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

This is the peer-reviewed author's version of a work that was accepted for publication in Journal of Organometallic Chemistry. Changes resulting from the publishing process, such as editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version is available at: http://dx.doi.org/10.1016/j.jorganchem.2010.08.019

Cite as:
Mansell, S. M., Perandones, B. F., & Arnold, P. L. (2010). New U^{III} and U^{IV} silylamides and an improved synthesis of $NaN(SiMe_2R)_2$ (R = Me, Ph). *Journal of Organometallic Chemistry*, *695*(25-26), 2814-2821.

Manuscript received: 14/05/2010; Accepted: 12/08/2010; Article published: 20/08/2010

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

Stephen M. Mansell,[1] Bernabé Fernandez Perandones[1] and Polly L. Arnold[1,*]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[*]Corresponding author; e-mail: polly.arnold@ed.ac.uk, tel.: +44 131 650 5429, fax: +44 131 650 6453

[**]We are grateful to the EPSRC and the University of Edinburgh for funding.

Supporting information:
CCDC 776998, 776999, 777000 contain the supplementary crystallographic data for the complexes $KN(SiMe_2H)_2$, $[U\{N(SiMe_2H)_2\}_4]$, and $[U\{N(SiMe_2Ph)_2\}_3]$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Keywords:
Uranium; amide ligands; actinide complexes; reduction; agostic; weak interactions

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 oxidation state uranium chemistry has caused much recent excitement due to the unusual reactions that can be accomplished [1], [2] and [3]. In this respect, convenient syntheses of suitable starting materials have been crucial to the development of this field such as uranium triiodide [4] and [5] for use in salt metathesis reactions with sodium and potassium ligand precursors. Uranium amides have also become very important precursors to many U(III) uranium complexes [6], and the synthesis of $[U\{N(SiMe_3)_2\}_3]$ in particular was a landmark in low-valent uranium chemistry [7] and [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] and [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], [14] and [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] and [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] and [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-^{i}Pr$_2$C$_6$H$_3$) [24]. From a U(IV) compound, $[U\{N(3,5\text{-}Me_2C_6H_3)^tBu\}_3(thf)]$ 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 both received attention in the field of f-element chemistry [30], [31], [32] and [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] and [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 [$\{(ArO)_3tacn\}U(cy\text{-}C_6H_{11}CH_3)$]· ($cy\text{-}C_6H_{11}CH_3$) [38],[39] and [40]. Despite in general being less well-documented, uranium has an extensive C‑H activation and cyclometallation chemistry [41] and [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] and [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.

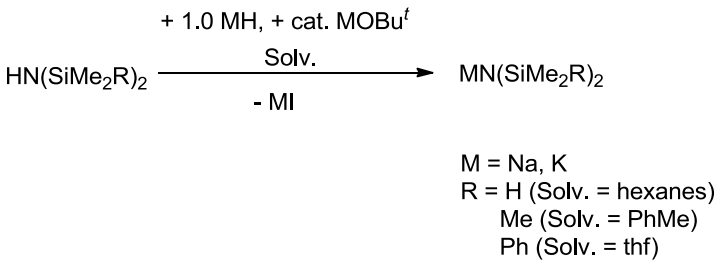
The structure of [{$(Me_2HSi)N(SiMe_3)K$}$_2$thf] is dimeric with one bridging thf molecule and one K atom has Si–H and Si–Me contacts as well as bonds to two nitrogen atoms [46].

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.



(1)

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 group *Pnma* showing an extended ladder structure parallel to the *a* axis with three nitrogen atoms surrounding each potassium atom. The N–K bond lengths that form the rungs of the ladder are the shortest (2.833(7) Å) and another bond is of a similar length (2.871(7) Å) with the other slightly longer (3.072(7) Å). Additional close contacts with all of the Si–H bonds are observed as well as several K···Me contacts. Unlike in the structure of [{$(PhMe_2Si)_2NK$(toluene)}$_2$], no molecules of toluene coordinate to the potassium atom presumably as a consequence of the extended nature of the structure.

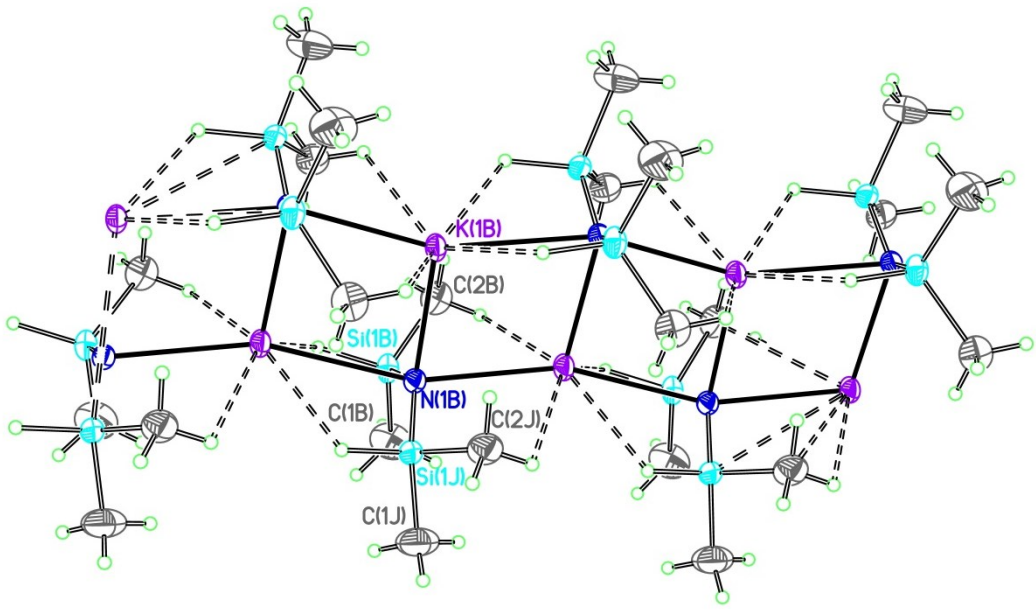
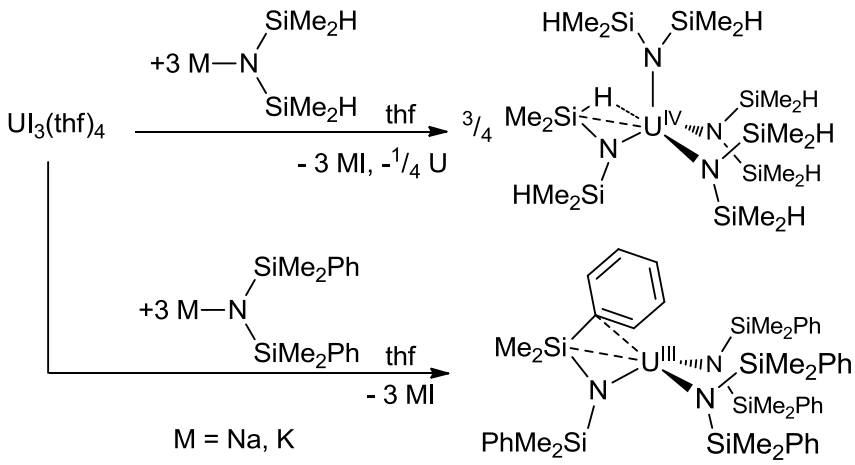


Figure 1. Thermal ellipsoid plot of $KN(SiMe_2H)_2$ (50 % ellipsoid probability). Selected distances (Å) and angles (°): K(1B)-N(1B) 2.833(7), K(1)-N(1)#1 2.871(7), K(1)-N(1)#2 3.072(7), , K(1)-Si(1)#3 3.437(2), K(1)-Si(1)#1 3.589(2).

