From Bent to Linear Uranium Metallocenes: Influence of Counterion, Solvent, and Metal Ion Oxidation State

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Reactions of $Cp^*_2UCl_2$ with a slight excess of Me_3SiI or Me_3SiOTf in acetonitrile provide convenient routes to $Cp^*_2UI_2$ (**1**) or $Cp^*_2U(OTf)_2$ (**2**) ($Cp^* = \eta\text{-}C_5Me_5$; $OTf = OSO_2CF_3$), which were isolated with excellent yields. Crystals of the bent metallocenes $Cp^*_2UI_2(NCR)$ (R = Me (**3**), ^tBu (**4**)) have been obtained by addition of excess RCN to a toluene solution of **1**. The triflate analogue $Cp^*_2U(OTf)_2$-(NCMe) (**5**) contains monodentate OTf ligands. Treatment of $Cp^*_2UMe_2$ with 2 equiv of $HNEt_3BPh_4$ in acetonitrile led to the immediate formation of $[Cp^*_2U(NCMe)_5][BPh_4]_2$ (**6**). The ^1H NMR spectra of **1** and **2** in acetonitrile are similar to that of **6**, indicating the presence of the dicationic species $[Cp^*_2U\text{-}(NCMe)_5][X]_2$ [X = I (**7**), OTf (**8**)] in this solvent. Compounds **6**–**8** are the first linear metallocenes of an f-element and exhibit an unprecedented structure with auxiliary donor ligands in the equatorial plane parallel to the cyclopentadienyl rings. When treated with Me_3SiOTf, the uranium(III) species $Cp^*_2UCl_2$-$Na(thf)_2$ did not afford the trivalent complex $Cp^*_2U(OTf)$ (**9**) but gave crystals of the dimeric uranium-(IV) "ate" compound $[Cp^*_2U(OTf)_3Na(thf)_2]_2 \cdot 2(CH_2)_4O$ (**10**·2(CH_2)_4O). The first organouranium(III) triflate, **9**, was isolated in 90% yield from the reaction of $U(OTf)_3$ with 2 equiv of KCp^* in thf. Dissolution of $Cp^*_2UI(py)$ in acetonitrile gave the adduct $Cp^*_2UI(NCMe)_2$ (**11**), which, like its cerium analogue, adopts a bent sandwich structure in its crystalline form. The ^1H NMR spectra of **11** and $Cp^*_2U(OTf)$-(NCMe)_2 are similar in benzene and acetonitrile, suggesting that the trivalent linear metallocene $[Cp^*_2U\text{-}(NCMe)_5][X]$ (X = I or OTf) is not present in pure acetonitrile. These observations are confirmed by the addition of 3 equiv or excess MeCN to a solution of $[Cp^*_2U(thf)_2][BPh_4]$ in thf, which afforded the stable $[Cp^*_2U(NCMe)_3][BPh_4]$ as the sole product.

Introduction

The nature of the halide and pseudo-halide X ligand in the starting materials $[M]X_n$ is of crucial importance in inorganic and organometallic chemistry since it has a strong influence on the synthesis, solubility, structure, and reactivity of the complexes. The nucleophilic character of the X group has a significant effect in metathesis reactions, and many efforts have been devoted to the preparation of useful precursors containing weakly coordinating anionic ligands and of highly reactive cationic complexes. In f-element chemistry, such compounds proved to be of major interest, permitting in particular the circumvention of the pervasive problem of the formation of "ate" species related to the retention of X on the metal center.[1]

The series of bis(pentamethylcyclopentadienyl) complexes, which are regarded as models in organouranium chemistry, were most generally synthesized from the dichloride precursor $Cp^*_2UCl_2$ and its reduced derivatives $[Cp^*_2UCl]_3$ and $Cp^*_2UCl_2Na(thf)_2$.[2,3] This situation has recently changed in uranium(III) chemistry with the discovery of practical routes to the new starting materials Cp^*_2UX (X = I,[4] BPh_4[5]) or $Cp^*_2U\text{-}(C_6H_6)UCp^*_2$.[6] These complexes were found to activate small unsaturated molecules, revealing unexpected reactions and new structural features and favoring a renewal of interest for the chemistry of U^{3+} reducing agents.[7] In contrast, the difficult or multistep preparations of the uranium(IV) compounds $Cp^*_2UX_2$ (X = I,[8] OTf[9]) certainly prevented their utilization as starting materials. Here we present new convenient syntheses of these complexes, their conversion in acetonitrile into the dicationic species $[Cp^*_2U(NCMe)_5][X]_2$ and the preparation of $[Cp^*_2U(NCMe)_5][BPh_4]_2$. With the aim to extend the variety of U(III) precursors, we also report the synthesis of the first organouranium(III) triflate complex $Cp^*_2U(OTf)$ and of $Cp^*_2UI(NCMe)_2$, a rare example of a crystallographically characterized Lewis base adduct of Cp^*_2UI. While the neutral compounds $Cp^*_2UX_2(NCMe)$ (X = I, OTf) and $Cp^*_2UI\text{-}(NCMe)_2$ adopt the familiar bent sandwich configuration, the cationic complexes $[Cp^*_2U(NCMe)_5][X]_2$ (X = I, OTf, BPh_4),

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resulting from total dissociation of the X ligands and saturation of the equatorial girdle, are the first linear metallocenes in the f-element series.[10] This finding led us to consider the possible formation of such complexes in the +3 oxidation state.

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 glove box. Solvents were dried over KH for pyridine and acetonitrile and over a mixture of sodium and benzophenone for thf, and distilled immediately 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 ^{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 were recorded at 23 °C when not otherwise specified. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). Me$_3$SiI (Aldrich) was stored under argon over 3 Å molecular sieves. Me$_3$SiOTf (Aldrich) was distilled and stored under argon over 3 Å molecular sieves. KH under mineral oil (Aldrich) was used after washings with toluene. KCp* was prepared by mixing a slight excess of C$_5$Me$_5$H with KH in thf. TlBPh$_4$ was precipitated as a white powder by mixing aqueous solutions of NaBPh$_4$ and TlNO$_3$; the compound was then washed with hot water followed with diethyl ether and dried under vacuum for 48 h. Cp*$_2$UCl$_2$,[2] Cp*$_2$UCl$_2$Na(thf)$_2$,[3] Cp*$_2$UMe$_2$,[2] UI$_3$(py)$_4$,[11] and U(OTf)$_3$[12] were synthesized as previously reported.

Synthesis of Cp*$_2$UI$_2$ (1). A flask was charged with Cp*$_2$UCl$_2$ (1061 mg, 1.83 mmol), and acetonitrile (50 mL) was condensed in. Addition of Me$_3$SiI (782 μL, 5.49 mmol) into the red suspension led immediately to a dark red solution. After stirring for 1 h at 20 °C, the solution was filtered and the solvent evaporated off, affording a brown powder, which was washed with pentane (10 mL) and dried under vacuum. Yield: 1263 mg (91%). Anal. Calcd for C$_{20}$H$_{30}$I$_2$U: C, 31.51; H, 3.97; I, 33.30. Found: C, 31.24; H, 3.90; I, 33.05. ^{1}H NMR (benzene-d_6): δ 18.1 (s, $w_{1/2}$ 37 Hz); (thf-d_8): δ 18.5 (s, $w_{1/2}$ 35 Hz); (pyridine-d_5): δ 18.8 (s, $w_{1/2}$ 33 Hz); (acetonitrile-d_3): δ 35.1 (s, $w_{1/2}$ 597 Hz).

