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Reactivity of a triamidoamine complex of trivalent uranium

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Reduction of [U(NN′$_3$)I] [NN′$_3$ = N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_3$] with potassium in pentane gives the purple trivalent monomer [U(NN′$_3$)] in good yield, this compound having previously been synthesised *via* fractional vacuum sublimation of mixed-valent [{U(NN′$_3$)}$_2$(μ-Cl)]. The magnetic susceptibility of this compound is consistent with the presence of U(III) centres, and this is confirmed by a characteristic near IR spectrum. Its reactions with Lewis bases to give *e.g.* [U(NN′$_3$)(Py)] and [U(NN′$_3$)(HMPA)] are reported, along with the molecular structure of the latter. The complex [U(NN′$_3$)] is readily oxidised, imido and hydrazido complexes being formed readily by reaction with trimethylsilyl-azide and -diazomethane, respectively. The reaction with methylene trimethylphosproane however led to the formation of an addition compound [U(NN′$_3$)(CH$_2$PMe$_3$)]. Reaction of this latter complex with air gave a few crystals of the unusual hydroxo complex [U(NN′$_3$)(OH)(CH$_2$PMe$_3$)] which was structurally characterised. Reaction of [U(NN′$_3$)(CH$_2$PMe$_3$)] with trimethylamine *N*-oxide gave pentavalent [U(NN′$_3$)(O)], or perhaps a dimer thereof. The latter complex reacted with [U(NN′$_3$)] to give the bridging oxo complex [{U(NN′$_3$)}$_2$(μ-O)] which could also be prepared directly by reaction of trimethylamine *N*-oxide with [U(NN′$_3$)].

Introduction

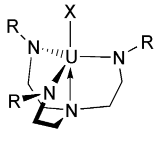
For the actinide An^{3+} ions in oxygen-free aqueous solution, stability increases across the series such that by Am this is the preferred oxidation state and the elements are quite lanthanide-like.[1] U^{3+} however, while kinetically stable, will eventually reduce water. The trivalent state of uranium in non-aqueous environments, rendered more accessible by the advent of useful starting materials,[2] has been stabilised by the use of sterically demanding alkyl,[3] amide[4] and phenolate ligands,[5] as well as by the more classical cyclopentadienyls.[6] Solvent-base free complexes of the former ligand classes have, by definition, coordination number 3; an unusual situation for any f element for which coordination numbers up to 9 are common. These two issues of high reducing power of U(III) and high susceptibility to incoming Lewis acids combine make uranium(III) systems among the most reactive of coordination and organometallic compounds.

Our contribution to the chemistry of triamidoamine[7] complexes has concentrated on the lanthanide[8,9] and actinide systems.[10] For uranium, the majority of compounds have contained U(IV) *e.g.* systems **I** (X = halides, alkoxides *etc.*), although a few other situations have arisen, such as in the mixed valence (III/IV) bimetallic [{U(NN′$_3$)}$_2$(μ-Cl)] **I**.[11] This latter compound acts as a source of trivalent uranium, liberating an equivalent quantity of the tetravalent component [U(NN′$_3$)Cl] (*e.g.* eqn. (1)). Although separation of the products in eqn. (1) was achieved, this process is generally difficult and certainly tiresome. We found it expedient, if inconvenient, to first separate the U(III) and U(IV) components *via* fractional sublimation (eqn. (2)).[12]

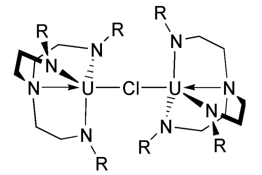
$$[\{U(NN'_3)\}_2(\mu\text{-Cl})] + Me_3SiN_3 \longrightarrow [U(NN'_3)({=}NSiMe_3)] + [U(NN'_3)Cl] \quad (1)$$

$$[\{U(NN'_3)\}_2(\mu\text{-Cl})] \longrightarrow [U(NN'_3)]\ \mathbf{1} + [U(NN'_3)Cl] \quad (2)$$

For the reasons alluded to earlier, compound **1** is an excellent candidate for the study of addition and oxidative addition reactions. This type of chemistry is well established for U(III) systems such as [U(OAr)$_3$] (Ar = 2,6-di-*tert*-butylphenyl) which readily give U(IV) complexes [U(OAr)$_3$X].[13]



I



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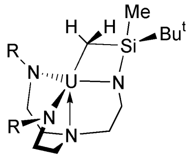

III

Results and discussion

Synthesis of [U(NN′$_3$)]

While the transition metal complexes [M(NN′$_3$)Cl] (M = Ti, V) are reduced to trigonal monopyramidal [M(NN′$_3$)],[14] reduction of [U(NN′$_3$)Cl] in pentane solution over a potassium film does not proceed further than the mixed valence (III/IV) compound [{U(NN′$_3$)}$_2$(μ-Cl)].[11] This is an example of the phenomenon of stabilisation of relatively high oxidation states for strongly Lewis acidic systems with conformationally-constrained ligand environments such as NN′$_3$.[9] Accordingly, complete reduction of [U(NN′$_3$)I][10] to **1** in good yield was achieved by stirring a suspension in pentane over potassium (Scheme 1); iodide is a poor bridging ligand for hard acids such as U(III). Like [U{N(SiMe$_3$)$_2$}$_3$], **1** is deep purple. Crystallisation of this very soluble compound was most readily achieved on a relatively large scale (*ca.* 4 g). It sublimes readily at *ca.* 90 °C/10^{-6} mbar. Traces of moisture or oxygen decompose **1** very rapidly.

