Synthesis and Reactions of Uranium(IV) Tetrathiolate Complexes†

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Uranium(IV) tetrathiolate complexes were made by (*a*) reaction of $U(NEt_2)_4$ with RSH (R = Et, Pr^i, Bu^n or Bu^t), (*b*) treatment of $U(BH_4)_4$ with RSH (R = Bu^n or Ph) or of $U(SBu^n)_4$ with PhSH or (*c*) oxidation of uranium metal by RSSR (R = Et, Pr^i or Ph). Rearrangement of $[U(SBu^t)_4(py)_3]$ (py = pyridine) in toluene gave the trinuclear cluster $[U_3S(SBu^t)_{10}]$ with liberation of Bu^tSH and $Me_2C{=}CH_2$. Reaction of $U(SPr^i)_4$ with $[NEt_3H][BPh_4]$ in the presence of hexamethylphosphoric triamide (hmpa) afforded the cationic compound $[U(SPr^i)_2(hmpa)_4][BPh_4]_2$ which presents a *trans*-octahedral crystal structure. Iodinolysis of $U(SPr^i)_4$ in pyridine led to the formation of $[U(SPr^i)_2I_2(py)_3]$ which adopts a pentagonal-bipyramidal configuration in its crystalline form. The trithiocarbonate $(Pr^iS)_2C{=}S$ was obtained by reaction of $U(SPr^i)_4$ with CS_2.

In 1956, Gilman and co-workers[1] prepared the first thiolate complexes of an f element, $U(SEt)_4$ and $U(SBu^n)_4$. Since then, these compounds have not received any further attention. This lack of consideration may be explained by at least two reasons. According to Gilman, the samples 'spontaneously burst into flames and burned vigorously' when exposed to the open air and the U–S bond between a 'hard' metal and a 'soft' donor was reputedly unstable. In 1993, Tatsumi *et al.*[2] pointed out that the instability of such d^0 metal–sulfur bonds has been 'more often presumed than actually proved'. A number of thermally stable homoleptic thiolate complexes of samarium, ytterbium and uranium have been recently synthesized, $[Sm(SC_6H_2Bu^t_3\text{-}2,4,6)_3]$,[3] $[\{Li(Me_2NCH_2CH_2NMe_2)\}_3][Ln(SBu^t)_6]$ (Ln = Sm or Yb),[2] $[\{Li(MeOCH_2CH_2OMe)\}_4][U(SCH_2CH_2S)_4]$[4] and $M_2[U(SPh)_6]$ [M = $Na(OC_4H_8)_3$,[5] NEt_2H_2 or $Cu(PPh_3)$[6]]. In this context, it seemed to us to be of interest to go back over the work of Gilman. We have already reported[7] the crystal structures of $[U_3S(SBu^t)_{10}]$ and $[U(SPr^i)_4(hmpa)_2]$ (hmpa = hexamethylphosphoric triamide). Here we present the new syntheses and reactions of some uranium tetrathiolate compounds, together with the crystal structures of $[U(SPr^i)_2(hmpa)_4][BPh_4]_2$ and $[U(SPr^i)_2I_2(py)_3]$ (py = pyridine).

Results

Syntheses and Reactions.—By following the original procedure of Gilman and co-workers[1] $U(SEt)_4$ and $U(SBu^n)_4$ were isolated as green insoluble powders from reaction (1) between

$$U(NEt_2)_4 + 4RSH \longrightarrow U(SR)_4 + 4NEt_2H \qquad (1)$$

$U(NEt_2)_4$ and an excess of the corresponding thiol in diethyl ether. We found that this reaction occurs with a stoichiometric quantity of RSH in dilute solutions of $U(NEt_2)_4$ in pentane, tetrahydrofuran (thf) or benzene; in all cases, the product was insoluble and easily separated by filtration. Reaction (1) represents the most general method for the preparation of $U(SR)_4$ complexes; it was also useful for the synthesis of secondary and tertiary uranium(IV) thiolates (see below). However, similar treatment of the uranium tetraamide with thiophenol did not afford $U(SPh)_4$ **1** but gave the hexathiolate complex $[NEt_2H_2]_2[U(SPh)_6]$.[6] This distinct behaviour is obviously due to the greater acidity of PhSH which is deprotonated by the liberated amine. Complex **1** could be prepared by three different routes represented by equations (2)–(4). Treatment of the uranium tetrahydroborate $U(BH_4)_4$

$$U(BH_4)_4 + 4(1 + n)PhSH \longrightarrow \underset{\mathbf{1}}{U(SPh)_4} + 4B(SPh)_nH_{3-n} + 4(1 + n)H_2 \qquad (2)$$

$$U(SBu^n)_4 + 4PhSH \longrightarrow U(SPh)_4 + 4Bu^nSH \qquad (3)$$

$$U + 2PhSSPh \longrightarrow U(SPh)_4 \qquad (4)$$

with an excess of thiophenol in toluene gave **1** in almost quantitative yield [equation (2)]; the soluble thiolato borane species $B(SPh)_nH_{3-n}$ were easily removed from complex **1** which precipitated as a dark red microcrystalline powder.