Synthesis of Cp*$_2$U(OTf)$_2$ (2). A flask was charged with Cp*$_2$UCl$_2$ (1270 mg, 2.19 mmol), and acetonitrile (50 mL) was condensed in. Addition of Me$_3$SiOTf (1190 μL, 6.57 mmol) at 20 °C to the red suspension gave immediately a dark red solution, which was stirred for 1 h at 20 °C. After filtration, evaporation of the solvent afforded a red-brown powder, which was washed with pentane (10 mL) and dried under vacuum. Yield: 1732 mg (98%). Anal. Calcd for C$_{22}$H$_{30}$F$_6$O$_6$S$_2$U: C, 32.75; H, 3.76; F, 14.13. Found: C, 32.61; H, 3.81; F, 13.97. ^{1}H NMR (toluene-d_8): δ 18.38 (s, $w_{1/2}$ 19 Hz); (acetonitrile-d_3): δ 35.4 (s, $w_{1/2}$ 715 Hz).

Crystals of Cp*$_2$UI$_2$(NCMe) (3) and Cp*$_2$UI$_2$(NC^{t}Bu)·C$_7$H$_8$ (4·C$_7$H$_8$). An NMR tube was charged with 1 (15.0 mg, 0.019 mmol) in toluene (0.5 mL), and an excess of MeCN or ^{t}BuCN (ca. 15 equiv) was introduced via a microsyringe. The solution was cooled at −5 °C, and dark brown crystals were deposited after 15 h.

An NMR tube was charged with 1 (15.0 mg, 0.019 mmol) in toluene-d_8 (0.5 mL), and MeCN (1 μL, 0.019 mmol) was introduced via a microsyringe. ^{1}H NMR (toluene-d_8): δ 18.51 (s, $w_{1/2}$ 10 Hz, 30 H, Cp*), −0.27 (s, $w_{1/2}$ 70 Hz, 3 H, MeCN). After addition of 15 molar equiv of MeCN, the ^{1}H NMR spectrum exhibits signals

at δ 18.72 (s, $w_{1/2}$ 20 Hz, 30 H, Cp*), 0.23 (s, $w_{1/2}$ 50 Hz, 45 H, MeCN).

Crystals of Cp*$_2$U(OTf)$_2$(NCMe) (5). An NMR tube was charged with 2 (17.2 mg, 0.021 mmol) in toluene (0.5 mL), and MeCN (1.1 μL, 0.021 mmol) was added via a microsyringe. Dark red crystals of 5 were deposited within a few hours at room temperature.

Synthesis of [Cp*$_2$U(NCMe)$_5$][BPh$_4$]$_2$ (6). Method 1. A flask was charged with Cp*$_2$UMe$_2$ (109.2 mg, 0.20 mmol) and HNEt$_3$BPh$_4$ (170.9 mg, 0.41 mmol). Acetonitrile (20 mL) was condensed into it, and an immediate release of gas was observed. After stirring for 30 min at 20 °C, the solvent was evaporated off, leaving a brown crystalline powder, which was washed with thf (3 mL) and dried under vacuum. Yield: 220.0 mg (80%). Anal. Calcd for C$_{78}$H$_{85}$B$_2$N$_5$U: C, 69.28; H, 6.34; N, 5.18. Found: C, 69.03; H, 6.53; N, 5.05.

Method 2. A flask was charged with Cp*$_2$UI$_2$ (200.0 mg, 0.26 mmol) and TlBPh$_4$ (274.8 mg, 0.52 mmol), and acetonitrile (50 mL) was condensed in. The brown solution was stirred for 2 h at room temperature, and the yellow precipitate of TlI was filtered off. The volume of the solution was reduced to 10 mL, and diethyl ether (50 mL) was slowly condensed into it at −78 °C. The red crystals that were deposited after 12 h at 20 °C were filtered off and washed twice with the solution in order to eliminate a fluffy white contaminant. Yield: 180 mg (51%). Anal. Calcd for C$_{78}$H$_{85}$B$_2$N$_5$U: C, 69.28; H, 6.34; N, 5.18. Found: C, 69.14; H, 6.35; N, 5.14. ^{1}H NMR (acetonitrile-d_3): δ 35.3 (s, $w_{1/2}$ 600 Hz, 30 H, Cp*), 7.06−6.95 (m, 40 H, BPh$_4$); (dmf-d_7): 36.6 (s, $w_{1/2}$ 385 Hz, 30 H, Cp*), 7.25−6.95 (m, 40 H, BPh$_4$), 2.20 (s, 15 H, MeCN); (pyridine-d_5): δ 35.82 (s, $w_{1/2}$ 33 Hz, 30 H, Cp*), 7.70−6.32 (m, 40 H, BPh$_4$), −44.50 (s, $w_{1/2}$ 750 Hz, 15 H, MeCN). IR spectrum: ν(CN) = 2262 and 2269 cm^{-1}. The dark red solution of 6 in dmf was evaporated to dryness and the brown residue dissolved in acetonitrile-d_3. The ^{1}H NMR spectrum exhibits signals at δ 35.0 (s, $w_{1/2}$ 110 Hz, 30 H, Cp*), 7.23−6.90 (m, 5 H + 40 H, dmf + BPh$_4$), 2.53 (s, $w_{1/2}$ 250 Hz, 30 H, dmf); at −40 °C: δ 43.5 (s, $w_{1/2}$ 260 Hz, 30 H, Cp*), 7.90 (s, $w_{1/2}$ 33 Hz, 5 H, dmf), 7.06−6.81 (m, 40 H, BPh$_4$), 2.91 (s, 15 H, dmf), 2.76 (s, 15 H, dmf).

Crystals of [Cp*$_2$U(NCMe)$_5$][I]$_2$·nMeCN (7·nMeCN) (n = 1, 2.5) and [Cp*$_2$U(NCMe)$_5$][OTf]$_2$·MeCN (8·MeCN). Brown crystals of 7·MeCN were obtained by slow diffusion of diethyl ether into an acetonitrile solution of 1. Crystals of 7·2.5MeCN were obtained by slow evaporation of an acetonitrile solution of 1. Brown crystals of 8·MeCN were deposited from a toluene solution of 2 in the presence of 15 equiv of MeCN. These crystals were converted into 1 and 2 upon drying under vacuum.

Synthesis of Cp*$_2$U(OTf) (9). A flask was charged with U(OTf)$_3$ (397.0 mg, 0.579 mmol) and KCp* (222.2 mg, 1.275 mmol), and thf (20 mL) was condensed in. The color of the solution rapidly turned dark green, and a white precipitate of KOTf was formed. The solution was stirred for 90 min at room temperature, and its volume was reduced to 10 mL. The dark green solution obtained after addition of pentane (30 mL) was filtered. Evaporation of the solvent and washing of the residue with pentane (20 mL) afforded a green powder of 9 after drying under vacuum. Yield: 350 mg (92%). Anal. Calcd for C$_{21}$H$_{30}$F$_3$O$_3$SU: C, 38.39; H, 4.60. Found: C, 38.13; H, 4.42. ^{1}H NMR (thf-d_8): δ −3.24 (s, $w_{1/2}$ 56 Hz); (acetonitrile-d_3): δ −2.64 (s, $w_{1/2}$ 35 Hz). Evaporation of an acetonitrile solution of 9 gave a brown powder of Cp*$_2$U(OTf)(NCMe)$_2$. ^{1}H NMR (benzene-d_6): δ −2.93 (s, $w_{1/2}$ 40 Hz, 30 H, Cp*), −31.6 (s, $w_{1/2}$ 85 Hz, 6 H, MeCN).

Crystals of [Cp*$_2$U(OTf)$_3$Na(thf)$_2$]$_2$·2(CH$_2$)$_4$O (10·2(CH$_2$)$_4$O). An NMR tube was charged with Cp*$_2$UCl$_2$ (17 mg, 0.03 mmol) and 2% Na(Hg) (34 mg, 0.03 mmol of Na), and thf (0.5 mL) was condensed in. The solution rapidly took the green color characteristic of the U(III) species Cp*$_2$UCl$_2$Na(thf)$_2$. A large excess of Me$_3$SiOTf (81.5 μL, 0.45 mmol) was then introduced, and the color

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of the solution immediately turned red-brown. After 5 min at room temperature, slow concentration of the solution led to the formation of red crystals of **10**·2(CH_2)$_4$O.

