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Synthesis and X-ray Crystal Structure of a Urana[1]ferrocenophane, the First Tris(1,1′-ferrocenylene) Metal Compound

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*Summary: Reaction of UCl$_4$ with Li$_2$fc·tmeda (fc = 1,1′-ferrocenylene, tmeda = tetramethylethylenediamine) gave the tris(1,1′-ferrocenylene) uranium complex [Li$_2$(py)$_3$U(fc)$_3$] (**1**) (py = pyridine). X-ray analysis of a pyridine solvate of **1** revealed the propeller type structure of the U(fc)$_3$ fragment, with the planar cyclopentadienyl rings of each fc group being parallel and with U−C and U−Fe bond distances of 2.52(7) and 3.14(2) Å, respectively.*

Ferrocenophanes have received much attention with respect to their peculiar structure−reactivity patterns and their potential in the synthesis of materials with novel electrochemical and magnetic properties;[1] of particular interest are their ring-opening polymerization reactions, which afford high molecular weight polyferrocenes.[2] Since the discovery in 1975 of the first [1]ferrocenophane, the silicon-bridged species Ph$_2$Si(fc) (fc = 1,1′-ferrocenylene),[3] this class of complexes has been extended to those bridged with main group elements from group 13 (B),[4] group 14 (Si, Ge, Sn),[5] group 15 (P, As),[5a,b,6] group 16 (S, Se),[7] and also group 4 transition metals (Ti, Zr, Hf).[8] Noteworthily, the homoleptic silicium- and germanium-bridged [1]ferrocenophanes M(fc)$_2$ (M = Si, Ge)[5a,c] are the only bis(1,1′-ferrocenylene) metal complexes to have been reported, and this work did not include any structural data. In our search of heteropolymetallic compounds containing a 3d transition metal in close proximity to uranium,[9] we isolated the UFe$_3$ complex [Li$_2$(py)$_3$U(fc)$_3$] (**1**) (py = pyridine). This complex is the first tris(1,1′-ferrocenylene) metal compound and the sole homoleptic metal-bridged [1]ferrocenophane to have been crystallographically characterized.

Reaction of uranium tetrachloride with the tetramethylethylenediamine adduct of 1,1′-dilithioferrocene (Li$_2$fc·tmeda) in tetrahydrofuran led to the immediate formation of a green-yellow precipitate; after filtration, the powder was dissolved in pyridine, and upon cooling to 0 °C, red microcrystals of **1** were obtained in 21% yield. It is noteworthy that **1** is the only compound isolated from the reaction of 1,1′-dilithioferrocene with a uranium halide, in addition to the ferrocenyl derivative $[(\eta\text{-}C_5H_5)_3U(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)]_2Fe$, which was synthesized by treating $(\eta\text{-}C_5H_5)_3UCl$ with Li$_2$fc·tmeda.[10] The ^{1}H NMR spectrum of **1** exhibits two signals of equal intensity at δ -10.8 and -28.5 corresponding to the equivalent protons at the α and β positions of the cyclopentadienyl rings; the most shifted resonance corresponds to the α protons which are the closest to the paramagnetic uranium center.

The structure of **1** was elucidated by X-ray analysis of a pyridine solvate; an ORTEP[11] view of one of the two independent and almost identical molecules is shown in Figure 1, while selected bond distances and angles are listed in Table 1. The most salient feature of the structure is the attachment of the three ferrocenylene units to the central uranium atom so that the molecule appears as three 1-metalla[1]ferrocenophanes sharing the same bridging metal atom. This structure

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(1) (a) Togni, A.; Hayashi, T. *Ferrocenes, Homogeneous Catalysis, Organic Synthesis, Materials Science*; VCH: Weinheim, 1995. (b) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(2) Manners, I. *Chem. Commun.* **1999**, 857.

(3) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

(4) (a) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338. (b) Berenbaum, A.; Braunschweig, H.; Dirk, R.; Englert, U.; Green, J. C.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765.

(5) (a) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345. (b) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91. (c) Blake, A. J.; Mayers, F. R.; Osborne, A. G.; Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2379. (d) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470. (e) Jäkle, F.; Rulkens, R.; Zech, G.; Massey, J. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 4231.