The proposed structure of **1** as a monometallic species is based principally on the molecular weight of *ca.* 710 deter-

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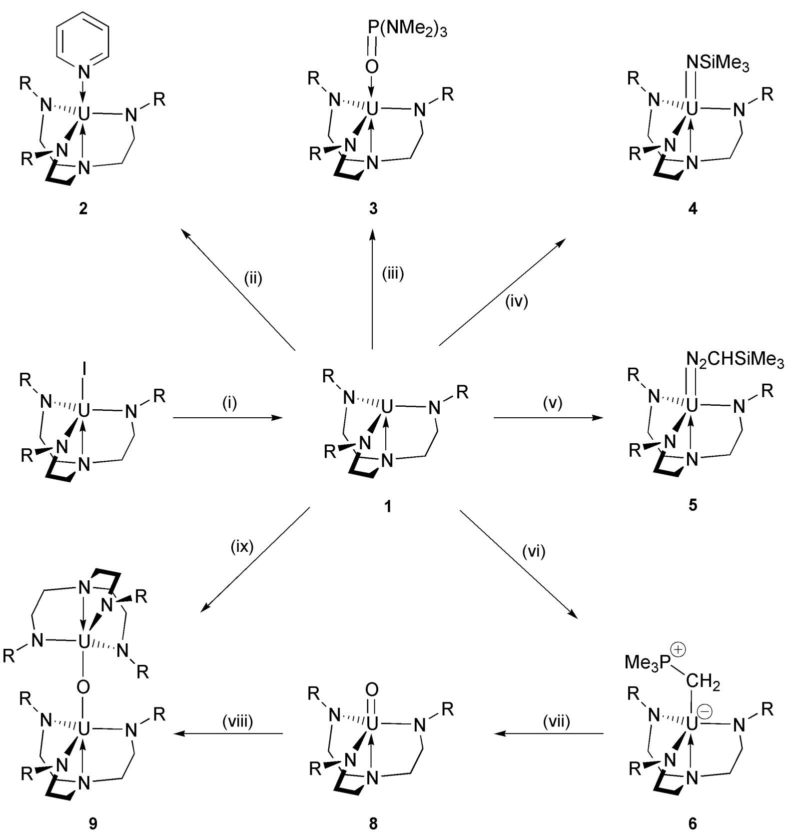

Scheme 1 Synthesis of the the complexes **1**–**6**, **8** and **9** (R = $SiMe_2Bu^t$); (i) K (ii) pyridine; (iii) HMPA; (iv) trimethylsilylazide; (v) trimethylsilyldiazomethane; (vi) methylene trimethylphosphorane; (vii) Me_3NO; (viii) **1**; (ix) Me_3NO. All reactions in pentane.

mined in cyclohexane solution. Molecular models based on X-ray structural data for $[\{U(NN'_3)\}_2(\mu\text{-Cl})]$[11] and other complexes of this ligand suggest that a dimer with *e.g.* bridging amido groups is sterically untenable.[15] The "free" apical coordination site in **1** may be protected by agostic C–H⟶U interactons between the alkylsilyl groups and the metal centre; we have evidence from Raman spectroscopy for the presence of such a feature in the related cerium system $[Ce(NN'_3)]$. While the instability of **1** prevented similar data being collected for this compound we know from the structure of the metallacycle **III** that a triamidoamine ligand conformation which would allow agostic interaction(s) is achieveable.[16]

The ^1H NMR spectrum of **1** contains four broad resonances ($w_{1/2}$ 150–400 Hz) between *ca.* 25 and −40 ppm which were assigned on the basis of integration. As a comparison, triamidoamines of tetravalent uranium have sharper resonances ($w_{1/2}$ *ca.* 20 to 100 Hz) which generally appear over a rather narrower chemical shift range. The magnetic moment of **1** (3.06 μ_B) is consistent with either U(III) or U(IV). The near-IR spectrum [Fig. 1(a)] contains several intense bands, typical of U(III).[16] The spectrum of $[U(NN'_3)Br]$ containing tetravalent uranium is given in Fig. 1(b) for comparison.

