)
U−Cp*1[a]	2.447
U−Cp*2[a]	2.445
C(1)−N(1)	1.169(9)
C(2)−N(2)	1.143(7)
C(3)−N(3)	1.162(8)
Cp*1−U−Cp*2[a]	144.6
U−C(1)−N(1)	177.6(5)
U−C(2)−N(2)	178.9(6)
U−C(3)−N(3)	175.0(5)
C(1)−U−C(2)	72.60(19)
C(2)−U−C(3)	71.54(19)

[a] Cp* is the centroid of the cyclopentadienyl ring.

The Linear Metallocenes. In contrast to the U(III) complex $[Cp^*_2U(CN)_3][NR_4]_2$, which was inert toward an excess of CN^- ions,[11] the U(IV) counterpart **3** or **3′** was readily transformed into the pentacyanide derivative $[Cp^*_2U(CN)_5][NR_4]_3$ (R = Et, **4**; R = ^nBu, **4′**). The latter was directly synthesized from $Cp^*_2UX_2$ (X = I, OTf) and 5 equiv of NR_4CN (R = Et, ^nBu) in acetonitrile, but it is only with X = OTf and R = Et that an analytically pure compound was easily obtained (eq 4); because of the poor solubility of **4** in thf, the released salt NEt_4OTf was easily eliminated by extraction in this solvent, leaving **4** as an orange powder in 75% yield.

$$Cp^*_2U(OTf)_2 + 5\,NEt_4CN \xrightarrow{MeCN} \underset{(\mathbf{4})}{[Cp^*_2U(CN)_5][NEt_4]_3} + 2\,NEt_4OTf \quad (4)$$

The infrared spectrum of **4** shows a strong absorption band at 2091 cm^{-1} assigned to the ν(CN) stretching frequency. Orange crystals of **4**·MeCN suitable for X-ray diffraction were formed after slow diffusion of diethyl ether into an acetonitrile solution of **4**.

A view of one of the three independent and quite identical anions of **4** is shown in Figure 3, and selected bond lengths and angles are listed in Table 3. The structure resembles that of the dication $[Cp^*_2U(NCMe)_5]^{2+}$ and provides a second example of a linear metallocene with auxiliary donor ligands in the equatorial plane.[15] The five CN groups and the metal center are coplanar with rms deviations of 0.016−0.024 Å, and this plane is equidistant from and parallel to the cyclopentadienyl

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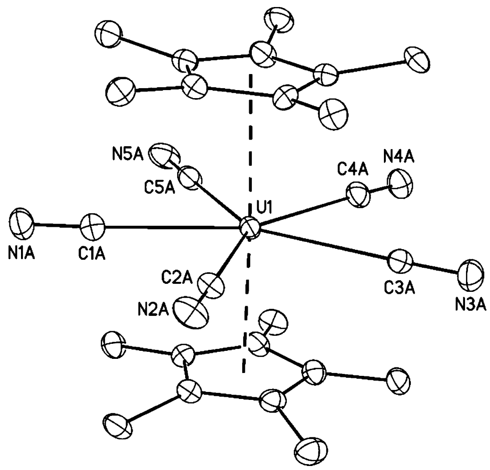

Figure 3. View of one of the three independent and quite identical anions of **4**. Hydrogen atoms have been omitted. Displacement parameters are drawn at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[Cp^*_2U(CN)_5][NEt_4]_3$ (4)

