Organometallics **2007,** *26,* 2623−2629 2623

Cyanide Metallocenes of Trivalent f-Elements

Jérôme Maynadié, Jean-Claude Berthet,* Pierre Thuéry, and Michel Ephritikhine*

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, Laboratoire Claude Fréjacques,
CEA/Saclay, 91191 Gif-sur-Yvette, France

Received December 14, 2006

Addition of N^nBu_4CN to $(C_5Me_5)_2UI(py)$, $(C_5Me_5)_2CeI$, or $(C_5Me_5)_2M(OTf)$ (M = U, Ce) in acetonitrile led to the precipitation of the neutral monocyanide species $[(C_5Me_5)_2M(\mu\text{-}CN)]_n$ [M = U (**1**), Ce (**2**)], which likely have an oligomeric structure, as shown by the trimeric cyanide-bridged complex $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$ (**3**) obtained by addition of excess ^tBuNC into a suspension of **2** in acetonitrile. The structure of the U(III,IV) mixed valence compound $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ (**4**), which crystallized from a thf solution of $(C_5Me_5)_2UI(py)$ in the presence of excess NaCN, reveals a unique example of an f-element−(μ-CN)−M interaction (M = main group or d transition metal). The anionic polycyanides $[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2$ [M = U (**5**), Ce (**6**)] were synthesized by treatment of **1** and **2** with 2 equiv or an excess of N^nBu_4CN in acetonitrile; they were also prepared in a one-pot procedure by stepwise addition of 1 equiv of KCN and 2 equiv of N^nBu_4CN to the parent iodides in acetonitrile. The bent metallocenes **5** and **6** are unique low-valent molecular polycyanide compounds of an f-element that have been structurally identified, while **5** is the first fully characterized actinide(III) cyanide. Comparison of the crystal structures of **5** and **6** shows that the M−C(C_5Me_5) and M−C(CN) distances are 0.02−0.03 Å shorter for M = U than for M = Ce, while the ionic radius of uranium(III) is 0.02 Å larger than that of cerium(III).

Introduction

The chemistry of d transition metal cyanide complexes has been extensively explored for a long time, leading to considerable developments in both its fundamental aspects and applications.[1−4] The prominent position of the CN^- ligand in various domains, from biology to materials science, is largely related to its ability to bind metal ions in both their low and high oxidation states and to adopt different ligation modes, thus giving a rich variety of homo- and heteropolynuclear compounds with interesting structures and physicochemical properties. The research in this field was much revitalized during the last decade with the discovery of compounds exhibiting fascinating magnetic behavior.[4] In contrast, it is surprising that the cyanide complexes of the f-elements have received little attention, while the chemistry of the lanthanides and actinides has witnessed significant advances during the recent period.[5] Besides the homoleptic lanthanide cyanides $[Ln(CN)_3]_\infty$, which were prepared by treatment of $LnCl_3$ with $Hg(CN)_2$,[6] the trivalent cyanide complexes are limited to the metallocenes $[(C_5H_5)_2M(CN)]_\infty$ (M = U, Nd, Yb),[7] obtained by reaction of $(C_5H_5)_3M$ with the extremely toxic HCN gas, and the oligomeric species $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNR)]_3$ (R = ^tBu, Cy)[8] and $[(C_5Me_5)_2Sm(\mu\text{-}CN)]_6$,[9] synthesized respectively by oxidation of $(C_5Me_5)_2Sm(thf)_2$ with the corresponding isocyanide and by hydrogenation of $(C_5Me_5)_2$-

---

* Authors to whom correspondence should be addressed. E-mail: jean-claude.berthet@cea.fr; michel.ephritikhine@cea.fr.

[1] (a) Vahrenkamp, H.; Geiss, A.; Richardson, G. N. *J. Chem. Soc., Dalton Trans.* **1997**, 3643. (b) Hanusa, T. P.; Burkey, D. J. In *Encyclopedia of Inorganic Compounds*; King, R. B., Ed.; J. Wiley and Sons: Chichester, 1994; Vol. 2, p 943. (c) Sharpe, A. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McClerverty, J. A., Eds.; 1987; Vol. 2, Chapter 12.1, p 7.

[2] (a) Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **1997**, *254*, 195. (b) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (c) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (d) Datta, A.; Karan, N. K.; Mitra, S.; Tiekink, E. R. T. *Polyhedron* **2002**, *21*, 2237. (e) Calhorda, M. J.; Drew, M. G. B.; Félix, V.; Fonseca, L. P.; Gamelas, C. A.; Godinho, S. S. M. C.; Gonçalves, I. S.; Hunstock, E.; Lopes, J. P.; Parola, A. J.; Pina, F.; Romão, C. C.; Santos, A. G. *J. Organomet. Chem.* **2001**, *632*, 94. (f) Sokol, J. J.; Shores, M. P.; Long, J. R. *Inorg. Chem.* **2002**, *41*, 3052.

[3] (a) Akitsu, T.; Einaga, Y. *Polyhedron* **2006**, *25*, 2655. (b) Estrader, M.; Ribas, J.; Tangoulis, V.; Solans, X.; Font-Bardia, M.; Maestro, M.; Diaz, C. *Inorg. Chem.* **2006**, *45*, 8239. (c) Li, G.; Akitsu, T.; Sato, O.; Einaga, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12396. (d) Du, B.; Ding, E.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2001**, *40*, 3637. (e) Yan, B.; Wang, H. D.; Chen, Z. D. *Polyhedron* **2001**, *20*, 591. (f) Liu, J.; Knoeppel, D. W.; Liu, S.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2001**, *40*, 2842. (g) Rawashdeh-Omary, M. A.; Larochelle, C. L.; Patterson, H. H. *Inorg. Chem.* **2000**, *39*, 4527.

[4] (a) Visinescu, D.; Desplanches, C.; Imaz, I.; Bahers, V.; Pradhan, R.; Villamena, F. A.; Guionneau, P.; Sutter, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 10202. (b) Yeung, W. F.; Lau, T. C.; Wang, X. Y.; Gao, S.; Szeto, L.; Wong, W. T. *Inorg. Chem.* **2006**, *45*, 6756. (c) Przychodzeń, P.; Lewiński, K.; Pelka, R.; Balanda, M.; Tomala, K.; Sieklucka, B. *Dalton Trans.* **2006**, 625. (d) Figuerola, A.; Ribas, J.; Llunell, M.; Casanova, D.; Maestro, M.; Alvarez, S.; Diaz, C. *Inorg. Chem.* **2005**, *44*, 6939. (e) Figuerola, A.; Ribas, J.; Casanova, D.; Maestro, M.; Alvarez, S.; Diaz, C. *Inorg. Chem.* **2005**, *44*, 6949. (f) Wang, S.; Zuo, J. L.; Gao, S.; Song, Y.; Zhou, H. C.; Zhang, Y. Z.; You, X. Z. *J. Am. Chem. Soc.* **2004**, *126*, 8900. (g) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096. (h) Rombaut, G.; Verelst, M.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *Inorg. Chem.* **2001**, *40*, 1151. (i) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (j) El Fallah, M. S.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947. (k) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397. (l) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701. (m) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (n) Mallah, T.; Thiébaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554. (o) Kahn, O. *Molecular Magnetism*; VCH Publishers Inc.: New York, 1993.