2.2. Syntheses of homoleptic $[U\{N(SiMe_2R)_2\}_n]$, *n* = 3, 4, R = H, Ph

Syntheses of two new homoleptic uranium(III) amides were attempted by treatment of three equivalents of either the sodium or potassium salts of $[N(SiMe_2H)_2]^-$[47] or $[N(SiMe_2Ph)_2]^-$[32] with $UI_3(thf)_4$ in thf (Scheme 1). The choice of sodium or potassium salt made no difference to the reaction outcome. However, the two different amide ligands gave very different products.



Scheme 1. Synthesis of U^{IV} and U^{III} amides

2.2.1. Synthesis of $[U\{N(SiMe_2H)_2\}_4]$

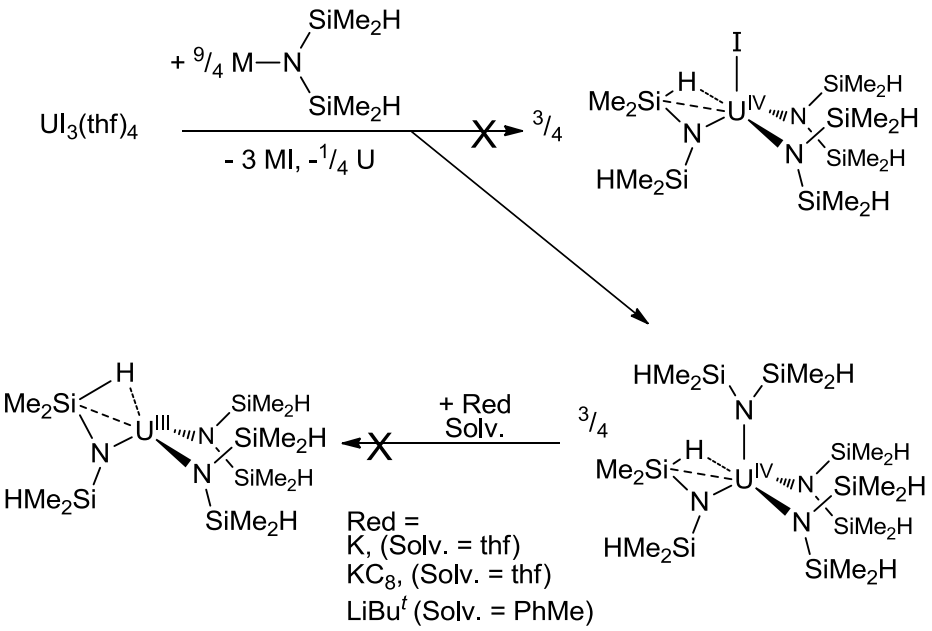
The reaction of $MN(SiMe_2H)_2$ and $UI_3(thf)_4$ in thf overnight affords a brown solution. Removal of the solvent and extraction of the product into *n*-hexane followed by filtration and crystallisation gave pale-blue crystals characterised as $[U\{N(SiMe_2H)_2\}_4]$ in good yield. The oxidation to uranium(IV) is not uncommon, and is accompanied by the formation of grey powdered uranium metal [25], [54], [55] and [56]; the smaller size of the ligand has clearly allowed the straightforward isolation of this complex which has never been observed in the $[U\{N(SiMe_3)_2\}_3]$ syntheses. The tetrakis complex can also be made independently from $UI_4(Et_2O)_2$ in good (46%) yield.

^{1}H NMR spectroscopy revealed a very low frequency resonance at −19.85 ppm caused by the close proximity of the Si-H to the paramagnetic uranium centre which demonstrates averaging of the two environments seen in the solid-state. Broad ^{29}Si satellites are observed (162 Hz) although no coupling is resolved for this resonance or the SiMe groups (observed as a singlet at 1.85 ppm) unlike in the alkali metal salts. ^{13}C NMR spectroscopy shows one resonance for the methyl groups at 7.46 ppm. The solution magnetic moment μ_{eff} (using Evans' NMR method) is 2.94 BM, which is larger than that measured for similar U^{IV} amides $[U\{N(SiMe_3)_2\}_3H]$ (2.6 BM) [50] and$[\{N(SiMe_3)_2\}_2U(CH_2Si)N(SiMe_3)]$ (2.7 BM) [51] although it is close to the value reported for $[U(NPh_2)_4]$ (2.84 BM) [52].

An I.R. spectroscopic study of$[U\{N(SiMe_2H)_2\}_4]$ revealed Si-H stretches in two different regions; two closely spaced bands at 2099.1 and 2075.5 cm^{-1} and another at 1975.2 cm^{-1} (in hexane: 2103.2, 2075.0 and 1982.2 cm^{-1}). This can be compared to $EN(SiMe_2H)_2$, E = H (2118 in nujol), E = Li (1990 cm^{-1} in nujol, 1996 in C_6H_6, increased to 2025 when thf is coordinated to the Li ion), E = Na (1961 and 1926 in nujol), 2004 in C_6H_6 and E = K (1980 in nujol, 1979 in C_6H_6). Si-H stretches at low wavenumber have also been reported in homoleptic lanthanide complexes of the $N(SiMe_2H)_2$ ligand with stretches observed in the range 1931-1970 cm^{-1} for agostic-type interactions [31]. It can be seen that the stretches at higher wavenumbers are from Si-H bonds without any interaction with the metal centre, whereas stretches at lower wavenumber indicate some form of interaction with f-element or alkali metal. Indeed, in $[(SALEN)Ln\{N(SiHMe_2)_2\}(thf)_n]$ (Ln = Y, La) compounds, bands at only high wavenumber (*ca.* 2040 cm^{-1}) were observed for the SiH moieties indicative of no agostic interaction [53].