	anion A	anion B	anion C
U−C(1)	2.584(6)	2.601(6)	2.612(6)
U−C(2)	2.634(7)	2.611(7)	2.607(7)
U−C(3)	2.668(6)	2.617(7)	2.596(7)
U−C(4)	2.648(7)	2.618(7)	2.619(7)
U−C(5)	2.599(7)	2.634(7)	2.644(7)
⟨U−C(Cp*)⟩[a]	2.86(3)	2.864(14)	2.868(13)
U−Cp*1[a]	2.596	2.602	2.594
U−Cp*2[a]	2.592	2.589	2.607
⟨C−N⟩	1.162(8)	1.153(5)	1.158(8)
Cp*1−U−Cp*2[a]	177.5	178.9	179.5
C(1)−U−C(2)	73.6(2)	71.65(19)	69.9(2)
C(2)−U−C(3)	75.80(19)	69.44(19)	70.3(2)
C(3)−U−C(4)	71.29(19)	71.2(2)	73.7(2)
C(4)−U−C(5)	70.2(2)	72.49(19)	73.16(19)
C(5)−U−C(1)	69.1(2)	75.28(19)	72.98(19)
U−C(1)−N(1)	175.8(6)	175.3(5)	176.3(5)
U−C(2)−N(2)	178.6(5)	176.2(5)	177.6(6)
U−C(3)−N(3)	177.4(6)	178.1(6)	175.0(6)
U−C(4)−N(4)	176.9(6)	174.8(5)	179.2(7)
U−C(5)−N(5)	177.9(6)	176.8(5)	177.6(6)

[a] Cp* is the centroid of the cyclopentadienyl ring.

rings, with dihedral angles of 0.3(2)−1.7(2)°. The pentagon of the CN carbon atoms is in a staggered conformation with respect to the eclipsed Cp* rings, thus minimizing the intramolecular steric interactions. The complex adopts a pentagonal bipyramidal configuration with the Cp* ligands, considered as monodentate, in apical positions; this geometry is reminiscent of that of the uranyl cyanide $[UO_2(CN)_5]^{3-}$.[12] The average U−C(Cp*) and U−C(CN) distances of 2.86(2) and 2.62(2) Å, respectively, are 0.10−0.13 Å larger than those in the bent metallocene **3**, in agreement with the increase of the coordination number and negative charge of the complex. The U−C(Cp*) distances are also 0.5 Å larger than in the cation $[Cp^*_2U(NCMe)_5]^{2+}$,[15] while the U−C(CN) distances are 0.5 Å larger than in the uranyl complex $[UO_2(CN)_5]^{3-}$.[12] The displacements of the methyl substituents away from the metal and out of the Cp* ring plane seem to be slightly less important in **4** than in $[Cp^*_2U(NCMe)_5]^{2+}$, with average values of 0.19(3) and 0.225(18) Å, respectively, likely reflecting the lesser steric saturation of the anionic cyanide complex; however, these displacements are greater than those observed in the bent metallocene **3**, which average 0.12(5) Å.

The easy formation of **4** by addition of cyanide ions to **3**, while the corresponding linear metallocene of uranium(III) could not be synthesized, was explained by theoretical calculations.[14] The MO diagrams indicate that the linear U(III) pentacyanide should not be stable because one of the three unpaired electrons would occupy an antibonding orbital. In contrast, both linear and bent structures could be adopted by the complexes in the +4 oxidation state, depending on the experimental conditions. The highest occupied MOs are energetically lower in the linear than in the bent complex, so that the former should be slightly favored, but the two unpaired electrons induce an electronic repulsion for the CN^- lone pairs, which is higher for the linear pentacyanide than for the bent triscyanide complex.

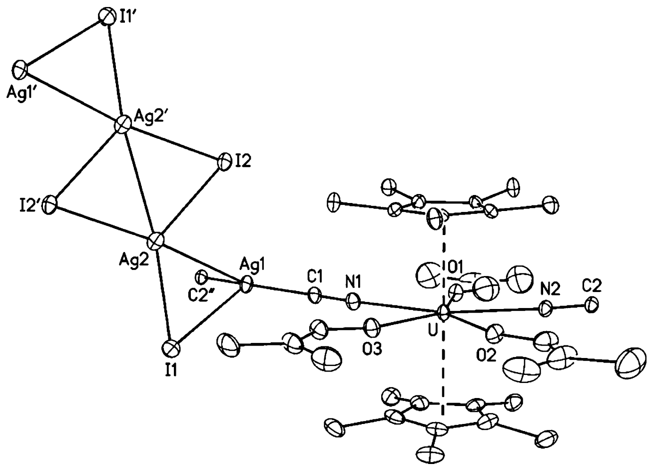

Figure 4. View of **5**·2dmf, showing the uranium and silver atoms' environment. Hydrogen atoms and solvent molecules have been omitted. Displacement parameters are drawn at the 30% probability level. Symmetry codes: $'$ = 1.5 − *x*, 1.5 − *y*, 1 − *z*; $''$ = *x*, 1 − *y*, *z* − 0.5.