[5] (a) Burns, C. J.; Eisen, M. S. In *The Chemistry of the Actinides and Transactinides Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands; 2006; Vol. 5, p 2799. (b) Ephritikhine, M. *Dalton Trans.* **2006**, 2501.

[6] McColm, I. J.; Thompson, S. J. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3801.

[7] Kanellakopulos, B.; Dornberger, E.; Billich, H. *J. Organomet. Chem.* **1974**, *76*, C42.

[8] Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797.

[9] Obora, Y.; Ohta, T.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 3745.

10.1021/om061131x CCC: $37.00 © 2007 American Chemical Society
Publication on Web 03/30/2007

$Sm(N\{SiMe_3\}CHPh\{NCHPh\})$. The latter two complexes are the sole crystallographically characterized cyanide compounds of trivalent f-elements. Here we report on the synthesis and characterization of the neutral oligomeric uranium(III) and cerium(III) cyanides $[(C_5Me_5)_2M(\mu\text{-}CN)]_n$ and their mononuclear anionic derivatives $[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2$ (M = U, Ce);[10] the crystal structures of the latter, of the trimeric isonitrile adduct $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$, and of the polymeric mixed valence U(III,IV) compound $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ are presented.

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 dried over KH for pyridine and acetonitrile and over a mixture of sodium benzophenone for thf, and distilled immediately before use. *tert*-Butyl isocyanide (98%), purchased from Aldrich, was stored under argon and over 3 Å molecular sieves. NaCN (97%, Fluka), KCN (98%, Fluka), and N^nBu_4CN (95%, Aldrich) have been used as received. KC_5Me_5 was prepared by mixing a slight excess of C_5Me_5H with KH (Aldrich) in thf. $(C_5Me_5)_2UI(py)$,[11] $(C_5Me_5)_2U(OTf)$,[12] $(C_5Me_5)_2CeI$,[13] and $U(OTf)_3$[14] were synthesized as previously reported. $Ce(OTf)_3$ (99%, Acros) was dried under vacuum for 48 h at 150 °C before use. 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 ^1H 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).

Synthesis of $(C_5Me_5)_2Ce(OTf)$. A flask was charged with $Ce(OTf)_3$ (279.4 mg, 0.476 mmol) and KC_5Me_5 (182.5 mg, 1.047 mmol), and thf (20 mL) was condensed in. The color of the solution readily turned yellow, and a white powder precipitated. The mixture was stirred for 90 min at 20 °C and the solvent evaporated off. The beige residue was extracted with diethyl ether (20 mL), and after evaporation of the solvent, the beige powder of $(C_5Me_5)_2Ce(OTf)$ was dried under vacuum (248 mg, 93%). Anal. Calcd for $C_{21}H_{30}CeF_3SO_3$: C, 45.07; H, 5.40. Found: C, 44.81; H, 5.24. ^1H NMR (thf-d_8): δ 4.46 (s, $w_{1/2}$ 28 Hz, 30H).

Synthesis of $[(C_5Me_5)_2U(\mu\text{-}CN)]_n$ (1). A flask was charged with $(C_5Me_5)_2UI(py)$ (222.3 mg, 0.311 mmol) and N^nBu_4CN (87.9 mg, 0.311 mmol), and acetonitrile (20 mL) was condensed in. The color of the solution readily turned brown, and a brown precipitate was deposited. The mixture was stirred for 2 h at 20 °C, and the volume of the solution was reduced to 10 mL by evaporation. The brown powder of **1** was filtered off, washed twice with acetonitrile (5 mL), and dried under vacuum (133 mg, 80%). Anal. Calcd for $C_{21}H_{30}UN$: C, 47.19; H, 5.66. Found: C, 46.90; H, 5.55. The poor solubility of **1** in organic solvents (thf, acetonitrile, and pyridine) prevented the collection of NMR spectra. IR (Nujol): $\nu(CN) = 2082$ cm^{-1}. Complex **1** was synthesized in a similar fashion from $(C_5Me_5)_2U(OTf)$ in place of $(C_5Me_5)_2UI(py)$.

Synthesis of $[(C_5Me_5)_2Ce(\mu\text{-}CN)]_n$ (2). A flask was charged with $(C_5Me_5)_2CeI$ (254.4 mg, 0.473 mmol) and N^nBu_4CN (133.8 mg, 0.473 mmol), and acetonitrile (20 mL) was condensed in. The color of the solution readily turned orange, and a yellow precipitate was deposited. The mixture was stirred for 2 h at 20 °C, and the volume of the solution was reduced to 10 mL. The yellow precipitate was filtered off, washed twice with acetonitrile (5 mL), and dried under vacuum for 15 h at room temperature, giving a mauve powder of **2** (177.6 mg, 86%). Anal. Calcd for $C_{21}H_{30}CeN$: C, 57.77; H, 6.93; N 3.21. Found: C, 57.59; H, 6.65; N, 2.92. The poor solubility of **2** in organic solvents (thf, acetonitrile, and pyridine) prevented the collection of NMR spectra. IR (Nujol): $\nu(CN) = 2104$ cm^{-1}. Complex **2** was synthesized in a similar fashion from $(C_5Me_5)_2Ce(OTf)$ in place of $(C_5Me_5)_2CeI$.

Crystals of $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$ (3). In an NMR tube, an excess of ^tBuNC (26 μL, 0.23 mmol) was added into a suspension of **2** (10 mg, 0.023 mmol) in acetonitrile (0.5 mL). After heating at 90 °C for 10 min, the yellow solution was slowly cooled to room temperature and deposited pale yellow crystals of **3**. IR (Nujol): $\nu(^tBuNC) = 2177$ (s), $\nu(CN) = 2135$(w) and 2102(s) cm^{-1}.

Crystals of $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ (4). Brown crystals were obtained by slow diffusion at 20 °C of diethyl ether into a thf solution of $(C_5Me_5)_2UI(py)$ containing an excess of NaCN.

