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An Unprecedented Type of Linear Metallocene with an f-Element

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Since the discovery of ferrocene $(C_5H_5)_2Fe$,[1] a milestone in the history of modern organometallic chemistry, metallocenes and their derivatives did not cease attracting considerable attention for their fascinating aspects, from theory to industrial applications.[2] A most intriguing feature of these so-called sandwich compounds concerns the arrangement of the biscyclopentadienyl metal fragment, which adopts either a linear or a bent structure, with the five-membered rings parallel or not. In addition to representing a synthetic challenge, changing the geometry of a metallocene complex from linear to bent 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.[3] Linear sandwich complexes, such as ferrocene and chromocene, were forced to bend by the introduction of an interannular bridge between the cyclopentadienyl rings.[4,5] On the opposite, it was possible to make bent metallocenes linear by increasing the steric bulk of the ring substituents. Thus, the plumbocene $(C_5Me_4SiMe_2{}^tBu)_2Pb$ or the titanocenes $[(C_5Me_4R)_2Ti]$ ($R = SiMe_3$, $SiMe_2{}^tBu$) 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).[6,7] Biscyclopentadienyl compounds of the f-elements constitute a large and varied range of metallocene derivatives which are found exclusively in a bent-sandwich configuration, whatever the 4f or 5f ion, the oxidation state, the electronic charge, and the nature and number of auxiliary ligands.[8] Here we present the synthesis and crystal structure of the uranium compounds $[(C_5Me_5)_2U(NCMe)_5]X_2$ (X = I, **1** or BPh_4, **2**), the first linear metallocenes of an f-element. In this novel type of π-sandwich complexes, the cyclopentadienyl rings are forced to be parallel through a new synthetic strategy, that is the full filling of the equatorial girdle of the $(C_5Me_5)_2U$ fragment with donor ligands.

As a preliminary, we noted that the ^1H NMR spectra of $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2UI_2$[9,10] are quite different in acetonitrile, exhibiting signals at δ 12.7 and 35.1, respectively, while the C_5Me_5 resonances are in the δ 9−18 range in benzene or pyridine; this observation strongly suggested that $(C_5Me_5)_2UI_2$ was converted into a new compound in acetonitrile. Elimination of the solvent under vacuum gave back $(C_5Me_5)_2UI_2$, but concentration of the solution led to the formation of dark brown crystals, suitable for X-ray diffraction analysis, of a solvate of $[(C_5Me_5)_2U(NCMe)_5]I_2$ **1** (Figure 1).[9,11] Most strikingly, the two cyclopentadienyl rings are quite parallel, forming a dihedral angle of 0.5(2)°, and are equidistant from and parallel to the plane defined by the metal center and nitrogen atoms of the five acetonitrile ligands. The $[(C_5Me_5)_2U(NCMe)_5]^{2+}$ cation is the first metallocene with auxiliary ligands which is linear. The C_5Me_5 rings are eclipsed, in a staggered conformation with respect to the pentagon of nitrogen atoms, a geometry which minimizes the intramolecular steric interactions. By taking into account the coordination number, the short average U−C bond length of 2.81(1) Å, in the range of analogous distances in bent-sandwich compounds of the type $(C_5Me_5)_2UX_2$, reflects the strength of the $U-C_5Me_5$ interaction. The average U−N distance of 2.547(8) Å is similar to that measured in other acetonitrile adducts of uranium(IV).[12]

