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Preliminary communication

Bis(tri-t-butylmethoxide)complexes of uranium(IV)

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Abstract

The compound (tritox)$_2$UCl$_2$(THF)$_2$ (I) (tritox = Bu$^t_3$CO; THF = tetrahydrofuran) has been prepared by treating UCl$_4$ with (tritox)Li. It is a precursor for a series of (tritox)$_2$UX$_2$ complexes (X = BH$_4$, CH$_3$COCHCOCH$_3$, η-C$_3$H$_5$, CH$_2$Ph).

Recent studies have revealed interesting properties of transition metal complexes bearing bulky alkoxide substituents [1,2]. Particular interest attaches to the tri-t-butylmethoxide ligand, denoted by tritox, which is sterically somewhat similar to the much used cyclopentadienyl group, but gives rise to a more electrophilic metal centre [2]. We report here on the synthesis of bis(tritox) complexes of uranium(IV), which, in contrast to most of the corresponding cyclopentadienyl derivatives, are fairly stable.

The uranium tetrachloride UCl$_4$ (0.92 g) reacted during 24 h at 20 °C with (tritox)Li [2] (1.0 g) in THF (25 ml) (THF = tetrahydrofuran) to give an orange solution, which after addition of toluene (10 ml) deposited air sensitive crystals of a THF-solvate of (tritox)$_2$UCl$_2$(THF)$_2$ (I). Compound I (1.59 g, 80%) was obtained from these crystals as a green powder by washing with toluene (20 ml) and/or drying in vacuo. The product was identified from its ^{1}H NMR spectrum and its reactions (vide infra); δ(60 MHz, 30 °C, toluene-d_8): 19.02 (54H, s, tritox), -3.10(8H, s, β-THF), -7.73(8H, s, α-THF). A satisfactory elemental analysis was not obtained because of contamination by LiCl.

Complex I is a precursor for a series of bis(tritox)uranium(IV) compounds (Scheme 1). In a typical experiment, I (300 mg) was treated in toluene (25 ml) at 20 °C with a slight excess of the relevant reagent; after filtration, the solution was evaporated in vacuo and the crude product was recrystallized from pentane (III, IV, V) or toluene (II and IV). The compounds were identified from their elemental analyses and ^{1}H NMR spectra; δ (60 MHz, 30 °C, toluene-d_8). II: 16.97 (54H, s, tritox), -84.65(8H, q, J 85 Hz, BH$_4$); III: 16.46(54H, s, tritox), -30.27(2H, s, CH), -66.81(8H, d, J 11 Hz, CH$_2$); V: 16.66(54H, s, tritox), -1.84(4H, t, J 7 Hz,

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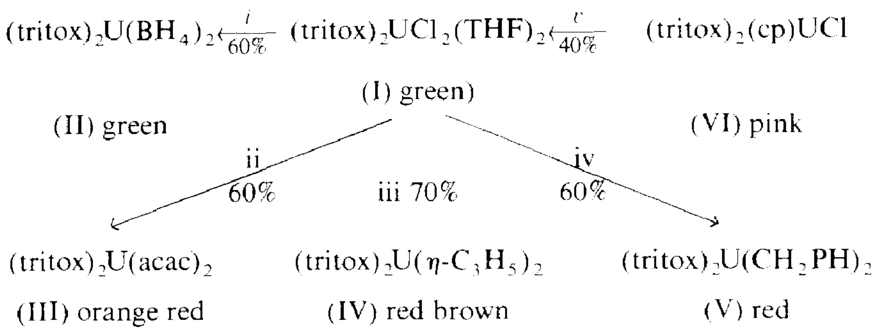

Scheme 1. Reagents and conditions: (i) $TlBH_4$, 24 h; (ii) acacNa, (acac = $CH_3COCHCOCH_3$), 2 h; (iii) allylMgCl, 2h; (iv) $PhCH_2Li$, 2 h; (v) CpTl, 12 h. All reactions in toluene.

m-Ph), −8.58(2H, t, *J* 7Hz, *p*-Ph), −20.03(4H, d, *J* 7 Hz, *o*-Ph), −173.9(4H, s, CH_2); VI: 14.17(54H, s, tritox), −35.97(5H, s, cp). Compound II is, to our knowledge, the first example of a mixed alkoxo-borohydride transition metal complex; the only alkoxouranium complexes containing hydrocarbon ligands to have been described appear to be some bis- and tris-cyclopentadienyl derivatives [3] and the allyl compounds $(\eta\text{-}C_3H_5)_2U(OR)_2$ (R = Et, Pr^i, Bu^t) [4]. The latter are dimeric in toluene; in the case of complexes I–VI, the bulk of the tritox ligand would prevent the formation of alkoxide bridges [2]. The other bis(alkyl)uranium(IV) complexes are those of the $(\eta\text{-}C_5Me_5)_2UR_2$ series [5].

Steric factors are generally invoked to account for the stability of some uranium complexes [6], especially the $CpUX_3L_2$ and Cp_2UX_2 derivatives ($Cp = \eta\text{-}C_5H_5$; L = oxygen donor ligands). We have recently found that, in contrast to their chloro analogues, the $CpU(BH_4)_3L_2$ compounds are not stable, and are readily transformed into mixtures of $U(BH_4)_4L_2$ and $Cp_2U(BH_4)_2$ [7]. This distinctive behaviour is obviously not due to steric parameters (the cone angles of the Cl and BH_4 groups are similar) [6], and can be attributed to the higher electron donating ability of the borohydride ligand [8]. The results reported here confirm that, not surprisingly, electronic factors can play an essential role in determining the stability of uranium compounds. In contrast to the Cp_2UX_2 complexes which, except for those with X = BH_4 or a bulky alkoxide group, [3], are elusive or undergo facile redistribution reactions, compounds I–VI are stable in the solid state and in toluene or THF solution.

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