An attempt to synthesise the mixed ligand halide complex $[U\{N(SiMe_2H)_2\}_3I]$, which we deemed a good candidate for reduction to the sterically unencumbered target $[U\{N(SiMe_2H)_2\}_3]$, with 2.25 equivalents of the amide anion yielded only $[U\{N(SiMe_2H)_2\}_4]$ in sub 30% yields in our hands, Scheme 2. Given the reported stability of the U^{III} complex $K[U(N\{SiMe_3\}_2)_4]$ [23], we anticipated that reduction of the tetraamide would be straightforward: Some reactivity with potassium or potassium graphite was observed, but no product could be

isolated, while surprisingly, no reaction with *tert*-butyl lithium, which could also act as a reductant, was observed, Scheme 2.



Scheme 2. Reactions of $[U\{N(SiMe_2H)_2\}_4]$ and to make related amide complexes.

2.2.2. Structure of $[U\{N(SiMe_2H)_2\}_4]$

The structure of this compound was ascertained as monomeric by X-ray diffraction (Fig. 2) with the uranium atom situated on a two-fold rotation axis. A uranium centre strongly distorted away from tetrahedral (109.5°) is evident from the different N-U-N angles; N(1A)-U(1)-N(1) 126.2(2), N(1A)-U(1)-N(2) 99.61(14), N(1)-U(1)-N(2) 104.15(14)°. The U-N bond lengths (U(1)-N(1) 2.280(4) and U(1)-N(2) 2.281(4) Å) are typical of U(IV) amides [6] and [48], Agostic-type interactions between the uranium atom and four Si-H bonds are suggested by the bent nature of the ligand as evidenced by the U-N-Si angles (Si(1)-N(1)-U(1) 103.45(18), Si(2)-N(1)-U(1) 129.3(2), Si(4)-N(2)-U(1) 103.83(18), Si(3)-N(2)-U(1) 127.5(2)°).This in turn leads to four short U···H contacts (2.705 and 2.773 Å) and short U···Si contacts (3.1462(14), 3.1566(14) Å). A distorted tetrahedral structure was also reported for $[U(NPh_2)_4]$ (N-U-N angles from 96.3(7) to 139.2(7)°) with very similar U-N bond lengths (2.21(2) to 2.35(2) Å) [29]. This structure can be also be compared with a transition metal analogue as the crystal structure of $[Hf\{N(SiMe_2H)_2\}_4]$ revealed a similar, if slightly less distorted, tetrahedral geometry with N-Hf-N angles varying from 102 to 115°, and with shorter Hf-N bonds lengths (2.062(2) to 2.079(2) Å) [49]. Agostic interactions were not mentioned in the paper, but the same

asymmetry in the $N(SiMe_2H)_2$ ligands was seen in the tilting of the group (Hf-N-Si angles of approximately 110° and 125°) with one set of shorter Si···Hf distances (3.090-3.169 Å) and one longer set (3.361-3.410 Å) [49].

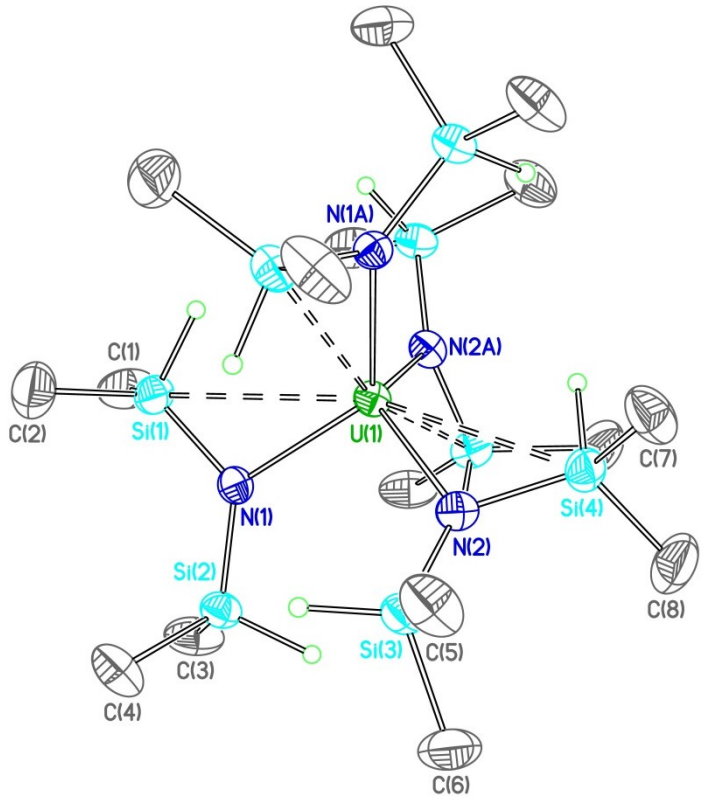


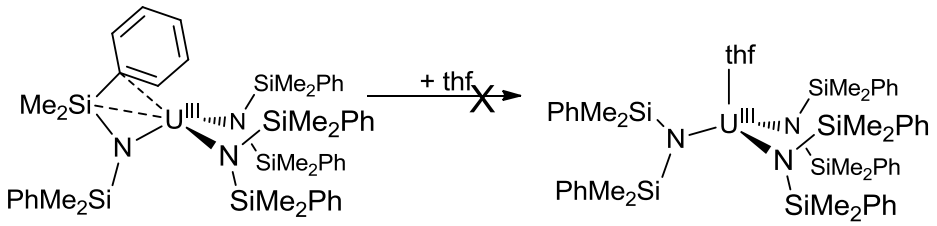
Figure 2. Thermal ellipsoid plot of $[U\{N(SiMe_2H)_2\}_4]$ (50 % ellipsoid probability). All hydrogen atoms except for Si-H have been omitted for clarity. Symmetry operator for symmetry generated atoms: *-x*, *y*, *-z* + 3/2. Selected bond lengths (Å) and angles (°): U(1)-N(1) 2.280(4), U(1)-N(2) 2.281(4), U(1)-Si(1) 3.1462(14) U(1)-Si(4) 3.1566(14), N(1)-Si(1) 1.701(4), N(1)-Si(2) 1.717(4), N(2)-Si(4) 1.704(4), N(2)-Si(3) 1.711(4), Si(1)-H(1) 1.32(6), Si(2)-H(2) 1.38(2), Si(3)-H(3) 1.30(6), Si(4)-H(4) 1.47(5), N(1A)-U(1)-N(1) 126.2(2), N(1A)-U(1)-N(2) 99.61(14), N(1)-U(1)-N(2) 104.15(14), Si(1)-N(1)-U(1) 103.45(18), Si(2)-N(1)-U(1) 129.3(2), Si(4)-N(2)-U(1) 103.83(18), Si(3)-N(2)-U(1) 127.5(2); Σ(angles at N1) 359.95, Σ (angles at N2) 359.83.

