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A convenient synthesis of $(\eta\text{-}C_8H_8)UI_2(THF)_2$ (THF = tetrahydrofuran), a precursor to monocyclooctatetraenyl uranium complexes

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Abstract

$(COT)_2U$ ($COT = \eta\text{-}C_8H_8$) reacts in tetrahydrofuran (THF) with I_2 to give the monocyclooctatetraenyl compound $(COT)UI_2(THF)_2$ (I) which is transformed into $(COT)UI_2(HMPA)_2$ (II) upon addition of 2 equiv. of hexamethylphosphoramide. Treatment of I with Kacac (acac = MeCOCHCOMe), KC_5Me_5 and $LiCH_2SiMe_3$ give $(COT)U(acac)_2$ (III), $(COT)(C_5Me_5)UI$ (IV) and $[(COT)U(CH_2SiMe_3)_3][Li(THF)_3]$ (V), respectively.

Monocyclooctatetraenyl uranium compounds are expected to possess a much varied chemistry, but the only well-characterized examples are the diamide derivative $(COT)U[N(SiMe_3)_2]_2$ [1*] and the borohydride compounds $(COT)U(BH_4)_2L$ ($L = THF$, $OPPh_3$) and $(COT)(C_5H_5)U(BH_4)(OPPh_3)$ [2*]. We describe here a convenient synthesis of $(COT)UI_2(THF)_2$ (I), which is a useful precursor for monocyclooctatetraenyl uranium complexes.

The mono-COT uranium diiodide I was obtained from the reaction of $(COT)_2U$ [3] with 1 equiv. of I_2 in THF; after 30 mn at 20 ° C, the solvent was evaporated and the red powder was washed with pentane and dried under vacuum. The product, I, obtained in this way in almost quantitative yield was analytically pure. Crystals were obtained from THF–pentane. This preparation of I represents the first synthesis of a monocyclooctatetraenyl uranium complex through degradation of the very stable uranocene; such a displacement of a π-coordinated ligand by oxidation is, to our knowledge, unprecedented in organoactinide chemistry. Compound I was found to decompose in toluene, presumably after the dissociation of a THF ligand, but the hexamethylphosphoramide derivative $(COT)UI_2(HMPA)_2$ (II) was stable in

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* Reference number with asterisk indicates a note in the list of references.

this solvent; it was formed readily in quantitative yield by treating **I** with 2 equiv. of HMPA in THF, and was isolated as brown crystals from THF–pentane. An equimolecular mixture of I and **II** in THF immediately gave (COT)UI$_2$(HMPA)(THF), which was characterized only by its NMR spectrum [4*]. It is noteworthy that two THF or HMPA molecules are coordinated in compounds **I** and **II**, whereas only adducts containing one Lewis base molecule, (COT)U(BH$_4$)$_2$L (L = THF, OPPh$_3$) [2], could be isolated in the case of the borohydride derivative, even though the borohydride ligand is smaller than the iodide group [5]. This difference can be attributed to the higher electron-donating ability of the BH$_4$ ligand [6].

Compound **I** reacted with 2 equiv. of Kacac in THF during 30 min at 20 °C to give a red solution of the bis acetylacetonate (COT)U(acac)$_2$ (III). After evaporation of the solvent, the residue was extracted with toluene, and addition of pentane gave red microcrystals of **III** (60%). Similar treatment of **I** with 1 equiv. of KCp* (Cp* = C$_5$Me$_5$) gave brown crystals of a THF solvate of the mixed-ring complex (COT)(Cp*)UI (**IV**) (60% yield).

It has been reported that the mono-COT uranium bis alkyl derivatives are not stable; in particular, (COT)U(CH$_2$SiMe$_3$)$_2$ and (COT)U[CH(SiMe$_3$)$_2$]$_2$ are elusive [1]. We found that the reaction of **I** with 3 equiv. of LiCH$_2$SiMe$_3$ in THF gave the anionic tris alkyl complex [(COT)U(CH$_2$SiMe$_3$)$_3$][Li(THF)$_3$] (**V**); after the usual work up, the yellow waxy product was isolated in 40% yield by evaporation of its pentane solution. Compound **V** is quite stable in THF and toluene.

Complexes **I**–**V** have been characterized by their elemental analyses (C, H, I, P, N, Li, Si) and by their ^{1}H NMR spectra [4*]. Synthesis of other derivatives of **I** and reactivity studies are in progress.

References and notes

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2 These complexes were synthesized by the intermediacy of (COT)U(BH$_4$)$_2$ which was isolated in toluene as an insoluble powder from the reaction of U(BH$_4$)$_4$ with (COT)$_2$U or C$_8$H$_8$. D. Baudry, E. Bulot, M. Ephritikhine, M. Nierlich, M. Lance and J. Vigner, J. Organomet. Chem., 388 (1990) 279.

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4 ^{1}H NMR spectra of the complexes in THF-d_8 except III and V in benzene-d_6. δ (60 MHz, 30 °C)**I**: −35.43 (s, COT); **II**: −32.31 (s, 8H, COT), 5,36 (d, J 10 Hz, 36H, HMPA); (COT)UI$_2$(HMPA)(THF): −34.05 (s, 8H, COT), 13.85 (d, J 10 Hz, 18H, HMPA); **III**: −29.18 (s, 8H, COT), −9.83 (s, 12H, CH$_3$), 10.32 (s, 2H, CH); **IV**: −34.02 (s, 8H, COT), 15.05 (s, 25H, Me); **V**: −26.04 (s, 6H, CH$_2$), −19.96 (s, 8H, COT), −4.71 (s, 27H, CH$_3$), 4.84 (s, 12H, β-THF), 10,77 (s, 12H, α-THF).

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