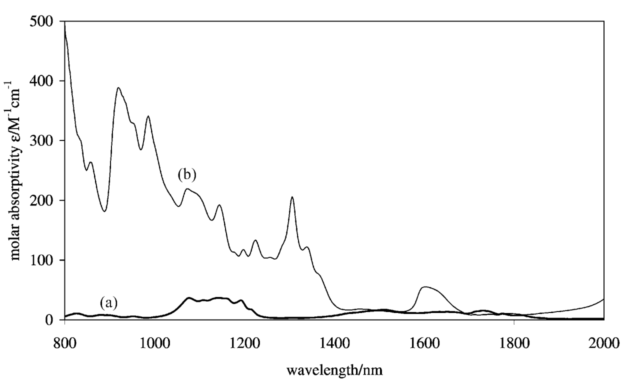

Fig. 1 Near-IR spectra of (a) the U(IV) complex $[U(NN'_3)Br]$ and (b) the U(III) complex $[U(NN'_3)]$ **1** measured in 5×10^{-2} mol dm^{-3} pentane solution.

Reaction of $[U(NN'_3)]$ with simple Lewis bases

Exposure of **1** in solution to THF led to instantaneous decomposition to a mixture of products. The reaction with pyridine however led to the formation of the surprisingly robust orange adduct $[U(NN'_3)(py)]$ **2**. Although the UV/VIS/NIR spectrum of **2** was similar to that of **1** in appearance, the ^1H NMR spectrum was rather more typical of a U(IV) complex, with relatively sharp resonances. Unusually also, the signal for the pyridine 4-H appears at *ca.* 33 ppm, well separated from the other aromatic signals at 17 and 16 ppm.

The reaction of **1** with one equivalent of HMPA led to an immediate colour change to black and formation of $[U(NN'_3)\{OP(NMe_2)_3\}]$ **3** in good yield. NMR and absorption spectra of this complex were typical of U(III).

The molecular structure of **3** is shown in Fig. 2. The inner coordination sphere of the triamidoamine unit is disposed with three-fold symmetry about the uranium centre, although the overall symmetry is lowered from the more usual[10] approximate C_{3v} as a result of the one of the $SiMe_2Bu^t$ groups having the opposite rotational orientation to the others. The amino U(1)–N(14) distance of 2.738(4) Å (see Table 1) is rather longer than those in the μ_2-η^2-dinitrogen adduct of the same ligand system[12] at 2.555(5) and 2.601(5) but similar to those in U(IV) complexes.[10] It seems that this parameter is more influenced by steric effects arising from twist orientations of the triamidoamine chelate than is it is by the formal oxidation state of the uranium centre.[10]

Reactions of 1 with one-electron oxidants

Not surprisingly,[13] **1** reacts with one equivalent of chloroform, chlorine, bromine and iodine to form the previously reported halides $[U(NN'_3)X]$.[10]

Disappointingly, although a wide range of alkoxide com-

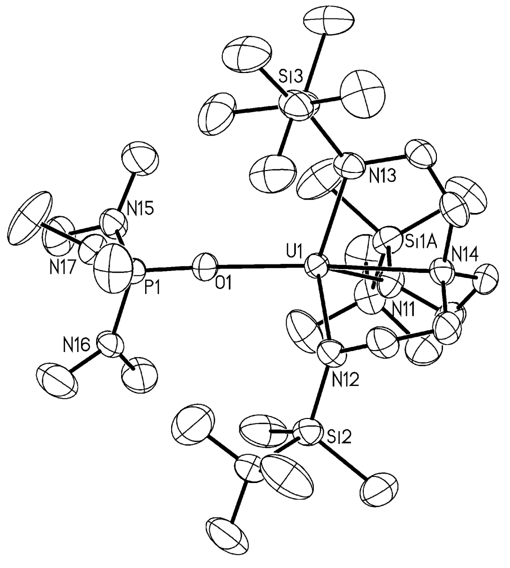

Fig. 2 Thermal ellipsoid plot of the molecular structure of [U(NN′$_3$){OP(NMe$_2$)$_3$] **3** (non-hydrogen atoms).

Table 1 Selected bond distances (Å) and angles (°) for complex [U(NN′$_3$){OP(NMe$_2$)$_3$] **3**

U(1)–N(11)	2.318(4)
U(1)–N(12)	2.345(4)
U(1)–N(13)	2.347(4)
U(1)–O(1)	2.460(3)
U(1)–N(14)	2.738(4)
P(1)–O(1)	1.495(4)
N(11)–U(1)–N(12)	105.43(14)
N(11)–U(1)–N(13)	103.29(15)
N(12)–U(1)–N(13)	112.97(15)
N(11)–U(1)–O(1)	109.96(13)
N(12)–U(1)–O(1)	109.92(13)
N(13)–U(1)–O(1)	114.65(13)
N(11)–U(1)–N(14)	68.18(13)
N(12)–U(1)–N(14)	68.30(13)
N(13)–U(1)–N(14)	68.79(14)
O(1)–U(1)–N(14)	176.53(12)
O(1)–P(1)–N(16)	112.7(2)
O(1)–P(1)–N(15)	110.3(2)
O(1)–P(1)–N(17)	109.9(2)
P(1)–O(1)–U(1)	168.7(2)

plexes of this system X = OR have been reported, reactions of **1** with alkyl and aryl disulfides and diselenides did not yield thiolates *etc.* although oxidation to a mixture of products was observed.