2.2.3. Synthesis of $[U\{N(SiMe_2Ph)_2\}_3]$

The reaction of three equivalents of $MN(SiMe_2Ph)_2$ with $UI_3(thf)_4$ in thf proceeded to give a dark brown solution, Scheme 1. The solvent was removed under reduced pressure and the residue was extracted with *n*-

hexane which was filtered and a small amount of impure solid precipitates after storage at −30 ° C. After the transfer of the supernatant to a new vessel, brown material crystallises upon storage at −30 ° C, characterised as [U{N(SiMe$_2$Ph)$_2$}$_3$]. The additional separation stage to remove impure material, along with the low volatility of the free amine makes this complex more difficult to isolate pure and in large quantities than the other silylamide analogues. ^{1}H NMR spectroscopy (C$_6$D$_6$) shows a single set of broad, paramagnetically shifted resonances at 5.34, 3.89 and 3.18 ppm for the phenyl groups and −6.50 ppm for the methyl groups. This is also observed by ^{13}C NMR spectroscopy with the phenyl resonances resonating at lower frequency (122.6, 120.5 and 112.0 ppm) than in the free amine (141.0, 133.4, 129.0 and 127.7) and in the K salt (149.2, 132.8 and 128.0 ppm) and a very broad resonance at −57.1 ppm for the methyl groups. The*ipso*-carbon was not observed.

The 5f^3 U^{III} centre gives rise to a magnetic moment for [U{N(SiMe$_2$Ph)$_2$}$_3$], determined in solution at room temperature, of 3.11 μ_B. This is very close to the values reported for the parent [U{N(SiMe$_3$)$_2$}$_3$] (the solid-state μ_{eff} is 3.07 μ_B at 300 K) [7], [37] and [57], and only slightly higher than that measured above for the 5f^2[U{N(SiMe$_2$H)$_2$}$_4$], but the range of room temperature magnetic moments of U^{III} (^{4}I$_{9/2}$ ground state) and U^{IV}(^{3}H$_4$ ground state) coordination complexes are know to have considerable overlap, and the values reported for both of these new uranium amides are within this range [58], [59] and [60].



(2)

Attempts to coordinate additional small molecules such as thf have shown no coordination by NMR spectroscopy, eq (2), in our hands to date, testifying to the protection of the U^{III} centre in this molecule.

2.2.4. Structure of [U{N(SiMe$_2$Ph)$_2$}$_3$]

Crystals of [U{N(SiMe$_2$Ph)$_2$}$_3$] suitable for X-ray diffraction were grown from a concentrated 1:1 *n*-hexane/toluene solution at −20 ° C and the high air- and moisture-sensitivity of the crystals meant the data collected is only of moderate quality. The complex [U{N(SiMe$_2$Ph)$_2$}$_3$] crystallised in the space group $R\bar{3}$ with the uranium atom sitting on a three-fold rotation axis. Interestingly, this leads to voids throughout the structure

which are not filled with solvent (no residual electron density could be identified in these voids) and do not appear to be interconnected, and their presence is reflected in a lower density (1.275 g cm^{-3}) compared with $[U\{N(SiMe_2H)_2\}_4]$ (1.407 g cm^{-3}). The molecular structure (Fig. 3) reveals a pyramidal uranium atom bonded to three nitrogen atoms (U–N distance 2.337(15) Å) with one phenyl group of every amide ligand pointing above the plane of the nitrogen atoms and directed towards the uranium atom, whilst the other three phenyl groups are below the plane and point away from the uranium atom. This pyramidal geometry is always seen in f-element tris(amide) complexes, such as $[U\{N(SiMe_3)_2\}_3]$ (U–N: 2.320(4) Å) [22], and can be explained for these compounds by the polarised-ion model [22]. Three Ph groups form close contacts with the uranium atom via the *ipso*-carbon and Si atom (U···Si: 3.319(5) Å) as has been seen in $[U\{N(^tBu)3,5\text{-}Me_2C_6H_3\}_3(thf)]$ which showed slightly shorter distances (U–N: 2.295(10) to 2.361(9) Å, U···*ipso* C: 2.886(12) to 2.980 (12) Å), and aryl interactions are also seen in uranium(IV) benzyl compounds[54] and [55]. This is seen most clearly in the top view of the complex, Fig. 3(b).

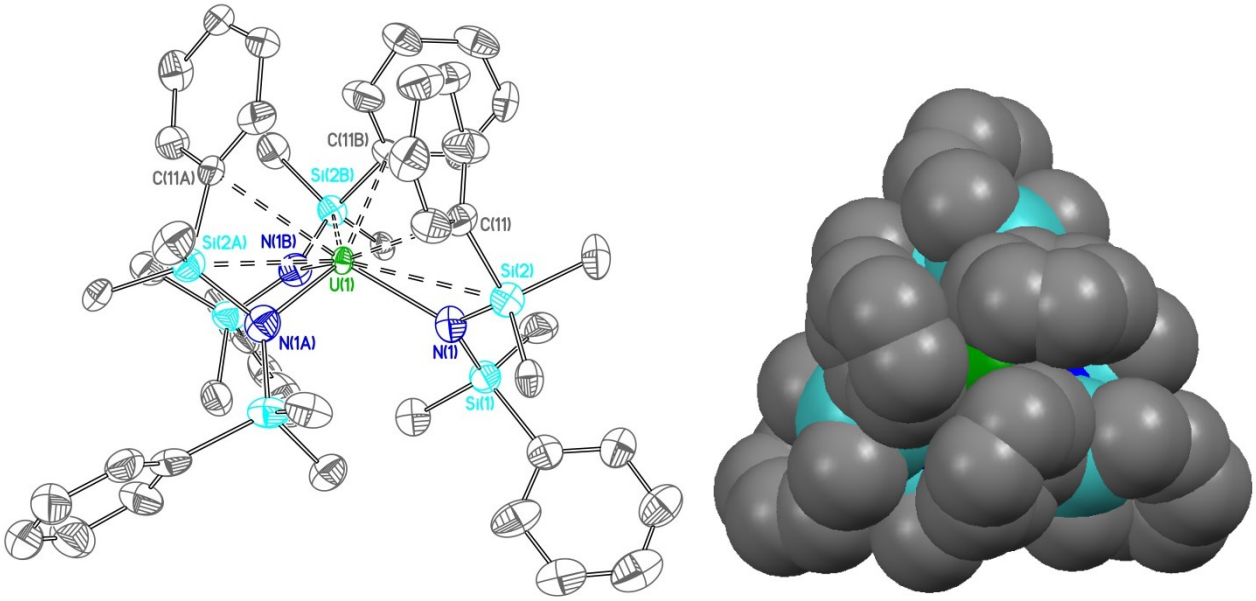


Figure 3. Thermal ellipsoid plot of $[U\{N(SiMe_2Ph)_2\}_3]$. (a) side view (50 % ellipsoid probability), (b) top view (space-fill). All hydrogen atoms have been omitted for clarity. Symmetry operators for symmetry generated atoms: $-x + y$, $-x + 1$, z and $-y + 1$, $x - y + 1$, z. Selected bond lengths (Å) and angles (°): U(1)-N(1) 2.337(15), U(1)-Si(2) 3.319(5), N(1)-Si(2) 1.720(16), N(1)-Si(1) 1.739(16).