Synthesis of $[(C_5Me_5)_2U(CN)_3][N^nBu_4]_2$ (5). A flask was charged with $(C_5Me_5)_2UI(py)$ (311.7 mg, 0.436 mmol) and KCN (43 mg, 0.660 mmol), and acetonitrile (20 mL) was condensed in. The mixture was stirred for 15 h at 20 °C, giving a brown solution and a brown precipitate. The latter was dissolved upon addition of N^nBu_4CN (246.6 mg, 0.872 mmol); after 4 h at 20 °C, the solvent was evaporated off and the residue extracted with thf (10 mL). After evaporation, the brown powder of **5** was dried under vacuum (388 mg, 83%). Anal. Calcd for $C_{55}H_{102}UN_5$: C, 61.65; H, 9.60; N, 6.54. Found: C, 61.87; H, 9.75; N, 6.49. ^1H NMR (acetonitrile-d_3): δ 2.77 (m, 16H, NCH_2), 1.37−0.90 (m, 56H, N^nBu_4), −6.50 (s, $w_{1/2}$ 20 Hz , 30H, C_5Me_5). IR (Nujol): $\nu(CN) = 2157$(w), 2091(s), and 2060(s) cm^{-1}.

Synthesis of $[(C_5Me_5)_2Ce(CN)_3][N^nBu_4]_2$ (6). A flask was charged with $(C_5Me_5)_2CeI$ (120.7 mg, 0.225 mmol) and KCN (22 mg, 0.338 mmol), and acetonitrile (20 mL) was condensed in. The mixture was stirred for 15 h at 20 °C, giving an orange solution and a yellow precipitate. The latter was dissolved upon addition of N^nBu_4CN (127.2 mg, 0.450 mmol); after 4 h at 20 °C, the solvent was evaporated off and the residue extracted with thf (10 mL). After evaporation, the yellow powder of **6** was dried under vacuum (177.4 mg, 81%). Anal. Calcd for $C_{55}H_{102}CeN_5$: C, 67.85; H, 10.56; N, 7.19. Found: C, 67.56; H, 10.84; N, 6.91. ^1H NMR (acetonitrile-d_3): δ 3.10 (m, 16H, NCH_2), 2.91 (s, $w_{1/2}$ 20 Hz , 30H, C_5Me_5), 1.62−0.90 (m, 56H, N^nBu_4). IR (Nujol): $\nu(CN) = 2086$(m) and 2065(m) cm^{-1}.

Complexes **5** and **6** were synthesized in an NMR tube by addition of 2 equiv of N^nBu_4CN into a solution of **1** or **2** (10 mg) in acetonitrile-d_3 (0.4 mL) or by addition of 3 equiv of the ammonium cyanide into a MeCN solution of $(C_5Me_5)_2MX$ (M = U, Ce; X = I, OTf). The tube was immersed in an ultrasound bath (80 W, 40 kHz) for 5 min at 20 °C, and the spectrum showed the quantitative formation of **5** or **6**. Crystals were obtained by slow diffusion of diethyl ether into an acetonitrile solution.

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[15] with graphite-monochromated 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 (φ and ω scans with 2° steps) were processed with HKL2000.[16] The structures were solved by direct methods or by Patterson map interpretation with

---

[10] Maynadié, J.; Barros, N.; Berthet, J. C.; Thuéry, P.; Maron, L.; Ephritikhine, M. *Angew. Chem.*, *Int. Ed.* **2007**, *46*, 2010.

[11] Avens, L. R.; Burns, C. J.; Butcher, R. J.; Clark, D. L.; Gordon, J. C.; Shake, A. R.; Scott, B. L.; Watkin, J. G.; Zwick, B. D. *Organometallics* **2000**, *19*, 451.

[12] Maynadié, J.; Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *Organometallics* **2006**, *25*, 5603.

[13] Mehdoui, T.; Berthet, J. C.; Thuéry, P.; Salmon, L.; Rivière, E.; Ephritikhine, M. *Chem.−Eur. J.* **2005**, *11*, 1.

[14] Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **1999**, 2005.

[15] Kappa-CCD Software; Nonius BV, Delft, 1998.

[16] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

Table 1. Crystal Data and Structure Refinement Details

	3	4	5[10]	6
empirical formula	$C_{78}H_{117}Ce_3N_6$	$C_{53}H_{76}N_5Na_2O_2U_2$	$C_{55}H_{102}N_5U$	$C_{55}H_{102}CeN_5$
M_r	1559.14	1337.23	1071.45	973.54
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pca2_1$	$C2/c$	$C2/c$	$C2/c$
a/Å	18.9720(18)	35.8003(15)	21.7791(10)	21.8298(4)
b/Å	23.084(3)	12.2794(5)	14.7214(7)	14.7017(3)
c/Å	18.993(2)	27.5754(13)	20.1912(8)	20.2229(4)
β /deg	90	106.107(3)	120.879(4)	120.9867(11)
V/Å^3	8318.0(16)	11646.5(9)	5556.1(4)	5564.0(2)
Z	4	8	4	4
D_{calcd}/g cm^{-3}	1.245	1.525	1.281	1.162
μ(Mo Kα)/mm^{-1}	1.654	5.609	2.959	0.855
F(000)	3204	5208	2236	2100
no. of reflns collected	130 877	134 572	18 874	88 329
no. of indep reflns	14 213	11 018	5026	5268
no. of obsd rflns ($I > 2\sigma(I)$)	6909	8533	4503	5118
R_{int}	0.072	0.066	0.052	0.020
no. of params refined	819	597	286	286
R1	0.071	0.038	0.027	0.018
wR2	0.155	0.102	0.058	0.047
S	0.893	1.032	1.013	1.055
$\Delta\rho_{min}$/e Å^{-3}	−0.58	−0.86	−1.03	−0.33
$\Delta\rho_{max}$/e Å^{-3}	1.08	1.88	0.54	0.28

SHELXS97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL97.[17] Absorption effects were corrected empirically with SCALEPACK[16] or DELABS.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters, with some restraints for the terminal carbon atoms of the ^{t}BuNC ligands in **3** and the carbon atoms of one thf molecule in **4**. The nitrogen and carbon atoms of the bidentate cyanide groups in **3** and **4** could not be discriminated; their location has been chosen so as to get equivalent isotropic parameters as close as possible to one another for the two atoms, but the difference between the two possibilities is not significant enough to permit an unambiguous choice. Some voids in the lattices of **3** and **4** likely indicate the presence of disordered, unresolved solvent molecules. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement details are given in Table 1. The molecular plots were drawn with SHELXTL.[19]