Uranium–element multiple bonds

In comparison to the transition metals, multiple bonds between the actinides and other elements (specifically N, O and C) are uncommon. Uranium imido U=N–R compounds are the most widely studied examples[17,18] and have recently been exploited in the catalytic reduction of azides and hydrazines.[19] Although the actinyl ions AnO$_2^{2+}$ are ubiquitous in aqueous chemistry of the early 5f series,[20] non-actinyl oxo compounds are curiously rare.[17,21] The synthesis of alkylidene complexes of the actinides remains something of a Holy Grail despite the detailed study of phosphorous ylid complexes with significant U–C multiple bond character.[22] Given the propensity for transition metal triamidoamine complexes to support metal-element multiple bonds,[7] we were particularly interested to attempt the synthesis of imido, oxo and alkylidene complexes from **1**.

Addition of one equivalent of trimethylsilylazide to the purple solution of **1** in pentane at −80 °C causes an immediate colour change to red and formation of a new uranium(V) complex [U(NN′$_3$)(NSiMe$_3$)] **4**. The ^{1}H NMR spectrum of this compound in solution was consistent with three-fold symmetry on this timescale. No peaks higher than *m*/*z* 811 (M$^+$) were observed in the EI-mass spectrum. Imido derivatives of uranium closely related to **4** have been described.[23]

In an attempt to synthesise a uranium alkylidene species, an equimolar amount of trimethylsilyldiazomethane was added to the deep purple solution of **1** in pentane. There was an immediate colour change to dark red, but no evolution of gas was observed. Cooling this solution to −30 °C gave dark red crystals of the hydrazido complex [U(NN′$_3$)(N$_2$CHSiMe$_3$)] **5** (Scheme 1). The ^{1}H NMR spectrum was unexpectedly complex but was assignable assuming a single vertical mirror plane rather than a three-fold symmetric complex. No peaks higher than *m*/*z* = 837 (M$^+$) were observed in the EI-mass spectrum. We were unsuccessful in our attempts to persuade **5** to eliminate dinitrogen; there was no evidence of formation of the target alkylidene [U(NN′$_3$)(CHSiMe$_3$)] after refluxing a solution of **5** in d$_6$-benzene or exposing it to UV radiation. A similar result was recorded for [V(NN$_3$)(N$_2$CHSiMe$_3$)].[24]

Another reagent that has been successfully used in the synthesis, for example, of a tantalum alkylidene *via* a formal two-electron oxidation process is methylene trimethylphosphorane (H$_2$C=PMe$_3$).[25] Addition of this compound to a purple solution of **1** in pentane caused an immediate and distinct colour change to dark green. Filtration and cooling to −30 °C afforded dark green crystals of [U(NN′$_3$)(CH$_2$PMe$_3$)] **6**. The ^{1}H NMR spectrum of **6** exhibited the usual four peaks for the NN′$_3$ ligand and two for the methylene trimethylphosphorane group. The EI-mass spectrum was similar to that of **1**, indicating that phosphorane is eliminated readily, and indeed attempts to sublime **6** led to production of **1** and free phosphorane. The UV/VIS spectrum of **6** was consistent with the presence of a trivalent uranium centre (*vide supra*) and hence this compound is best described as a phosphorane adduct of **1** as shown in Scheme 1.

In one of several attempts to measure the molecular structure of **6** we isolated a few dark green crystals which were shown to be the remarkable uranium (IV) hydroxide [U(NN′$_3$)(OH)(CH$_2$PMe$_3$)] **7** (Fig. 3). Since we have been unable to crystallise further samples of this compound we can offer no corroborative evidence for its formulation, but a brief discussion is included here because of its highly unusual nature. The triamidoamine unit is disposed about a distorted octahedron in a manner similar to that for the complex [U(NN$_3$)(BH$_4$)(THF)].[26] The U–C(25) distance of 2.706(12) Å (see Table 2) is very much greater than that found in most uranium alkyls and is

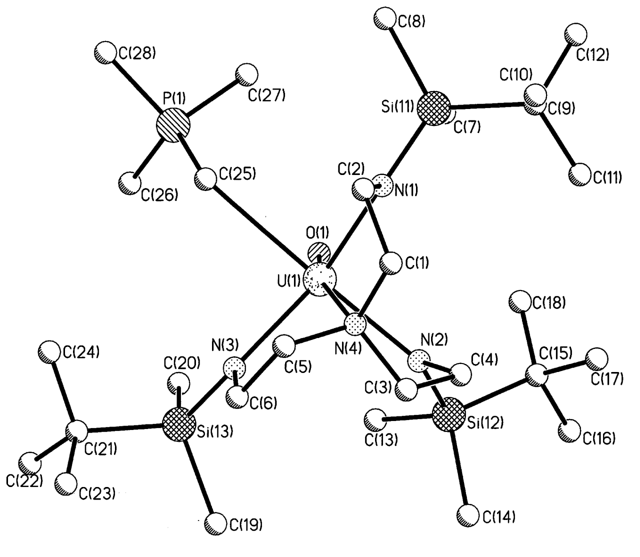

Fig. 3 Molecular structure of [U(NN′$_3$)(OH)(CH$_2$PMe$_3$)] **7** (non-hydrogen atoms).