In fact, the bent and linear metallocenes **3** and **4** were found to be in equilibrium in solution. The ^1H NMR spectrum of **4** in acetonitrile at 23 °C exhibits a broad signal at δ 24.35 corresponding to the Cp* ligands; this resonance is out of the region characteristic of the bent uranium(IV) metallocenes, being shifted downfield like the Cp* resonance of $[Cp^*_2U(NCMe)_5]^{2+}$ (δ 35.3).[15] The spectrum also shows a broad Cp* resonance at δ 6.3, revealing that **4** was partly dissociated into **3**, according to eq 5. The ratio of the molar fractions of **4** and **3**, x_4/x_3, was

$$\underset{(\mathbf{3})}{[Cp^*_2U(CN)_3][NEt_4]} + 2\,NEt_4CN \rightleftarrows \underset{(\mathbf{4})}{[Cp^*_2U(CN)_5][NEt_4]_3} \qquad (5)$$

found to depend markedly on the temperature and the initial concentration C_0 of **4**; for $C_0 = 3.99\ 10^{-2}$ M, x_4/x_3 is equal to 83/17 and 27/73 at 25 and 45 °C, respectively. The value of the equilibrium constant $K = 4x_3{}^3C_0{}^2/x_4$ is $4.24(4) \times 10^{-5}$ at 25 °C, and the linear dependence of ln *K* vs 1/*T* allowed the determination of the thermodynamic parameters ΔH and ΔS for the dissociation of **4**, which are respectively equal to +199(6) kJ mol^{-1} and +586(20) J mol^{-1} K^{-1} (see Supporting Information). The ligand exchange reaction between **3** and **4** was also evidenced by spin saturation transfer experiments; irradiation of the Cp* signals of **3** (or **4**) induced a decrease in the intensity of the signal of **4** (or **3**).

The fortuitous formation of the uranium(V) compound $[Cp^*_2U(CN)_5][N^nBu_4]_2$ in an attempt to prepare the tetravalent derivative $[Cp^*_2U(CN)_5][N^nBu_4]_3$ (**4′**)[14] led us to consider a rational and reproducible synthesis of uranium(V) cyanido metallocenes by oxidation of U(III) and U(IV) precursors; AgCN seemed to be an appropriate reagent as both an oxidizing agent and a source of cyanide ions. Treatment of $[Cp^*_2U(CN)_3]$-