Results and Discussion

Synthesis of the Monocyanide Complexes $[(C_5Me_5)_2M(\mu\text{-}CN)]_n$ (M = U or Ce) and $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$. Treatment of $(C_5Me_5)_2UI(py)$ or $(C_5Me_5)_2CeI$ with 1 equiv of N^nBu_4CN in acetonitrile at 20 °C readily afforded a brown or yellow precipitate, which was filtered off, washed with MeCN, and dried under vacuum to give a brown or mauve powder of $[(C_5Me_5)_2M(CN)]_n$ [M = U (**1**) or Ce (**2**)], respectively (eq 1); the yields were 80 and 86%, respectively. Complexes **1** and **2** were similarly synthesized from the triflate precursors $(C_5Me_5)_2M(OTf)$ (M = U, Ce). These trivalent f-element compounds are extremely air sensitive, but proved to be stable for months when kept in an inert atmosphere of argon. While the $(C_5Me_5)_2M$ moiety generally enhances the solubility of the complexes in nonpolar solvents, the poor solubility of **1** and **2** in coordinating solvents such as acetonitrile or pyridine likely reflects the presence of oligomers with cyanide bridges, as previously suggested for the highly insoluble tetravalent tris(cyclopentadienyl) compounds $[(C_5H_4R)_3U(CN)]_\infty$ (R = H, Me, Me_3Si, ^tBu).[7,20]

$$(C_5Me_5)_2MI + N^nBu_4CN \xrightarrow{MeCN} [(C_5Me_5)_2M(CN)]_n + N^nBu_4I \quad (1)$$

$$M = U\ (\mathbf{1}),\ Ce\ (\mathbf{2})$$

Attempts to crystallize **1** or **2** from hot acetonitrile were unsuccessful, but the slow cooling of a hot acetonitrile suspension of **2** in the presence of an excess of *tert*-butyl isocyanide led to the formation of pale yellow crystals of the trimeric adduct $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$ (**3**), suitable for X-ray diffraction (vide infra). Following the same procedure, crystals of the analogous uranium compound could not be obtained. The structure of **3** strongly suggests that **2** as well as **1**, in view of the similar radii of the Ce^{3+} and U^{3+} ions,[21] also have a trimeric structure in the solid state since isocyanides, though they are suitable ligands for f-elements,[8,22] seem not to be able to cleave strong cyanide bridges.[1b] It is possible that the change of color of **2**, from mauve in the dried solid to yellow in the acetonitrile suspension, is related to the reversible coordination of MeCN to the cerium ions in the trimeric complex.

The infrared spectra of **1** and **2** show strong absorption bands assigned to the ν(CN) stretching frequencies at 2082 and 2104 cm^{-1}, respectively, while the IR vibrational frequency of the cyanide ion in NEt_4CN is 2050 cm^{-1}. The CN^- ion can act as a strong σ-donor and a weak π-acid ligand, and the ability of low-valent uranium compounds to behave as π-donors is well documented with the formation of stable carbonyl[23] and nitrogen complexes[24] and through lanthanide(III)/actinide(III) differentiation studies.[13,25] However, the ν(CN) values in **1** and **2** suggest

---

[17] Sheldrick, G. M. *SHELXS97* and *SHELXL97*; University of Göttingen, 1997.

[18] Spek, A. L. *PLATON*; University of Utrecht, 2000.

[19] Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1999.

[20] (a) Bagnall, K. W.; Plews, M. J.; Brown, D.; Fischer, R. D.; Kläne, E.; Landgraf, G. W., Sienel G. R. *J. Chem. Soc., Dalton Trans.* **1982**, 1999. (b) Berthet, J. C.; Ephritikhine, M. Unpublished results.

[21] Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

[22] del Mar, Conejo, M.; Parry, J. S.; Carmone, E.; Schultz, M.; Brennann, J. G.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. *Chem.−Eur. J.* **1999**, *5*, 3000.

[23] (a) Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc*. **2005**, *127*, 11242. (b) Evans, W. J.; Kozimor, S. A.; Nyce, G. W.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 13831. (c) Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649.

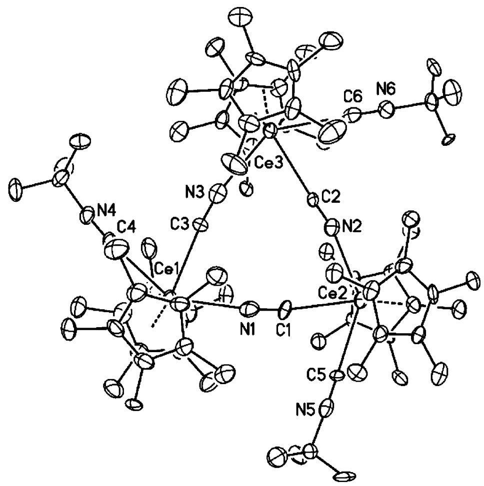


Figure 1. View of complex **3**. Hydrogen atoms have been omitted. Displacement parameters are drawn at the 20% probability level.

the absence of π back-bonding from the M^{3+} ion to the cyanide ligand. Moreover, the higher ν(CN) value for the cerium compound **2** would indicate a stronger σ-donating interaction compared to the uranium(III) analogue. Compound **3** displays two strong frequencies in the ν(CN) region at 2102 and 2177 cm^{-1}. By comparing the IR spectra of **1**−**3**, together with that of $[Ce(CN)_3]_\infty$, which exhibits two ν(CN) absorptions at 2095 and 2125 cm^{-1},[6] the lowest frequency at 2102 cm^{-1} in **3** can be assigned to the cyanide ligand and the highest to the isocyanide group. These frequencies match those of the CN and RNC ligands, which were found respectively at 2110 and 2180 cm^{-1} or 2105 and 2180 cm^{-1} in the ^tBuNC or CyNC adducts $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNR)]_3$.[8] The isocyanide ν(CN) frequency in **3** can also be compared with those found in a series of $(R_nC_5H_{5-n})_3Ce(CNR)$ complexes, which are in the range 2150−2200 cm^{-1}.[22] The positive difference between the ν(CN) absorption of ^tBuNC in the trimeric compounds $[(C_5Me_5)_2Ln(\mu\text{-}CN)(CN^tBu)]_3$ (Ln = Sm, Ce) and that of the free molecule (2134 cm^{-1}) indicates that the isocyanide molecule acts only as an efficient σ donor toward the trivalent lanthanides.[22] The C≡N stretching modes of the cyanide ligands in the organometallic species **1**−**3** compare well with that measured in $(C_5H_5)_2U(CN)$ (2112 cm^{-1}),[6] $(C_5H_5)_3U(CN)$ (2110 or 2116 cm^{-1}),[26,7] $(C_5H_2{}^tBu_3)_2U(CN)(OSiMe_3)$ (2040 cm^{-1}),[27] and $(C_5H_5)_2Ln(CN)$ (2187 and 2116 cm^{-1} for Ln = Nd; 2198 and 2136 cm^{-1} for Ln = Yb),[7] but differ from those reported for $[(C_5Me_5)_2Sm(\mu\text{-}CN)]_6$ (2332 and 2360 cm^{-1}).[9]