Table 2 Selected bond distances (Å) and angles (°) for complex $[U(NN'_3)(OH)(CH_2PMe_3)]$ **7**

U(1)–O(1)	2.145(6)
U(1)–N(1)	2.301(8)
U(1)–N(2)	2.308(9)
U(1)–N(3)	2.322(8)
U(1)–N(4)	2.620(8)
U(1)–C(25)	2.706(12)
P(1)–C(25)	1.723(11)
P(1)–C(27)	1.776(11)
P(1)–C(26)	1.794(11)
P(1)–C(28)	1.814(12)
O(1)–U(1)–N(1)	109.6(3)
O(1)–U(1)–N(2)	93.3(3)
N(1)–U(1)–N(2)	97.0(3)
O(1)–U(1)–N(3)	118.0(3)
N(1)–U(1)–N(3)	129.5(3)
N(2)–U(1)–N(3)	96.2(3)
O(1)–U(1)–N(4)	165.3(3)
N(1)–U(1)–N(4)	69.2(3)
N(2)–U(1)–N(4)	72.5(3)
N(3)–U(1)–N(4)	68.9(3)
O(1)–U(1)–C(25)	84.9(3)
N(1)–U(1)–C(25)	82.1(3)
N(2)–U(1)–C(25)	177.6(3)
N(3)–U(1)–C(25)	86.0(3)
N(4)–U(1)–C(25)	109.2(3)
C(25)–P(1)–C(27)	111.2(6)
C(25)–P(1)–C(26)	111.1(6)
C(27)–P(1)–C(26)	106.7(6)
C(25)–P(1)–C(28)	116.9(6)
C(27)–P(1)–C(28)	104.4(6)
C(26)–P(1)–C(28)	105.7(6)
Si(13)–N(3)–U(1)	124.1(4)
P(1)–C(25)–U(1)	125.2(6)

comparable to that found in a highly strained (triamidoamine)uranium metallacycle.[16] U–C distances of *ca.* 2.60 Å have been measured in related complexes of chelating phosphorus ylids.[27] The nominal distance C(25)–P(1) of 1.723(11) is rather longer than the C=P bond in the solid state structure of the phosphorane [1.678(2) Å][28] and only slightly shorter than to the three C–P single bonds (1.77–1.81 Å). This supports that valence bond description in Scheme 1. The U(1)–O(1) distance 2.145(6) Å, similar to the distance in alkoxides (*ca.* 2.2 Å)[29] rules out the presence of and oxo species (*ca.* 1.8 Å), hence the assignment as U–OH. To our knowledge, no terminal U–OH compounds are known, the closest comparisons with the structure found here is with Andersen's rather better authenticated $Cp_2U(\mu\text{-}OH)_2UCp_2$ compounds where the U–O distances are 2.295(3) and 2.299(3) Å.

We sought a reagent to promote the elimination of trimethylphosphine from **6**, the target being the uranium(V) alkylidene species $[U(NN'_3)(CH_2)]$ or perhaps its dimer. Addition of an equimolar amount of intensely green **6** to a suspension of rigorously dry trimethylamine *N*-oxide in pentane caused evolution of a gas, trimethylamine, and production of a light orange solution. Filtration of this solution and cooling to −30 °C afforded orange microcrystals of the complex $[U(NN'_3)(O)]$ **8** (Scheme 1). No peaks higher than *m*/*z* = 739 (M^+) were observed in the EI-mass spectrum, militating against (but not ruling out) the formulation of **8** as the di-μ-oxo dimer $[(NN'_3)U(\mu\text{-}O)_2U(NN'_3)]$. Attempts to measure the molecular weight of **8** by cryoscopy were thwarted since, like $[U(NN'_3)Cl]$, it crystallises from suitable solvents at low temperatures. The ^1H NMR spectrum was as expected, except that the two methylene signals overlapped at 15.2 ppm. In the IR spectrum, terminal *ν*(U–O) stretching vibration would be expected between *ca.* 750 and 900 cm^{-1},[30] but this region in **8** is complicated by several bands arising from the NN'_3 ligand; ^{18}O labelling experiments did not permit assignment. That the UV/VIS spectrum of **8** contained no bands in the region 200 to 900 nm is consistent with the presence of a pentavalent species. This was also observed for the imido complex **4**. The magnetic susceptibility of **8** as measured by the Evans method gave $\mu_{eff} = 1.47\ \mu_B$, also consistent with a formal oxidation state of V.