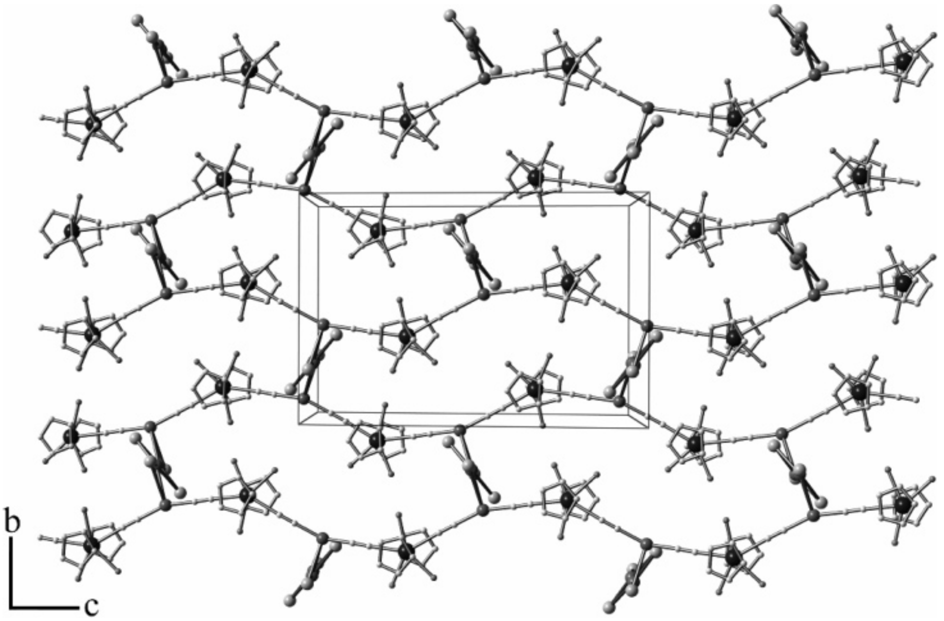

Figure 5. 2D layer structure of **5**. Hydrogen atoms and the methyl groups of the Cp* ligands have been omitted and only the oxygen atoms of the dmf ligands are represented for clarity. Atoms are represented as spheres of arbitrary radii.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[Cp^*{}_2U(dmf)_3(\mu\text{-}NC)_2(AgI)_2]_n$ (5)

U−N(1)	2.527(6)	Ag(1)−C(1)	2.085(7)	Cp*1−U−Cp*2[a]	179.2
U−N(2)	2.530(6)	Ag(1)−C(2″)	2.093(7)	N(1)−U−O(1)	71.44(18)
U−O(1)	2.415(5)	Ag(1)−I(1)	3.1595(8)	O(1)−U−N(2)	72.30(18)
U−O(2)	2.476(5)	Ag(2)−I(1)	2.7046(8)	N(2)−U−O(2)	71.97(18)
U−O(3)	2.431(5)	Ag(2)−I(2)	2.7650(8)	O(2)−U−O(3)	71.57(18)
⟨U−C(Cp*)⟩[a]	2.843(5)	Ag(2)−I(2′)	2.8188(8)	N(1)−U−O(3)	72.72(18)
U−Cp*1[a]	2.580	C(1)−N(1)	1.147(9)	N(1)−U−N(2)	143.72(19)
U−Cp*2[a]	2.573	C(2)−N(2)	1.148(9)	C(1)−Ag(1)−C(2″)	158.5(3)

[a] Cp* is the centroid of the cyclopentadienyl ring. Symmetry codes: ′ = 1.5 − *x*, 1.5 − *y*, 1 − *z*; ″ = *x*, 1 − *y*, *z* − 0.5.

$[N^nBu_4]_2$ with 1 equiv of AgCN in thf gave an equilibrating 1:1 mixture of the bent and linear uranium(IV) metallocenes **3′** and **4′**. Further addition of AgCN led to the formation of a unique new compound, characterized by a Cp* signal at δ 6.95, but this could not be isolated in a pure form and crystals suitable for X-ray diffraction were not obtained.