Crystal Structure of $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$ (3). A view of **3** is shown in Figure 1, and selected bond lengths and angles are listed in Table 2. The structure, which is quite similar to that of a toluene solvate of $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCy)]_3$,[8] is built up of three bent metallocene $(C_5Me_5)_2Ce(CN^tBu)$ moieties connected via μ-CN ligands. This arrangement is reminiscent of that of the trimetallic complexes $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$[28] and $[(Me_3SiC_5H_4)_2U(\mu\text{-}O)]_3$,[29] but the nine-coordination of the metal centers in **3** is much less common in the series of bis(cyclopentadienyl) complexes of the f-elements.[30] The X-ray data do not differentiate between the carbon and nitrogen atoms in the CN bridging ligands due to their equivalent electron densities and similar metal bond distances. This is a common problem in crystallographic studies of cyanide complexes, which has also been encountered with the structures of $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCy)]_3$[8] and $[(C_5Me_5)_2Sm(\mu\text{-}CN)]_6$.[9] The $\{Ce(\mu\text{-}CN)\}_3$ framework is planar with an rms deviation of 0.10 Å, and the three cerium atoms define an equilateral triangle with an average Ce⋯Ce distance of 6.398(14) Å. The isocyanide ligand coordinated to Ce(2) is close to the plane, whereas the other two are not, the C(4) and C(6) atoms being on opposite sides at a distance of 0.54(2) Å. The average $Ce{-}C(C_5Me_5)$ and Ce−C/N(μ-CN) distances of 2.81(3) and 2.64(4) Å are respectively 0.06 and 0.07 Å smaller than the corresponding distances in $[(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCy)]_3$,[8] in agreement with the variation of 0.065 Å in the radii of the nine-coordinate Ce^{3+} and Sm^{3+} ions.[21] However, the mean Ce−C(isocyanide) bond length of 2.70(4) Å is 0.11 Å larger than the Sm−C(CNR) distance in the samarium complex.[8] This would correspond to a weaker Ce−C(isocyanide) interaction but is not reflected in the infrared data, which show quite identical isocyanide ν(CN) frequencies in the Sm and Ce compounds.

Synthesis of the Polycyanide Complexes $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ and $[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2$ (M = U, Ce). To the best of our knowledge, the uranyl(VI) compounds $[UO_2(CN)_5][NEt_4]_3$[31a] and $[(C_5Me_5)UO_2(CN)_3][NEt_4]_2$[31b] the uranium(IV) compounds $[(C_5Me_5)_2U(CN)_n]^{(n-2)-}$ (n = 3, 5)[10] and the homoleptic lanthanide complexes $Ln(CN)_3$[6] are the sole polycyanide compounds of f-elements, but only the uranium complexes have been recently crystallographically characterized. Synthesis of low-valent molecular f-element polycyanides was often attempted. Thus, treatment of $[(C_5H_4R)_3U(CN)]_n$ (R = H, Me) with an excess of alkali metal cyanide in water or various organic solvents (thf, MeCN) failed to give the expected anionic uranium complexes $[(C_5H_4R)_3U(CN)_2]^-$; it was then suggested that the cleavage of the U−CN−U bridges of $[(C_5H_4R)_3U(CN)]_n$ toward the formation of monomeric species with terminal cyanide ligands is thermodynamically unfavorable.[20a]

In a first attempt to prepare such monomeric polycyanide species of trivalent uranium by mixing $(C_5Me_5)_2UI(py)$ with an excess of NaCN in thf, brown crystals of the mixed valence U(III/IV) complex $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)\{(\mu\text{-}CN)_2Na(thf)\}_2]_\infty$ (**4**) were obtained after several days at room temperature (Figure 2). This compound certainly resulted from accidental oxidation of a U(III) polycyanide species by traces of air. The formation of **4** via the likely oligomeric intermediate $[(C_5Me_5)_2U(CN)]_n$ clearly indicates that the cleavage of the U−CN−U bridges by addition of CN^- ions is possible and that the nature of the M^+

---

[24] (a) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264. (b) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070.

[25] (a) Berthet, J. C.; Nierlich, M.; Miquel, Y.; Madic, C.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **2005**, 369. (b) Mehdoui, T.; Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *Chem. Commun.* **2005**, 2860. (c) Karmazin, L.; Mazzanti, M.; Bezombes, J. P.; Gateau, C.; Pécaut, J. *Inorg. Chem.* **2004**, *43*, 5147. (d) Jensen, M. P.; Bond, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 8970. (e) Berthet, J. C.; Miquel, Y.; Iveson, P. B.; Nierlich, M.; Thuéry, P.; Madic, C.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3265. (f) Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J. M.; Maldivi, P.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389. (g) Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. *Inorg. Chem.* **2001**, *40*, 4428. (h) Wietzke, R.; Mazzanti, M.; Latour, J. M.; Pécaut, J. *J. Chem. Soc., Dalton Trans.* **2000**, 4167.

[26] Adam, R.; Villiers, C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *445*, 99.

[27] Zi, G.; Jia, L.; Werkema, E. L.; Walter, M. D.; Gottfriedsen, J. P.; Andersen, R. A. *Organometallics* **2005**, *24*, 4251.

[28] Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075.

[29] Berthet, J. C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *460*, 47.

[30] (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Hazin, P. N.; Lakshminarayan, C.; Brinen, L. S.; Knee, J. L.; Bruno, J. W.; Streib,W. E.; Folting, K. *Inorg. Chem.* **1988**, *27*, 1393.

[31] (a) Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *Chem. Commun.* **2007**, 604. (b) Maynadié, J.; Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *Chem. Commun.* **2007**, 486.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[(C_5Me_5)_2Ce(\mu\text{-}CN)(CN^tBu)]_3$ (3)

Ce(1)−N(1)	2.615(14)	Ce(1)−C(4)	2.719(17)	Cp*1[a]−Ce(1)−Cp*2	134.4
Ce(2)−N(2)	2.612(14)	Ce(2)−C(5)	2.642(14)	Cp*1−Ce(2)−Cp*2	134.1
Ce(3)−N(3)	2.701(16)	Ce(3)−C(6)	2.736(17)	Cp*1−Ce(3)−Cp*2	133.4
Ce(1)−C(3)	2.596(15)	C(1)−N(1)	1.186(13)	Ce(1)−N(1)−C(1)	171.0(13)
Ce(2)−C(1)	2.641(13)	C(2)−N(2)	1.131(14)	Ce(2)−N(2)−C(2)	165.1(11)
Ce(3)−C(2)	2.704(14)	C(3)−N(3)	1.174(15)	Ce(3)−N(3)−C(3)	169.1(12)
Ce(1)−C(C_5Me_5)	2.83(2)	C(4)−N(4)	1.129(16)	Ce(1)−C(3)−N(3)	173.5(13)
Ce(2)−C(C_5Me_5)	2.80(4)	C(5)−N(5)	1.140(16)	Ce(2)−C(1)−N(1)	170.8(13)
Ce(3)−C(C_5Me_5)	2.80(2)	C(6)−N(6)	1.133(16)	Ce(3)−C(2)−N(2)	177.0(11)

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

ion in the MCN salt is crucial since it may participate in the formation of polynuclear species. This can be detrimental to the formation of materials containing only the M_f−CN−M_f pattern (M_f = f-element) that can display specific physicochemical properties.

