Neutral, Anionic, and Cationic Bis(cyclohexadienyl) and Bis(pentadienyl) Uranium(III) Complexes

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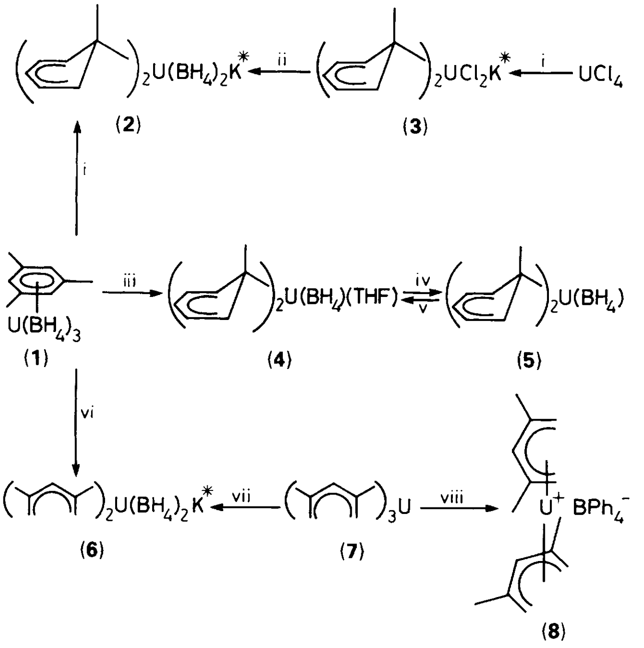
The compounds [(dmch)$_2$UX$_2$][K(18-crown-6)] [dmch = η-6,6-dimethylcyclohexadienyl; X = Cl, (**3**); X = BH$_4$, (**2**)], (dmch)$_2$U(BH$_4$)(tetrahydrofuran) (**4**), (dmch)$_2$U(BH$_4$) (**5**), and [(dmpd)$_2$U(BH$_4$)$_2$][K(18-crown-6)] (**6**) (dmpd = η-2,4-dimethylpentadienyl) were prepared from the reaction of UCl$_4$ or (η-mesitylene)U(BH$_4$)$_3$ (**1**) with the corresponding potassium dienyl anions; complex (**6**) was alternatively obtained by treatment of (dmpd)$_3$U (**7**) with KBH$_4$ whereas protonation of (**7**) with (Et$_3$NH)(BPh$_4$) afforded the cationic derivative [(dmpd)$_2$U][BPh$_4$] (**8**).

We recently described the first acyclic pentadienyl and cyclohexadienyl complexes of uranium(IV), the latter being unique examples of cyclohexadienyl derivatives of an f-element.[1] It was of interest to examine the possible use of the 2,4-dimethylpentadienyl (dmpd) and 6,6-dimethylcyclohexadienyl (dmch) ligands in organouranium(III) chemistry, a less explored field.[2] In addition to a variety of neutral and anionic bis(dienyl)uranium(III) compounds, we prepared the (dmpd)$_2$U$^+$ cation, which is, to our knowledge, the first organometallic cation of an f-element in the +3 oxidation state.

The (dmch)$_2$U(BH$_4$)$_2$$^-$ anion was formed in tetrahydrofuran (THF)(20 ml) by treatment of the arene complex (**1**)[1] (250 mg) with 2 equivalents of the potassium salt of the dimethylcyclohexadienyl anion (Scheme 1); after stirring for 2 h at 20 °C, the suspension was filtered and evaporated under vacuum, leaving a brown powder of [(dmch)$_2$U(BH$_4$)$_2$][K(thf)$_x$]. In the presence of 18-crown-6 (165 mg), bronze crystals of (**2**) (450 mg, 90%) were isolated from THF–diethyl ether, whereas the bronze neutral compound (**4**) was obtained by extraction of the same brown powder with pentane (3 × 10 ml) and crystallized from this



Scheme 1. *Reagents and conditions*: i, dmchK, 18-crown-6; ii, KBH$_4$; iii, dmchK and extraction with pentane; iv, evaporation of a toluene solution; v, THF; vi, dmpdK, 18-crown-6; vii, KBH$_4$, 18-crown-6; viii, (Et$_3$NH)(BPh$_4$). All reactions, except iv, in THF, K* means K(18-crown-6).

solvent at −78 °C (218 mg, 65%). Evaporation of a toluene solution of (**4**) afforded bronze microcrystals of (**5**) and this compound, as well as (**4**), reacted with a stoicheiometric amount of triphenylphosphine oxide in toluene to give brown–green crystals of (dmch)$_2$U(BH$_4$)(OPPh$_3$) in almost quantitative yield. The anionic dichloride (**3**) was obtained in 90% yield from the reaction of UCl$_4$ (400 mg) with dmchK (460 mg) in the presence of 18-crown-6 ether (290 mg); the mixture was stirred for 1 h at 20 °C and after the usual work-up, the product was isolated as red–brown crystals from THF–pentane. Reaction of (**3**) with KBH$_4$ led to the formation of (**2**), which was identified by n.m.r. spectroscopic experiments.