Crystals of Cp*$_2$UI(NCMe)$_2$ (11). Dark brown crystals of **11** were obtained by cooling at 4 °C a toluene solution of Cp*$_2$UI(py) in the presence of 15 equiv of acetonitrile. Evaporation of an acetonitrile solution of Cp*$_2$UI(py), under vacuum for 15 h at room temperature, afforded the stable adduct **11** in quantitative yield. ^{1}H NMR (benzene-d_6): δ −1.59 (s, $w_{1/2}$ 43 Hz, 30 H, Cp*), −32.12 (s, $w_{1/2}$ 93 Hz, 6 H, MeCN); (acetonitrile-d_3): δ −1.09 (s, $w_{1/2}$ 65 Hz, Cp*).

Behavior of [Cp*$_2$U(thf)$_2$][BPh$_4$] in Acetonitrile. ^{1}H NMR of [Cp*$_2$U(thf)$_2$][BPh$_4$] (thf-d_8, 23 °C): δ 5.59−5.14 (m, 20 H, Ph), 0.10 (s, $w_{1/2}$ 100 Hz, 30 H, Cp*); (acetonitrile-d_3): δ 7.17−6.84 (m, 20 H, Ph), 3.76 (s, $w_{1/2}$ 7 Hz, 8 H, thf), 2.02 (s, $w_{1/2}$ 100 Hz, 8 H, thf), −2.59 (s, $w_{1/2}$ 30 Hz, 30 H, Cp*). Evaporation to dryness of an acetonitrile solution of [Cp*$_2$U(thf)$_2$][BPh$_4$] (15.2 mg, 0.016 mmol) gave a brown powder of [Cp*$_2$U(NCMe)$_3$][BPh$_4$]. ^{1}H NMR (thf-d_8, 23 °C): δ 5.63−5.18 (m, 20 H, Ph), 0.16 (s, $w_{1/2}$ 30 Hz, 30 H, Cp*), the resonances of MeCN are not visible; (thf-d_8, −80 °C): δ 4.33, 3.81, 3.19 (s, $w_{1/2}$ 30 Hz, 20 H, Ph), −0.49 (s, $w_{1/2}$ 100 Hz, 30 H, Cp*), −76.7 (s, $w_{1/2}$ 100 Hz, 9 H, MeCN). After addition of MeCN (2.5 μL, 0.048 mmol), the spectrum at −80 °C was unchanged, except for the appearance of the signal of free MeCN at δ 1.82 ($w_{1/2}$ 60 Hz).

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[13] with graphite-monochromated Mo Kα radiation (λ = 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.[14] The structures were solved by direct methods or by Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[15] Absorption effects were corrected empirically with SCALEPACK[14] or DELABS.[16] All non-hydrogen atoms were refined with aniso-tropic displacement parameters. In compound **7**·2.5CH$_3$CN, one acetonitrile molecule is disordered around a binary axis and has been given an occupancy parameter of 0.5. Restraints on C−F bond lengths and on displacement parameters were applied for the badly resolved triflate moiety in compound **8**. In compound **10**, restraints on one bond length and some displacement parameters have been applied for the atoms of one thf molecule. 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. Crystal data and structure refinement details are given in Table 1. The molecular plots were drawn with SHELXTL.[17]

Results and Discussion

Synthesis of Cp*$_2$UX$_2$ (X = I, OTf) and Crystal Structures of Cp*$_2$UI$_2$(NCR) (R = Me, [t]Bu) and Cp*$_2$U(OTf)$_2$(NCMe). The halide or pseudo-halide silane Me$_3$SiX molecules are useful substituting reagents in organic, inorganic, and organometallic chemistry.[18] Their efficiency in the conversion of low- and high-valent actinide compounds was also demonstrated.[19,20] In particular, we reported that the transformation [U]−Cl → [U]−I with Me$_3$SiI was rapid and quantitative in acetonitrile, which

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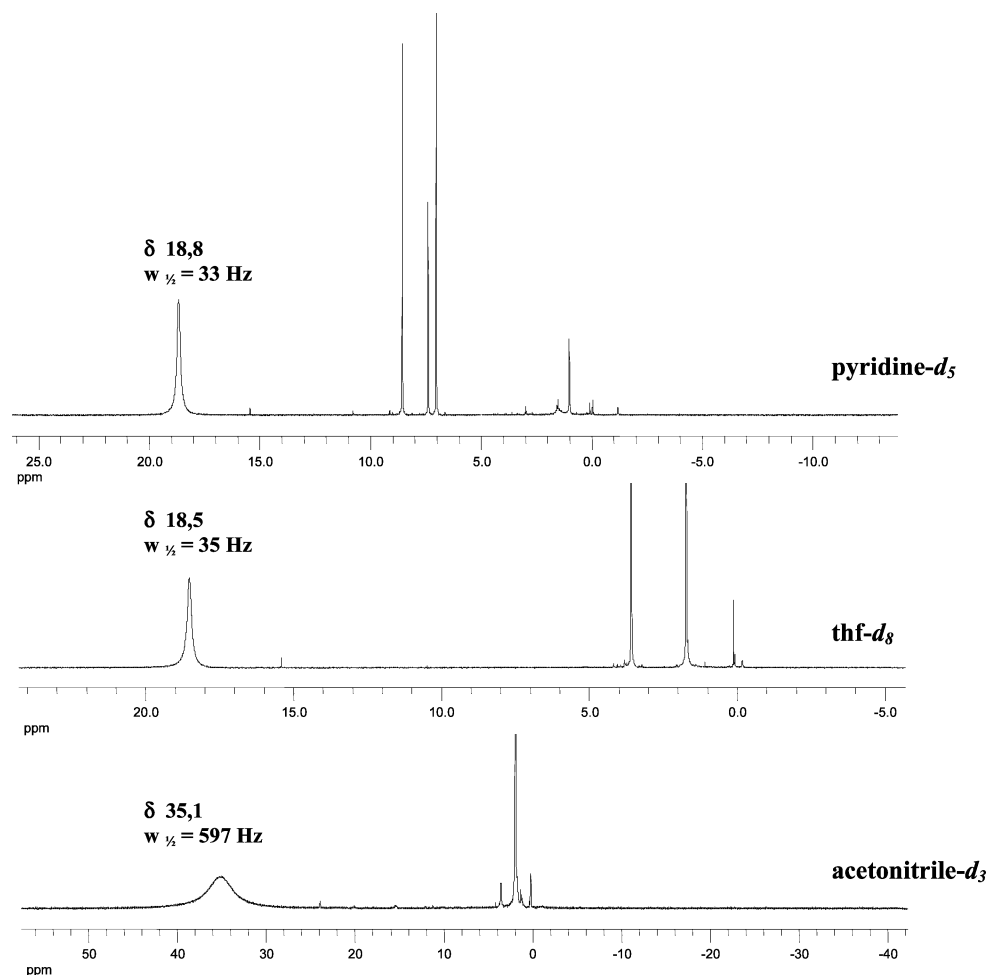(17) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1999.

