Novel ring-opening reaction of tetrahydrofuran promoted by a cationic uranium amide compound

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The cationic uranium amide compound $[U(cp^*)_2(NMe_2)(thf)][BPh_4]$ (cp* = η-C_5Me_5) reacts with tetrahydrofuran (thf) in the presence of free amine as catalyst to give the heterocyclic metallacycle $[(cp^*)_2\overline{U(O\{CH_2\}_4NMe_2\{CH_2\}_4O})][BPh_4]\cdot0.5thf$; the crystal structure of the pyridine solvate is determined.

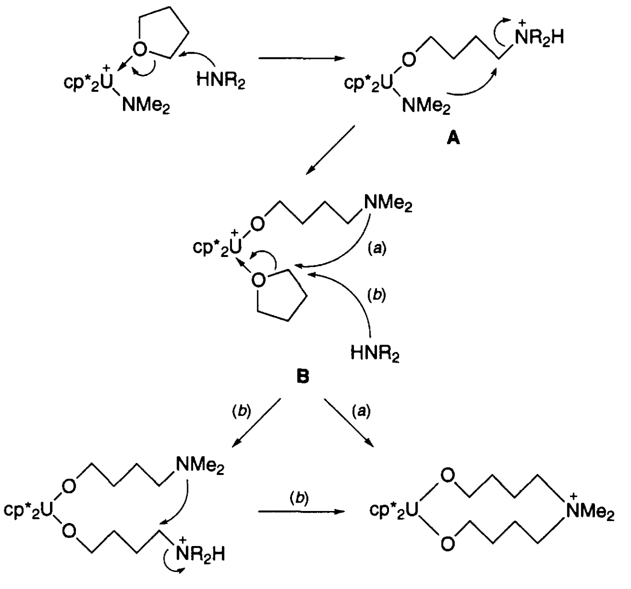
Cationic metal compounds with dialkylamide ligands were unknown until the synthetic approach[1] exemplified by the preparation of the uranium complex $[U(cp^*)_2(NMe_2)(thf)][BPh_4]$ **1** (cp* = η-C_5Me_5, thf = tetrahydrofuran) was designed, according to eqn. (1).[2] While studying the reactivity of such cationic species, we found a novel ring-opening reaction of thf promoted by **1**, leading to the formation of

$$[U(cp^*)_2(NMe_2)_2] + NHEt_3BPh_4 \xrightarrow{thf} \underset{\mathbf{1}}{[U(cp^*)_2(NMe_2)(thf)][BPh_4]} + NHMe_2 + NEt_3 \quad (1)$$

$[(cp^*)_2\overline{U(O\{CH_2\}_4NMe_2\{CH_2\}_4O})][BPh_4]\cdot0.5thf$ **2**, a unique example of a heterocyclic metallacycle containing both oxygen and nitrogen atoms.