Reaction of $Cp^*{}_2UI_2$ and 2 molar equiv of AgCN in dmf did not afford an uranium(V) complex but crystals of the polymeric compound $[Cp^*{}_2U(dmf)_3(\mu\text{-}NC)_2(AgI)_2\cdot 2dmf]_n$ (**5**·2dmf), which is, to the best of our knowledge, the first cyanometalate of uranium(IV); a view of complex **5** is shown in Figure 4, and selected bond lengths and angles are listed in Table 4. The $Cp^*{}_2U$ fragment adopts a linear sandwich configuration with the equatorial plane containing three dmf molecules and two nonadjacent bridging NC groups (rms deviation 0.012 Å). Complex **5** is the first linear metallocene of an f element with distinct donor ligands in its equatorial girdle. As observed in the structure of **4**, this plane is parallel to and equidistant from the Cp* rings, with dihedral angles of 0.4(2)° and 0.5(2)°. The pentagon of the O and N atoms is in a staggered conformation with respect to the eclipsed Cp* rings (average U−C distance of 2.843(5) Å). The U−N distances of 2.527(6) and 2.530(6) Å are slightly larger than those measured in the uranyl(VI) complexes $[UO_2(H_2O)_4(dmf)_2]_{0.5}[UO_2\{M(CN)_6\}(dmf)_2]$ [2.490(1) and 2.495(3) Å for M = Fe and Co, respectively],[25a] the only other actinide cyanometalates to have been crystallographically characterized, and are similar to the average U−N distance of 2.55(2) Å in the cationic nitrile adduct $[Cp^*{}_2U(NCMe)_5]^{2+}$.[15] The U−O distances, which average 2.423(8) Å, can be compared with those in the eight-coordinate cationic complexes $[UCl_3(dmf)_5]_2[UCl_6]$ [2.29(3)−2.45(2) Å],[26] $[UCl(dmf)_7]_2[UO_2Cl_4]_3$ [2.30(1)−2.40(1) Å].[27] and $[UCl(dmf)_7]Cl_3$ [2.315(2)−2.391(2) Å][28] and the nine-coordinate compound $[U(dmf)_9]I_4$ [2.35(1)−2.47(1) Å].[29] The metallocenes are attached to the silver atom Ag(1) via the C(1) and C(2) atoms of the bridging CN groups, to form 1D wavy chains directed along the *c* axis (Figure 5); the undulated shape of the chain results from the C(1)−Ag−C(2) and N(1)−U−N(2) angles of 158.5(3)° and 143.72(19)°, respectively. Each chain is linked to two others through centrosymmetric $[Ag(1)I(1)Ag(2)I(2)]_2$ units, resulting in the formation of 2D corrugated layers in the *bc* plane. The average Ag−C distance of 2.089(4) Å is comparable with those in the $Ag_x(CN)_y$-based complexes.[30] Among the numerous AgI oligomers present in the Cambridge Structural Database (Version 5.28),[31] none is similar to the present Ag_4I_4 assembly. The Ag−I distances, which are in the large range 2.7046(8)−3.1595(8) Å, and the average Ag−Ag separation of 3.15(10) Å, which reflects argentophilic interactions, are unexceptional. The whole

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2D network of **5**, which exhibits a “brick wall” pattern,[32] is built from a tessellation of elongated [UAgUAg$_4$]$_2$ rings with approximate dimensions of 26 × 9.5 Å; these layers, with an approximate thickness of 11 Å and an interlayer spacing of about 2.8 Å, are stacked so as to form channels along the [1 1 0] direction.

Conclusion

Successive addition of CN$^-$ ions to Cp*$_2$UI$_2$ afforded the neutral complex Cp*$_2$U(CN)$_2$ and its anionic mononuclear derivatives [Cp*$_2$U(CN)$_3$][NR$_4$] and [Cp*$_2$U(CN)$_5$][NR$_4$]$_3$, which are the first polycyanide complexes of uranium(IV). The pentacyanide compound, which is a novel linear metallocene resulting from complete saturation of the equatorial girdle, was found to be in equilibrium with the bent triscyanido metallocene. The 2D polymeric complex [Cp*$_2$U(dmf)$_3$(μ-NC)$_2$(AgI)$_2$]$_n$, which is the first cyanometalate of uranium(IV), represents a unique example of a linear metallocene with distinct donor ligands in its equatorial plane.

