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# Cyclometallation following coordination of anionic and neutral Lewis bases to a uranium(IV) dialkyl complex

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ABSTRACT

Addition of 3.05 equiv of dme (1,2-dimethoxyethane) to an *n*-pentane solution of $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**; $XA_2$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) and $LiCH_2SiMe_3$ (~1:1) precipitated the tris(alkyl) 'ate' complex, $[Li(dme)_3][(XA_2)U(CH_2SiMe_3)_3]$ (**2-dme**). Sterically encumbered **2-dme** is thermally unstable in solution, eliminating $SiMe_4$ to form $[Li(dme)_3][(XA_2{}^*)U(CH_2SiMe_3)_2]$ (**3-dme**; $XA_2{}^*$ = $XA_2$ cyclometallated at the methine carbon of an isopropyl group) as the major product. Compound **1** did not react with $PMe_3$, 2,2′-bipyridine (bipy), or quinuclidine in benzene at 40 °C. However, **1** reacted with 2.1 equiv of 4-(dimethylamino)pyridine (DMAP) or 9-azajulolidine (AJ; a DMAP derivative featuring a fused tricyclic structure) at 22 °C to afford $[(XA_2)U(CH_2SiMe_3)(\eta^2$*CN*-DMAP*)(DMAP)] (**4**) and $[(XA_2)U(CH_2SiMe_3)(\eta^2$*CN*-AJ*)(AJ)] (**5**), respectively, where DMAP* and AJ* are DMAP and AJ ligands cyclometallated at the 2-position. Reaction of **1** with DMAP-$d_2$ (deuterated in the *ortho* positions) confirmed that **4** is formed via a direct σ-bond metathesis mechanism. All newly-isolated uranium complexes (**2**–**5**) were crystallographically characterized.

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## 1. Introduction

Multidentate non-carbocyclic ancillary ligands provide enormous opportunity to tune the steric, electronic and geometric environment at coordinated metal centres, providing a mechanism to influence and control a broad range of properties, including thermal stability and catalytic activity. One program of research in the Emslie group involves the application of highly-rigid pincer ligands to the development of thermally-robust organo-f-element complexes, and we previously reported the synthesis of a range of f-element complexes bearing 4,5-bis(anilido)xanthene dianions (these xanthene-backbone ligands are rigid in the sense that they ensure tridentate coordination, and strongly encourage meridional coordination, although the ligand backbone can bend to a significant degree, especially upon coordination to smaller metals [1,2] or upon cyclometallation; *vide infra*). These complexes include neutral dialkyl thorium [3] and uranium [4] species, cationic monoalkyl thorium complexes [5,6], neutral monoalkyl yttrium [2] and lutetium [7] complexes, and an anionic dialkyl complex of lanthanum [7] (Fig. 1).

During the course of our investigations into the organometallic chemistry of uranium(IV), we uncovered the unusual reaction of $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**; $XA_2$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) with 2 equiv of $LiCH_2CMe_3$ in $C_6D_6$ to form the bis(neopentyl) complex $[(XA_2)U(CH_2CMe_3)_2]$, with release of 2 equiv of $LiCH_2SiMe_3$ (Scheme 1). This reaction resembles salt metathesis, but with elimination of a lithium alkyl rather than a lithium halide, and presumably proceeds via $[(XA_2)U(CH_2SiMe_3)_2(CH_2CMe_3)]^-$. However, no tris(alkyl) 'ate' complex could be detected in the reaction, or upon treatment of **1** with 20 equiv of $LiCH_2SiMe_3$ in $C_6D_6$ (Scheme 1). By contrast, neutral **1** reacted readily with $LiCH_2SiMe_3$ in THF-$d_8$ to afford $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ (**2-THF**), which was characterized *in-situ* by $^1$H NMR spectroscopy [4].

Herein we report the isolation and structural characterization of $[Li(dme)_3][(XA_2)U(CH_2SiMe_3)_3]$ (**2-dme**) and its thermal decomposition product, in which a 2,6-diisopropylphenyl group is cyclometallated at the isopropyl methine position. Additionally, we describe the ability of pyridine Lewis bases to coordinate and subsequently engage in cyclometallation upon reaction with $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**).

