

Preliminary communication

Tricyclopentadienyluranium azide complexes

Jean-Claude Berthet, Monique Lance, Martine Nierlich, Julien Vigner
 and Michel Ephritikhine

*Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA-CEN Saclay,
 91191 Gif sur Yvette (France)*

(Received July 15th, 1991)

Abstract

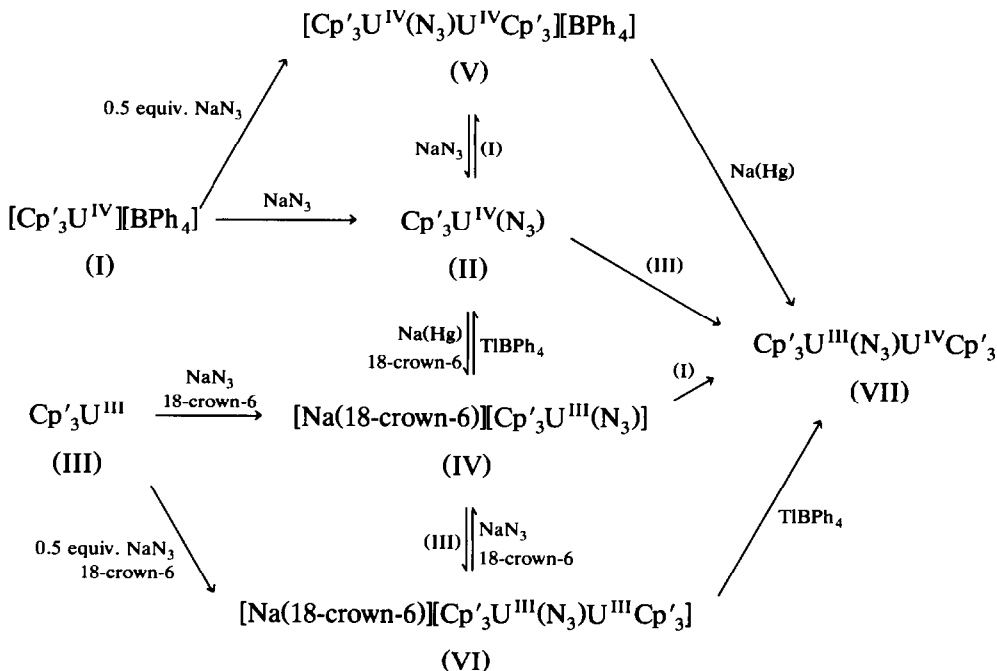
The synthesis and characterization of $A(N_3)$, $[Na(18\text{-crown-6})][A(N_3)]$, $[A(N_3)A][BPh_4]$, $[Na(18\text{-crown-6})][A(N_3)A]$ and $A(N_3)A$ [$A = (C_5H_4SiMe_3)_3U$] are reported.

Metallic and organometallic azide complexes have been extensively studied and a variety of original structures and reaction types have been discovered [1]. Although derivatives of the Main Group and *d* transition metals are numerous, only one azide compound of an *f* element, $[Li(\text{dimethoxyethane})_3][Cp_3Sm(N_3)-SmCp_3]$ ($Cp = C_5H_5$), has been so far described [2]. Here we report the synthesis and characterization of a series of triscyclopentadienyluranium azide compounds including mononuclear U^{III} and U^{IV} derivatives with terminal N_3 ligands, binuclear $U^{III}-U^{III}$ and $U^{IV}-U^{IV}$ compounds with 1,3- μ -azido-groups and the first mixed valence ($U^{III}-U^{IV}$) azido-bridged binuclear complex.

The neutral uranium(IV) azide complex $(C_5H_4SiMe_3)_3UN_3$ (II) was synthesized by treatment of the cation I [3] with a slight excess of NaN_3 in tetrahydrofuran (THF) (Scheme 1); the reaction mixture was stirred at 20 °C for 1.5 h, evaporated to dryness, and the product was extracted in pentane and isolated as pale-brown microcrystals after crystallization from this solvent (88% yield). Similar reaction of $(C_5H_4SiMe_3)_3U$ (III) [4] in the presence of 1 equivalent of 18-crown-6-ether led to the formation of the red-brown anionic U^{III} azido-compound(IV), which was crystallized from toluene (90% yield). This was also obtained in almost quantitative yield by $Na(Hg)$ reduction of II and could be reoxidized to II by $TIBPh_4$.