Experimental Section

All reactions were carried out under argon with the rigorous exclusion of air and water (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried by standard methods and distilled immediately before use. NaCN (97%, Fluka), KCN (98%, Fluka), NEt$_4$CN (94%, Aldrich), and N^{n}Bu$_4$CN (95%, Aldrich) have been used as received. Cp*$_2$UCl$_2$,[16] Cp*$_2$UI$_2$, Cp*$_2$U(OTf)$_2$,[15b,c] and Cp*$_2$UI(py)[33] were synthesized as previously reported. IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded on a Perkin-Elmer FT-IR 1725X spectrometer. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The spectra are recorded at 23 °C when not otherwise specified. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Crystals of [Cp*$_2$UCl$_2$(μ-CN)]$_2$Mg(thf)$_4$ (1). Slow diffusion of pentane into a solution of Cp*$_2$UCl$_2$ (15.8 mg, 0.027 mmol) and NaCN (2.9 mg, 0.059 mg) in thf (0.4 mL) led to the formation of a few orange crystals of **1**, which obviously resulted from the presence of traces of MgCl$_2$ in the sample of Cp*$_2$UCl$_2$.

Synthesis of Cp*$_2$U(CN)$_2$ (2). A flask was charged with Cp*$_2$UI$_2$ (120.3 mg, 0.158 mmol) and KCN (21.6 mg, 0.362 mg), and thf (30 mL) was condensed in at −78 °C. After stirring for 12 h at 20 °C, the red solution was filtered and evaporated to dryness, leaving a red microcrystalline powder of **2** (75 mg, 85%). Anal. Calcd for C$_{22}$H$_{30}$UN$_2$: C, 47.14; H, 5.39; N, 5.00. Found: C, 46.90; H, 5.55; N, 4.88. ^{1}H NMR (pyridine-d_5): δ 8.13 (s, $w_{1/2}$ 60 Hz, 30H, Cp*). IR (Nujol): ν(CN) = 2134(s), 2094(m), 2040(m) cm^{-1}.

Synthesis of [Cp*$_2$U(CN)$_3$][NEt$_4$] (3). A flask was charged with Cp*$_2$UI$_2$ (163.1 mg, 0.214 mmol) and Et$_4$NCN (106.7 mg, 0.642 mmol), and thf (30 mL) was condensed in at −78 °C. The mixture was stirred under reflux for 24 h; an orange solution and a white precipitate of Et$_4$NI were obtained. The orange solution was filtered and evaporated to dryness, leaving a brown powder of **3** (127.3 mg, 83%). Anal. Calcd for C$_{31}$H$_{50}$UN$_4$: C, 51.94; N, 7.82. Found: C, 51.56; N, 7.96. ^{1}H NMR (thf-d_8): δ 6.75 (s, $w_{1/2}$ 50 Hz, 30H, Cp*), −4.14 (s, $w_{1/2}$ 16 Hz, 12H, NCH$_2$C*H*$_3$), −4.48 (s, $w_{1/2}$ 23 Hz, 8H, NC*H*$_2$CH$_3$). IR (Nujol): ν(CN) = 2188(s), 2104(m), 2053(s) cm^{-1}.

Crystals of [Cp*$_2$U(CN)$_3$][N^{n}Bu$_4$]·1.5thf (3′·1.5thf). Slow diffusion of diethyl ether into a solution of Cp*$_2$UI$_2$ (15.1 mg, 0.020 mmol) and N^{n}Bu$_4$CN (16.8 mg, 0.053 mmol) in thf (0.4 mL) led to the formation of dark orange crystals of **3′**·1.5thf.

Oxidation of [Cp*$_2$U(CN)$_3$][N^{n}Bu$_4$]$_2$ with Iodine. The uranium(III) complex was readily prepared in an NMR tube by treating Cp*$_2$UI(py) (16.3 mg, 0.022 mmol) with N^{n}Bu$_4$CN (18.4 mg, 0.066 mmol) in thf-d_8 (0.4 mL). The brown solution immediately turned red upon addition of I$_2$ (2.9 mg, 0.011 mmol), and the NMR spectrum showed the quantitative formation of the U(IV) compound **3′** characterized by its Cp* signal at δ 6.60.