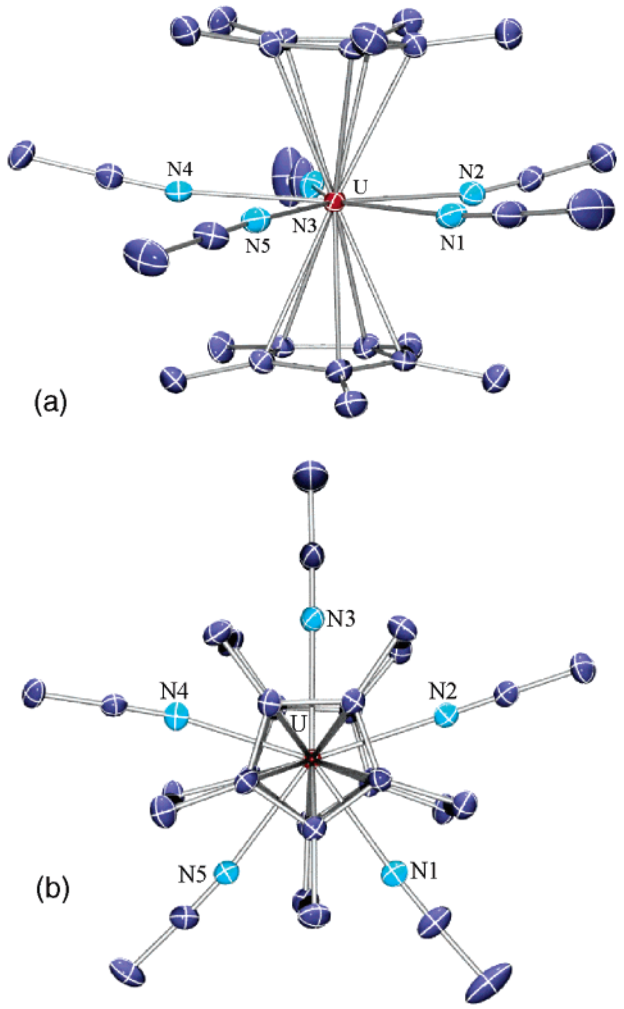

Figure 1. Views of the dication $[(C_5Me_5)_2U(NCMe)_5]^{2+}$ parallel (a) and perpendicular (b) to the cyclopentadienyl rings.

The easy formation of **1** highlights the major influence of both the solvents and the counterions. Though acetonitrile is known to dissociate the U−I bond of U(III) and U(IV) complexes, thus favoring the formation of polycationic species,[10b,12,13] the weaker lability of Cl^- versus I^- explains why the dication $[(C_5Me_5)_2U(NCMe)_5]^{2+}$ could not be obtained from $(C_5Me_5)_2UCl_2$. However, as noted before, $(C_5Me_5)_2UI_2$ was recovered when the crystals of **1** were dried under vacuum. Suppressing the back-coordination of the counterion by replacement of the iodide with the less coordinating tetraphenylborate group afforded $[(C_5Me_5)_2U(NCMe)_5][BPh_4]_2$ **2**, which proved to be stable toward elimination of the MeCN ligands. Dark red crystals of **2** were obtained in 51% yield after

10.1021/ja057226s CCC: $33.50 © 2006 American Chemical Society

treatment of $(C_5Me_5)_2UI_2$ with $TlBPh_4$ in acetonitrile;[11,14] compound **2** was isolated with a better yield of 80% from the reaction of $(C_5Me_5)_2UMe_2$ and $HNEt_3BPh_4$ in acetonitrile.[14] The crystal structure of the cation of **2** is practically identical to that of **1**.

Complexes **1** and **2** open attractive perspectives in the chemistry of linear metallocenes. Their novel structure raises the theoretical problem of the nature of the metal−ligand interaction and of its occurrence with other f-elements. Extending the variety of these compounds is in progress, either by changing the donor ligands or the metal and its oxidation state.[15]

Supporting Information Available: Crystallographic data in CIF format for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) $(C_5Me_5)_2UI_2$ was previously spectroscopically characterized from the in situ oxidative reactions of $(C_5Me_5)_2UCl$ with I_2 or alkyl iodides and by iodide transfer from BI_3 to $(C_5Me_5)_2UCl_2$.[10a] Recently, a benzonitrile adduct of $(C_5Me_5)_2UI_2$ was isolated in poor yields by reacting $UI_4(NCPh)_4$ and Cp*MgCl.thf.[10b] We found a high yield route to $(C_5Me_5)_2UI_2$ by treatment of $(C_5Me_5)_2UCl_2$ with Me_3SiI in acetonitrile. **Synthesis of $(C_5Me_5)_2UI_2$:** The reaction was performed under argon in a glovebox. Me_3SiI (782 μL, 5.49 mmol) was introduced into a flask charged with $(C_5Me_5)_2UCl_2$ (1061 mg, 1.83 mmol) in acetonitrile (50 mL). After 1 h at 20 °C, the red solution was evaporated to dryness, leaving a brown powder of $(C_5Me_5)_2UI_2$ which was washed with pentane (10 mL) and dried under vacuum (1263 mg, 91%). Anal. Calcd for $C_{20}H_{30}I_2U$: C, 31.51; H, 3.97; I, 33.30. Found: C, 31.24; H, 3.90; I, 33.05. ^1H NMR (benzene-d_6): δ 18.1 (s, $w_{1/2}$ 37 Hz); (tetrahydrofuran-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 (br s, $w_{1/2}$ 600 Hz). Dark brown crystals of $[(C_5Me_5)_2U(NCMe)_5]I_2{\cdot}2.5MeCN$ (**1**·2.5MeCN) were deposited upon concentration of an acetonitrile solution of $(C_5Me_5)_2UI_2$.