Similar reaction of $U(BH_4)_4$ with Bu^nSH yielded $U(SBu^n)_4$ but in the presence of Pr^iSH and Bu^tSH, the uranium tetrahydroborate was transformed into unidentified compounds, presumably some mixed thiolate–hydroborate derivatives or their decomposition products. The thiol exchange reaction of $U(SBu^n)_4$ with PhSH [equation (3)] afforded the desired compound **1** in quantitative yield. However, this method was not effective for the preparation of $U(SPr^i)_4$ and $U(SBu^t)_4$, as $U(SBu^n)_4$ was inert towards the corresponding thiol.

Finally, compound **1** was isolated in 10% yield from the reaction of freshly prepared uranium turnings[8] with an excess of PhSSPh in toluene [equation (4)]. Small quantities of $U(SEt)_4$ and $U(SPr^i)_4$ were similarly obtained when the metal was sonicated in the pure disulfide. These oxidation reactions started immediately but stopped after a few hours, because of the eventual passivation of the metal surface.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and ^{1}H NMR data for compounds **1**–**7**

	Analysis^a (%)				
Compound	C	H	S	N	^{1}H NMR (δ)^b
1 $\mathrm{U(SPh)_4}$	42.45 (42.7)	2.9 (3.0)	18.75 (19.0)	—	20.56 (s, 2 H, *o*-Ph), 9.54 (s, 2 H, *m*-Ph), 4.59 (t, 1 H, *J* 7, *p*-Ph)
2 $[\mathrm{U_3S(SBu^t)_{10}}]^c$	29.05 (29.35)	5.4 (5.5)	21.5 (21.5)	—	13.62, 10.19 and −21.78 (3 × s, 3 × 27 H, μ-SBu^t, terminal SBu^t), −5.51 (s, 9 H, μ_3-SBu^t)
3 $[\mathrm{U(SBu^t)_4(py)_3}]$	44.4 (44.75)	6.0 (6.2)	15.25 (15.4)	4.85 (5.05)	7.84 (s, SBu^t)
4 $\mathrm{U(SPr^i)_4}$	26.6 (26.75)	5.1 (5.2)	23.5 (23.8)	—	12.42 (s, 6 H, CH*Me*$_2$), 27.23 (s, 1 H, C*H*Me$_2$)
5 $[\mathrm{U(SPr^i)_4(hmpa)_2}]^c$	32.0 (32.15)	7.05 (7.15)	14.05 (14.3)	—	6.02 (spt, 4 H, *J* 6, C*H*Me$_2$), 4.14 (d, 36 H, *J* 10, hmpa), 0.75 (d, 24 H, *J* 6, CH*Me*$_2$)
6 $[\mathrm{U(SPr^i)_2(hmpa)_4][BPh_4]_2}$	54.0 (53.75)	7.2 (7.3)	—	9.8 (9.65)	10.42 (spt, 2 H, *J* 6, C*H*Me$_2$), 7.96 (s, 40 H, Ph), 2.35 (d, 72 H, *J* 10, hmpa), 2.07 (d, 12 H, *J* 6, CH*Me*$_2$)
7 $[\mathrm{U(SPr^i)_2I_2(py)_3}]$	28.55 (28.7)	3.2 (3.3)	—	4.95 (4.8)	85.73, (s, 1 H, C*H*Me$_2$), 39.89 (s, 6 H, CH*Me*$_2$)

^{a} Calculated values in parentheses. ^{b} Recorded at 60 MHz, 30 °C, in [^{2}H$_5$]pyridine unless stated otherwise; coupling constant *J* in Hz; half-height widths of singlets = 10–20 Hz. ^{c} ^{1}H NMR spectrum recorded in [^{2}H$_6$]benzene.

Reaction of $\mathrm{U(NEt_2)_4}$ with $\mathrm{Bu^tSH}$ in benzene or tetrahydrofuran did not lead to the expected tetrathiolate $\mathrm{U(SBu^t)_4}$ but gave the trinuclear compound $[\mathrm{U_3S(SBu^t)_{10}}]$ **2**; the crystal structure of this first uranium–sulfur cluster has already been described.[7] Complex **2** was also synthesized on a preparative scale by protonation of $[\mathrm{Na(thf)_3}]_2[\mathrm{U(SBu^t)_6}]$ by means of $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$. These reactions are likely to proceed by the intermediacy of $\mathrm{U(SBu^t)_4}$ but no intermediate could be characterized during the formation of the trinuclear unit. When reaction (1) was carried out in pyridine, $[\mathrm{U(SBu^t)_4(py)_3}]$ **3** was obtained immediately and was isolated as a dark red microcrystalline powder in 77% yield. Complex **3** was quite stable in pyridine but after 15 min in refluxing benzene, it was totally and cleanly converted into the cluster **2**, with concomitant liberation of 2-methylpropane-2-thiol and 2-methylpropene, according to equation (5).

$$\underset{\mathbf{3}}{3[\mathrm{U(SBu^t)_4(py)_3}]} \longrightarrow \underset{\mathbf{2}}{[\mathrm{U_3S(SBu^t)_{10}}]} + 9\mathrm{py} + \mathrm{Bu^tSH} + \mathrm{Me_2C{=}CH_2} \quad (5)$$