Compound **1** was prepared readily in thf and was isolated easily in a very good yield.[2] However, when the reaction mixture was kept at room temperature for a longer period, the red solution of **1** progressively deposited a yellow microcrystalline powder. The ^1H NMR spectrum† exhibited, in addition to the resonances attributed to the cp* ligands (30 H) and the NMe_2 group (6 H), four signals of equal intensities (4 H), thus suggesting the occurrence of thf ring opening. The new compound **2** was identified after X-ray diffraction analysis of the solvate obtained by crystallization from pyridine (*vide infra*);‡ it was then clear that **1** was transformed slowly into **2** (*ca.* 20% after 4 days) by reaction with two molecules of thf. In fact, **1** was found to be inert towards thf, except in the presence of free amine; the reactivity sequence was $NHMe_2 > NHEt_2 > NEt_3$. This observation revealed that the coordinated thf molecule in **1** did not undergo nucleophilic attack by the NMe_2 ligand but rather that of the free amine. Similar reactions of NMe_3 with the zirconium alkyl cations $[Zr(\eta\text{-}C_5H_5)_2(R)(thf)]^+$ (R = Me, Ph or CH_2Ph) afforded the ring-opened derivatives $[Zr(\eta\text{-}C_5H_5)_2(R)(O\{CH_2\}_4NMe_3)]^{+}$.[3] Since **2** was obtained by treating **1** with either $NHMe_2$ or $NHEt_2$, the first intermediate **A** in Scheme 1, $[U(cp^*)_2(NMe_2)(O\{CH_2\}_4NR_2H)]^+$, should then rearrange into $[U(cp^*)_2(O\{CH_2\}_4NMe_2)(thf)]^+$, following nucleophilic substitution by the NMe_2 group and liberation of NHR_2. The coordinated thf in this second intermediate, **B**, would be attacked either by the amino group of the $O(CH_2)_4NMe_2$ ligand to afford **2** directly [path (*a*)] or, as before, by NHR_2 to give $[U(cp^*)_2(O\{CH_2\}_4NMe_2)(O\{CH_2\}_4NR_2H)]^+$ which would then cyclize into the final product **2** [path (*b*)]. The free amine NHR_2 plays a catalytic role in the formation of **2**. Although nucleophilic ring-opening reactions of thf are well documented,[3,4] the synthesis of **2** provides the first example of such a transformation where two molecules are opened on a single metal centre to give a heterocyclic metallacycle.

The crystal structure of the cation in the pyridine solvate $[(cp^*)_2\overline{U(O\{CH_2\}_4NMe_2\{CH_2\}_4O})][BPh_4]\cdot NC_5H_5$ is shown in Fig. 1 together with selected data.§ The uranium atom is in a pseudo-tetrahedral environment which is quite familiar for complexes of the type $[M(cp^*)_2(X)_2]$. The short U–O distances and the large U–O–C angles reflect the strong π-bonding interaction between the uranium and oxygen atoms.[5] The other



Scheme 1

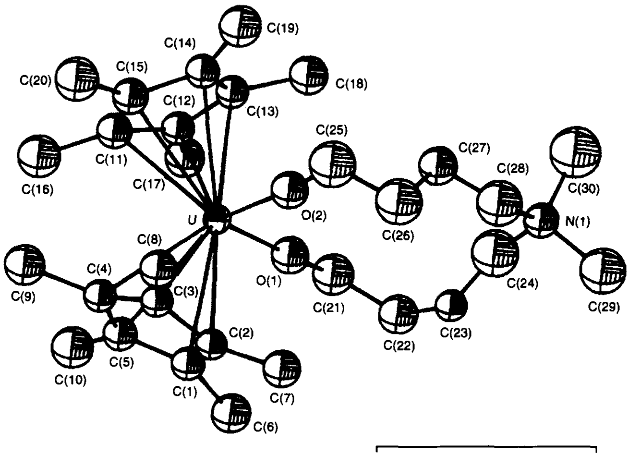


Fig. 1 The X-ray crystal structure of $[(cp^*)_2\overline{U(O\{CH_2\}_4NMe_2\{CH_2\}_4O})]^+$. Only one position of C(21) and C(27) is represented. Selected bond distances (Å) and angles (°): U–O(1) 2.08(1), U–O(2) 2.09(1), av. U–C 2.77(3), U–1 2.50(1), U–2 2.50(1); O(1)–U–O(2) 99.8(4), 1–U–O(1) 105.9(4), 1–U–O(2) 104.5(4), 2–U–O(1) 103.8(4), 2–U–O(2) 105.2(4), 1–U–2 133.1(4), U–O(1)–C(21) 170.2(5), U–O(2)–C(25) 172.8(5). 1 and 2 are the centroids of the rings C(1)–C(5) and C(11)–C(15) respectively.

interatomic distances and angles within the metallacycle are typical, as is the tetrahedral configuration of the nitrogen atom. The conformation of the 12-membered cycle is not strained; two carbon atoms, C(23) and C(27), occupy two sites with equal probability. The U, O(1), O(2) and N(1) atoms are located in the equatorial plane (±0.05 Å) of the bent-sandwich complex and the distances of the carbon atoms from this plane do not exceed 1.0 Å; the twelve atoms of the ring are within ±0.8 Å of their mean plane.