Table 1. Crystal Data and Structure Refinement Details

	3	4·C$_7$H$_8$	5	6	7·MeCN	7·2.5MeCN	8·MeCN	10·2(CH$_2$)O	11
empirical formula	C$_{22}$H$_{33}$I$_2$NU	C$_{32}$H$_{47}$I$_2$NU	C$_{24}$H$_{33}$F$_6$NO$_6$S$_2$U	C$_{78}$H$_{85}$B$_2$N$_5$U	C$_{32}$H$_{48}$I$_2$N$_6$U	C$_{35}$H$_{52.5}$I$_2$N$_{7.5}$U	C$_{34}$H$_{48}$F$_6$N$_6$O$_6$S$_2$U	C$_{70}$H$_{108}$F$_{18}$Na$_2$O$_{24}$S$_6$U$_2$	C$_{24}$H$_{36}$IN$_2$U
M_r	803.32	937.54	847.68	1352.16	1008.59	1070.18	1052.95	2390.02	717.48
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$Pnma$	$Pnma$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$Pnma$	$Pbca$	$Pbcn$
a/Å	17.5655(6)	17.0969(6)	17.8654(8)	10.0055(1)	16.0984(10)	21.0005(5)	22.8466(10)	29.475(3)	12.9263(7)
b/Å	15.4579(5)	12.9933(9)	10.5923(5)	27.7679(6)	11.2243(7)	19.4352(5)	20.4868(9)	9.9062(7)	14.6453(8)
c/Å	8.8755(2)	15.0916(7)	15.9315(4)	24.2432(6)	21.1510(9)	22.9247(3)	9.2103(3)	30.888(4)	13.9515(5)
β/deg	90	90	104.406(3)	97.678(1)	105.096(4)	116.103(1)	90	90	90
V/Å^3	2409.93(13)	3352.5(3)	2920.0(2)	6675.1(2)	3690.0(4)	8402.4(3)	4310.9(3)	9018.8(16)	2641.2(2)
Z	4	4	4	4	4	8	4	4	4
D_{calcd}/g cm^{-3}	2.214	1.857	1.928	1.345	1.816	1.692	1.622	1.760	1.804
μ(Mo Kα)/mm^{-1}	9.304	6.703	5.779	2.479	6.100	5.364	3.935	3.841	7.325
$F(000)$	1480	1776	1640	2760	1920	4104	2080	4736	1356
no. of rflns collected	17 162	136 365	91 116	139 757	81 294	78 796	84 653	168 083	30 355
no. of indep rflns	2350	3312	5539	12 292	6983	7941	4197	8527	2307
no. of obsd rflns ($I > 2\sigma(I)$)	2296	3072	4440	10577	6405	7042	3798	4396	1615
R_{int}	0.038	0.015	0.020	0.064	0.067	0.043	0.022	0.093	0.038
no. of params refined	133	184	372	790	385	442	271	560	134
R1	0.047	0.048	0.026	0.030	0.019	0.024	0.055	0.060	0.037
wR2	0.123	0.130	0.063	0.095	0.046	0.083	0.139	0.123	0.116
S	1.313	1.089	1.001	1.162	1.039	1.163	1.229	0.990	0.973
$\Delta\rho_{min}$/e Å^{-3}	−2.54	−1.97	−1.12	−0.79	−0.86	−1.29	−1.13	−0.85	−1.46
$\Delta\rho_{max}$/e Å^{-3}	1.67	1.22	0.57	0.55	0.44	0.69	1.74	1.37	0.73

Figure 1. ^{1}H NMR spectra of Cp*$_2$UI$_2$ in pyridine, thf, and acetonitrile.

proved to be more suitable than thf or other ethereal or aromatic solvents in these metathesis reactions.[20] Treatment of Cp*$_2$UCl$_2$ with a slight excess of Me$_3$SiX (X = I, OTf) in acetonitrile at 20 °C led to an immediate change of color from red to dark red and the formation of the corresponding Cp*$_2$UX$_2$ compounds (eq 1). After stirring for 1 h to ensure complete reaction, gram quantities of pure Cp*$_2$UI$_2$ (**1**) or Cp*$_2$U(OTf)$_2$ (**2**) were obtained in almost quantitative yields. Complex **1** was previously characterized by NMR spectroscopy in the oxidative reaction of Cp*$_2$UCl with I$_2$ or alkyl iodides or the metathesis exchange between Cp*$_2$UCl$_2$ and BI$_3$.[21] Recently, the benzonitrile adduct Cp*$_2$UI$_2$(NCPh) was isolated in 36% yield from the reaction of UI$_4$(NCPh)$_4$ and Cp*MgCl(thf) in toluene.[8] We reported that **2**

can be obtained by protonolysis of Cp*$_2$UX$_2$ (X = Me, NMe$_2$) with HpyOTf in thf.[9] The syntheses presented here are more practical and straightforward routes to **1** and **2**, which are isolated with better yields.
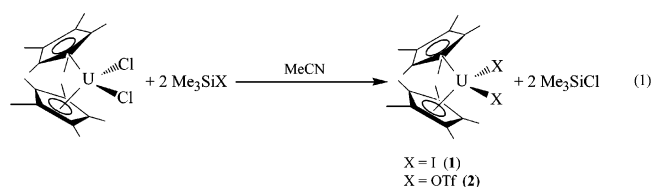
Complexes **1** and **2** were characterized by their elemental analyses and ^{1}H NMR spectra, which indicate the absence of free or coordinated acetonitrile molecules. They are both quite soluble in benzene, thf, and pyridine, and the NMR spectra exhibit a single paramagnetic signal corresponding to the Cp* ligands around δ 18. These values are characteristic of neutral Cp*$_2$UX$_2$ complexes with a bent sandwich geometry for which the Cp* resonance in these solvents is visible in the δ 5−18 region.[2] Most strikingly, the spectra of **1** and **2** in acetonitrile show a significant shift of the Cp* signal at δ 35.1 and 35.4, respectively (Figure 1). In contrast, the chemical shifts of the Cp* signal of Cp*$_2$UCl$_2$ are very close in benzene and acetonitrile, with δ values of 13.6 and 12.7, respectively. These differences in the NMR spectra strongly suggest that **1** and **2** were converted into new compounds in acetonitrile.

The NMR spectrum of an equimolar mixture of **1** and MeCN in toluene indicated that the nitrile molecule is coordinated to

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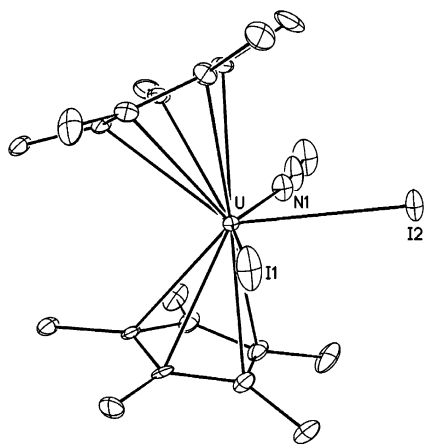
Figure 2. View of Cp*$_2$UI$_2$(NCMe) (**3**). The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.
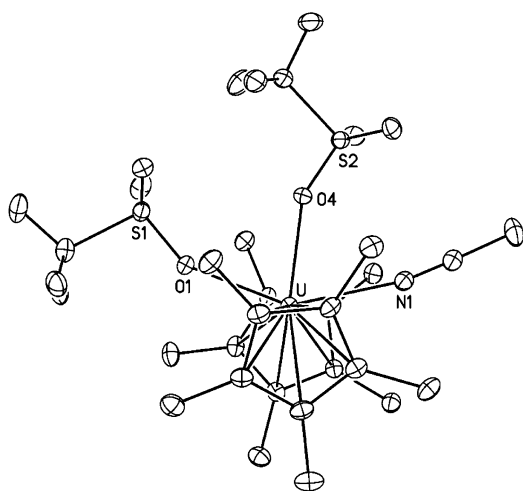

Figure 3. View of Cp*$_2$U(OTf)$_2$(NCMe) (**5**). The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

the metal center, its broad signal being visible at δ −0.27. After addition of 15 molar equiv of MeCN, this signal became less broad and was shifted to the diamagnetic region at δ 0.23, reflecting the rapid exchange between free and coordinated molecules. Whatever the quantity of MeCN, the Cp* ligands give rise to a single signal, which is little displaced from δ 18, showing that in these conditions the geometry of the Cp*$_2$UI$_2$ fragment is not greatly modified upon coordination of the nitrile ligand. Dark brown crystals of Cp*$_2$UI$_2$(NCMe) (**3**) and Cp*$_2$UI$_2$(NC^{t}Bu)·C$_7$H$_8$ (**4**·C$_7$H$_8$) suitable for X-ray diffraction analysis were obtained by addition of an excess of the corresponding nitrile into solutions of **1** in toluene. A solution of an equimolar mixture of **2** and MeCN in toluene rapidly deposited dark red crystals of Cp*$_2$U(OTf)$_2$(NCMe) (**5**). The lability of the nitrile ligand in compounds **3**, **4**, and **5** was evidenced by its ready dissociation upon drying the crystals under vacuum, giving back **1** and **2**.