(6) (a) Seyferth, D.; Withers, H. P. *J. Organomet. Chem.* **1980**, *185*, C1. (b) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275. (c) Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Organometallics* **1982**, *1*, 1283. (d) Evans, C. E. B.; Lough, A. J.; Grondey, H.; Manners, I. *New J. Chem.* **2000**, *24*, 447. (e) Brunner, H.; Klankermayer, J.; Zabel, M. *J. Organomet. Chem.* **2000**, *601*, 211.

(7) (a) Pudelski, J. K.; Gates, D. P.; Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1506. (b) Rulkens, R.; Gates, D. P.; Balaishis, D.; Pudelski, J. K.; McIntosh, D. F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 10976.

(8) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817.

(9) (a) Arliguie, T.; Ephritikhine, M.; Lance, M.; Nierlich, M. *J. Organomet. Chem.* **1996**, *525*, 293. (b) Cendrowski-Guillaume, S. M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1487. (c) Le Borgne, T.; Rivière, E.; Marrot, J.; Girerd, J. J.; Ephritikhine, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1647.

(10) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1974**, *96*, 3650.

(11) Farrugia, L. J. ORTEP3 for Windows. *J. Appl. Cryst.* **1997**, *30*, 565.

10.1021/om000483f CCC: $19.00

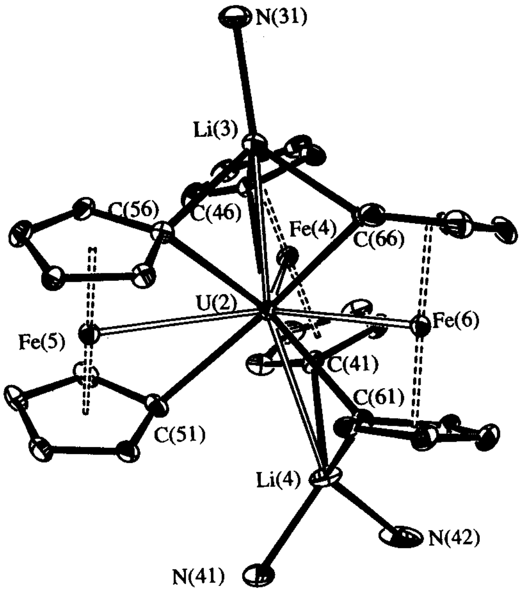

Figure 1. ORTEP view of one of the two independent molecules of $[Li_2(py)_3U(fc)_3]\cdot py$ with thermal elipsoids at the 30% probability level. Carbon atoms of the pyridine ligands have been omitted for clarity.

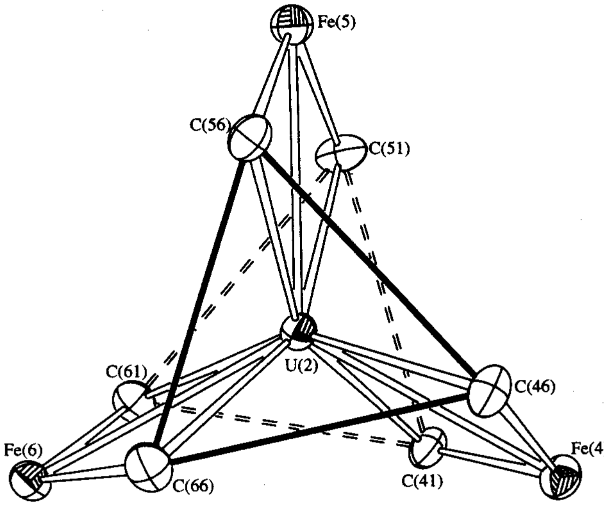

Figure 2. Projection on the UFe_3 plane showing the distorted environment around the uranium atom.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Li_2(py)_3U(fc)_3]\cdot py$

U(2)−C(41)	2.502(14)	U(2)−C(46)	2.536(13)
U(2)−C(51)	2.473(12)	U(2)−C(56)	2.593(13)
U(2)−C(61)	2.543(13)	U(2)−C(66)	2.532(12)
U(2)−Fe(4)	3.122(2)	U(2)−Fe(5)	3.165(2)
U(2)−Fe(6)	3.149(2)	U(2)−Li(3)	2.814(14)
U(2)−Li(4)	3.184(16)		