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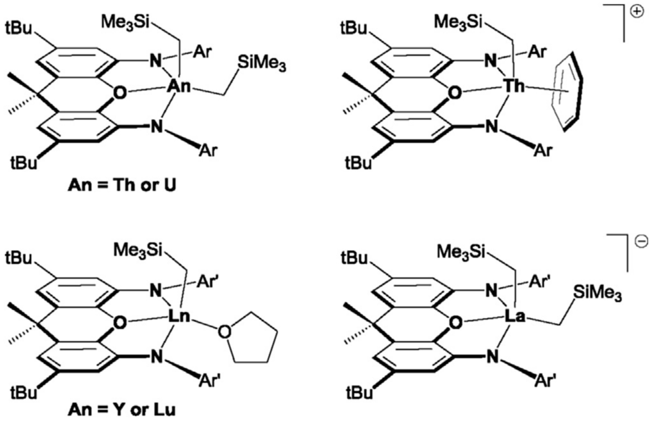


**Fig. 1.** Selected 4,5-bis(anilido)xanthene f-element alkyl complexes (Ar = $C_6H_3^iPr_2$-2,6; Ar' = $C_6H_2^iPr_3$-2,4,6).

## 2. Results and discussion

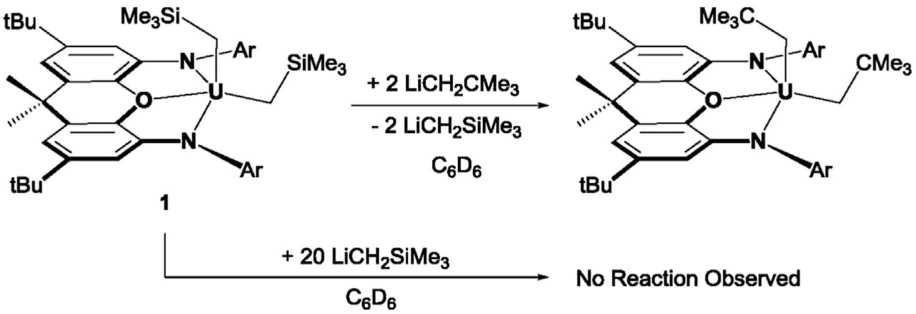
### 2.1. Reaction of [$(XA_2)U(CH_2SiMe_3)_2$] (*1*) with $LiCH_2SiMe_3$

As noted above, [$Li(THF)_x$][$(XA_2)U(CH_2SiMe_3)_3$] (**2-THF**) could be generated via the reaction of [$(XA_2)U(CH_2SiMe_3)_2$] (**1**) with 1 equiv of $LiCH_2SiMe_3$ in THF [4]. However, **2-THF** is unstable in solution at room temperature; decomposition is noticeable in the $^1$H NMR spectrum after 1 h, and proceeds to completion over the course of 1 week, accompanied by a solution colour change from yellow to dark-amber. Given the instability of **2-THF** in solution, previous attempts to isolate pure samples of **2-THF** were unsuccessful. The synthesis of **2** was also conducted in dme (1,2-dimethoxyethane) rather than THF, in the hope of improving product crystallinity, and while this approach afforded single crystals of [$Li(dme)_3$][$(XA_2)U(CH_2SiMe_3)_3$]·2 dme (**2-dme**·2 dme; *vide infra*), bulk material generated by this method was impure. Analytically pure **2-dme** was ultimately prepared by cooling an *n*-pentane solution of [$(XA_2)U(CH_2SiMe_3)_2$] (**1**) and $LiCH_2SiMe_3$ (approx 1:1 stoichiometry) to −30 °C, followed by addition of 3.05 equiv of dme, resulting in rapid precipitation of **2-dme** as a yellow powder in 95% yield (Scheme 2).