The tetrathiolate $\mathrm{U(SPr^i)_4}$ **4** was isolated as a green powder in 82% yield by using the procedure of Gilman and co-workers,[1] *i.e.* treatment of $\mathrm{U(NEt_2)_4}$ with $\mathrm{Pr^iSH}$ in diethyl ether [equation (1)]. Compound **4** was soluble in pyridine, forming an adduct with the strong Lewis base. In the presence of hmpa, the thiolate **4** was transformed in thf into $[\mathrm{U(SPr^i)_4(hmpa)_2}]$ **5**, the first uranium tetrathiolate to have been structurally characterized.[7] Protonation of **4** or **5** by means of $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$ in the presence of hmpa gave the cationic complex $[\mathrm{U(SPr^i)_2(hmpa)_4}][\mathrm{BPh_4}]_2$ **6** which precipitated in thf and was isolated in 83% yield as a light green microcrystalline powder [equation (6)]. Treatment of the thiolate **4** with $\mathrm{I_2}$ in pyridine afforded

$$\underset{\mathbf{5}}{[\mathrm{U(SPr^i)_4(hmpa)_2}]} + 2\mathrm{hmpa} + 2[\mathrm{NEt_3H}][\mathrm{BPh_4}] \longrightarrow \underset{\mathbf{6}}{[\mathrm{U(SPr^i)_2(hmpa)_4}][\mathrm{BPh_4}]_2} + 2\mathrm{NEt_3} + 2\mathrm{Pr^iSH} \quad (6)$$

successively the iodo derivatives $[\mathrm{U(SPr^i)_{4-\mathit{n}}I_\mathit{n}(py)_\mathit{x}}]$ (n = 1–3) which were characterized by their ^{1}H NMR spectra; $\mathrm{Pr^iSSPr^i}$ was liberated during the reaction [equation (7)]. The

$$\underset{\mathbf{4}}{\mathrm{U(SPr^i)_4}} + \mathrm{I_2} \xrightarrow{\mathrm{py}} \underset{\mathbf{7}}{[\mathrm{U(SPr^i)_2I_2(py)_3}]} + \mathrm{Pr^iSSPr^i} \quad (7)$$

monoiodide was found to be in equilibrium with **4** and the diiodide. Yellow crystals of $[\mathrm{U(SPr^i)_2I_2(py)_3}]$ **7** were isolated in 74% yield after crystallization from pyridine. The green powder **4** became a red oil in carbon disulfide from which yellow crystals of the trithiocarbonate $(\mathrm{Pr^iS})_2\mathrm{C{=}S}$ were isolated by sublimation (10^{-3} mm Hg, *ca.* 0.133 Pa, 20 °C), leaving a dark red residue which was not identified.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

$[\mathrm{U(SPr^i)_2(hmpa)_4}][\mathrm{BPh_4}]_2$ *			
U(1)–O(11)	2.27(4)	U(1)–S(11)	2.61(5)
U(1)–O(12)	2.25(6)	U(1)–S(12)	2.61(5)
U(1)–O(13)	2.03(6)	U–S(av.)	2.65(7)
U–O(av.)	2.2(2)		
S(11)–U(1)–S(12)	177(2)	O(11)–U(1)–O(11$^{\mathrm{II}}$)	176(2)
O(12)–U(1)–O(13)	169(2)	O(11)–U(1)–O(12)	92(1)
O(11)–U(1)–O(13)	88(1)	O(11)–U(1)–S(11)	90(1)
O(11)–U(1)–S(12)	90(1)	O(12)–U(1)–S(11)	88(2)
O(12)–U(1)–S(12)	95(2)	O(13)–U(1)–S(11)	103(2)
O(13)–U(1)–S(12)	74(2)	U(1)–S(12)–C(102)	139(8)
U(1)–S(11)–C(100)	157(5)		
$[\mathrm{U(SPr^i)_2I_2(py)_3}]$			
U–S	2.62(2)	U–I	3.093(4)
U–N(1)	2.56(9)	U–N(2)	2.56(8)
S–U–S$^{\mathrm{I}}$	176(1)	S–U–I	82.7(3)
S–U–N(1)	88.2(5)	S–U–N(2)	97(2)
I–U–N(1)	74.1(1)	I–U–N(2$^{\mathrm{I}}$)	73(1)
N(2)–U–N(2$^{\mathrm{I}}$)	68(3)	U–S–C(9)	117(3)

* Only the data corresponding to the independent cation shown in Fig. 1 are given. The average values were calculated from the data of both independent cations. Symmetry codes: I $x - y, -y, \frac{1}{2} - z$; II $x, \frac{1}{2} - y, z$.

Complexes **1**–**7** have been characterized by their elemental analyses and their ^{1}H NMR spectra (Table 1); the crystal structures of **2** and **5** have already been described and those of **6** and **7** are presented below.