The crystal structures of **3** and **5** are shown in Figures 2 and 3, respectively; the structure of **4** is very similar to that of **3**. Selected bond distances and angles are listed in Table 2. The complexes adopt the familiar bent sandwich configuration with an asymmetric arrangement of the RCN and I or OTf ligands in the equatorial plane. This geometry is similar to that found in Cp*$_2$UI$_2$(NCPh)[8] or Cp*$_2$U(OTf)$_2$(H$_2$O)[22] but differs from that of Cp*$_2$UCl$_2$L (L = pyrazole,[23] HNPPh$_3$[24]), where the

neutral ligand L is located between the two chloride groups. Compounds **3** and **4** possess a plane of symmetry containing the uranium center and the atoms N(1), I(1), and I(2). The U−C bond lengths in **3**−**5** are unexceptional, with average values of 2.75(2), 2.75(1), and 2.72(3) Å, respectively. The U−(ring centroid) distances and the (ring centroid)−U−(ring centroid) angles [2.465 Å and 135.8° in **3**, 2.474 Å and 139.2° in **4**, and 2.435 Å and 135.2° in **5**] are close to those measured in Cp*$_2$UI$_2$(NCPh) [2.45(2) and 2.48(2) Å, 136.7(5)°] or Cp*$_2$U-(OTf)$_2$(H$_2$O) [2.439 and 2.469 Å, 134.7°]. The U−N distances of 2.515(14), 2.541(9), and 2.523(3) Å in **3**−**5** can be compared with those found in Cp*$_2$UI$_2$(NCPh) [2.53(1) Å],[8] UI$_4$(NCPh)$_4$ [2.56(1) Å], or [UI$_2$(NCMe)$_7$][UI$_6$] [2.53(1) Å average value].[20] In both **3** and **4**, the two U−I bond lengths are quite identical, with mean values of 3.07(2) and 3.072(1) Å, respectively, which is in contrast to what is observed in Cp*$_2$UI$_2$(NCPh), where the two U−I bond lengths are quite distinct [2.942(3) and 3.092(2) Å].[8] These U−I bond lengths are in the range of distances reported for uranium(IV) iodide compounds, in particular [UI$_2$(NCMe)$_7$][UI$_6$] [3.001(2) Å] and UI$_4$(py)$_3$ [3.00-(4) Å average value].[20] The U−O(OTf) distances of 2.375(2) and 2.371(2) Å in **5** are similar to those found in the other bis-(cyclopentadienyl) uranium(IV) compounds with monodentate triflate ligands, Cp*$_2$U(OTf)$_2$(H$_2$O) [2.36(1) and 2.40(1) Å],[22] Cp*$_2$U(OTf)(η^2(*N*,*N'*)-MeNN=CPh$_2$) [2.395(14) Å],[25] and Cp$_2$U-(OTf)$_2$(py)$_2$ [2.395(4) and 2.385(4) Å].[9]

The nature of the complexes present in acetonitrile solutions of **1** and **2** was intriguing. In view of the high polarity of acetonitrile and the high lability of the iodide and triflate counterions, the most plausible hypothesis was the formation of cationic species.

Syntheses and Crystal Structures of the Linear Uranium-(IV) Metallocenes [Cp*$_2$U(NCMe)$_5$][X]$_2$ (X = I, OTf, BPh$_4$). Cationic complexes proved to be valuable precursors in inorganic and organometallic chemistry and active species in catalysis due to their strong Lewis acidic character. Protonolytic cleavage reactions of [An]−X bonds (An = Th, U; X = H,[26] alkyl,[27] BH$_4$,[28] NR$_2$[29]) with HNR$_3$BPh$_4$ represent convenient routes to such actinide compounds. This method was particularly efficient for the synthesis of monocationic complexes but much less for the preparation of polycationic derivatives.[29] In the bisCp* series, the monocationic metallocenes [Cp*$_2$ThMe(thf)$_2$]-[BPh$_4$][27] and [Cp*$_2$UX(thf)][BPh$_4$] (X = NMe$_2$, NEt$_2$)[30] were easily obtained from Cp*$_2$ThMe$_2$ and Cp*$_2$UX$_2$, whereas formation of the dication [Cp*$_2$U(L)$_n$][BPh$_4$]$_2$ by subsequent protonolysis of the U−C or U−N bond could not be achieved in thf.[29] However, this reaction was possible only by using MeCN as the solvent. Treatment of Cp*$_2$UMe$_2$ with 2 equiv of HNEt$_3$BPh$_4$ in acetonitrile led to the straightforward formation

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Bent Trivalent and Tetravalent Metallocenes 3−5 and 11

	Cp*$_2$UI$_2$(NCMe) (3)	Cp*$_2$UI$_2$(NC^{t}Bu)·C$_7$H$_8$ (4·C$_7$H$_8$)		Cp*$_2$U(OTf)$_2$(NCMe) (5)		Cp*$_2$UI(NCMe)$_2$ (11)
⟨U−C⟩	2.75(2)	2.75(1)	⟨U−C⟩	2.72(3); 2.72(2)	⟨U−C⟩	2.79(1)
U−Cp*	2.465	2.474	U−Cp*1	2.435	U−Cp*	2.514
			U−Cp*2	2.437		
U−I(1)	3.0536(13)	3.0707(8)	U−O(1)	2.375(2)	U−I	3.2076(7)
U−I(2)	3.0920(12)	3.0732(8)	U−O(4)	2.371(2)		
⟨U−I⟩	3.07(2)	3.072(1)	⟨U−O⟩	2.373(2)		
U−N(1)	2.515(14)	2.541(9)	U−N(1)	2.523(3)	U−N(1)	2.595(6)
N(1)−C(1)	1.18(3)	1.134(14)	N(1)−C(3)	1.142(5)	N(1)−C(1)	1.119(7)
Cp*−U−Cp*^{a}	135.8	139.2	Cp*1−U−Cp*2	135.2	Cp*−U−Cp*	134.9
N(1)−U−I(1)	152.7(3)	71.7(2)	N(1)−U−O(1)	146.58(9)	N(1)−U−I	74.10(12)
N(1)−U−I(2)	72.5(3)	155.0(2)	N(1)−U−O(4)	70.77(9)	N(1)−U−N(1′)	148.2(2)
I(1)−U−I(2)	80.13(3)	83.29(2)	O(1)−U−O(4)	75.82(9)		
U−N(1)−C(1)	170.2(14)	171.1(9)	U−N(1)−C(3)	169.0(3)	U−N(1)−C(1)	156.5(5)

^{a} Cp* is the centroid of the cyclopentadienyl ring. Symmetry code: ′ = −x, y, 1.5 − z.