Preparations of the azido-bridged binuclear complexes V and VI were similar to those of II and IV, but employed 0.5 equivalent of sodium azide; not surprisingly, compounds V and VI were respectively transformed into II and IV in the presence of an excess of NaN_3 . The crystal structure of the anion $[(C_5H_4SiMe_3)_3U-N-N-N-U(C_5H_4SiMe_3)_3]^-$ (Fig. 1) resembles that of the samarium analogue $[Cp_3Sm-N-N-N-SmCp_3]^-$ [2] and reveals the 1,3- μ -form of the linear azide ligand [5*].

* A reference number with an asterisk indicates a note in the list of references.



Scheme 1. Synthesis of tricyclopentadienyluranium azide complexes, $\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$. All reactions in THF at 20°C .

The orange-brown binuclear $\text{U}^{\text{IV}}\text{-U}^{\text{IV}}$ derivative V was alternatively obtained in 95% yield from an equimolecular mixture of I and II, whereas the red crystalline $\text{U}^{\text{III}}\text{-U}^{\text{III}}$ compound VI was formed by mixing III and IV (72% isolated yield). Such a use of mononuclear azide complexes as ligands is, to our knowledge, unprecedented.

It was of special interest to prepare the first mixed valence azido-bridged binuclear complex $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UN}_3\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$ (VII). This was synthesized by several routes: a) from equimolecular mixtures of II and III, I and IV or V and VI, b) by $\text{Na}(\text{Hg})$ reduction of V and c) by oxidation of VI with TIBPh_4 . All these reactions afforded VII in almost quantitative yield, and the product was isolated as red microcrystals after the usual work-up and crystallization from cold pentane. Complex VII was reduced to VI by sodium amalgam and its oxidation as well as those of V and VI, by AgI , afforded a 1:1 mixture of II and $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UI}$ [6].

The synthesis of bimetallic azido-bridged derivatives containing an *f* element and a *d* transition metal, and the reactivity and the magnetic properties of such compounds are under investigation. Complexes II–VII have been characterized by their elemental analyses (C, H, N, Si, Na, B) and their ^1H NMR spectra [7*].