Crystal Structures of $[\mathrm{U(SPr^i)_2(hmpa)_4}][\mathrm{BPh_4}]_2$ **6** *and* $[\mathrm{U(SPr^i)_2I_2(py)_3}]$ **7**.—An ORTEP[9] drawing of one of the two identical independent cations of complex **6** is shown in Fig. 1; selected bond distances and angles are listed in Table 2. The uranium atom is in a distorted *trans*-octahedral environment. The S–U–S axis shows little deviation from linearity and is not

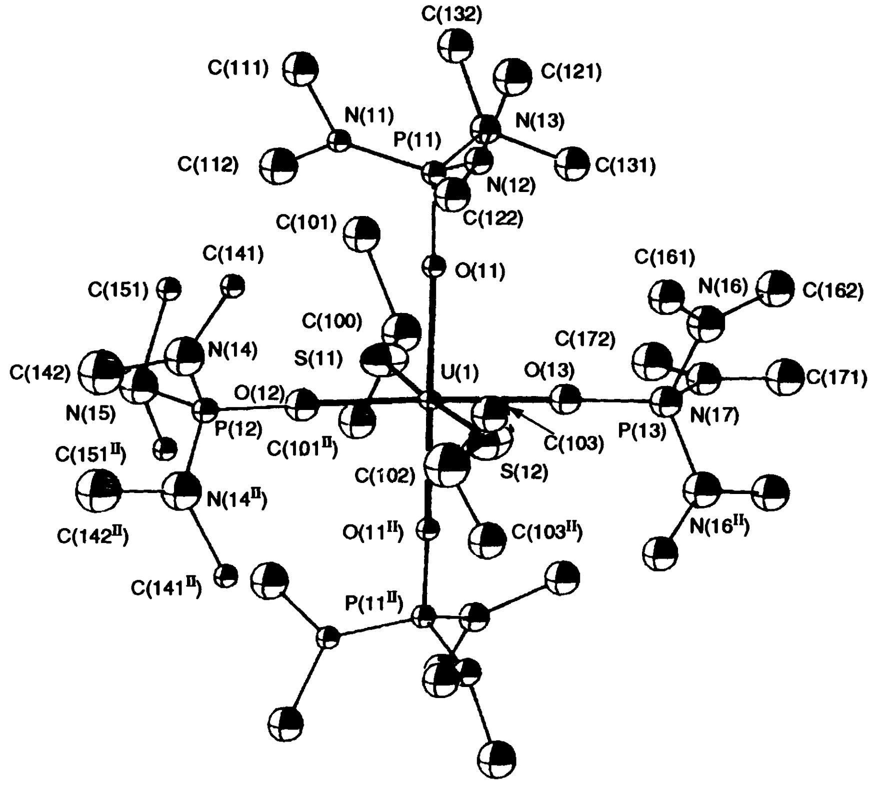


Fig. 1 Perspective view of one of the two independent cations $[\mathrm{U(SPr^i)_2(hmpa)_4}]^{2+}$; atoms labeled II are related by a plane of symmetry

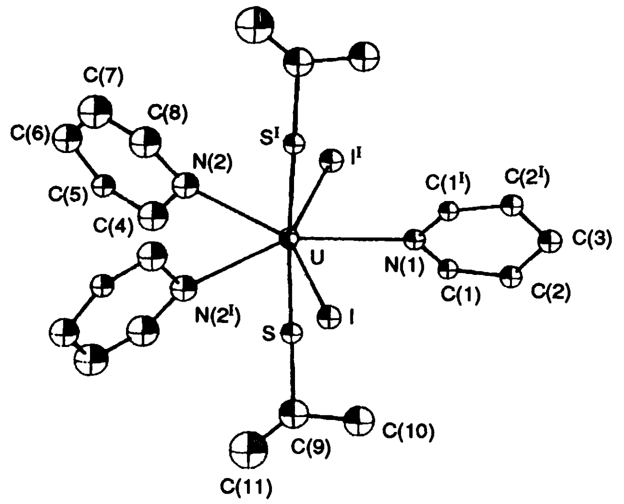


Fig. 2 Perspective view of $[\mathrm{U(SPr^i)_2I_2(py)_3}]$; atoms labeled I are related by a two-fold axis of symmetry

perfectly orthogonal to the equatorial plane defined by the uranium and four oxygen atoms. The U–S bond distances vary from 2.61(5) to 2.72(3) Å [average 2.65(7) Å] and are within the limits of the range found for uranium–S(thiolate) bond lengths, but the U–S–C angles lie between 121(3) and 157(5)° and are much larger than those measured in $[\mathrm{U(SPr^i)_4(hmpa)_2}]$ and other uranium thiolates,[7] which are typically 110–115°. These distinct values suggest that the π bonding between the uranium and sulfur atoms is stronger in the cationic compound **6**. The mean U–O distance of 2.2(2) Å compares favourably with values of 2.31(1) Å in $[\mathrm{U(SPr^i)_4(hmpa)_2}]$, 2.31(1) or 2.18(1) Å in $[\mathrm{UX_4(hmpa)_2}]$ (X = Cl or Br)[10] and 2.29(1) Å in $[\mathrm{U(C_5H_5)Cl_3(hmpa)_2}]$.[11]