Scheme 1. Syntheses of the Linear Metallocenes [Cp*$_2$U(NCMe)$_5$][X]$_2$ (X = BPh$_4$, I, OTf)
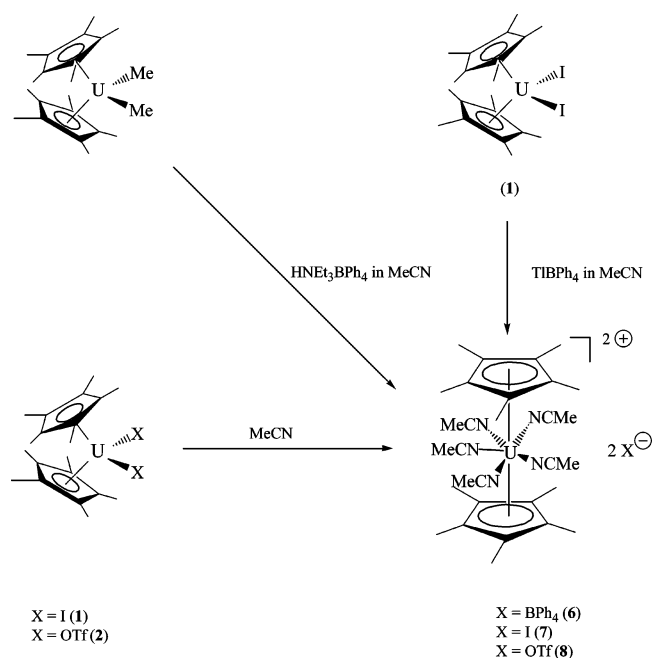
of a compound analyzed as [Cp*$_2$U(NCMe)$_5$][BPh$_4$]$_2$ (6) with concomitant evolution of CH$_4$ (Scheme 1). After evaporation of the solvent, washing with thf, and drying under vacuum, the analytically pure brown powder of 6 was isolated in 80% yield. The visible release of methane clearly indicates that the synthesis of 6 proceeds by protonolysis of the U−Me bonds of Cp*$_2$UMe$_2$ before the latter was transformed into the bisketimine derivative Cp*$_2$U(N=CMe$_2$)$_2$ by insertion of the nitrile molecule into the U−Me bonds.[31] The synthesis and the reactivity of the bisketimine compound will be reported elsewhere. Complex 6 was alternatively synthesized from 1 by reaction with 2 equiv of TlBPh$_4$ in acetonitrile; the precipitate of TlI was filtered off and the crystals of 6 that slowly deposited upon addition of diethyl ether were, after usual workup, recovered with a lower yield (51%).

The infrared spectrum of 6 exhibits two bands at 2262 and 2269 cm^{-1}, corresponding to the vibrational frequencies of bound nitriles; the increase of the nitrile CN stretching frequencies with respect to free MeCN (2254 cm^{-1}) reflects the σ-donor character of the acetonitrile ligand.[32]

The ^{1}H NMR spectrum of 6 in acetonitrile shows a peak at δ 35.3 corresponding to the Cp* ligands; the MeCN resonance is observed at its diamagnetic position due to the rapid exchange between free and coordinated nitrile molecules. While 6 is insoluble in thf, it dissolves readily in pyridine, and the presence of five coordinating acetonitrile molecules was confirmed. The MeCN ligands are not displaced by pyridine, and two NMR signals of relative intensities 30:15 are visible at δ 35.82 and −44.50, respectively. In contrast, a singlet corresponding to free MeCN was observed when 6 was dissolved in dmf, with the signal of the Cp* ligands at δ 36.6. Evaporation of a dmf solution of 6 afforded a brown powder of [Cp*$_2$U(dmf)$_5$][BPh$_4$]$_2$, which was characterized by its ^{1}H NMR spectrum in acetonitrile; broad resonances corresponding to the dmf molecules at their diamagnetic position indicate that these molecules have been almost totally displaced by the solvent.

The observation that the chemical shifts of the Cp* signals of 1 and 2 in MeCN (δ 35.1 and 35.4) are very close to those of 6 in acetonitrile, dmf, and pyridine (δ 35.3−36.6) strongly suggests that the iodide and triflate complexes were converted into the dicationic compounds [Cp*$_2$U(NCMe)$_5$][X]$_2$ (X = I (7), OTf (8)) in acetonitrile. The easy formation of these complexes highlights the major influence of both the solvents and the counterions. Though acetonitrile is known to dissociate the U−I bond of U(IV) and U(III) complexes,[20,33] thus favoring the formation of polycationic species, the weaker lability of Cl$^-$ versus I$^-$ and OTf$^-$ explains why the dication [Cp*$_2$U-(NCMe)$_5$]$^{2+}$ could not be obtained from Cp*$_2$UCl$_2$. However, in contrast to 6, which is stable toward desolvation, complexes 1 and 2 were recovered after evaporation of their acetonitrile solutions, due to elimination of the MeCN ligands and back-coordination of the iodide and triflate ions.

The determination of the structure of the dication [Cp*$_2$U-(NCMe)$_5$]$^{2+}$ was exciting since a linear geometry of the Cp*$_2$U fragment, which would permit it to accommodate a large number of auxiliary ligands, could be anticipated, and this type of linear metallocene was unknown. Dark red crystals of 6 and brown crystals of [Cp*$_2$U(NCMe)$_5$][I]$_2$·MeCN (7·MeCN) were obtained by slow diffusion of diethyl ether into an acetonitrile solution of 6 and 1, respectively, and brown crystals of 7·2.5MeCN were deposited upon concentration of an acetonitrile solution of 1. Brown crystals of [Cp*$_2$U(NCMe)$_5$][OTf]$_2$·MeCN (8·MeCN) were readily formed upon addition of 15 equiv of MeCN into a toluene solution of 2; formation of 8 was thus more facile than that of 7, which crystallized only from pure

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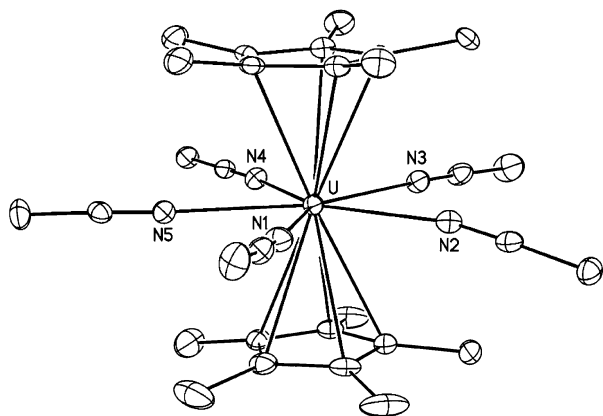**Figure 4.** View of the cation $[Cp^*_2U(NCMe)_5]^{2+}$ in **6**. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

acetonitrile solutions. Crystals of **6** were found to be stable in air, an unusual feature for U(IV) complexes, which can be explained by the steric saturation of the coordination sphere that protects the metal center against oxidation and hydrolysis.

Crystals of **6** and solvates of **7** and **8** are composed of discrete $[Cp^*_2U(NCMe)_5]^{2+}$ cations and BPh_4^-, I^-, or OTf^- anions in the ratio 1:2 and free solvent molecules. The crystal structure of the cation of **6**, which is quite identical to those in the other compounds, is shown in Figure 4, while selected bond distances and angles are listed in Table 3. The planar Cp* rings are almost parallel, with a dihedral angle varying from 0.5(2)° in **7**·2.5MeCN to 2.8(2)° in **7**·MeCN, and are equidistant from and parallel to the plane defined by the uranium and five nitrogen atoms (rms deviation 0.003−0.042 Å). The Cp* ligands are eclipsed, in a staggered conformation with respect to the pentagon of nitrogen atoms, thus minimizing the intramolecular steric interactions. The displacements of the methyl substituents away from the metal and out of the Cp* ring plane seem to be slightly more important in the linear than in the bent metallocenes, with average values of 0.225(18) and 0.18(8) Å, respectively. However, the maximum displacement of 0.244 Å is much less than the value of 0.42 Å, which was considered as the upper limit for cyclopentadienyl complexes with conventional $M-C(C_5R_5)$ bond distances and angles and no unusual ring reactivity.[34] The complexes adopt a pentagonal bipyramidal configuration, with the Cp* ligands, considered as monodentate, in apical positions and the five acetonitrile molecules in the equatorial plane; this geometry is reminiscent of that of the uranyl(VI) complexes $[UO_2(L)_5]^{2+}$.[35] The mean U−C distance in **6**−**8** is 0.05−0.1 Å larger than in the bent metallocenes **3**−**5**, as expected from the increase of the coordination number by two units, whereas the average lengthening of the U−N distance is only 0.02 Å, likely reflecting the higher Lewis acidic character of the metal center in the dicationic complex.