The synthesis of the pentadienyl derivative (**6**) was similar to that of its cyclohexadienyl analogue (**2**); the red–brown product crystallized from THF–pentane (90% yield). Compound (**6**) was alternatively obtained by treatment of the tris(pentadienyl)complex (**7**)[3] with KBH$_4$ in the presence of 18-crown-6. Protonation of (**7**) (200 mg) by (Et$_3$NH)(BPh$_4$) (150 mg) in THF (10 ml) gave immediately a red–brown solution containing dimethylpentadiene, triethylamine, and the cationic complex (**8**); the latter was isolated as dark brown crystals from THF–pentane (255 mg, 90%). The remarkable stability of (**8**) is reminiscent to that of many 'open metallocenes';[4] in particular, (dmpd)$_2$Ti contrasts markedly with its cyclic analogue (η-C$_5$H$_5$)$_2$Ti, in being quite stable thermally and in forming much more labile adducts with Lewis bases.[5] The low temperature n.m.r. spectrum† indicated the unsymmetrical ground state of (**8**), which presumably adopts a nearly *gauche* eclipsed conformation (shown in Scheme 1), as is generally observed in the series of the 'open metallocenes' of the d-elements.[4] The other organoactinide cations so far reported are Cp'$_2$ThMe$^+$, $Cp'_2\overline{Th(o\text{-}C_6H_4CH_2N}Me_2)^+$ (Cp' = η-C$_5$Me$_5$),[6] and Cp$_3$M$^+$ (Cp = η-C$_5$H$_5$ and its substituted derivatives; M = U, Th).[6,7]

The new complexes have been characterized by their elemental analyses (C,H,B,K,P,Cl) and their ^{1}H n.m.r. spectra.†

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References

1 D. Baudry, E. Bulot, and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1988, 1369; D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich, and J. Vigner, *J. Organomet. Chem.*, in press.
2 T. J. Marks and R. D. Ernst, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, vol. 3, Pergamon, Oxford, 1982, ch. 21; P. C. Blake, M. L. Lappert, J. L. Atwood, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1988, 1436, and references cited.
3 T. H. Cymbaluk, J. Z. Liu, and R. D. Ernst, *J. Organomet. Chem.*, 1983, **255**, 311.
4 R. D. Ernst, *Chem. Rev.*, 1988, **88**, 1255.
5 L. Stahl and R. D. Ernst, *J. Am. Chem. Soc.*, 1987, **109**, 5673.
6 Z. Lin, J. F. LeMarechal, M. Sabat, and T. J. Marks, *J. Am. Chem. Soc.*, 1987, **109**, 4127.
7 H. Aslan, K. Yünlü, R. D. Fischer, G. Bombieri, and F. Benetollo, *J. Organomet. Chem.*, 1988, **354**, 63.

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† *Spectral data*. N.m.r. of the complexes {(**2**), (**3**), (**6**), (**8**) in [^{2}H$_8$]THF; (**4**), (**5**) in [^{2}H$_8$]toluene}, δ (60 MHz, 30 °C): (**2**) 72.72 (8H, q, *J* 80 Hz, BH$_4$), 3.05 (24H, s, 18-crown-6), 1.18 and −4.17 (6H and 6H, s, CH$_3$), −10.18 and −17.98 (4H and 4H, br., $W_{\frac{1}{2}}$ 23 and 16 Hz, 1,5-H and/or 2,4-H), −30.40 (2H, br., $W_{\frac{1}{2}}$ 23 Hz, 3-H); (**3**) 2.81 (24H, s, 18-crown-6), 1.59 and −6.91 (6H and 6H, s, CH$_3$), −4.54 and −21.04 (4H and 4H, br., $W_{\frac{1}{2}}$ 40 and 27 Hz, 1,5-H and/or 2,4-H), −24.55 (2H, br., $W_{\frac{1}{2}}$ 40 Hz, 3-H); (**4**) 90 (4H, br., $W_{\frac{1}{2}}$ 900 Hz, BH$_4$), 6.19 and −9.88 (6H and 6H, s, CH$_3$), −4.28 and −22.63 (4H and 4H, br., $W_{\frac{1}{2}}$ 60 and 40 Hz, 1,5-H and/or 2,4-H), −7.20 (4H, br., $W_{\frac{1}{2}}$ 20 Hz, β-THF), −17.51 (4H, br., $W_{\frac{1}{2}}$ 45 Hz, α-THF), −37.90 (2H, br., $W_{\frac{1}{2}}$ 90 Hz, 3-H); (**5**) 10.74 and −12.24 (6H and 6H, s, CH$_3$), −2.66 and −20.11 (4H and 4H, br., $W_{\frac{1}{2}}$ 100 Hz, 1,5-H and/or 2,4-H), −47.32 (2H, br., $W_{\frac{1}{2}}$ 100 Hz, 3-H); (**6**) 72.52 (8H, br., $W_{\frac{1}{2}}$ 320 Hz, BH$_4$), 3.56 (24H, s, 18-crown-6), −12.01 (12H, s, CH$_3$), −18.75 and −46.12 (4H and 4H, br., $W_{\frac{1}{2}}$ 25 and 50 Hz, CH$_2$), −26.46 (2H, br., $W_{\frac{1}{2}}$ 25 Hz, CH); (**8**) 6.91 and 6.58 (20H, m, Ph), −15.58 (12H, s, CH$_3$), −21.39 and −79.08 (4H and 4H, br., $W_{\frac{1}{2}}$ 40 and 100 Hz, CH$_2$), −28.41 (2H, br., $W_{\frac{1}{2}}$ 65 Hz, CH). At −55 °C, the spectrum exhibited 2 signals (3H and 3H, $W_{\frac{1}{2}}$ 200 and 175 Hz) at δ 15.03 and −31.82, and 5 signals of equal intensity (2H, $W_{\frac{1}{2}}$ 200—350 Hz) at δ −5.76, −16.23, −67.47, −108.96, and −154.84. Spin saturation transfer was observed between the methyl peaks.