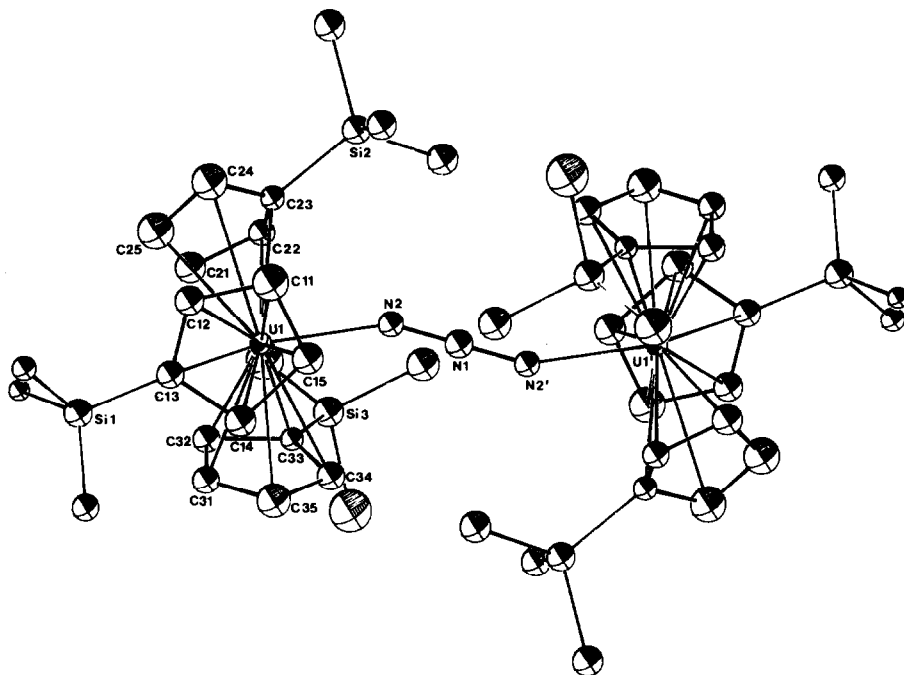


Fig. 1. ORTEP drawing of the centrosymmetric anion $[(C_5H_4SiMe_3)_3U-N_3-U(C_5H_4SiMe_3)_3]^-$. The N(1) atom lies on an inversion centre and primed atoms are related by this centre. Selected bond distances (Å) and angles ($^\circ$) for one of two independent molecules: U(1)–N(2) 2.40(2), N(1)–N(2) 1.19(2), U(1)–U(1') 7.0868(1), U(1)–1 2.54(2), U(1)–2 2.56(2), U(1)–3 2.53(2); U(1)–N(2)–N(1) 160(1), N(2)–U(1)–1 98.9(7), N(2)–U(1)–2 101.9(7), N(2)–U(1)–3 94.6(6), 1–U(1)–2 116.2(7), 1–U(1)–3 118.0(7), 2–U(1)–3 119.4(6). 1 is the centroid of the cyclopentadienyl ring 1, etc.

References and notes

- Z. Dori and R.F. Ziolo, *Chem. Rev.*, 73 (1973) 247; K. Vrieze and G. van Koten, in R.D. Gillard, J.A. McCleverty and G. Wilkinson (Eds.), *Comprehensive Coordination Chemistry*, Vol. 2 Pergamon, Oxford, 1987, 189; J. Strahle, *Comments Inorg. Chem.*, 4 (1985) 295.
- H. Schumann, C. Janiak and J. Pickardt, *J. Organomet. Chem.*, 349 (1988) 117.
- J.-C. Berthet, J.-F. LeMarechal and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, (1991) 360.
- J.G. Brennan, R.A. Andersen and A. Zalkin, *Inorg. Chem.*, 25 (1986) 1756.
- Crystal data for VI·2THF: $C_{68}H_{118}Si_6N_3O_8NaU_2$, $M = 1773.28$, monoclinic, space group $P2_1/n$, $a = 23.24(2)$, $b = 16.588(8)$, $c = 23.48(2)$ Å, $\beta = 113.20(7)^\circ$, $V = 8319(3)$ Å³, $Z = 4$, 2θ max = 40° . Diffraction data were recorded on an Enraf–Nonius CAD4 diffractometer using graphite monochromatized Mo- K_α radiation ($\lambda = 0.71073$ Å). 2571 reflections with $I > 3\sigma(I)$ were considered observed out of 7734 unique data collected. The structure was solved by the heavy-atom method and refined by full-matrix least-squares (F). Current final residuals are $R = 0.054$ and $R_w = 0.065$. Full lists of atomic parameters, thermal parameters and observed and calculated structure factors are available from M.N.
- L.E. Schock, A.M. Seyam, M. Sabat and T.J. Marks, *Polyhedron*, 7 (1988) 1517.
- ¹H NMR spectra of the complexes. δ (60 MHz, THF- d_8 , 30 °C): the first three chemical shifts given in each case are singlets (half-width 10–20 Hz when not specified) assigned to the Si(CH₃)₃ and CH hydrogen atoms of the cyclopentadienyl rings (intensity ratio 9:2:2). II: –7.22, –13.80 and 16.08; IV: –4.80, –18.88 and –2.69, 3.11 (s, 18H, 18-crown-6); V: –7.56 (br, half-width 50 Hz), –11.4 and 6.6 (br, half-width 170 Hz), 6.64 and 6.94 (m, 20H, Ph); VI: –7.37, –20.45 and –6.72, 4.18 (s, 18H, 18-crown-6); VII: –5.77, –15.34 and 15.23 (half-width ca. 100 Hz). The IR spectra exhibit intense absorption bands at ca. 2100 cm^{–1} associated with the azide antisymmetric stretch, and weaker bands at ca 1300 cm^{–1} corresponding to the symmetric stretch [1].