Footnotes

† ^1H NMR spectrum of **2** δ (60 MHz, 30 °C, in $[^2H_5]$pyridine): 16.92 (4 H, t, *J* 7 Hz, α-CH_2), 7.8 and 7.1 (Ph and solvent resonances), 3.55 and 1.51 (2 H + 2 H, m, thf), 0.87 (6 H, NMe_2), 0.0 (34 H, cp* and β-CH_2), −1.7 (4 H, m, δ-CH_2), −9.0 (4 H, m, γ-CH_2). α, β, γ and δ are the positions of the carbon atoms of the metallacycle, with respect to the oxygen atoms; assignments was made after decoupling experiments. When not specified the signals are singlets with half-height width between 10 and 30 Hz.

‡ Compound **2** gave satisfactory elemental analyses (C, H, N).

§ *Crystal data* for $[(cp^*)_2\overline{U(O\{CH_2\}_4NMe_2\{CH_2\}_4O})][BPh_4]\cdot NC_5H_5$: $C_{59}H_{77}BN_2O_2U$, $M = 1095.12$, crystal dimensions (mm): 0.45 × 0.45 × 0.30; triclinic, space group $P\bar{1}$, $a = 10.091(2)$, $b = 15.839(3)$, $c = 17.114(6)$ Å, $\alpha = 78.75(3)$, $\beta = 83.72(2)$, $\gamma = 81.73(2)°$, $U = 2646(2)$ Å^3, $Z = 2$, $D_c = 1.375$ g cm^{-3}, $\mu = 29.48$ cm^{-1}, $F(000) = 1116$, $T_{min} = 0.777$, $T_{max} = 0.999$, $R = 0.048$ and $R_w = 0.057$ ($w = 1$) for 4335 observed reflections with $I > 3\sigma(I)$ and 274 refined parameters, residual electron density: 0.97 e Å^{-3}. Data were collected at room temperature using an Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, λ = 0.710 73 Å) in the range $2 < 2\theta < 40°$. Accurate unit-cell parameters were obtained from least-squares refinement of the setting angles of 25 reflections with $8 < \theta < 12°$. The intensities of three standard reflections were measured after each hour: a decay was observed (2% in 74 h) and was linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[6] The structure was solved by the heavy-atom method and refined by full-matrix least squares (*F*) with anisotropic thermal parameters for the U atom; H atoms were not introduced. Two C atoms of the metallacycle, C(23) and C(27), are disordered. Analytical scattering factors for neutral atoms were corrected for f' and f''. Crystallographic calculations were carried out on a VAX 4200 computer using the MolEN Enraf-Nonius package.[7] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogrpahic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/196.

References

1 J. C. Berthet and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1993, 1566; J. C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1995, 3019.

2 J. C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1995, 3027.

3 S. L. Borkowsky, R. F. Jordan and G. D. Hinch, *Organometallics*, 1991, **10**, 1268.

4 H. van der Heijden, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1989, **8**, 255; W. J. Evans, T. A. Ulibarri, L. R. Chamberlain, J. W. Ziller and D. Alvarez, *Organometallics*, 1990, **9**, 2124; T. L. Breen and D. W. Stephan, *Inorg. Chem.*, 1992, **31**, 4019; L. R. Avens, D. M. Barnhart, C. J. Burns and S. D. McKee, *Inorg. Chem.*, 1996, **35**, 537.

5 T. Arliguie, D. Baudry, M. Ephritikhine, M. Nierlich, M. Lance and J. Vigner, *J. Chem. Soc., Dalton Trans.*, 1992, 1019.

6 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

7 MolEN, *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands, 1990.

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