An ORTEP[9] drawing of the molecule **7** is shown in Fig. 2. The uranium atom is seven-co-ordinate in a slightly distorted pentagonal-bipyramidal arrangement. The metal centre, the two iodide ligands and the nitrogen atoms of the three pyridine ligands are almost coplanar, within ±0.3 Å; the angles within this equatorial plane range from 68(3) to 74.1(1)° and their sum is equal to 362°. The pyramid axis, defined by the uranium and two sulfur atoms, is quasi linear and perpendicular to the equatorial plane. One of the equatorial pyridine ligands is located between the iodide groups and the U–N distances are 2.56(9) and 2.56(8) Å; these values compare with that of 2.64(1) Å in $[\mathrm{U(C_8H_8)Cl_2(py)_2}]$.[12] Although the crystal structures of many uranium(IV) chloride and some uranium(IV) bromide compounds are known, those of uranium(IV) iodide derivatives are very rare; the U–I bond distance of 3.093(4) Å can only be compared with the mean value of 3.01(1) Å found in $[\mathrm{UI_4\{OC(NMe_2)_2\}_2}]$[13] and 2.98(1) Å in $[\mathrm{UI_2\{OP(NC_4H_8)_3\}_4}][\mathrm{BPh_4}]_2$.[14] The U–S bond distance [2.62(2) Å] and the U–S–C(9) angle [117(3)°] are similar to those determined in other uranium thiolate compounds.[7]

Discussion

The reaction of the uranium tetraamide complex $\mathrm{U(NEt_2)_4}$ with thiols [equation (1)], first used by Gilman and co-workers[1] to prepare $\mathrm{U(SEt)_4}$ and $\mathrm{U(SBu^n)_4}$, was also quite effective for the synthesis of uranium tetrathiolate compounds with secondary and tertiary SR ligands, such as $\mathrm{U(SPr^i)_4}$ **4** and $[\mathrm{U(SBu^t)_4(py)_3}]$ **3**. However, other synthetic methods have been considered, especially for the preparation of $\mathrm{U(SPh)_4}$ since the more acidic benzenethiol reacted with $\mathrm{U(NEt_2)_4}$ to give the anionic complex $[\mathrm{NEt_2H_2}]_2[\mathrm{U(SPh)_6}]$.[6] Most of these alternative routes ought to be parallel to those which have been successfully followed for the preparation of actinide alkoxides. It is not surprising that Gilman reported in the same paper the synthesis of the uranium(IV) thiolates and that of the parent alkoxides $\mathrm{U(OR)_4}$ (R = Me or Et), by alcoholysis of $\mathrm{U(NEt_2)_4}$ or by metathesis of the chloride ligands of $\mathrm{UCl_4}$ with the corresponding LiOR reagent.[1] However, $\mathrm{UCl_4}$ reacted with NaSR to give the anionic complexes $[\mathrm{Na(thf)_3}]_2[\mathrm{U(SR)_6}]$ (R = Pr^i, Bu^t or Ph); this difference has been explained by the less electron-donating ability of the SR ligand.[5] Other representative syntheses of thorium and uranium alkoxides are: (*a*) treatment of $U(BH_4)_4$ with alcohols which gave the complexes $[U(OR)_n(BH_4)_{4-n}]$ (n = 1–4),[15] (*b*) alcohol-exchange reactions of $Th(OPr^i)_4$ which led to a variety of primary, secondary and tertiary thorium(IV) alkoxides[16] and (*c*) reaction of uranium metal with ethanol[17] or with isopropyl alcohol in the presence of iodine[18] which gave $U(OEt)_4$ and $[\{UI_2(OPr^i)_2(Pr^iOH)\}_2]$ respectively. Moreover, a common approach to metal thiolate complexes involves the use of disulfides RSSR as oxidative-addition type reagents with low-valent metal complexes, particularly metal(0) carbonyl or tertiary phosphine species.[19] The compounds $U(BH_4)_4$ or $U(SBu^n)_4$ effectively reacted with PhSH to yield the tetrabenzenethiolate $U(SPh)_4$ **1**, according to equations (2) and (3), but these two methods were not valid for the synthesis of $U(SPr^i)_4$ and $U(SBu^t)_4$. The SR ligand substitution reaction (3) was driven most likely by the formation of the weaker acid [pK_a (dimethyl sulfoxide): PhSH = 10.3, Bu^nSH = 17.03].[20] However, since $Th(OPr^i)_4$ could be converted into a number of tertiary alkoxide complexes $Th(OCRR'R'')_4$ by alcohol exchange,[16] the acidity of the thiol RSH, which is greater than that of the corresponding alcohol ROH, is not the sole determining factor in these reactions. In this context, it was noted that $[U(C_5H_5)_3(SPr^i)]$ was inert towards an excess of Pr^iSH whereas $[U(C_5H_5)_3(OR)]$, in the presence of two equivalents of ROH, was readily transformed into $[U(C_5H_5)(OR)_3]$, with liberation of cyclopentadiene.[21] It is possible that the distinct reactivity of RSH and ROH is due to the weaker co-ordination of the thiol to the hard uranium(IV) centre.[22] However, it was reported that both isopropyl alcohol and propane-2-thiol were able to protonate the cyclopentadienyl ligands of the trivalent compound $[U(C_5H_4Me)_3(thf)]$.[23] Amalgamated uranium did not react with the thiols and its oxidation by disulfides [equation (4)] was impeded by rapid passivation of the metal surface; the reasons for this phenomenon are not clear.