In order to avoid the formation of U−CN−Na bridges and to favor the synthesis of mononuclear $[(C_5Me_5)_2U(CN)_n]^{(n-1)-}$ complexes, NaCN was replaced with N^nBu_4CN in its reactions with **1** and **2**. The anionic tris(cyanide) complexes $[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2$ [M = U (**5**), Ce (**6**)] were readily prepared in almost quantitative yield either by treatment of **1** or **2** with 2 equiv of N^nBu_4CN or by addition of 3 equiv or an excess of the ammonium cyanide to $(C_5Me_5)_2MX$ (M = U, Ce; X = I, OTf) in acetonitrile, according to eqs 2 and 3; brown (M = U) or pale yellow (M = Ce) crystals suitable for X-ray diffraction were formed upon slow diffusion of diethyl ether into the acetonitrile solution (Figure 3). Analytically pure powders of **5** and **6** were conveniently obtained in a one-pot procedure by successive addition of 1 equiv of KCN and 2 equiv of N^nBu_4CN to $(C_5Me_5)_2MI$ in acetonitrile; the products were easily separated from the released KI by extraction with thf. The choice of the NR_4CN salt is important in these reactions; using NEt_4CN in place of N^nBu_4CN did not permit the isolation of **5** and **6** in a pure form, free from NEt_4X.

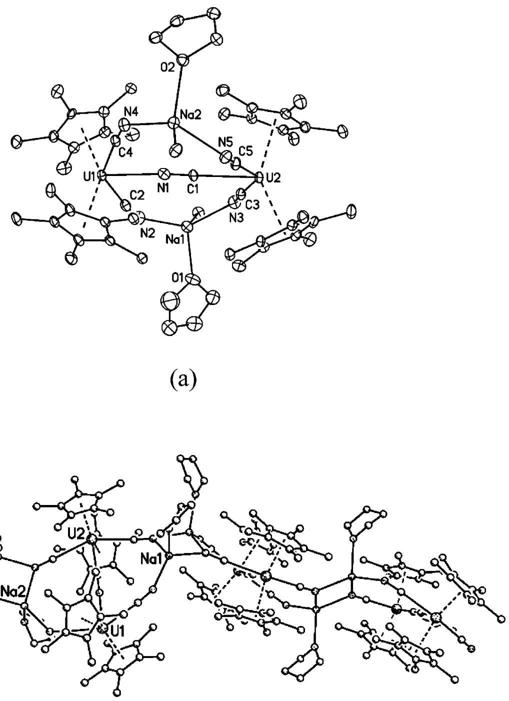
$$\underset{M = U\ (\mathbf{1}),\ Ce\ (\mathbf{2})}{[(C_5Me_5)_2M(CN)]_n} + 2\,N^nBu_4CN \xrightarrow{MeCN} \underset{M = U\ (\mathbf{5}),\ Ce\ (\mathbf{6})}{[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2} \quad (2)$$

$$\underset{X = I,\ OTf}{(C_5Me_5)_2MX} + 3\,N^nBu_4CN \xrightarrow{MeCN} \underset{M = U\ (\mathbf{5}),\ Ce\ (\mathbf{6})}{[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2 + N^nBu_4X} \quad (3)$$

The infrared spectra of **5** and **6** show two strong absorption bands in the ν(CN) region at 2091 and 2060, and 2086 and 2065 cm^{-1}, respectively. As expected for terminal cyanide ligands,[1b] these values are smaller than those corresponding to the bridging CN groups in the oligomeric parents **1** and **2** and can be compared with that of 2040 cm^{-1} in the mononuclear uranium(IV) compound $(C_5H_2{}^tBu_3)_2U(CN)(OSiMe_3)$.[27]

Contrary to the uranium(IV) compound $[(C_5Me_5)_2M(CN)_3][N^nBu_4]$, which was readily transformed into the linear metallocene $[(C_5Me_5)_2M(CN)_5][N^nBu_4]_3$,[10] complexes **5** and **6** were found to be inert in the presence of an excess of cyanide ions, which reveals that their stability is related to the electronic configuration of the f-element and evidences the role of the f orbitals, as previously observed with cationic U(III) and U(IV) metallocenes.[12]

Crystal Structures of $[\{(C_5Me_5)_2U\}_2(\mu\text{-}CN)_5\{Na(thf)\}_2]_\infty$ (4) and $[(C_5Me_5)_2M(CN)_3][NBu^n{}_4]_2$ (M = U (5), Ce (6)). Views of **4** are shown in Figures 2a and 2b, and selected bond lengths and angles are listed in Table 3. The structure of the tetranuclear Na_2U_2 moiety (Figure 2a) is reminiscent of that of the triflate compound $[(C_5Me_5)_2U(OTf)_3Na(thf)_2]_2$[12] and can be formally viewed as the association of the uranium(III) species $[(C_5Me_5)_2U(CN)_3\{Na(thf)\}_2]$ and the uranium(IV) derivative



(a)

(b)

Figure 2. (a) View of complex **4**. Hydrogen atoms have been omitted. Displacement parameters are drawn at the 20% probability level. Symmetry codes: ′ = 1 − *x*, *y*, 1.5 − *z*; ″ = 1.5 − *x*, 1.5 − *y*, 2 − *z*. (b) View of the 1D chain.

