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Synthesis and reactions of $(\eta^5\text{-}C_5Me_4\text{-}2\text{-}C_5H_4N)_2UCl_2$ and its derivatives, including the puzzling formation of the *ansa*-metallocene $C_2H_4(\eta^5\text{-}C_5Me_3\text{-}2\text{-}C_5H_4N)_2UCl_2$

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Abstract

Reaction of UCl_4 with $Li(C_5Me_4\text{-}2\text{-}C_5H_4N)$ (LiCp*Py) gave $(Cp^*Py)_2UCl_2$ (**1**), which was subsequently transformed into $(Cp^*Py)_2UX_2$ [X = Me (**2**), BH_4 (**3**)]. Treatment of **3** with $HNEt_3BPh_4$ afforded the cationic derivative $[(Cp^*Py)_2U(BH_4)][BPh_4]$. The *ansa*-metallocene $C_2H_4(\eta^5\text{-}C_5Me_3\text{-}2\text{-}C_5H_4N)_2UCl_2$ (**5**) was unexpectedly obtained in one reaction of **2** and $CuCl_2$. The crystal structures of **1** and **5** have been determined. ***To cite this article: L. Moisan et al., C. R. Chimie 10 (2007).***

Résumé

La réaction de UCl_4 et de $Li(C_5Me_4\text{-}2\text{-}C_5H_4N)$ (LiCp*Py) donne $(Cp^*Py)_2UCl_2$ (**1**), qui a été transformé en les dérivés $(Cp^*Py)_2UX_2$ [X = Me (**2**), BH_4 (**3**)]. Le traitement de **3** avec $HNEt_3BPh_4$ fournit le complexe cationique $[(Cp^*Py)_2U(BH_4)][BPh_4]$. Le composé *ansa*-métallocène $C_2H_4(\eta^5\text{-}C_5Me_3\text{-}2\text{-}C_5H_4N)_2UCl_2$ (**5**) a été obtenu de façon inexpliquée lors d'une réaction de **2** avec $CuCl_2$. Les structures cristallines de **1** et **5** ont été déterminées. ***Pour citer cet article : L. Moisan et al., C. R. Chimie 10 (2007).***

Keywords: Actinide; Uranium; Functionalized cyclopentadienyl; Pyridyl; *Ansa*-metallocene; Crystal structure

Mot-sclés : Actinide ; Uranium ; Cyclopentadiényle fonctionnalisé ; Pyridyl ; *Ansa*-métallocène ; Structure cristalline

1. Introduction

Cyclopentadienyl ligands with side chains containing donor functionalities are extensively used in organometallic chemistry, giving unique chemical and physical properties to the complexes [1]. Because of

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their hemilability and assembling capacity, such ligands have found significant applications, especially in catalysis and the construction of molecular materials. It is noteworthy that among these functionalized cyclopentadienyl ligands, those substituted with a pyridyl group seem to have been coordinated to Fe ions exclusively, and the resulting ferrocene derivatives served as building blocks for oligonuclear organometallic assemblies [2,3]. In this paper we present the introduction in f-element chemistry of the 2-pyridyl tetramethylcyclopentadienyl ligand η^5-C_5Me_4-2-C_5H_4N, hereafter denoted as Cp*Py, with the synthesis and characterization of the uranium(IV) compounds $(Cp^*Py)_2UX_2$ (X = Cl, Me, BH_4) and $[(Cp^*Py)_2U(BH_4)][BPh_4]$; we also describe the crystal structure of the chloride complex $(Cp^*Py)_2UCl_2$ and the ethylene bridged *ansa*-metallocene derivative $C_2H_4(\eta^5\text{-}C_5Me_3\text{-}2\text{-}C_5H_4N)_2UCl_2$ which was obtained in an unexpected and unreproducible manner from the reaction of $(Cp^*Py)_2UMe_2$ and $CuCl_2$.