Reduction of Cp*$_2$U(CN)$_2$ with Potassium Amalgam. A flask was charged with **2** (118.2 mg, 0.212 mmol) and 2% K(Hg) (617 mg, 0.316 mmol of K), and thf (40 mL) was condensed in at −78 °C. After stirring for 12 h at 20 °C, N^{n}Bu$_4$CN (118 mg, 0.390 mmol) was added into the suspension, giving a brown solution, which deposited brown crystals of the U(III) complex [Cp*$_2$U(CN)$_3$][N^{n}Bu$_4$]$_2$, characterized by X-ray diffraction analysis.

Synthesis of [Cp*$_2$U(CN)$_5$][NEt$_4$]$_3$ (4). A flask was charged with Cp*$_2$U(OTf)$_2$ (157.0 mg, 0.195 mmol) and NEt$_4$CN (162.1 mg, 0.975 mmol), and MeCN (20 mL) was condensed in at −78 °C. After stirring for 30 min at 20 °C, the solvent was evaporated off, and thf (30 mL) was condensed into the flask at −78 °C. The mixture was heated at 50 °C for 1 h, and the orange powder of **4** was filtered off, washed three times with thf (20 mL), and dried under vacuum (150 mg, 75%). Anal. Calcd for C$_{49}$H$_{90}$UN$_8$: C, 57.18; H, 8.81; N, 10.89. Found: C, 56.86; H, 8.58; N, 11.08. ^{1}H NMR (acetonitrile-d_3): δ 24.35 (s, $w_{1/2}$ 360 Hz, 30H, Cp*), 2.40 (q, J 7 Hz, 24H, NC*H*$_2$CH$_3$), 0.69 (s, $w_{1/2}$ 20 Hz, 36H, NCH$_2$C*H*$_3$). IR (Nujol): ν(CN) = 2091(s), 2066(w), 2062(w), 2050(w) cm^{-1}.

Study of the Equilibrium between 3 and 4. In a typical experiment, an NMR tube was charged with **4** (18.5 mg, 0.0180 mmol) in acetonitrile-d_3 (450 μL); the initial concentration, C_0, of **4** is thus 0.0399 M. The ^{1}H NMR spectra were recorded from +25 to +45 °C with intervals of 5 °C. The relative proportions of **3** and **4**, $x_\mathbf{3}$ and $x_\mathbf{4}$, were measured by integration of the respective Cp* signals. The dissociation constant of **4** at 25 °C, $K = 4x_\mathbf{3}{}^3C_0{}^2/x_\mathbf{4}$, is equal to 4.24(4) × 10^{-5}, and the thermodynamic parameters ΔH and ΔS, which were determined from the linear dependence of ln K vs 1/T, are respectively equal to +199(6) kJ mol^{-1} and +586(20) J mol^{-1} K^{-1} (see Supporting Information).

Oxidation of [Cp*$_2$U(CN)$_3$][N^{n}Bu$_4$]$_2$ with Silver Cyanide. The uranium(III) complex was readily prepared in an NMR tube by treating Cp*$_2$UI(py) (17.3 mg, 0.023 mmol) with N^{n}Bu$_4$CN (19.5 mg, 0.072 mmol) in thf-d_8 (0.4 mL). After addition of AgCN (1.6 mg, 0.012 mmol), the reaction mixture was heated at 80 °C for 10 min and a black precipitate of Ag metal was formed. The spectrum of the red solution showed a broad signal ($w_{1/2}$ 195 Hz) at δ 20.1, attributed to **4′**, and a very broad signal at ca. δ 0, reflecting the rapid and reversible electron-transfer reaction between the U(III) and U(IV) complexes [Cp*$_2$U(CN)$_3$][N^{n}Bu$_4$]$_2$ and **3′**. Irradiation at δ 0 lowered the intensity of the signal at δ 20.1 to ca. 20% of its original value. After further addition of AgCN (1.6 mg, 0.012 mmol) and heating at 80 °C for 10 min, the spectrum showed the presence of an equimolar mixture of **3′** and **4′**, characterized by their Cp* signals at δ 6.6 and 20.1, respectively. Each of these signals disappeared completely when the other one was irradiated.