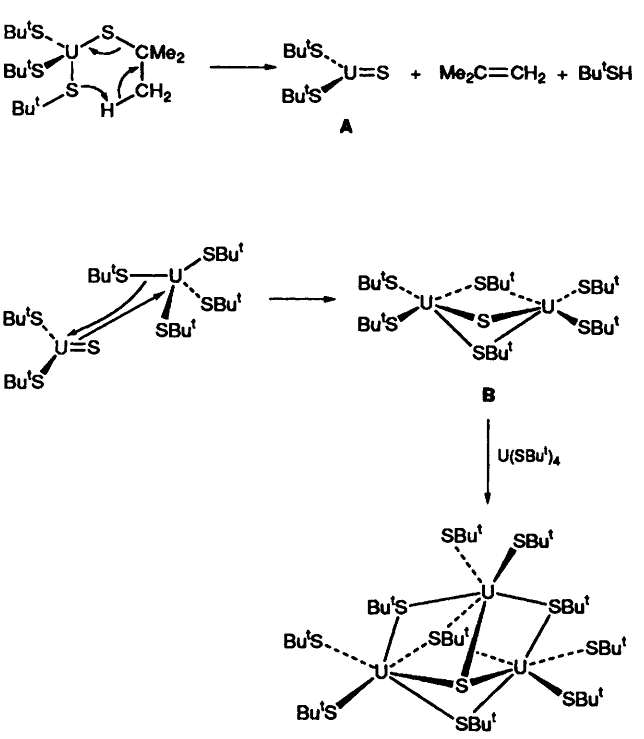
The tetrathiolate $U(SBu^t)_4$ could be isolated only in the form of the pyridine adduct $[U(SBu^t)_4(py)_3]$ **3**, from the Gilman reaction[1] in this solvent. Rearrangement of **3** in toluene and other reactions which were expected to afford $U(SBu^t)_4$ led to the formation of the cluster $[U_3S(SBu^t)_{10}]$ **2**. These preparations of **2** are reminiscent of those of $[U_3O(OBu^t)_{10}]$[24] and $[Zr_3S(SBu^t)_{10}]$,[25] from attempted syntheses of $U(OBu^t)_4$ and $Zr(SBu^t)_4$ and of $[Ce_3O(OBu^t)_{10}]$, by conversion of $[Ce(OBu^t)_4(thf)_2]$ in toluene.[26] It was found that $[U_3O(OBu^t)_{10}]$ could be obtained by careful hydrolysis of $[U_2(OBu^t)_8(Bu^tOH)]$, according to equation (8).[27] However, the synthesis

$$3[U_2(OBu^t)_8(Bu^tOH)] + 2H_2O \longrightarrow 2[U_3O(OBu^t)_{10}] + 7Bu^tOH \quad (8)$$

of $[U_3S(SBu^t)_{10}]$ cannot be explained by the reaction of $U(SBu^t)_4$ with an adventitious (and improbable) trace of water which would give oxygenated products such as $[U_3O(SBu^t)_{10}]$. In fact, hydrolysis of **3** led to the formation of Bu^tSH and of an insoluble green compound, presumably an oxo uranium derivative. The presence of 2-methylpropene in the organic products of reaction (5) and of a μ_3-S ligand in **2** indicate that dealkylation of a SBu^t group occurred during the transformation of $U(SBu^t)_4$ into $[U_3S(SBu^t)_{10}]$. Such C–S bond cleavage is a common decomposition pathway for SBu^t ligands[28,29] and was in particular observed in the synthesis of the sulfido-bridged dimer $[\{Mo(\mu\text{-}S)(SBu^t)_2(PMe_2Ph)\}_2]$ from the molybdenum tetrathiolate $Mo(SBu^t)_4$ [equation (9)].[30] It is

$$2Mo(SBu^t)_4 + 2PMe_2Ph \longrightarrow [\{Mo(\mu\text{-}S)(SBu^t)_2(PMe_2Ph)\}_2] + 2Bu^tSH + Me_2C{=}CH_2 \quad (9)$$

possible that this reaction proceeds by a concerted mechanism, as shown in Scheme 1. A similar rearrangement of $U(SBu^t)_4$ would produce the monosulfide intermediate $[U(SBu^t)_2(=S)]$ **A** (these species would exist as Lewis-base adducts with solvent molecules and/or as dimers). A speculative mechanism of the formation of **2** is proposed in Scheme 1. The first step would be the addition of a U–SBu^t bond of $U(SBu^t)_4$ to the U=S bond[31] of **A** leading, after bridging of two SBu^t groups, to intermediate **B** which contains a $M(\mu\text{-}SR)_2(\mu\text{-}S)M$ unit, like that found in $[(C_4H_8S)Cl_2W(\mu\text{-}SEt)_2(\mu\text{-}S)WCl_2(SC_4H_8)]$.[32] The cluster would be then built up by combination of **B** with a second molecule of $U(SBu^t)_4$.