Finally, a comparison of the NIR-UV-vis spectra of hexanes solutions of $[U\{N(SiMe_2Ph)_2\}_3]$ and $[U\{N(SiMe_2H)_2\}_4]$ (Fig. 4) show maxima with molar absorptivities in the 100s for the U^{III} amide and absorptions with molar absorptivities in the 10s the U^{IV} amide, confirming the assigned oxidation states.

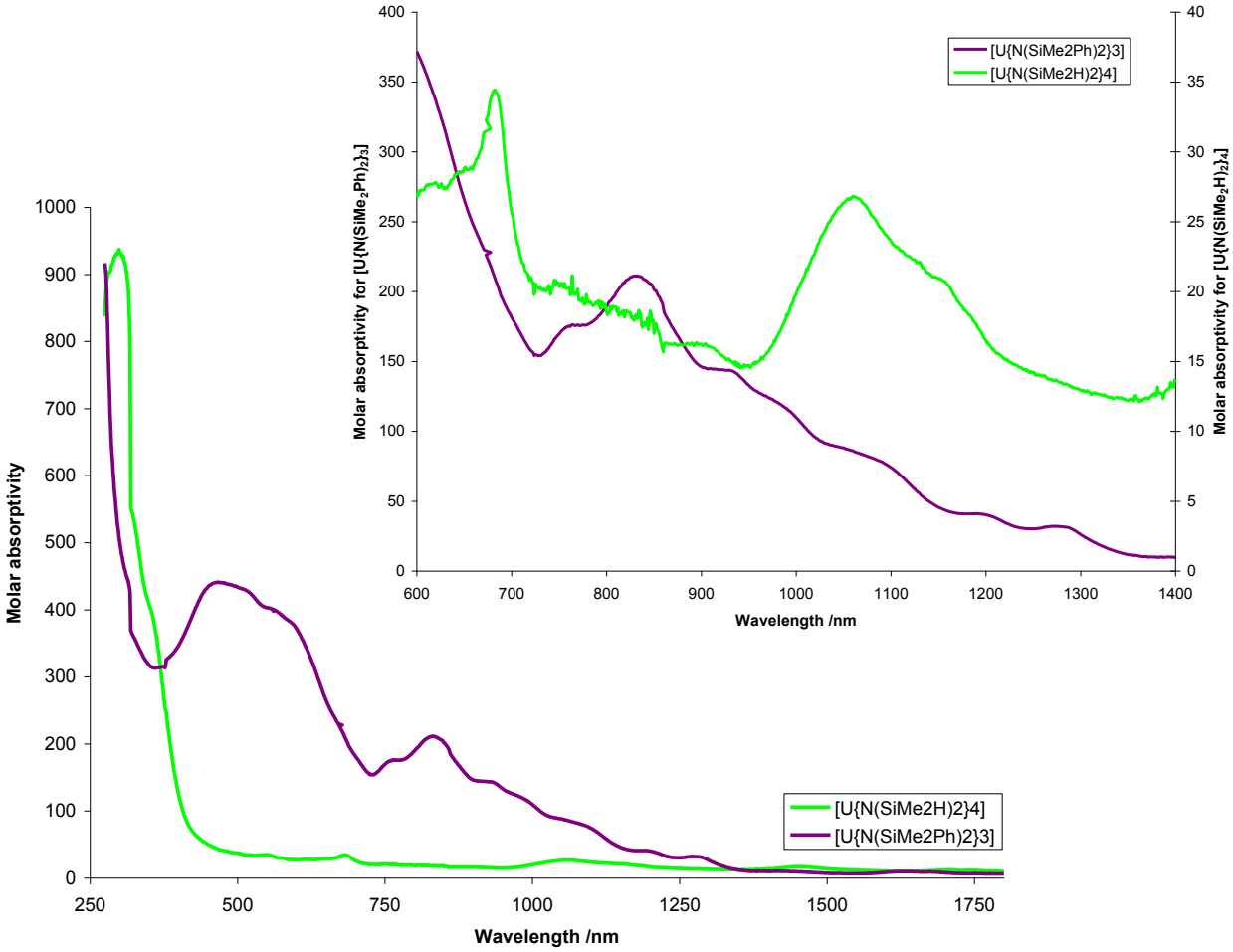


Figure 4. NIR-Uv-vis spectra of hexane solutions of $[U\{N(SiMe_2H)_2\}_4]$ and $[U\{N(SiMe_2Ph)_2\}_3]$ (1.9 x 10^{-5} M and 1.5 x 10^{-5} M respectively).

3. Conclusions

A fast, efficient synthesis of Group 1 bis(silylamide) salts $NaN(SiMe_2R)_2$, R = H, Me, Ph, using $NaOBu^t$ as a catalyst, has been described, which reduced the time required to make the sterically most hindered compound, $NaN(SiMe_2Ph)_2$, from three days to 16 h. The recent renaissance in multi-electron-chemistry reported for f-block metals using 'sterically induced reduction' suggests that this protocol for the acceleration of kinetically difficult deprotonations of bulky ligands might have more widespread use. These amide anions allow the synthesis of U^{IV} and U^{III} complexes $[U\{N(SiMe_2H)_2\}_4]$ and$[U\{N(SiMe_2Ph)_2\}_3]$, both of which display weak interactions between the uranium centre and silane Si–H atoms (the former) and Si–Ph *ipso* C atoms (the latter). We have been unable to isolate the sterically unencumbered trivalent $[U\{N(SiMe_2H)_2\}_3]$ but we anticipate that both amide complexes will prove useful starting materials for further redox and ligand exchange reactivity.

4. Experimental

4.1. General details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in MBraun Unilab or Vacuum Atmospheres OMNI-lab gloveboxes unless otherwise stated. THF and hexane were degassed and purified by passage through activated alumina towers prior to use. All deuterated solvents were boiled over potassium, vacuum transferred, and freeze-pump-thaw degassed three times prior to use. The compounds $NaN(SiMe_2H)_2$[47], $KN(SiMe_2H)_2$[47], $KN(SiMe_2Ph)_2$[32], and $UI_3(thf)_4$(from stirring UI_3[61] in thf), were made as previously described in the literature, whilst all other reagents were used as purchased without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker AVA 400 or 600 MHz NMR spectrometers at 298 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances calibrated against external TMS. Infrared spectra were recorded on Jasco 410 spectrophotometers. Solutions for UV–vis spectrophotometry were made in a nitrogen filled glovebox and spectra were recorded in either a Teflon-tapped 10 mm quartz cell or a 1 mm quartz cell sealed by a tight fitting Subaseal on a Unicam UV1 spectrophotometer.