In an attempt to prepare directly the pentavalent complex **8**, a solution of **1** in pentane was added to an excess of trimethylamine *N*-oxide. The solution immediately changed colour to light brown and evolution of trimethylamine was detected. Filtration and cooling to −30 °C gave light brown plates of bridging oxo complex $[\{U(NN'_3)\}_2(\mu\text{-}O)]$ **9**. The ^1H NMR spectrum showed four peaks attributable to the NN'_3 ligand. No peaks higher than *m*/*z* = 1462 (M^+) were observed in the EI-mass spectrum of **9**. The UV/VIS spectrum and the magnetic moment ($\mu_{eff} = 2.55\ \mu_B$) are consistent with the presence of tetravalent uranium centres. Interestingly, even with excess trimethylamine *N*-oxide the U(V) oxide **8** species was not formed. Bridging oxo complexes have previously been prepared by oxidative addition of trivalent uranium centres.[31]

The direct production of the bridging oxo compound **9** from trivalent **1** and trimethylamine *N*-oxide when the analogous reaction of methylenephosphorane **6** gives only terminal oxo **8** requires explanation. Presumably **1** reacts with trimethylamine *N*-oxide to give first **8**. As a result of the very low solubility of trimethylamine *N*-oxide in the reaction medium (pentane), further **1** will react much more rapidly with **8** to give **9**. We propose that this latter process is much slower when **6** is used as a source of the trivalent centre by the virtue of its steric bulk, hence in this case the whole sample is converted to **8**. In support of the above mechanism we have found that addition of one equivalent of **1** to a solution **8** in d_6-benzene gave **9** in quantitative yield.

Experimental

Standard Schlenk techniques were used. Argon (not dinitrogen) for this purpose was purified by passage through a 500 ml stainless steel sample cylinder containing BASF deoxygenation catalyst and 3A molecular sieves. Solids were transferred in a THF-free MBraun dry-box operating under argon at <1 pmm O_2/H_2O. All glassware was dried *in vacuo* while heating with a paint-stripper heat gun before use. NMR samples were made up in the dry box in d^6-benzene and the sample tubes were sealed *in vacuo* or using Young's type concentric stopcocks. All ^1H NMR resonances reported below are singlets unless otherwise stated. HPLC grade pentane was pre-dried over sodium wire and then distilled over sodium–potassium alloy under an atmosphere of nitrogen before degassing and saturation with argon. Deuterated benzene was dried over molten potassium and distilled trap-to-trap *in vacuo*. NMR spectra were recorded on Bruker WM-360, Bruker AC-250, AC-400 or DMX-300 spectrometers at 293 K and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ = 0 ppm). Infrared spectra were obtained as Nujol mulls in an air-tight holder using a Perkin-Elmer FTIR spectrometer. Ultra violet/visible/near IR spectra were obtained as pentane solutions in an air-tight quartz cell (*l* = 1 mm) a Jasco V-540 spectrophotometer. EI mass spectra were obtained on a VG Autospec mass spectrometer. Elemental analyses were performed by Warwick Analytical Services. Cryoscopic solution molecular weight determinations were performed on *ca.* 200 mg samples in cyclohexane.[32]

Crystallography

Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the Siemens SMART three-circle diffractometer equipped with a CCD area detector. The structures were solved by direct methods (SHELXS[33]) with additional light atoms found by Fourier methods, and refined using SHELXTL;[34] see Table 3 for crystallographic details. One Si

Table 3 Experimental data for the X-ray diffraction studies of **3** and **7**

	[U(NN′$_3$){OP(NMe$_2$)$_3$] **3**	[U(NN′$_3$)(OH)(CH$_2$PMe$_3$)] **7**
Molecular formula	$C_{30}H_{75}N_7OPSi_3U$	$C_{28}H_{69}N_4OPSi_3U$
Formula weight	903.24	831.14
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a/Å	11.6213(3)	11.5920(3)
b/Å	19.6503(5)	12.4323(2)
c/Å	19.6564(5)	13.6752(3)
α/°	—	89.4280(10)
β/°	—	87.7850(10)
γ/°	—	84.1600(10)
V/Å^3	4488.8(2)	1959.07(7)
Z	4	2
μ/mm^{-1}	3.761	4.300
Total reflections	27147	11548
Independent reflections	10376 [R(int) = 0.0495]	8248 [R(int) = 0.0413]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0405, 0.0580	0.0690, 0.1588

group in **3** was found to be slightly disordered (occupancy 0.957 : 0.043).[35] H atoms were included in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups.

CCDC reference numbers 171263 and 171264.

See http://www.rsc.org/suppdata/dt/b1/b108584k/ for crystallographic data in CIF or other electronic format.