Scheme 1 Speculative mechanism of the formation of $[U_3S(SBu^t)_{10}]$ from $U(SBu^t)_4$

The inaugural reactivity studies on $U(SPr^i)_4$ revealed that the uranium tetrathiolate complexes possess an interesting chemistry. Cleavage of U–S bonds was performed by protonation or iodinolysis [equations (6) and (7)]; $[U(SPr^i)_2(hmpa)_4][BPh_4]_2$ **6** and $[U(SPr^i)_2I_2(py)_3]$ **7** are unique examples of cationic thiolate and iodo thiolate compounds of uranium. It has been pointed out that the availability of electron density on the sulfur atom would encourage attack by electrophiles at this site,[28] as it was observed in the protonation or alkylation reactions of the cation[33] $[Co(H_2NCH_2CH_2NH_2)_2(SCH_2CH_2NH_2)]^{2+}$ and of the anion[34] $[Fe(CO)_4(SPh)]^-$. Reaction (7) provides another example of the tendency for thiolates to act as reducing agents with formation of disulfides.[28] Cleavage of metal–sulfur bonds by iodine has previously been observed in the iodinolysis of $[Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2]$ leading to $[OsI_2(CO)_2(PPh_3)_2]$ and elemental sulfur.[35] Formation of $(Pr^iS)_2C{=}S$ from $U(SPr^i)_4$ in carbon disulfide certainly proceeds by initial insertion of CS_2 into a U–S bond of **4**;[36] further studies are necessary to determine the mechanism of this unusual reaction.

Experimental

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy (benzene) or molecular sieves (pyridine).

Elemental analyses were performed by Analytische

Table 3 Crystallographic data and experimental details *

	$[U(SPr^i)_2(hmpa)_4][BPh_4]_2$	$[U(SPr^i)_2I_2(py)_3]$
Formula	$C_{78}H_{126}B_2N_{12}O_4P_4S_2U$	$C_{21}H_{29}I_2N_3S_2U$
M	1743.63	884.49
Crystal size/mm	0.45 × 0.4 × 0.3	0.35 × 0.3 × 0.15
Colour	Green	Yellow
Crystal system	Orthorhombic	Trigonal
Space group	*Abm*2	*R*-3*c*
a/Å	36.15(3)	21.671(6)
b/Å	26.914(5)	21.671(6)
c/Å	19.539(7)	33.41(7)
α/°	90	90
β/°	90	90
γ/°	90	120
U/Å^3	19 010(26)	13 588(36)
Z	8	18
D_c/g cm^{-3}	1.218	1.934
μ(Mo-Kα)/cm^{-1}	17.73	72.661
F(000)	7232	9744
T/K	243	223
Range of absolute transmission	0.605, 1.648	0.750, 1.238
Range h, k, l	0–18, 0–25, 0–34	0–15, 0–15, 0–30
Reflections collected:		
total	4972	2319
unique	4708	682
with $I > 3\sigma(I)$	2605	315
No. of parameters	464	62
$R = \Sigma\Vert F_o\vert - \vert F_c\Vert/\Sigma\vert F_o\vert$	0.080	0.051
$R' = [\Sigma w\Vert F_o\vert - \vert F_c\Vert^2/\Sigma w(\vert F_o\vert)^2]^{\frac{1}{2}}$	0.109	0.061
$w = 1/(\sigma F)^2 = 4F^2/[\sigma I^2 + (pF^2)^2]^{\frac{1}{2}}$	$p = 0.04$	$w = 1$

* Details in common: θ limits 1–20°; scan type ω–2θ; scan width 0.8 + 0.35 tan θ.

Laboratorien at Engelskirchen (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The commercial thiols and disulfides (Aldrich and Janssen) were dried over molecular sieves. The salt $[NEt_3H][BPh_4]$ was made by mixing NEt_3HCl and $NaBPh_4$ in water. Amalgamated uranium metal turnings,[8] $U(NEt_2)_4$,[37] $U(BH_4)_4$[38] and $[Na(thf)_3]_2[U(SBu^t)_6]$[5] were prepared by published methods.

$U(SPh)_4$ **1**.—(*a*) Benzenethiol (1500 mg, 13.6 mmol) was added to a suspension of $U(BH_4)_4$ (200 mg, 0.67 mmol) in toluene (50 cm^3). A gas was immediately evolved and the pale green solution turned red. The reaction mixture was heated at 60 °C for 12 h and a red powder precipitated; this was filtered off, washed with thf (3 × 20 cm^3) and dried under vacuum (440 mg, 97%).

(*b*) A round-bottom flask (50 cm^3), charged with $U(SBu^n)_4$ (150 mg, 0.25 mmol) in PhSH (2.5 g, 22.7 mmol), was immersed for 1 h in an ultrasound bath (60 W, 40 kHz). The green powder turned progressively red; this was filtered off, washed with pentane (3 × 10 cm^3) and dried under vacuum (164 mg, 96%).

(*c*) A round-bottom flask (50 cm^3) was charged with freshly prepared uranium turnings (150 mg, 0.63 mmol) and PhSSPh (2.5 g, 11.5 mmol) in toluene (20 cm^3). The flask was immersed in an ultrasound bath. A red powder was formed immediately but the reaction slowed down after 3 h. After 24 h, the remaining metal turnings were discarded, the red powder was filtered off, washed with toluene (3 × 10 cm^3) and dried under vacuum (41 mg, 10%). The pieces of metal were found to be unreactive when put again in the presence of the disulfide.

$[U_3S(SBu^t)_{10}]$ **2**.—(*a*) A round-bottom flask (100 cm^3) was charged with $[Na(thf)_3]_2$ $[U(SBu^t)_6]$ (300 mg, 0.24 mmol) and $[NEt_3H][BPh_4]$ (210 mg, 0.50 mmol) and diethyl ether (50 cm^3) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 12 h and after evaporation the residue was extracted in benzene (30 cm^3). The solution was evaporated to dryness, leaving a red powder; recrystallization from pentane afforded red microcrystals of compound **2**, which were filtered off and dried under vacuum (72 mg, 50%).