4.2. Improved synthesis of $NaN(SiMe_3)_2$ and $NaN(SiMe_2Ph)_2$

NaH (102 mg, 4.2 mmol) and NaO^tBu (7 mg, 0.02 mol) was dissolved in thf (10 cm^3) and $HN(SiMe_2Ph)_2$(1 cm^3, 3.5 mmol) was added and the mixture was heated under reflux for 16 h. All of the solvent was removed under reduced pressure and the colourless solid was extracted into hot *n*-hexane and filtered. Removal of the solvent under reduced pressure and extended heating with a hot water bath gave $NaN(SiMe_2Ph)_2$ with only very small amounts of residual coordinated thf (882 mg, 2.9 mmol, 83%).

NaH (1.21 g, 50.4 mmol) and NaO^tBu (97 mg, 1.0 mmol) was suspended in toluene (20 cm^3) and $HN(SiMe_3)_2$(20 cm^3, 48.0 mmol) was added and the mixture was heated under reflux for 48 h. The solution was filtered and all of the solvent was removed under reduced pressure and the colourless solid was washed with *n*-hexane (*ca*. 3 cm^3) and dried under reduced pressure (7.530 g, 41.1 mmol 86%).

4.3. Synthesis of uranium(III) and uranium(IV) amides

4.3.1. $[U\{N(SiMe_2H)_2\}_4]$

(a) A solution of $NaN(SiMe_2H)_2$ (490 mg, 3.15 mmol) in thf (10 cm^3) was added to a blue solution of $UI_3(thf)_4$ (954 mg, 1.05 mmol) in thf (10 cm^3) giving a brown solution which was stirred at room temperature for 16 h. The volatiles were removed under reduced pressure and the brown solid was extracted with *n*-hexane (20

cm^3). This was filtered via cannula and the supernatant was reduced in volume under reduced pressure and pale-blue crystals were obtained after storage of a saturated solution overnight at −30 °C (182 mg, 0.24 mmol, 30%).

^{1}H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 1.85 (s, 48H, Me), −19.85 (s with ^{29}Si satellites $^1J(^1H–^{29}Si)$ = 162 Hz, 8 H, Si–H). ^{13}C NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 7.46 (Me). μ_{eff} (Evans' NMR method) 2.94. I.R. (nujol mull) υ (cm^{-1}) 2099.1m, 2075.5m, 1975.2m, 1260.3s, 1093.4s, 1018.7s, 896.7s and 797.4s. I.R. (hexane solution) υ (cm^{-1}) 2103.2s, 2075.0s, 1982.2m, 1255.2m, 1099.0m, 943.5m, 843.7m, 684.6m. Anal. Calcd. for $C_{16}H_{56}N_4Si_8U$: C, 25.04; H, 7.36; N, 7.30. Found: C, 24.31; H, 7.31; N, 7.27.

b) Instead of $NaN(SiMe_2H)_2$, $KN(SiMe_2H)_2$ (573 mg, 3.34 mmol) was added to $UI_3(thf)_4$ (1.011 g, 1.11 mmol) in thf (20 cm^3), yield: 313 mg, 0.41 mmol, 37%.

c) Four equivalents of $NaN(SiMe_2H)_2$ (61 mg, 0.39 mmol) were added to $UI_4(OEt_2)_2$ (88 mg, 0.099 mmol) in thf (2 cm^3) and the pale yellow solution was stirred for 24 h. The solvent was removed under reduced pressure and the solid was extracted with *n*-hexane (10 cm^3), filtered and the solvent removed under reduced pressure yielding a yellow solid (35 mg, 0.046 mmol, 46%) which was identified as $[U\{N(SiMe_2H)_2\}_4]$ by NMR spectroscopy.

4.3.2. Attempted synthesis of $[U\{N(SiMe_2H)_2\}_3I]$

In an attempt to synthesise $[U\{N(SiMe_2H)_2\}_3I]$, $NaN(SiMe_2H)_2$ (290 mg, 1.87 mmol) reacted with $[UI_3(thf)_4]$ (753 mg, 0.83 mmol) yielding instead $[U\{N(SiMe_2H)_2\}_4]$ (140 mg, 0.18 mmol, 29%).

4.3.3. Reactions of $[U\{N(SiMe_2H)_2\}_4]$

4.3.3.1. $[U\{N(SiMe_2H)_2\}_4]$ with KC_8

A solution of $[U\{N(SiMe_2H)_2\}_4]$ (150 mg, 0.20 mmol) in thf (10 cm^3) was added to a bronze suspension of KC_8(26 mg, 0.20 mmol) in thf (10 cm^3) and this mixture was stirred for 72 h. Black graphite was observed, and the brown supernatant was isolated by filtration and the solvent removed under reduced pressure. Extraction into C_6D_6 with a few drops of thf allowed the identification of resonances for the starting material as well a numerous paramagnetically shifted resonances including δ (ppm); 21.6 (s), 12.7 (s), 9.1 (s), −0.8 (s), −3.6 (s), −4.9 (s), −10.9 (s), −22.9 (s).

4.3.3.2. [U{N(SiMe$_2$H)$_2$}$_4$] with K

Potassium (20 mg, in excess) was added to a solution of [U{N(SiMe$_2$H)$_2$}$_4$] (150 mg, 0.20 mmol) in thf (15 cm^3) and the brown solution was stirred for 16 h, after which time, potassium metal was still visible in the dark brown solution. The supernatant was isolated by filtration and the solvent removed under reduced pressure. ^{1}H NMR spectroscopy in C_6D_6 showed no U starting material and no resonances outside the diamagnetic region: δ (ppm) 5.13 (bs, 2H), 3.37 (bs, thf), 1.29 (bs, thf), 0.36 (bs, 12H).

4.3.3.3. [U{N(SiMe$_2$H)$_2$}$_4$] with ^{t}BuLi

^{t}BuLi (0.15 cm^3, 1.7 M in pentane, 0.25 mmol) was added to a solution of [U{N(SiMe$_2$H)$_2$}$_4$] (190 mg, 0.25 mmol) in toluene and was stirred for 72 h. The supernatant was isolated by filtration and the solvent removed under reduced pressure. ^{1}H NMR spectroscopy revealed only resonances for the starting material, [U{N(SiMe$_2$H)$_2$}$_4$].

4.3.4. [U{N(SiMe$_2$Ph)$_2$}$_3$]

a) A solution of NaN(SiMe$_2$Ph)$_2$ (406 mg, 1.32 mmol) in thf (10 cm^3) was added to a blue solution of UI$_3$(thf)$_4$ (399 mg, 0.44 mmol) in thf (10 cm^3) giving a brown solution which was stirred at room temperature for 16 h. The volatiles were removed under reduced pressure and the brown solid was extracted with *n*-hexane (40 cm^3). This was cannula filtered and reduced in volume under reduced pressure; upon storage at −30 °C an impure solid precipitates. The supernatant solution was transferred into a new Schlenk vessel and dark brown crystals were obtained after storage of this saturated solution overnight at −30 °C (234 mg, 0.21 mmol, 49%).