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(11) The data were collected at 100(2) K on a Nonius Kappa-CCD diffractometer with Mo Kα radiation. The crystals were placed inside glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The structures were solved with SHELXS-97 and subsequent Fourier difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97. Absorption effects were corrected empirically with the program DELABS in PLATON. Crystal data for **1**·2.5MeCN: $C_{35}H_{52.5}I_2N_{7.5}U$, $M = 1070.18$, monoclinic, space group $C2/c$, $a = 21.0005(5)$, $b = 19.4352(5)$, $c = 22.9247(3)$ Å, $\beta = 116.1030(10)°$, $V = 8402.4(3)$ Å^3, $Z = 8$, μ(Mo Kα) = 5.364 mm^{-1}, 78 796 measured reflections, 7941 independent, 7042 with $I > 2\sigma(I)$, 442 parameters, $R1 = 0.024$, $wR2 = 0.083$. Crystal data for **2**: $C_{78}H_{85}B_2N_5U$, $M = 1352.16$, monoclinic, space group $P2_1/c$, $a = 10.0055(1)$, $b = 27.7679(6)$, $c = 24.2432(6)$ Å, $\beta = 97.6780(10)°$, $V = 6675.1(2)$ Å^3, $Z = 4$, μ(Mo Kα) = 2.479 mm^{-1}, 139 757 measured reflections, 12 292 independent, 10 577 with $I > 2\sigma(I)$, 790 parameters, $R1 = 0.030$, $wR2 = 0.095$. CCDC-286203 (**1**·2.5MeCN) and CCDC-286204 (**2**).

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(14) **Syntheses of $[(C_5Me_5)_2U(NCMe)_5][BPh_4]_2$ (2):** All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. (a) A flask was charged with $(C_5Me_5)_2UI_2$ (200 mg, 0.26 mmol) and $TlBPh_4$ (275 mg, 0.52 mmol), and acetonitrile (50 mL) was condensed into it. The reaction mixture was stirred for 2 h at 20 °C, and after filtration, the volume of the brown solution was reduced to 10 mL. The dark red crystals of **2**, which were deposited after addition of diethyl ether (50 mL), were filtered off, washed with diethyl ether, and dried under vacuum (180 mg, 51%). Anal. Calcd for $C_{78}H_{85}B_2N_5U$: C, 69.28; H, 6.34; N, 5.18. Found: C, 69.14; H, 6.35; N, 5.14. ^1H NMR (acetonitrile-d_3): δ 35.3 (br s, $w_{1/2}$ 600 Hz, 30 H, C_5Me_5), 7.06−6.95 (m, 40 H, BPh_4), 1.98 (s, 15 H, MeCN); (pyridine-d_5): δ 35.82 (br s, $w_{1/2}$ 680 Hz, 30 H, C_5Me_5), 7.7−6.32 (m, 40 H, BPh_4), −44.50 (br s, $w_{1/2}$ 750 Hz, 15 H, MeCN). (b) A flask was charged with $(C_5Me_5)_2UMe_2$ (109.2 mg, 0.20 mmol) and $HNEt_3BPh_4$ (170.9 mg, 0.41 mmol), and acetonitrile (20 mL) was condensed into it. After 30 min at 20 °C, the solution was evaporated to dryness, leaving a brown microcrystalline powder of **2**, which was washed with tetrahydrofuran (3 mL) and dried under vacuum (220 mg, 80%). Dark red crystals of **2** were obtained by slow diffusion of diethyl ether into an acetonitrile solution. Anal. Calcd for $C_{78}H_{85}B_2N_5U$: C, 69.28; H, 6.34; N, 5.18. Found: C, 69.03; H, 6.53; N, 5.05. IR spectrum (Nujol): ν(CN) = 2262 and 2269 cm^{-1}.

(15) We already found that the MeCN ligands of **1** and **2** can be replaced with neutral polydentate aromatic amines such as *o*-phenanthroline or the anionic cyanide groups (CN^-) to give the anionic species $[(C_5Me_5)_2U(CN)_5]^{3-}$, without changing the linear configuration of the metallocene. The synthesis and crystal structures of these complexes will be reported in a forthcoming paper.

JA057226S