C(41)−U(2)−C(46)	83.0(4)	C(51)−U(2)−C(56)	81.4(4)
C(61)−U(2)−C(66)	81.2(4)	C(41)−U(2)−Li(3)	128.1(6)
C(51)−U(2)−Li(3)	125.8(5)	C(61)−U(2)−Li(3)	127.4(5)
Fe(4)−U(2)−Fe(6)	121.59(5)	Fe(4)−U(2)−Fe(5)	120.22(5)
Fe(5)−U(2)−Fe(6)	117.68(5)	C(46)−U(2)−Li(4)	128.0(5)
C(56)−U(2)−Li(4)	144.8(4)	C(66)−U(2)−Li(4)	120.3(5)
Li(3)−U(2)−Li(4)	165.5(6)		

confers great stability to **1**, in contrast with the uranium hexaalkyl complexes Li_2UR_6 and the other homoleptic uranium hydrocarbyls UR_4 and Li_3UR_8, which are not thermally stable and which could only be partially characterized at low temperature.[12] The U−C bond distances vary from 2.490(12) to 2.563(13) Å and average 2.52(7) Å; these values are within the range typically found for other uranium−carbon σ bonds (2.4−2.6 Å).[13] The polyhedron defined by the six carbon atoms is distorted from the trigonal prism toward the octahedron, as shown in Figure 2. The two equal equilateral triangles C(41)−C(51)−C(61) and C(46)−C(56)−C(66) are parallel and rotated from the eclipsed conformation by a twist angle of 23.9° (23.2° for molecule 1). These two triangles are parallel and equidistant to the equilateral triangle formed by the Fe atoms, which contains the U atom at its center. Also noteworthy are the distances between the U and Fe atoms, which range between 3.122(2) and 3.165(2) Å and average 3.14(2) Å; these are equal to the sum of the atomic radii of these elements (1.75 and 1.40 Å).[14] These values would suggest the occurrence in **1** of a direct U−Fe interaction; similar intermetallic closed contacts have been observed in the zircona[1]ferrocenophane $[Zr(C_5H_4Bu^t)_2(fc)]$[8] and some rare actinide−transition metal compounds.[15] It is possible that such dative bonds, although weak, contribute to the stability of the molecular building. The most favoring factor for the stability of **1** is certainly the total lack of strain in the separate fc units, as shown notably by the planar cyclopentadienyl rings which are perfectly parallel. This is in contrast with the other [1]-ferrocenophanes, where ring tilting has always been observed, with tilt angles varying from 32° to 6° in the B- and Zr-bridged [1]ferrocenophanes, respectively;[4,8] this variation is inversely proportional to the distance between the bridging atom and the *ipso*-carbon atom of the five-membered ring.[8] Also indicative of the strain relief in **1** are the $C_{ipso}−U−C_{ipso}$ angles, which average 82(1)° and are significantly smaller than the corresponding angles in the other [1]ferrocenophanes, which vary from 100° to 86° in the B and Zr complexes, respectively. In each fc unit, the plane defined by the U, Fe, and two C_{ipso} carbons, which is perpendicular to the eclipsed cyclopentadienyl rings, deviates from orthogonality to the UFe_3 plane by an angle of about 13.7° (mean value). The $U(fc)_3$ fragment thus adopts a propeller type structure with angles of 29.6° (mean value) between the five-membered rings of adjacent fc units; this arrangement would minimize the steric interactions between the cyclopentadienyl groups. One of the two lithium atoms is located on the pseudo C_3 axis of the $U(fc)_3$ fragment, capping a triangular face of the coordination prism, while the second Li atom is bound only to two C_{ipso} carbon atoms of adjacent cyclopentadienyl groups; each Li atom completes its tetrahedral coordination sphere with pyridine ligands. The Li−C and Li−N bond lengths are unexceptional, but the U−Li distances, especially U(1)−Li(1) and

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(12) (a) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo- f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Reidel: Dordrecht, 1985; p 115. (b) Sigurdson, E. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 812. (c) Marks, T. J.; Seyam, A. M. *J. Organomet. Chem.* **1974**, *67*, 61.