Complexes **6**−**8** are the first linear metallocenes of an f-element. Their structure is novel since they are unique examples of linear metallocenes containing auxiliary ligands.

In addition to representing a synthetic challenge, changing the geometry of a metallocene complex from bent to linear or vice versa is of major significance for the control of distinct physicochemical properties and/or reactivity and for the evaluation of the relative importance of covalent, electrostatic, and steric interactions in the metal−cyclopentadienyl bonding.[36] Bent metallocenes of the main group and d transition metals were forced to be linear by increasing the steric bulk of the ring substituents. Thus, the plumbocene $(C_5Me_4SiMe_2{}^tBu)_2Pb$ or the titanocenes $(C_5Me_4R)_2Ti$ (R = $SiMe_3$, $SiMe_2Bu^t$) exhibit parallel cyclopentadienyl rings, and the latter are reluctant to form bent derivatives of the type $(C_5H_5)_2TiL_2$ (L = PF_3, PMe_3, CO).[37,38] The full filling of the equatorial girdle of the Cp^*_2U fragment with donor molecules represents a new strategy for making bent metallocenes linear, which is exclusive to f-element sandwich compounds.

Behavior of the Uranium(III) Metallocenes Cp^*_2UX (X = I, OTf, BPh_4) in Acetonitrile. From the above results, it was of interest to determine if the linear trivalent metallocenes $[Cp^*_2U(NCMe)_5]X$ could be obtained by dissolving the uranium(III) compounds Cp^*_2UX (X = I, OTf, BPh_4) in acetonitrile.

The syntheses of $Cp^*_2UI(L)$ (L = thf,[4] py[39]), $[Cp^*_2U(thf)_2]$-$[BPh_4]$,[40] and $[Cp^*_2U][BPh_4]$[5] were previously reported. Attempts to synthesize Cp^*_2UOTf (**9**) by treating $Cp^*_2UI(py)$ or $Cp^*_2UCl_2Na(thf)_2$ with Me_3SiOTf were unsuccessful. In one of these reactions of uranium(III) chloride, red crystals were obtained and found by X-ray diffraction analysis to represent a unique example of an "ate" complex of the type $Cp^*_2UX_3Na$. The crystals of $[Cp^*_2U(OTf)_3Na(thf)_2]_2\cdot2(CH_2)_4O$ (**10**·$2(CH_2)_4O$) are composed of the tetranuclear Na_2U_2 complex and the organic polymer resulting from thf ring opening reaction. The centrosymmetric structure of the dimeric complex is shown in Figure 5, and selected bond distances and angles are listed in Table 4. The two $Cp^*_2U(OTf)_3$ fragments, which feature a typical bent metallocene framework, are linked to two $Na(thf)_2$ moieties through the three equatorial triflate ligands. The two lateral OTf groups are bidentate, whereas the central one is tridentate in bridging position between the two sodium atoms, giving the first example of a μ_3-coordination mode of a triflate ligand with an f-element. The U and Na atoms and SO_2 groups in μ_2 position are almost coplanar, with an rms deviation of 0.306 Å, and the O(4) and S(2) atoms of the tridentate triflate ligand are at 0.893(5) and 1.399(3) Å from this mean plane. The U−O distances of the bridging triflates, which range from 2.381(5) to 2.408(6) Å [mean value 2.39(1) Å], are only slightly larger than those of the monodentate triflate in **5**, in agreement with the presence of σ U−O and dative Na−O bonds. The Na−O(OTf) and Na−O(thf) distances are unexceptional.

Eventually, the triflate derivative **9** was prepared in a manner similar to that of $Cp^*_2UI(thf)$, by treating $U(OTf)_3$ with 2 equiv of KCp* in thf (eq 2), and was isolated after usual workup as a green powder in 90% yield. The absence of coordinating thf

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Linear Metallocenes 6−8

	[Cp*$_2$U(NCMe)$_5$][BPh$_4$]$_2$ (6)	[Cp*$_2$U(NCMe)$_5$][I]$_2$· MeCN (7·MeCN)	[Cp*$_2$U(NCMe)$_5$][I]$_2$· 2.5MeCN (7·2.5MeCN)	[Cp*$_2$U(NCMe)$_5$][OTf]$_2$· MeCN (8·MeCN)
⟨U−C⟩	2.80(1)	2.81(2)	2.81(1)	2.809(8)
U−Cp*1[a]	2.540	2.549	2.539	2.541
U−Cp*2	2.528	2.531	2.541	2.532
U−N(1)	2.521(4)	2.545(3)	2.547(4)	2.558(10)
U−N(2)	2.576(3)	2.577(3)	2.548(4)	2.563(8)
U−N(3)	2.529(3)	2.549(2)	2.535(4)	2.539(7)
U−N(4)	2.570(3)	2.518(2)	2.551(4)	
U−N(5)	2.537(3)	2.562(3)	2.556(4)	
⟨U−N⟩	2.55(2)	2.55(2)	2.547(7)	2.55(1)
⟨N−C⟩	1.142(7)	1.141(3)	1.14(1)	1.12(1)
Cp*1−U−Cp*2	178.6	178.0	179.9	179.5
N(1)−U−N(2)	71.21(11)	72.23(8)	72.49(12)	72.04(16)
N(2)−U−N(3)	73.10(11)	73.81(8)	71.47(12)	71.9(2)
N(3)−U−N(4)	72.16(11)	74.22(8)	72.51(12)	72.2(3)[b]
N(4)−U−N(5)	70.48(11)	69.21(8)	71.09(12)	
N(5)−U−N(1)	73.07(12)	70.54(8)	72.53(11)	

[a] Cp* is the centroid of the cyclopentadienyl ring. [b] N(3)−U−N(3′); symmetry code: ′ = x, 0.5 − y, z.
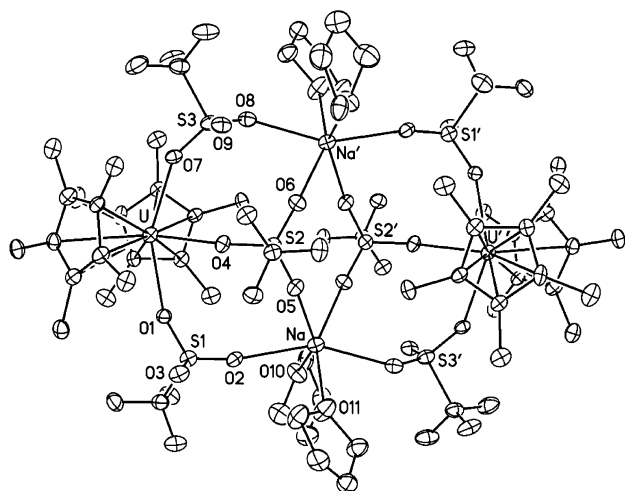

Figure 5. View of [Cp*$_2$U(OTf)$_3$Na(thf)$_2$]$_2$ (**10**). The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Symmetry code: ′ = −x, 1 − y, −z.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in [Cp*$_2$U(OTf)$_3$Na(thf)$_2$]$_2$·2(CH$_2$)$_4$O (10·2(CH$_2$)$_4$O)

⟨U−C⟩	2.732(6); 2.75(3)
U−Cp*1[a]	2.453
U−Cp*2	2.468
U−O(1)	2.401(6)
U−O(4)	2.381(5)
U−O(7)	2.408(6)
⟨U−O⟩	2.39(1)
Na−O(2)	2.453(7)
Na−O(5)	2.325(7)
Na−O(6′)	2.416(6)
Na−O(8′)	2.431(7)
⟨Na−O(OTf)⟩	2.41(5)
O(1)−U−O(4)	75.06(18)
O(4)−U−O(7)	75.72(19)
O(1)−U−O(7)	150.75(18)
Cp*1−U−Cp*2	131.2