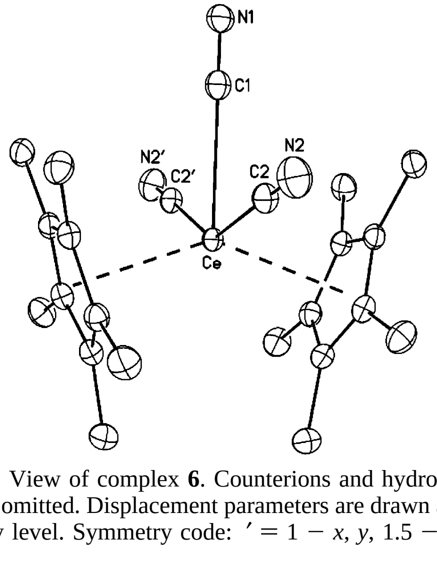


Figure 3. View of complex **6**. Counterions and hydrogen atoms have been omitted. Displacement parameters are drawn at the 50% probability level. Symmetry code: ′ = 1 − *x*, *y*, 1.5 − *z*.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[\{(C_5Me_5)_2U\}_2(\mu\text{-CN})\{(\mu\text{-CN})_2Na(thf)\}_2]_\infty$ (4)

U(1)−N(1)	2.482(6)	Na(1)−N(2)	2.335(7)	Cp*1−U(1)−Cp*2[a]	143.8
U(1)−C(2)	2.521(8)	Na(1)−N(3)	2.395(7)	Cp*1−U(2)−Cp*2[a]	140.6
U(1)−C(4)	2.508(7)	Na(1)−N(3′)	2.343(6)	N(1)−U(1)−C(2)	71.86(19)
U(2)−C(1)	2.599(6)	Na(2)−N(4)	2.347(6)	N(1)−U(1)−C(4)	72.92(18)
U(2)−C(3)	2.600(7)	Na(2)−N(5)	2.364(6)	C(2)−U(1)−C(4)	144.8(2)
U(2)−C(5)	2.615(7)	Na(2)−N(5″)	2.380(6)	C(1)−U(2)−C(3)	72.91(19)
U(1)−C(C_5Me_5)	2.732(9)	Na(1)−O(1)	2.288(6)	C(1)−U(2)−C(5)	71.02(19)
U(2)−C(C_5Me_5)	2.78(2)	Na(2)−O(2)	2.289(5)	C(3)−U(2)−C(5)	143.6(2)
				U(1)−N(1)−C(1)	175.2(5)
		C(1)−N(1)	1.172(8)	U(1)−C(2)−N(2)	172.9(6)
		C(2)−N(2)	1.142(8)	U(1)−C(4)−N(4)	176.1(6)
		C(3)−N(3)	1.168(8)	U(2)−C(1)−N(1)	178.5(6)
		C(4)−N(4)	1.154(8)	U(2)−C(3)−N(3)	176.4(6)
		C(5)−N(5)	1.154(8)	U(2)−C(5)−N(5)	177.7(5)

[a] Cp* is the centroid of the cyclopentadienyl ring. Symmetry codes: ′ = 1 − *x*, *y*, 1.5 − *z*; ″ = 1.5 − *x*, 1.5 − *y*, 2 − *z*.

$(C_5Me_5)_2U(CN)_2$. Their assemblage is ensured by a central cyanide group, which bridges the two uranium atoms, while the four lateral cyanide ligands trap, at the periphery, the two $Na(thf)^+$ entities. The U(1)···U(2) line is a pseudo-C_2 axis of symmetry. As in the case of **3**, the crystal data do not differentiate between the C and N atoms of the CN bridges, but it is likely that the N atoms are coordinated to the alkali metal. The four metal centers are coplanar with an rms deviation of 0.074 Å, and this plane, which coincides with the equatorial girdle of the $(C_5Me_5)_2U$ fragments, also contains the cyanide ligands within 0.801(6) Å. The Na(1) and Na(2) atoms are in a distorted tetrahedral environment, being linked respectively to the O(1) and O(2) atoms of a thf molecule and to the N(3) and N(5) atoms of neighboring units, thus leading to the formation of infinite zigzag chains running along the [1 0 1] direction (Figure 2b). Such triply bridging cyanide ligands have been found in d transition metal complexes.[32] The U−C(C_5Me_5) and U−C/N(CN) distances are smaller for U(1) than for U(2). The average U(1)−C(C_5Me_5) distance of 2.732(9) Å is typical of U(IV) bis(pentamethylcyclopentadienyl) complexes, as observed in $(C_5Me_5)_2UI_2(NCR)$ [2.71(2) and 2.75(2) Å for R = ${}^tBu$ and Me, respectively],[12] $(C_5Me_5)_2U(OTf)_2(NCMe)$ [2.72(2) Å],[12] or $(C_5Me_5)_2UCl_2(C_3H_4N_2)$ [2.74(2) Å],[33] whereas the larger mean U(2)−C(C_5Me_5) distance of 2.78(2) Å is close to the value of 2.79 Å usually found in nine-coordinate U(III) species, such as $(C_5Me_5)_2UI(CNMe)_2$ [2.79(1) Å],[12] $(C_5Me_5)_2UH(dmpe)$ [2.79(4) Å],[34] or $[(C_5Me_5)_2U(terpy)]I$ [2.78(3) Å].[25a] The mean U(1)−C/N(CN) distance of 2.504(16) Å is 0.10 Å smaller than the mean U(2)−C/N(CN) distance, 2.605(7) Å, which is similar to the average Ce−C/N(CN) distance of 2.64(5) Å in **3**. These structural features are in agreement with the uranium atoms U(1) and U(2) being in the +4 and +3 oxidation states, respectively. However, the differences between the U(1)−ligand and U(2)−ligand bond lengths could also be related to the distinct ligation modes of the cyanide groups coordinated to U(1), C(2)N(2), and C(4)N(4) and those coordinated to U(2), C(3)N(3), and C(5)N(5), since the latter ensure the polymeric structure of the complex. The asymmetry in the structure of **4** is further shown with the Na(1)−N(3) and Na(2)−N(5) distances of 2.395(7) and 2.364(6) Å, which are respectively 0.06 and 0.02 Å larger than the Na(1)−N(2) and Na(2)−N(4) distances. The C−N distances, which average 1.158(11) Å, are quite identical to those measured in the free cyanide anion[1b] and the bridging or terminal cyanide ligands of transition metal compounds. Complex **4** is likely to be the first compound exhibiting f-element−CN−M bridges (M = main group or d transition metal) since, in the uranyl(VI) compounds $[UO_2(H_2O)_4(dmf)_2]_{0.5}[UO_2\{M(CN)_6\}(dmf)_2]$ (M = Fe, Co)[35] and the series of lanthanide cyanometalates,[3,4] the bridging CN ligands are coordinated to the f-element via the nitrogen atom.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[(C_5Me_5)_2M(CN)_3][N^nBu_4]_2$ [M = U (5), Ce (6)]

	5	6
M−C(1)	2.636(5)	2.674(2)
M−C(2)	2.643(3)	2.6630(14)
M−C(C_5Me_5)	2.808(16)	2.83(2)
C(1)−N(1)	1.154(6)	1.154(3)
C(2)−N(2)	1.159(4)	1.161(2)
Cp*1[a]−M−Cp*2	142.0	141.3
M−C(1)−N(1)	180	180
M−C(2)−N(2)	177.6(3)	177.46(12)
C(1)−M−C(2)	73.69(7)	74.89(3)