^{1}H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 5.34 (bs, 8H, *para*-C_6H_5), 3.89 (bs, 16H, *ortho*-C_6H_5), 3.18 (bs, 16H, *meta*-C_6H_5), −6.50 (bs, 48H, Me). ^{13}C NMR (600 MHz, 298 K, C_6D_6) δ (ppm) 122.6 (*meta*-C), 120.5 (*para*-C), 112.0 (*ortho*-C), −57.1 (Me). μ_{eff} (Evans' NMR method) 3.11 μ_B. I.R. (nujol mull) υ (cm^{-1}) 1259.1 (m), 1102.8 (m), 933.1 (m), 832.1 (w), 799.8 (w), 722.2 (w). I.R. (hexane solution) υ (cm^{-1}) 1255.7 (w), 1181.2 (w), 1111.0 (m), 942.1 (m), 833.8 (w), 699.1 (w).

b) Instead of NaN(SiMe$_2$Ph)$_2$, KN(SiMe$_2$Ph)$_2$ (539 mg, 1.67 mmol) was added to UI$_3$(thf)$_4$ (504 mg, 0.56 mmol) in thf (40 cm^3), yield: 320 mg, 0.29 mmol, 52%.

A drop of thf (excess) was added to a solution of [U{N(SiMe$_2$Ph)$_2$}$_3$] (60 mg) in C_6D_6 (0.7 cm^3) and was sealed in an NMR tube equipped with a Young's tap. NMR spectroscopy revealed no change in any of the resonances indicating no coordination of thf.

4.4. Crystallographic details

Crystals suitable for X-ray diffraction analysis were grown from saturated toluene or hexane solutions, mounted in an inert oil and then transferred to the cold gas stream of the diffractometer. Diffraction experiments were on an Oxford diffraction Excalibur four-circle diffractometer employing Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct or Patterson methods and refined by least squares on weighted F^2 values for all reflections [62]. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters except the SiH in [U{N($SiMe_2H$)$_2$}$_4$] which were located in the Fourier difference map and refined with isotropic parameters equal to 1.5 times that of the attached Si atom. Refinement proceeded smoothly to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used. Data for KN($SiMe_2H$)$_2$ and [U{N($SiMe_2Ph$)$_2$}$_3$] were twinned and individual domains could not be separated from the main domain and hence the residuals are higher than is desirable.

Table 1. Selected experimental crystallographic details for Compounds KN($SiMe_2H$)$_2$, [U{N($SiMe_2H$)$_2$}$_4$] and [U{N($SiMe_2Ph$)$_2$}$_3$].

Compound	KN($SiMe_2H$)$_2$	[U{N($SiMe_2H$)$_2$}$_4$]	[U{N($SiMe_2Ph$)$_2$}$_3$]
Colour, habit	Colourless, block	Pale-blue, shard	Brown, block
Size/mm	0.50 × 0.50 × 0.20	0.12 × 0.07 × 0.02	0.15 × 0.15 × 0.03
Empirical Formula	$C_8H_{28}K_2N_2Si_4$	$C_{16}H_{56}N_4Si_8U$	$C_{48}H_{66}N_3Si_6U$
M	342.88	767.40	1091.61
Crystal system	Orthorhombic	Monoclinic	Trigonal
Space group	*Pnma*	*C*2/*c*	*R*-3
a/Å	5.8432(6)	17.3799(7)	18.6138(10)
b/Å	15.1901(19)	11.6699(5)	18.6138(10)
c/Å	11.2466(17)	18.4494(8)	28.426(3)
α/°	90	90	90
β/°	90	104.478(4)	90
γ/°	90	90	120
V/Å^3	998.2(2)	3623.1(3)	8529.5(11)
Z	2	4	6
μ/mm^{-1}	0.699	4.756	3.012
T/K	173(2)	173(2)	171(2)
$\theta_{min,max}$	3.62, 27.49	3.33, 27.48	2.91, 24.10
Completeness to θ_{max}	95.1	99.8	99.7
Reflections: total/independent	2486, 1131	16093, 4156	7691, 3013
R_{int}	0.0842	0.0468	0.1036
Final $R1$ ($I > 2\sigma$) and $wR2$ (all data)	0.0923, 0.2637	0.0360, 0.0830	0.0929, 0.2591
Largest peak, hole/e Å^{-3}	0.876, −0.755	3.441, −1.024	3.880, −1.459
ρ_{calc}/g cm^{-3}	1.141	1.407	1.275

References

[1] M. Ephritikhine, *Dalton Trans.* (2006), **p. 2501.**

[2] O.P. Lam, C. Anthon, K. Meyer, *Dalton Trans.* (2009), **p. 9677.**

[3] M.J. Monreal, P.L. Diaconescu, *Nat. Chem.*, 2 (2010), **p. 423.**

[4] L.R. Avens, S.G. Bott, D.L. Clark, A.P. Sattelberger, J.G. Watkin, B.D. Zwick, *Inorg. Chem.*, 33 (1994), **p. 2248.**

[5] D.L. Clark, A.P. Sattelberger, S.G. Bott, R.N. Vrtis, *Inorg. Chem.,* 28 (1989), **p. 1771.**

[6] J.C. Berthet, M. Ephritikhine, *Coord. Chem. Rev.*, 178 (1998), **p. 83.**

[7] R.A. Andersen, *Inorg. Chem.,* 18 (1979), **p. 1507.**

[8] D.L. Clark, A.P. Sattelberger, R.A. Andersen, *Inorg. Synth.*, 31 (1997), **p. 307.**

[9] R. Kempe, *Angew. Chem., Int. Ed.*, 39 (2000), **p. 468.**

[10] S.C. Bart, F.W. Heinemann, C. Anthon, C. Hauser, K. Meyer, *Inorg. Chem.*, 48 (2009), **p. 9419.**

[11] Castro-Rodriguez, K. Olsen, P. Gantzel, K. Meyer, *J. Am. Chem. Soc.*, 125 (2003), **p. 4565.**

[12] Z.R. Turner, R. Bellabarba, R.P. Tooze, P.L. Arnold, *J. Am. Chem. Soc.,* 132 (2010), **p. 4050.**

[13] W.J. Evans, S.A. Kozimor, *Coord. Chem. Rev*., 250 (2006), **p. 911.**

[14] W.J. Evans, B.L. Davis, *Chem. Rev.*, 102 (2002), **p. 2119.**

[15] H. Schumann, J.A. Meesemarktscheffel, L. Esser, *Chem. Rev.*, 95 (1995), **p. 865.**

[16] P. Roussel, P. Scott, *J. Am. Chem. Soc.*, 120 (1998), **p. 1070.**

[17] S.T. Liddle, J. McMaster, D.P. Mills, A.J. Blake, C. Jones, W.D. Woodul, *Angew. Chem., Int. Ed.*, 48 (2009), **p. 1077.**