Syntheses

[U(NN′$_3$)] 1. A slurry of [U(NN′$_3$)I][10] (5 g, 5.8 mmol) in pentane (40 cm^3) was added *via* large bore cannula to a Schlenk vessel containing a potassium mirror (excess) and was magnetically stirred vigorously for 24 h. Best results were obtained when the stir-bar became "decoupled" from the stirrer such that it rattled about in the Schlenk and eroded the mirror. The resultant purple solution was transferred without filtration to a second Schlenk vessel containing a fresh potassium film and again stirred vigorously for 24 h. After filtration through a thoroughly dry glass microfibre disk fitted to the end of a cannula, the deep purple solution was concentrated and cooled to −30 °C to give an intense purple crystalline solid (3.87 g, 91%). When performed on a smaller scale it was found that crystallisation was less reliable. In these instances, sublimation of the material at *ca.* 100 °C/10^{-5} mbar along a glass tube was usually successful.

Anal. Calc. for $C_{24}H_{57}N_4Si_3U$: C, 39.81; H, 7.93; N, 7.73. Found C, 39.14; H, 7.73; N, 7.44%. ^{1}H NMR, δ 26.6 (6H, CH$_2$), 9.9 (27H, Bu^t), −5.6 (18H, Me$_2$Si), −38.5 (CH$_2$, 6H). MS (EI), *m*/*z* 723 (100%, M+), 685 (15, M+ − Bu^t). IR (Nujol), 1377(w), 1345(w), 1247(m), 1123(m), 1077(w), 1038(w), 1005(w), 957(w), 936(s), 915(s), 823(s), 807(s), 771(s), 722(s), 649(w). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}), 337 (2254), 538 (1390), 680 (843), 775 (573), 832 (302), 855 (260). Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 3.06\ \mu_B$.

[U(NN′$_3$)(NC$_5$H$_5$)] 2. An excess of dry pyridine (0.1 ml) was added to a stirred solution of **1** (0.36 g, 0.50 mmol) in pentane (10 cm^3) at 0 °C. An orange/pink solid was precipitated, which was isolated by filtration and washed with pentane. (0.36 g, 89%). Anal. Calc. for $C_{29}H_{62}N_5Si_3U$: C, 43.39; H, 7.73; N, 8.73. Found C, 44.39; H, 7.37; N, 8.81%. ^{1}H NMR, δ 33.0 (1H, Py-4-H), 17.3 (2H, Py), 15.9 (2H, Py), 13.7 (6H, CH$_2$), 10.2 (6H, CH$_2$), −1.5 (27H, Bu^t), −8.44 (18H, Me$_2$Si). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}), 304 (2520), 670 (1200), 708 (600), 850 (305), 1038 (270). Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 2.95\ \mu_B$.

[U(NN′$_3$){OP(NMe$_2$)$_3$}] 3. Dry HMPA (0.56 cm^{-3} of 0.89 M solution in pentane, 0.5 mmol) was added to a stirred solution of **1** (0.36 g, 0.50 mmol) in pentane (10 cm^3) at 0 °C. The resulting black solution was filtered and concentrated to *ca.* 3 cm^{-3}. Cooling to −40 °C gave large black cubes (0.31 g, 68%). Anal. Calc. for $C_{30}H_{75}N_7OPSi_3U$: C, 39.91; H, 8.31; N, 10.86. Found C, 39.71; H, 8.40; N, 12.31%. ^{1}H NMR, δ 10.9 (6H, CH$_2$), 2.2 (27H, Bu^t), 1.75 (12 H, NMe$_2$), −1.3 (6H, CH$_2$), −8.5 (18H, Me$_2$Si). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}), 372 (2430), 538 (1773), 710 (1325), 778 (400), 928 (155), 1048, (184), 1128 (125), 1268 (100). Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 2.80\ \mu_B$.

[U(NN′$_3$)(NSiMe$_3$)] 4. Trimethylsilylazide (0.04 g, 0.34 mmol) was added to a stirred solution of **1** (0.25 g, 0.34 mmol) in pentane (10 cm^3) to give a dark red solution and evolution of a gas. The solution was filtered and cooled to −30 °C to give dark red octahedra (0.252 g, 90%).

Anal. Calc. for $C_{27}H_{66}N_5Si_4U$: C, 39.98; H, 8.20; N, 8.63. Found C, 39.85; H, 8.25; N, 7.87%. ^{1}H NMR, δ 28.4 (6H, CH$_2$), 15.7 (9H, Me$_3$Si), 6.5 (6H, CH$_2$), −4.2 (27H, Bu^t), −12.8 (18H, Me$_2$Si). MS (EI), *m*/*z* 811 (14%, M$^+$), 723 (64%, M$^+$ − NSiMe$_3$). IR (Nujol), 1248(m), 1143(w), 1076(m), 1020(w), 987(m), 925(m), 895(w), 830(s), 801(m), 793(m), 723(m). UV/VIS: no peaks observed in the range 200–900 nm. Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 2.17\ \mu_B$.

[U(NN′$_3$)(N$_2$CHSiMe$_3$)] 5. Trimethylsilyldiazomethane (0.17 cm^3, 2.0 M in hexanes, 0.34 mmol) was added to a stirred solution of **1** (0.25 g, 0.34 mmol) in pentane (10 cm^3) to give a dark red solution which was filtered and cooled to −30 °C to give dark red crystals (0.165 g, 57%).