2. Results and discussion

Reaction of UCl_4 with two equivalents of LiCp*Py in THF gave the bis(cyclopentadienyl) compound $(Cp^*Py)_2UCl_2$ (**1**) which, after evaporation of the solvent and extraction with toluene, was isolated as an orange powder in 88% yield (Eq. (1)); orange crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a THF solution.

$$UCl_4 + 2LiCp^*Py \rightarrow \underset{(\mathbf{1})}{(Cp^*Py)_2UCl_2} + 2LiCl \qquad (1)$$

The crystal structure of **1** is shown in Fig. 1 together with selected bond lengths and angles. The asymmetric unit contains half a molecule, the other half being generated by the binary axis. In contrast to what was observed with ferrocene type complexes containing the Cp*Py ligand or its equivalent without methyl groups (CpPy), where the pyridyl moiety is either not coordinated or bound to a distinct metal centre in a dinuclear assembly [3], both the Cp* ring and the N atom are linked to the uranium(IV) ion in **1**. This ligation mode of the Cp*Py ligand is also found in the previously described compounds $[(Cp^*Py)(Cp^*PyH)Fe]_2[U_8Cl_{24}O_4(Cp^*Py)_2]$ [4a] and $\{(Cp^*Py)UCl(Et_2O)\}_2(\mu\text{-}O)_2$ [4b] which were, respectively, formed by reaction of UCl_4 and $(Cp^*Py)_2Fe$ in CH_2Cl_2, and crystallization of **1** in a mixture of THF and Et_2O, in the presence of adventitious traces of air. The average U–C distance of 2.78(11) Å is similar to those measured in the aforementioned compounds [2.72(9) and 2.78(8) Å] and in bis (pentamethylcyclopentadienyl) uranium(IV) complexes [5], while the U–N distance of 2.757(6) Å is significantly larger, by 0.2 Å, and is even out of the range of the U–N(Py) distances found in uranium(IV) compounds, which is 2.54–2.70 Å [6]. The impeded approach of the Py unit to the metal centre is likely due to the steric crowding of the coordination sphere; contacts as short as 1.97 and 2.07 Å are present between hydrogen atoms bound to C(1) and C(12′) or C(13′) (symmetry code ′ = −*x*, *y*, 0.5−*z*). This situation is also indicated by the displacements of atoms C(2) and C(5) out of the tetramethylcyclopentadienyl mean plane, 1.138(19) and 0.307(11) Å, and the dihedral angle between the five- and six-membered rings, 60.4(3)°, which are smaller than in the previous di- and octanuclear complexes (ca. 1.65 and 0.45 Å and 73°, respectively). The U–Cl distance of 2.6874(16) Å can be compared with the average value of 2.69(5) Å in $(Cp^*)_2UCl_2(HNPPh_2)$ (Cp* = η^5-C_5Me_5) [7].

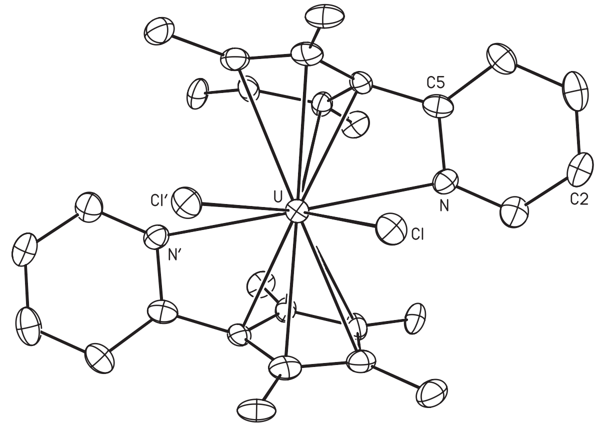

Fig. 1. View of $(Cp^*Py)_2UCl_2$ (**1**) with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted. Symmetry code: ′ = −*x*, *y*, 0.5 − *z*. Selected bond lengths (Å) and angles (°): U–Cl 2.6874(16), U–N 2.757(6), ⟨U–C⟩ 2.78(11); Cl–U–Cl 76.65(7), (Cp* centroid)–U–(Cp* centroid) 142.2.

Complex **1** was treated with a slight excess of LiMe or $LiBH_4$ in THF for giving, after usual work-up, the pale brown methyl and dark red borohydride derivatives, $(Cp^*Py)_2UMe_2$ (**2**) and $(Cp^*Py)_2U(BH_4)_2$ (**3**), in 77% and 23% yield, respectively, (Eqs. (2) and (3)). In the IR spectrum of **3**, the strong singlet at 2466 cm^{-1} and the broad bands at 2213 and 2133 cm^{-1} are characteristic of a tridentate BH_4 group [8].

$$\underset{(\mathbf{1})}{(Cp^*Py)_2UCl_2} + 2LiMe \rightarrow \underset{(\mathbf{2})}{(Cp^*Py)_2UMe_2} + 2LiCl \qquad (2)$$

$$\underset{(\mathbf{1})}{(Cp^*Py)_2UCl_2} + 2LiBH_4 \rightarrow \underset{(\mathbf{3})}{(Cp^*Py)_2U(BH_4)_2} + 2LiCl \qquad (3)$$