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

Crystals of **5** and **6** are isomorphous; a view of the anion of the cerium derivative **6** is shown in Figure 3, and selected bond lengths and angles for both compounds are listed in Table 4. These unique examples of mononuclear $[(C_5Me_5)_2MX_3]^{n-}$ complexes[10,12] adopt the familiar bent-sandwich configuration with the three CN groups lying in the equatorial girdle of the $(C_5Me_5)_2M$ fragment; the line passing through the metal center and the C(1) and N(1) atoms of the central cyanide ligand is a C_2 axis of symmetry. The average M−C(C_5Me_5) distances of 2.808(16) and 2.83(2) Å for M = U and Ce, respectively, are unexceptional, but the ring centroid−M−ring centroid angles of 142.0° and 141.3°, respectively, are larger than those usually observed in $(C_5Me_5)_2MXL_2$ complexes, which are in the range 135−139°;[12,30,36] this difference is likely due to the weak steric requirement of the equatorial CN ligands, which does not force the bending of the cyclopentadienyl rings. The high accuracy of the structures of **5** and **6** helps determine unambiguously the M−C bonding mode of the CN ion. The average U−C(CN) distance of 2.641(3) Å in **5** is larger than that of 2.52(2) Å in the uranium(IV) congener $[(C_5Me_5)_2U(CN)_3][N^nBu_4]\cdot 1.5thf$[10] and is quite similar to that of 2.62(3) Å in the pentacyano derivative $[(C_5Me_5)_2U(CN)_5][NEt_4]_3$,[10] in agreement with the variation in the coordination numbers and the radii of the U^{4+} and U^{3+} ions.[21] This could indicate the similar nature of the U−CN bonds in the U(III) and U(IV) polycyanide metallocene complexes. The U−C(CN) bond lengths are also larger than

---

[32] (a) Liaw, W. F.; Tsai, W. T.; Gau, H. B.; Lee, C. M.; Chou, S. Y.; Chen, W. Y.; Lee, G. H. *Inorg. Chem.* **2003**, *42*, 2783. (b) Klose, A.; Hesschenbrouck, J.; Solari, E.; Latronico, M.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Organomet. Chem.* **1999**, *591*, 45.

[33] Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

[34] Duttera, M. R.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc*. **1982**, *104*, 865.

[35] Zhang, L. P.; Tanner, P. A.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2006**, *8*, 1543.

[36] Enriquez, A. E.; Scott, B. L.; Neu, M. P. *Inorg. Chem.* **2005**, *44*, 7403.

those in $(C_5HMe_4)_3U(CN)_{0.6}(Cl)_{0.4}$ [2.31(4) Å][22] and in $(C_5H_2{}^tBu_3)_2U(CN)(OSiMe_3)$[27] [2.415(6) Å], reflecting the different coordination numbers and/or the negative charge of the anionic compound. The mean U−C distance for the terminal CN ligands in **5** is slightly larger than that of the mean U(2)−C/N distance for the bridging CN groups in **4** [2.608(8) Å]; the same trend is observed between the Ce−C(CN) distances in **6** [2.666(5) Å] and **3** [2.64(5) Å].

Comparison of the crystal structures of **5** and **6** shows that the U−C(C_5Me_5) and U−C(CN) distances are shorter, by 0.02−0.03 Å, than the Ce−C(C_5Me_5) and Ce−C(CN) distances, while the ionic radius of uranium(III) is 0.02 Å longer than that of cerium(III).[21] Such deviations of U−X distances (X = C, N, I, P, S) from a purely ionic bonding model, which have been observed in a variety of analogous uranium(III) and lanthanide(III) complexes,[13,25,37] are explained by a stronger, more covalent actinide−ligand interaction. In these anionic and monomeric complexes, the shortening of the U−C(CN) distance with respect to the corresponding Ce−C(CN) bond lengths could be an indication of a stronger σ-donation of the ligand toward uranium rather than π back-bonding, as supported by the ν(CN) frequencies in **5** and **6**.

Conclusion

Successive addition of N^nBu_4CN to $(C_5Me_5)_2MX$ (M = U, Ce; X = I, OTf) afforded the neutral oligomeric complexes $[(C_5Me_5)_2M(CN)]_n$ and their anionic mononuclear derivatives $[(C_5Me_5)_2M(CN)_3][NBu^n{}_4]_2$, which are the first polycyanide complexes of a trivalent f-element to have been crystallographically characterized. After the characterization of uranyl(VI) and uranium(IV) tri- and pentacyanide compounds, these results show the ability of the cyanide ligand to stabilize low-valent uranium species The crystal structure of the U(III,IV) mixed valence compound $[\{(C_5Me_5)_2U\}_2(\mu\text{-CN})\{(\mu\text{-CN})_2Na(thf)\}_2]_\infty$, which was obtained accidentally, contains μ_2- and μ_3-bridging cyanides and demonstrates the potential of uranium cyanides in the elaboration of polynuclear f-element compounds. Comparison of the crystal structures of the analogous uranium(III) and cerium(III) complexes $[(C_5Me_5)_2M(CN)_3][NBu_4]_2$ (M = U, Ce) indicates that the covalent contribution to the U−C(C_5Me_5) and U−C(CN) bonds could be more important in the actinide compound. These trivalent complexes could not be transformed into the linear pentacyano metallocenes $[(C_5Me_5)_2M(CN)_5][N^nBu_4]_4$. The distinct cyanide chemistry of uranium(IV) metallocenes will be detailed in a forthcoming paper.

Acknowledgment. We thank the Nuclear Fission Safety Program of the European Union for support under the EUROPART (FI6W-CT-2003-508854) contract and the postdoctoral situation of J. Maynadié. We also thank the Direction de l'Energie Nucléaire of the Commissariat à l'Energie Atomique for its financial support.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061131X

---

(37) (a) Roger, M.; Barros, N.; Arliguie, T.; Thuéry, P.; Maron, L.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006**, *128*, 8790. (b) Roger, M.; Belkhiri, L.; Thuéry, P.; Arliguie, T.; Fourmigué, M.; Boucekkine, A.; Ephritikhine, M. *Organometallics* **2005**, *24*, 4940. (c) Mehdoui, T; Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans*. **2004**, 579. (d) Mehdoui, T.; Berthet, J. C.; Thuéry, P.; Ephritikhine, M. *Dalton Trans.* **2005**, 1263. (e) Villiers, C.; Thuéry, P.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2004**, 4624. (f) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Polyhedron* **2003**, *22*, 3475. (g) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1329.