(13) Hall, S. W.; Huffman, J. C.; Miller, M. M.; Avens, L. R.; Burns, C. J.; Arney, D. S. J.; England, A. F.; Sattelberger, A. P. *Organometallics* **1993**, *12*, 752.

(14) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

(15) (a) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501. (b) Hay, P. J.; Ryan, R. R.; Salazar, K. V.; Wrobleski, D. A.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1986**, *108*, 313.

U(2)−Li(3) [2.85(1) Å], are quite short by comparison with the sum of the covalent radii of U (1.75 Å) and Li (1.40 Å).[14] Together with the acute U−C_{ipso}−Li angles of 73(1)°, these features give argument to the presence of a bonding interaction between the uranium and lithium atoms, which would reinforce the stability of **1**.

Complex **1** has been found to undergo a reversible one-electron oxidation reaction, and studies on the structure and magnetic properties of the resulting compound are in progress.

Experimental Section

All experiments were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuterated solvents were dried over Na−K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H NMR spectrum was recorded on a Bruker DPX 200 instrument and was referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). UCl_4[16] and Li_2Fc·tmeda[17] were prepared by published methods.

[$Li_2(py)_3U(fc)_3$] (1). A flask was charged with UCl_4 (0.250 g, 0.66 mmol) and Li_2Fc·tmeda (0.830 g, 2.63 mmol), and THF (50 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 10 h at 20 °C, and after filtration, the green-yellow precipitate was dissolved in pyridine (10 mL). Upon cooling to 0 °C, red microcrystals of **1** were deposited; these were filtered off and dried under vacuum (140 mg, 21%). Anal. Calcd for $C_{45}H_{39}N_3Fe_3Li_2U$: C, 51.9; H, 3.7; N, 4.0. Found: C, 50.25; H, 3.55; N, 3.75; the systematic low values (calc/found = 1.03−1.06) reflect the difficult combustion of the product. ^{1}H NMR (pyridine-d_5): δ −10.80 (s, 12 H, β-CH), −28.5 (s, 12 H, α-CH).

X-ray Crystal Structure of [$Li_2(py)_3U(fc)_3$]·py. The X-ray data were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The structure was solved by direct methods (SIR97)[18] and refined by least-squares procedures on F^2. All H atoms attached to carbon were introduced in calculation in idealized positions [d(CH) = 0.96 Å] and treated as riding models with isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Most of the pyridine moieties display very large thermal anisotropic components, especially within the $Li(py)_2$ fragment attached to U(1) and the two free pyridines. However, attempts to introduce reasonable disordered models failed, and so ordered models were kept using restrained refinements for the pyridine groups. Least-squares refinements were carried out by minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$ and $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$, having values listed in Table 2. The calculations were carried out with the SHELXL-97 program[19] running on a PC.

Table 2. Experimental Data for the X-ray Diffraction Studies of [$Li_2(py)_3U(fc)_3$]·py

formula	$C_{50}H_{44}N_4Fe_3Li_2U$
fw	1120.35
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	20.278(3)
b (Å)	17.755(4)
c (Å)	24.739(4)
β (deg)	111.108(17)
V (Å^3)	8309(2)
Z	8
D(calcd) (g/cm^3)	1.791
μ (cm^{-1})	4.954
cryst size (mm)	0.27 × 0.27 × 0.24
radiation type	Mo Kα
temp (K)	160(2)
θ range (deg)	1.76−24.17
no. of reflns collected	54 138
no of reflns merged	15 208 ($R_{int} = 0.0611$)
no of reflns observed	7661 ($F \geq 4\sigma(F_o)$)
R, wR2 ($F > 4\sigma(F_o)$)	0.0569, 0.1570
R, wR2 (all data)	0.0902, 0.1655
goodness of fit	1.031

Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

(17) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

(18) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97, a Program for Automatic Solution of Crystal Structures by Direct Methods. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(19) Sheldrick, G. M. *SHELXL97*, Program for Crystal Structure Refinement; University of Göttingen, 1997.