[18] B.M. Gardner, J. McMaster, W. Lewis, S.T. Liddle, *Chem. Commun.* (2009), **p. 2851.**

[19] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed*., 38 (1999), **p. 428.**

[20] F.T. Edelmann, D.M.M. Freckmann, H. Schumann, *Chem. Rev.*, 102 (2002), **p. 1851.**

[21] J. Drożdżyński, *Coord. Chem. Rev.*, 249 (2005), **p. 2351.**

[22] J.L. Stewart, R.A. Andersen, *Polyhedron*, 17 (1998), **p. 953.**

[23] W.J. Evans, D.S. Lee, D.B. Rego, J.M. Perotti, S.A. Kozimor, E.K. Moore, J.W. Ziller, *J. Am. Chem. Soc.*, 126 (2004), **p. 14574.**

[24] J.E. Nelson, D.L. Clark, C.J. Burns, A.P. Sattelberger, *Inorg. Chem.*, 31 (1992), **p. 1973.**

[25] A.L. Odom, P.L. Arnold, C.C. Cummins, *J. Am. Chem. Soc.,* 120 (1998), **p. 5836.**

[26] R.G. Jones, G. Karmas, G.A. Martin, H. Gilman, *J. Am. Chem. Soc.,* 78 (1956), **p. 4285.**

[27] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, L.K. Templeton, *Inorg. Chem.*, 15 (1976), **p. 2498.**

[28] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, *Inorg. Chem.*, 16 (1977), **p. 1858.**

[29] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, *Inorg. Chem.*, 16 (1977), **p. 1090.**

[30] O. Runte, T. Priermeier, R. Anwander, *Chem. Commun.* (1996), **p. 1385.**

[31] R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, *Dalton Trans.* (1998), **p. 847.**

[32] W.J. Evans, D.B. Rego, J.W. Ziller, *Inorg. Chem.,* 45 (2006), **p. 3437.**

[33] W.A. Herrmann, R. Anwander, F.C. Munck, W. Scherer, V. Dufaud, N.W. Huber, G.R.J. Artus, *Z. Naturforsch., B: Chem. Sci.*, 49 (1994), **p. 1789.**

[34] M. Brookhart, M.L.H. Green, G. Parkin, *Proc. Natl. Acad. Sci. U.S.A.*, 104 (2007), **p. 6908.**

[35] M. Brookhart, M.L.H. Green, *J. Organomet. Chem.*, 250 (1983), **p. 395.**

[36] W. Scherer, D.J. Wolstenholme, V. Herz, G. Eickerling, A. Bruck, P. Benndorf, P.W. Roesky, *Angew. Chem., Int. Ed.,* 49 (2010), **p. 2242.**

[37] W.G. Van der Sluys, C.J. Burns, A.P. Sattelberger, *Organometallics*, 8 (1989), **p. 855.**

[38] J.T. Lyon, L. Andrews, H.S. Hu, J. Li, *Inorg. Chem.*, 47 (2008), **p. 1435.**

[39] Korobkov, S. Gorelsky, S. Gambarotta, *J. Am. Chem. Soc.,* 131 (2009), **p. 10406.**

[40] Castro-Rodriguez, H. Nakai, P. Gantzel, L.N. Zakharov, A.L. Rheingold, K. Meyer, *J. Am. Chem. Soc.*, 125 (2003), **p. 15734.**

[41] Korobkov, S. Gambarotta, G.P.A. Yap, *Organometallics*, 20 (2001), **p. 2552.**

[42] Korobkov, S. Gambarotta, *Inorg. Chem.,* 49 (2010), **p. 3409.**

[43] H.M. Dietrich, C. Meermann, K.W. Tornroos, R. Anwander, *Organometallics*, 25 (2006), **p. 4316.**

[44] H.F. Yuen, T.J. Marks, *Organometallics*, 27 (2008), **p. 155.**

[45] M.G. Klimpel, H.W. Gorlitzer, M. Tafipolsky, M. Spiegler, W. Scherer, R. Anwander, *J. Organomet. Chem.,* 647 (2002), **p. 236.**

[46] J. Schneider, E. Popowski, H. Reinke, *Z. Anorg. Allg*. Chem., 629 (2003), **p. 55.**

[47] J. Eppinger, E. Herdtweck, R. Anwander, *Polyhedron*, 17 (1998), **p. 1195.**

[48] M. Roger, N. Barros, T. Arliguie, P. Thuery, L. Maron, M. Ephritikhine, *J. Am. Chem. Soc.,* 128 (2006), **p. 8790.**

[49] E.D. Jimenez, S. Javed, D.M. Hoffman, *Inorg. Chim. Acta,* 362 (2009), **p. 385.**

[50] H.W. Turner, S.J. Simpson, R.A. Andersen*, J. Am. Chem. Soc.*, 101 (1979), **p. 2782.**

[51] S.J. Simpson, H.W. Turner, R.A. Andersen, *J. Am. Chem. Soc.,* 101 (1979), **p. 7728.**

[52] J.G. Reynolds, A. Zalkin, D.H. Templeton, N.M. Edelstein, *Inorg. Chem.,* 16 (1977), **p. 599.**

[53] Q.C. Liu, C. Meermann, H.W. Gorlitzer, O. Runte, E. Herdtweck, P. Sirsch, K.W. Tornroos, R. Anwander, *Dalton Trans.* (2008), **p. 6170.**

[54] S. Duhović, S. Khan, P.L. Diaconescu, *Chem. Commun.,* 46 (2010), **p. 3390.**

[55] M.J. Monreal, P.L. Diaconescu, *Organometallics*, 27 (2008), **p. 1702.**

[56] P.L. Diaconescu, C.C. Cummins, *J. Am. Chem. Soc*., 124 (2002), **p. 7660.**

[57] H. Nakai, X. Hu, L.N. Zakharov, A.L. Rheingold, K. Meyer, *Inorg. Chem.*, 43 (2004), **p. 855.**

[58] N.M. Edelstein, G.H. Lander, **Magnetic Properties,** L.R. Morss, N.M. Edelstein, J. Fuger, J.J. Katz (Eds.), *The Chemistry of the Actinide and Transactinide Elements*, Springer (2006), **p. 2225.**

[59] J.G. Brennan, R.A. Andersen, A. Zalkin, *Inorg. Chem.,* 25 (1986), **p. 1756.**

[60] E.J. Schelter, R. Wu, B.L. Scott, J.D. Thompson, T. Cantat, K.D. John, E.R. Batista, D.E. Morris, J.L. Kiplinger, *Inorg. Chem.,* 49 (2009), **p. 924.**

[61] C.D. Carmichael, N.A. Jones, P.L. Arnold, *Inorg. Chem.*, 47 (2008), **p. 8577.**

[62] G.M. Sheldrick, *Acta Crystallogr. A*, 64 (2008), **p. 112.**