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New U^{III} and U^{IV} silylamides and an improved synthesis of $NaN(SiMe_2R)_2$ ($R = Me, Ph$)

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ABSTRACT

It is shown that the deprotonation of bulky amides such as $HN(SiMe_2Ph)_2$ may be accelerated by the use of catalytic quantities of an alkali metal *tert*-butoxide salt, affording, for example, overnight syntheses of $NaN(SiMe_2Ph)_2$. The new uranium(IV) and uranium(III) complexes $[U\{N(SiMe_2H)_2\}_4]$ and $[U\{N(SiMe_2Ph)_2\}_3]$ are both accessible from the Group 1 salts of the amides and $UI_3(thf)_4$ in thf. The choice of sodium or potassium salt made no difference to the reaction outcome. Both exhibit Weak interactions between uranium and with silyl-H or silyl-Ph groups in the solid-state.

1. Introduction

Low-valent uranium chemistry has caused much recent excitement due to the unusual reactions that can be accomplished [1–3]. In this respect, convenient syntheses of low-valent starting materials have been crucial to the development of this field such as uranium triiodide [4,5] for use in salt metathesis reactions with sodium and potassium ligand precursors. Uranium amides have also become very important precursors to many low-valent uranium complexes [6], and the synthesis of $[U\{N(SiMe_3)_2\}_3]$ in particular was a landmark in low-valent uranium chemistry [7,8] allowing the facile exploration of uranium(III) and its comparison with lanthanide(III) chemistry [9]. Examples where this methodology has been used include in the synthesis of tripodal trisalkoxideuranium(III) systems [10,11] and in the synthesis of an alkoxy-tethered uranium(III) carbene complex [12]. Compared to the cyclopentadienyl and pentamethylcyclopentadienyl ligands, which have a very rich f-element chemistry [13–15], simple amido species are comparatively underdeveloped, but glimpses of fascinating chemistry have been observed including reversible coordination of dinitrogen between two uranium centres supported by trisamidoamine ligands [16] and the ability of the same ligand to stabilise U-metal bonding. [17,18] It is increasingly important to investigate the fundamental chemistry of these species in order to expand on known chemistry and find new reactivity unachievable with the cyclopentadienyl ligand system [19,20].

Homoleptic uranium(III) amides are relatively rare [21], and apart from $[U\{N(SiMe_3)_2\}_3]$, the structure of which was published in 1998 [22], other examples include the "ate" complex $[U\{N(SiMe_3)_2\}_4][K(thf)_6]$ [23], and along with the La, Ce and Pr analogues, these represent the only crystallographically characterised complexes with four $N(SiMe_3)_2$ ligands around one metal centre [23]. Another "ate" complex that has been identified is $[K(THF)_2]_2[U(N(H)Dipp)_5]$ ($Dipp = 2,6\text{-}{}^{i}Pr_2C_6H_3$) [24]. From a U(IV) compound, $[U\{N(3,5\text{-}Me_2C_6H_3){}^{t}Bu\}_3(thf)]$ was synthesised by potassium reduction and was crystallographically characterised [25].

Homoleptic uranium(IV) amides were investigated initially in the search for volatile uranium compounds for separations technologies; the highly volatile tetravalent complex $[U(NEt_2)_4]$ was reported in 1956 [26]. This compound is dimeric with a five-coordinate uranium centre in the solid-state [27], but the methyl analogue $[U(NMe_2)_4]$ has a trimeric structure with six-coordinate uranium centres, again characterised as containing ligands bridging through the N atoms [28]. Using the proligand $MeN(H)CH_2CH_2N(H)Me$, a tetrameric cluster was characterised [28] whereas $[U(NPh_2)_4]$ is monomeric with a four-coordinate uranium centre [29].

Amides which are similar to the ubiquitous and highly useful $N(SiMe_3)_2$ ligand include $N(SiMe_2H)_2$ and $N(SiMe_2Ph)_2$ which have