[a] Cp* is the centroid of the cyclopentadienyl ring. Symmetry code: ′ = −x, 1 − y, −z.

in the product, confirmed by the elemental analysis and the ^{1}H NMR spectrum, suggests that **9** is likely oligomeric in the solid state with bridging OTf ligands, as observed, for example, in the polymeric compound [U(OTf)$_3$(MeCN)$_3$]$_n$.[41] Compound **9**
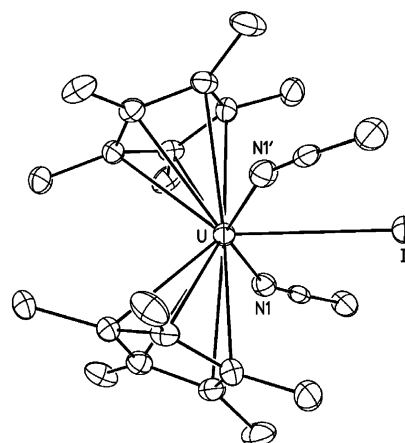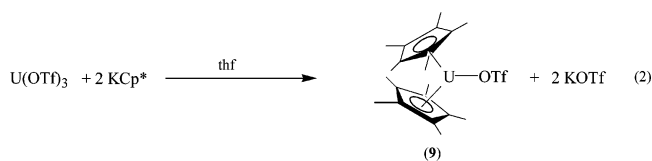

Figure 6. View of Cp*$_2$UI(NCMe)$_2$ (**11**). The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ′ = −x, y, 1.5 − z.

is, to the best of our knowledge, the first organouranium(III) triflate to have been isolated.

$$U(OTf)_3 \; + \; 2 \, KCp* \quad \xrightarrow{thf} \quad \text{Cp*}_2U-OTf \; + \; 2 \, KOTf \quad (2)$$

(9)

Evaporation of an acetonitrile solution of Cp*$_2$UI(py) gave a brown powder of Cp*$_2$UI(NCMe)$_2$ (**11**), and dark brown crystals of **11** were obtained by cooling a toluene solution of Cp*$_2$UI(py) in the presence of 15 equiv of MeCN. In contrast to the U(IV) complexes **3−5**, but as observed with the cerium counterpart Cp*$_2$CeI(NCMe)$_2$, which was obtained by crystallization of the "ate" complex Cp*$_2$CeI$_2$K(thf)$_2$ in acetonitrile,[42] the nitrile ligands of **11** are not removed by evacuation. A view of **11**, which is a rare example of a crystallographically characterized Lewis base adduct of Cp*$_2$UI,[39] is shown in Figure 6; the complex is isostructural to Cp*$_2$CeI(NCMe)$_2$ and will not be discussed further. It is only noteworthy that the U−C, U−I, and U−N distances (Table 2) seem to be slightly smaller than the corresponding distances in the cerium counterpart, by 0.01−0.03 Å, while the ionic radius of U^{3+} is 0.01 Å larger than that of Ce^{3+};[43] this trend has been observed in a variety of

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analogous uranium(III) and lanthanide(III) compounds and is explained by the more covalent character of the uranium−ligand bond.[44]

The ^{1}H NMR spectrum of **11** in benzene exhibits two signals at δ −1.59 and −32.12 attributed to the Cp* and MeCN ligands, respectively; the Cp* resonance is slightly shifted at δ −1.09 in acetonitrile. In the ^{1}H NMR spectra of Cp*$_2$CeI in thf and acetonitrile, the signals corresponding to the Cp* ligands are visible at δ 5.35[39] and 4.95,[42] respectively. These observations, in contrast to those made with Cp*$_2$UI$_2$, suggest that the geometry of the Cp*$_2$M fragment (M = U, Ce) in the trivalent metallocenes is not modified by changing the solvent and that the cationic complex [Cp*$_2$M(NCMe)$_5$]I is not formed. The same conclusion can be drawn from the NMR spectra of **9** in thf and MeCN, with the Cp* signals at δ −3.24 and −2.64, respectively. Evaporation of an acetonitrile solution of **9** gave a brown powder of the triflate analogue of **11**, Cp*$_2$U(OTf)-(MeCN)$_2$, which is also stable toward desolvation and exhibits in benzene two ^{1}H NMR resonances in the ratio 30:6 at δ −2.93 (Cp*) and −31.6 (MeCN). A greater shift of the Cp* resonance was observed in the case of [Cp*$_2$U(thf)$_2$][BPh$_4$] in thf or acetonitrile, with δ values of 0.10 and −2.59 respectively. Unfortunately, no crystal suitable for X-ray diffraction analysis could be obtained from an acetonitrile solution of [Cp*$_2$U(thf)$_2$]-[BPh$_4$]. However, evaporation to dryness of this solution afforded a brown powder of a product analyzed as [Cp*$_2$U-(NCMe)$_3$][BPh$_4$] since the ^{1}H NMR spectrum in thf at −80 °C shows two broad signals at δ −0.49 and −76.7, in relative intensities of 30:9, corresponding to the Cp* and MeCN ligands; these resonances were not affected upon addition of acetonitrile (3 equiv), which gave rise to the signal of the free ligand in the diamagnetic region. Although the structure of the cation [Cp*$_2$U-(NCMe)$_3$]$^+$ is not determined unambiguously, these results clearly indicate that the linear uranium(III) metallocene [Cp*$_2$U-(NCMe)$_5$][BPh$_4$] was not formed.

The formation of the linear uranium(IV) metallocenes **6**−**8**, which contain five MeCN ligands in the equatorial girdle, could be related, in addition to the role of the counterion and the solvent, to the large size of the actinide ion and the small steric hindrance of the acetonitrile molecule. These sole steric effects are, however, not determinant, as shown by the results obtained with the trivalent compounds Cp*$_2$MX (M = U and X = I, OTf, BPh$_4$; M = Ce and X = I), where the ionic radii of the M^{3+} ions are larger than that of U^{4+}.[43] It is likely that the number of f-electrons in the valence shells and the availability of empty f-orbitals in the metal−ligand interactions have a major influence on the bent or linear structure of the metallocenes. Recently, relativistic DFT calculations revealed that the 5f orbitals give an important contribution to the metal−cyclopentadienyl bonding in the hypothetical [Cp$_2$U]$^{2+}$ complex, predicting that the more stable configuration of this dication is linear with D_{5h} symmetry.[45]

Conclusion

The easy syntheses of Cp*$_2$UI$_2$ and Cp*$_2$U(OTf)$_2$ by treatment of Cp*$_2$UCl$_2$ with Me$_3$SiX (X = I, OTf) in acetonitrile provide new entries into organouranium chemistry. The combined use of weakly coordinating anions (I$^-$ and OTf$^-$) and of acetonitrile as the polar solvent led to the discovery of the first linear metallocenes of the f-elements, [Cp*$_2$U(NCMe)$_5$][X]$_2$ (X = I, OTf), which exhibit a novel type of structure, with the presence of five additional ligands in the equatorial girdle of the linear Cp*$_2$U fragment. The use of acetonitrile as solvent was also beneficial for the double protonolysis reaction of Cp*$_2$UMe$_2$, affording the dicationic species [Cp*$_2$U(NCMe)$_5$][BPh$_4$]$_2$. In contrast, the MeCN adducts of Cp*$_2$UX (X = I, OTf, BPh$_4$), as well as that of Cp*$_2$CeI, retain a bent configuration, suggesting that the stability of linear metallocenes is likely related to the electronic configuration of the f-element and the role of the f-orbitals. Further work devoted to the enlargement of this new class of linear metallocenes, by changing the nature of either the auxiliary ligands, or the cyclopentadienyl groups, or the metal ion and/or its oxidation state, together with theoretical studies, will be presented in forthcoming papers.

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.

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