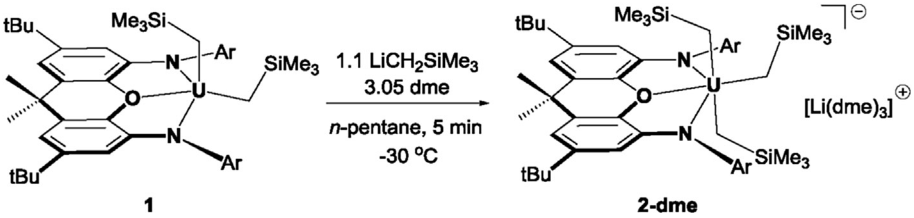
In the solid-state, **2-dme**·2 dme features two independent but structurally similar ion-pairs in the unit cell, each comprised of an $XA_2$-uranium(IV) trialkyl anion (Fig. 2) and a distal [$Li(dme)_3$]$^+$ cation. Uranium is six-coordinate with the five anionic donors {N(1), N(2), C(48), C(52), and C(56)} in a distorted trigonal-bipyramidal arrangement around the metal centre; the N(1)–U–N(2), N(1)–U–C(48) and N(2)–U–C(48) angles in the equatorial plane are 123.5(3)–124.2(3), 102.2(3)–108.4(3), and 127.4(4)–134.2(3)° respectively, and the C(52)–U–C(56) angle between axial substituents is 159.1(3)–172.8(4)° ($\tau_{avg} = 0.59$ for the two anions in the unit cell) [8]. The neutral diarylether donor is coordinated between the two amido groups, located 0.75 and 0.83 Å out of the N(1)/U/N(2) plane, resulting in a capped trigonal-bipyramidal geometry with an O–U–C(56) angle of 76.5(3)–86.3(3)° and an O–U–C(52) angle of 110.0(3)–110.5(3)°.

The U–N, U–O, and U–$CH_2$ distances in **2-dme** are 2.374(9)–2.398(8), 2.515(6)–2.551(6), and 2.42(1)–2.50(1) Å, respectively. The average U–N bond distance in **2-dme** is elongated by 0.12 Å, relative to those of the neutral bis(trimethylsilylmethyl) precursor **1**, likely a result of the increased coordination number, reduced electrophilicity, and steric crowding at the uranium centre. Indeed, uranium–ligand bond elongation has previously been observed in 'ate' derivatives relative to their neutral precursors. For example, Liddle and co-workers observed U=C and U–$N_{pincer}$ bond elongations of at least 0.08 Å in the mixed imido/amido bis(iminophosphorane) methanediide 'ate' derivative [$(BIPM^{TMS})U{=}NCPh_3(NHCPh_3)(K)$] ($BIPM^{TMS} = \kappa^3$-$\{C(PPh_2NSiMe_3)_2\}^{2-}$) relative to those of the neutral bis(amido) precursor [$(BIPM^{TMS})U(NHCPh_3)_2$] [9]. The U–$CH_2$ distances in **2-dme** are likely also elongated relative to those in **1**, but the differences fall within the error associated with the measurements; the range of distances observed for **2-dme** does include that observed in Hayton's tris(trimethylsilylmethyl) 'ate' complex [$Li(dme)_3$][$U(O^tBu)_2(CH_2SiMe_3)_3$] (U–C = 2.49(1) Å) [10].

Crystallographically-characterized examples of monomeric actinide(IV) tris(alkyl) complexes are surprisingly rare; prominent examples are [$Li(dme)_3$][$U(O^tBu)_2(CH_2SiMe_3)_3$] [10], [$(BDPP^*)Th(\mu$-$Me)_2Li(dme)$] ($BDPP^* = [2,6$-$(NC_5H_3)(CH_2NAr)(CH_2N\{C_6H_3^iPr(CMe_2)$-



**Scheme 1.** Treatment of [$(XA_2)U(CH_2SiMe_3)_2$] (**1**) in $C_6D_6$ with (a) 2 equiv of $LiCH_2CMe_3$ to afford [$(XA_2)U(CH_2CMe_3)_2$], and (b) 20 equiv of $LiCH_2SiMe_3$ (Ar = $C_6H_3^iPr_2$-2,6).



**Scheme 2.** Synthesis of [$Li(dme)_3$][$(XA_2)U(CH_2SiMe_3)_3$] (**2-dme**) (Ar = $C_6H_3^iPr_2$-2,6).

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