Anal. Calc. for $C_{28}H_{67}N_6Si_4U$: C, 40.80; H, 8.19; N, 8.50. Found C, 40.87; H, 8.16; N, 8.51%. ^{1}H NMR, δ 26.84 (4H, CH$_2$), 11.58 (9H), 7.49 (12H, Me$_2$Si), 1.21 (4H, CH$_2$), 0.87 (4H, CH$_2$), −5.39 (18H, Bu^t), −7.33 (6H, Me$_2$Si), −22.83 (9H). MS (EI), *m*/*z* 838 (20%, M$^+$), 736 (41%, M$^+$ − NCHSiMe$_3$), 723 (58%, M$^+$ − N$_2$CHSiMe$_3$). IR (Nujol), 1246(s), 1146(w), 1061(s), 1034(s), 970(s), 895(s), 807(s), 723(s), 657(s). UV/VIS: no peaks observed in the range 200–900 nm.

[U(NN′$_3$)(CH$_2$PMe$_3$)] 6. Methylene trimethylphosphorane[35] (0.69 cm^3, 0.5 M solution in pentane, 0.34 mmol) was added to a stirred solution of **1** (0.25 g, 0.34 mmol) in pentane (10 cm^3) to give an intense green solution. The solution was filtered and cooled to −30 °C to give dark green needles (0.25 g, 89%).

Anal. Calc. for $C_{28}H_{68}N_4Si_3PU$: C, 41.31; H, 8.42; N, 6.88. Found C, 40.94; H, 8.41; N, 6.88%. ^{1}H NMR, δ 8.94 (s, 6H, CH$_2$), 5.21 (s, 27H, Bu^t), −4.60 (s, 9H, PMe$_3$), −5.88 (s, 18H, Me$_2$Si), −14.37 (s, 6H, CH$_2$), −54.33 (br.s, 2H, CH$_2$). MS (EI), *m*/*z* 723 (100%, M$^+$ − CH$_2$PMe$_3$), 701 (36%, M$^+$ − CH$_2$PMe$_3$ − Bu^t). IR (Nujol), 1148(s), 1078(s), 1057(s), 1031(s), 1006(s), 978(s), 932(s), 894(s), 823(s), 666(s). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}) 388 (2184), 579 (1530). Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 3.60\ \mu_B$.

[U(NN′$_3$)(O)] 8. Pentane (20 cm^3) was added to a Schlenk vessel containing **6** (0.3 g, 0.37 mmol) and trimethylamine *N*-oxide (0.028 g, 0.37 mmol) to give a light orange solution. The solution was stirred for 1 h, filtered and cooled to −30 °C to afford light orange cubes (0.204 g, 74%).

Anal. Calc. for $C_{24}H_{57}N_4Si_3OU$: C, 38.95; H, 7.76; N, 7.57. Found C, 38.85; H, 7.63; N, 7.03%. ^{1}H NMR (293 K d$_6$-benzene), δ 15.2 (12H, CH$_2$), −2.16 (27H, Bu^t), −8.8 (18H, Me$_2$Si). MS (EI), m/z 739 (45%, M$^+$), 721 (27%, M$^+$ − O). IR (Nujol), 1299(m), 1290(w), 1258(m), 1240(m), 1085(w), 1061(w), 1025(w), 1006(w), 976(w), 943(m), 931(m), 902(m), 824(m), 773(m), 722(s). UV/VIS: no peaks observed in the range 200–900 nm. Magnetic susceptibility (Evans' method: 225–293 K), $\mu_{eff} = 1.47\ \mu_B$.

[{U(NN′$_3$)}$_2$(μ-O)] 9. Pentane (10 cm^3) was added to a Schlenk vessel containing **1** (0.25 g, 0.34 mmol) and trimethylamine *N*-oxide (0.026 g, 0.34 mmol) to give a light brown solution. The solution was stirred for 5 min and was filtered and cooled to −30 °C to afford light brown plates (0.151 g, 60%).

Anal. Calc. for $C_{48}H_{114}N_8Si_6OU_2$: C, 39.38; H, 7.85; N, 7.65. Found C, 39.08; H, 7.95; N, 7.39%. ^{1}H NMR, δ 74.19 (12H, CH$_2$), 14.64 (12H, CH$_2$), −9.97 (54H, Bu^t), −25.76 (36H, Me$_2$Si). MS (EI), m/z 1462 (27% M$^+$), 1446 (31%, M$^+$ − O), 740 (3%, M^+ − UNN′$_3$), 724 (52%, M^+ − UNN′$_3$ − O). IR (Nujol), 1143(m), 1136(m), 1082(s), 1027(s), 1005(m), 927(s), 829(s), 723(s), 652(s). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}) 542 (32), 693 (23). Magnetic susceptibility (Evans' method: 225–293 K) $\mu_{eff} = 2.55\ \mu_B$.

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