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both received attention in the field of f-element chemistry [30–33]. Considering steric factors, replacement of a methyl group for a hydrogen atom would be expected to decrease the kinetic stabilisation of the metal centre whereas the effect of replacement of a methyl group by phenyl is less clear. Since agostic and other weak interactions can be hard to predict *a priori* but can play significant roles in the chemistry of low-coordinate metal complexes, it is notable that both ligands offer the potential for weak interactions with the metal centre through Si–H agostic-type interactions or η^n-Ph interactions. Examples of agostic interactions in low-coordinate d-block chemistry are well-documented [34,35], including a notable recent example of β C–H agostic interactions in titanium amido compounds [36]. The most notable weak C–H interactions in uranium(III) coordination chemistry are the silylmethyl agostic interactions found in the pyramidal $[U\{N(SiMe_3)_2\}_3]$ [22] and $[U\{CH(SiMe_3)_2\}_3]$ [37], and the interaction with trapped hydrocarbon solvent in $[\{(ArO)_3tacn\}U(cy\text{-}C_6H_{11}CH_3)]\cdot(cy\text{-}C_6H_{11}CH_3)$ [38–40]. Despite in general being less well-documented, uranium has an extensive C–H activation and cyclometallation chemistry [41,42]. Homoleptic lanthanide complexes of the $N(SiMe_2H)_2$ ligand (Ln = Lu, Y, Er, Nd, La) have been shown to form agostic-type interactions as observed by I.R. spectroscopy with a stretch at lower wavenumber (1931–1970 cm^{-1}) as well as one at higher wavenumber (2051–2072 cm^{-1}) [31]. Their solid-state structures showed two molecules of coordinated thf and limited evidence for Ln···Si interactions (Lu···Si distances 3.271(1) to 3.476(1) Å, La···Si distances 3.337(3) to 3.575(3) Å) [31]. Recently, thf-free structures have been realised by the reaction of $HN(SiMe_2H)_2$ with either $[(YMe_3)_n]$ or $[La\{N(SiMe_3)_2\}_3]$ and dimeric, four-coordinate lanthanide complexes were formed with bridging $N(SiMe_2H)_2$ ligands [43,44]. Agostic interactions were clearly evident both by X-ray crystallography (Y···Si: 3.0521(7) and Y···H: 2.41(3) Å, La···Si: 3.191(2) and La···H: 2.56(6) Å) and by I.R. spectroscopy via identification of the Si–H stretch (Ln = Y; 2095 – non-agostic, 1931 cm^{-1} – agostic, Ln = La; 2092 and 2060 – non-agostic, 2023, 1920 cm^{-1} – agostic). However, lanthanide complexes containing only one $N(SiMe_2H)_2$ ligand with Cp* (Cp* = C_5Me_5) coligands gave much lower stretching frequencies for Si–H agostic interactions (as low as 1827 cm^{-1}) [45]. The amide $N(SiMe_2Ph)_2$ has been characterised coordinating to a bis(Cp*) lanthanum fragment and showed agostic interactions with the methyl groups (La···C distances of 3.121(2) and 3.388(2) Å, La···H distances of 2.86(2) to 3.46(2) Å) despite the presence of phenyl groups with their associated electron density [32]. Interestingly, $NaN(SiMe_2H)_2$ forms an extended ladder structure in the solid-state with Si–H···Na interactions and $NaN(SiMe_2Ph)_2$ shows coordination of thf (retained from the synthesis) whereas $KN(SiMe_2Ph)_2$ forms a dimeric structure with bridging amide groups and incorporated toluene molecules indicating incomplete encapsulation of the potassium atom by the ligand despite the larger steric bulk and presence of Si–Ph groups. The structure of $[\{(Me_2HSi)N(SiMe_3)K\}_2thf]$ is dimeric with one bridging thf molecule and one K atom has Si–H and Si–Me contacts as well as bonds to two nitrogen atoms [46].

2. Results and discussion

2.1. An improved synthesis of $MN(SiMe_2R)_2$ and the solid-state structure of $KN(SiMe_2H)_2$

We started our survey of new uranium amides by noting an efficient and general route to improving the synthesis of the Group 1 metal salts, and investigating the solid-state structure of one of the ligand precursors, $KN(SiMe_2H)_2$. This ligand contains a β Si–H bond which could lead to interesting interactions or reactivity with low-valent uranium centres.

We note that for bulkier silyl substituents R, the synthesis of $MN(SiMe_2R)_2$ from reaction of the amine with NaH can take over 72 h even in refluxing thf or toluene to react completely with the amine. We find that the addition of a catalytic amount of $NaOBu^t$ can act as a transfer agent, reducing the synthetic time required for even $NaN(SiMe_2Ph)_2$ to only 16 h in thf at reflux, eq. (1). After 7 h the $NaOBu^t$-catalysed synthesis of $NaN(SiMe_2Ph)_2$ is almost complete, whereas the uncatalysed reaction has formed only *ca*. 45% product.

$$HN(SiMe_2R)_2 \xrightarrow[-\mathrm{MI}]{\frac{+1.0\mathrm{MH},\ +\mathrm{cat.MOBu}^t}{\mathrm{Solv}}} MN(SiMe_2R)_2 \qquad (1)$$

M = Na, K
R = H(Solv. = hexanes)
Me(Solv. = PhMe)
Ph(Solv. = thf)

Colourless crystals of $KN(SiMe_2H)_2$ were obtained from a toluene solution of the reaction of the amine with KH. Its structure, Fig. 1, is isomorphous to the sodium analogue in the space

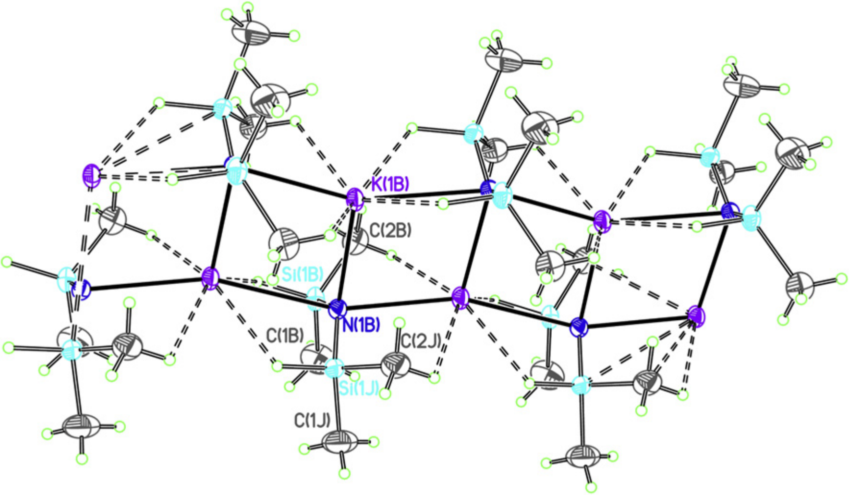

Fig. 1. Thermal ellipsoid plot of $KN(SiMe_2H)_2$ (50% ellipsoid probability). Selected distances (Å) and angles (°): K(1B)–N(1B) 2.833(7), K(1)–N(1)#1 2.871(7), K(1)–N(1)#2 3.072(7),, K(1)–Si(1)#3 3.437(2), K(1)–Si(1)#1 3.589(2).