Crystals of [Cp*$_2$U(dmf)$_3$(μ-NC)$_2$(AgI)$_2$·2dmf]$_n$ (5·2dmf). Slow diffusion of diethyl ether into a solution of Cp*$_2$UI$_2$ (14.6 mg, 0.019 mmol) and AgCN (5.2 mg, 0.039 mmol) in dmf (0.4 mL) led to the formation of orange crystals of **5**.

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[34] with graphite-monochromated

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Table 5. Crystal Data and Structure Refinement Details

	1	**3′**·1.5thf	**4**·MeCN	**5**·2dmf
empirical formula	$C_{58}H_{92}Cl_4MgN_2O_4U_2$	$C_{45}H_{78}N_4O_{1.5}U$	$C_{51}H_{93}N_9U$	$C_{37}H_{65}Ag_2I_2N_7O_5U$
M_r	1523.51	937.14	1070.37	1395.53
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$Fdd2$	$P2_1/c$	$C2/c$
a/Å	9.3093(12)	33.605(2)	38.6077(8)	32.5453(12)
b/Å	32.315(4)	41.640(3)	12.1228(4)	13.9298(3)
c/Å	10.4798(13)	13.5465(6)	38.4765(14)	21.5528(8)
β/deg	106.958(6)		118.949(2)	105.331(2)
V/Å^3	3015.6(7)	18956(2)	15758.2(9)	9423.3(5)
Z	2	16	12	8
D_{calcd}/g cm^{-3}	1.678	1.314	1.354	1.967
μ(Mo Kα)/mm^{-1}	5.596	3.460	3.131	5.607
F(000)	1500	7680	6648	5344
no. of rflns collected	32 595	73 891	228 313	100 878
no. of indep rflns	5703	8850	29 774	8916
no. of obsd rflns ($I > 2\sigma(I)$)	4080	7637	23 090	7816
R_{int}	0.083	0.051	0.082	0.073
no. of params refined	332	502	1713	547
R1	0.064	0.034	0.047	0.044
wR2	0.156	0.074	0.141	0.114
S	1.112	1.010	1.075	1.036
$\Delta\rho_{min}$/e Å^{-3}	−1.12	−0.64	−1.21	−1.52
$\Delta\rho_{max}$/e Å^{-3}	1.41	0.87	2.92	2.29

Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protective "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to $\theta = 25.7°$ and a minimum redundancy of 3 for 90% of the reflections) were processed with HKL2000.[35] The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[36] Absorption effects were corrected empirically with SCALEPACK[35] or DELABS.[37] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Special details are as follows.

Compound **1**. The carbon and nitrogen atoms of the cyanide ions were unambiguously located on the basis of their displacement parameters.

Compound **3′**. One of the thf molecules was affected with a 0.5 occupancy factor so as to retain acceptable displacement parameters. Some restraints on bond lengths and/or displacement parameters were applied for some atoms of the solvent molecules.

Compound **4**. Some restraints on bond lengths, angles, and displacement parameters were applied for the very badly resolved tetraethylammonium ion containing N(9). Some short H···H contacts involving the counterions are likely due to the imperfect location and possible unresolved disorder of some of the latter. Numerous intramolecular C···C contacts (>3.10 Å) are due to the steric congestion of the complex molecules.

Compound **5**. The carbon and nitrogen atoms of the cyanide ions were unambiguously located on the basis of their displacement parameters. Two solvent dmf molecules are disordered around symmetry elements and have been refined with occupancy parameters of 0.5 and restraints for some bond lengths and displacement parameters.

Crystal data and structure refinement details are given in Table 5. The molecular plots were drawn with SHELXTL[38] and Balls & Sticks.[39]

Acknowledgment. We thank the Direction de l'Energie Nucléaire of the Commissariat à l'Energie Atomique (DEN-DSOE) for its financial support, which made possible the postdoctoral position of J.M..

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. Plots of ln K vs $1/T$ for the equilibrium between compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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