(*b*) An NMR tube charged with $[U(SBu^t)_4(py)_3]$ **3** (*ca.* 10 mg) in $[^2H_6]$benzene (0.25 cm^3) was heated at 60 °C for 15 min. The spectrum showed that **3** was totally converted into **2** with liberation of pyridine (9 equivalents), Bu^{t}SH (1 equivalent) and 2-methylpropene (0.6 equivalents). 2-Methylpropene was also detected in the vapour phase by GLC (phenyl isocyanate column). The products were identified by comparison of their ^1H NMR spectra and GLC retention times with those of authentic samples.

$[U(SBu^t)_4(py)_3]$ **3**.—2-Methylpropane-2-thiol (1700 mg, 18.8 mmol) was added to a solution of $U(NEt_2)_4$ (1000 mg, 1.9 mmol) in pyridine (15 cm^3). The solution turned red immediately and a red microcrystalline powder precipitated; this was filtered off, washed with diethyl ether (3 × 20 cm^3) and dried under vacuum (1220 mg, 77%).

$U(SPr^i)_4$ **4**.—(*a*) Propane-2-thiol (115 mg, 1.5 mmol) was added to a solution of $U(NEt_2)_4$ (200 mg, 0.38 mmol) in diethyl ether (50 cm^3). A green powder immediately precipitated; this was filtered off, washed with diethyl ether (3 × 20 cm^3) and dried under vacuum (168 mg, 82%). The product was soluble in pyridine, giving a red solution, and was recovered as a green powder after evaporation to dryness.

(*b*) A round-bottom flask (50 cm^3), charged with uranium metal turnings (150 mg, 0.63 mmol) in Pr^{i}SSPr^i (2.5 g, 17 mmol) was immersed for 24 h in an ultrasound bath. The remaining metal turnings were discarded and the green powder was filtered off, washed with toluene (3 × 10 cm^3) and dried under vacuum (27 mg, 8%).

$[U(SPr^i)_4(hmpa)_2]$ **5**.—A round-bottom flask (100 cm^3) was charged with compound **4** (290 mg, 0.54 mmol) and hmpa (190

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for $[U(SPr^i)_2(hmpa)_4][BPh_4]_2$

Atom	*x*	*y*	*z*
U(1)	0.869 77(8)	0.750	0.900
U(2)	0.622 68(8)	0.750	1.438 1(2)
S(11)	0.811 5(7)	0.750	0.979(2)
S(12)	0.925 5(8)	0.750	0.815(2)
S(21)	0.689 8(6)	0.750	1.500(1)
S(22)	0.552 9(7)	0.750	1.391(2)
P(11)	0.859 5(4)	0.889 1(5)	0.911 8(7)
P(12)	0.929 6(6)	0.750	1.058(1)
P(13)	0.829 4(7)	0.750	0.727(1)
P(21)	0.609 2(3)	0.887 7(5)	1.434 1(7)
P(22)	0.596 7(6)	0.750	1.628(1)
P(23)	0.671 3(6)	0.750	1.268(1)
O(11)	0.868 7(9)	0.834(1)	0.898(2)
O(12)	0.905(1)	0.750	0.995(2)
O(13)	0.848(1)	0.750	0.804(2)
O(21)	0.617 1(8)	0.833(1)	1.426(1)
O(22)	0.600(1)	0.750	1.553(2)
O(23)	0.646(1)	0.750	1.334(2)
N(11)	0.871(1)	0.906(1)	0.984(2)
N(12)	0.889(1)	0.910(1)	0.850(2)
N(13)	0.818(1)	0.903(2)	0.894(2)
N(14)	0.954(2)	0.792(2)	1.056(3)
N(15)	0.901(2)	0.750	1.133(4)
N(16)	0.829(1)	0.802(2)	0.690(3)
N(17)	0.782(2)	0.750	0.722(4)
N(21)	0.637 7(9)	0.915(1)	1.484(2)
N(22)	0.568(1)	0.900(1)	1.461(2)
N(23)	0.612(1)	0.906(1)	1.354(2)
N(24)	0.629(2)	0.784(2)	1.665(3)
N(25)	0.557(2)	0.781(2)	1.644(4)
N(26)	0.684(1)	0.805(2)	1.252(3)
N(27)	0.634(2)	0.750	1.204(4)
N(241)	0.601(2)	0.798(2)	1.658(3)
C(1)	0.776(1)	0.986(2)	0.634(2)
C(2)	0.817(1)	0.979(2)	0.647(3)
C(3)	0.840(1)	0.948(2)	0.595(3)
C(4)	0.825(2)	0.931(2)	0.541(3)
C(5)	0.792(2)	0.927(3)	0.505(4)
C(6)	0.764(2)	0.965(2)	0.566(3)
C(7)	0.772(2)	1.061(2)	0.716(3)
C(8)	0.788(2)	1.056(2)	0.778(3)
C(9)	0.811(2)	1.090(2)	0.812(3)
C(10)	0.814(2)	1.126(3)	0.780(4)
C(11)	0.798(2)	1.143(3)	0.717(4)
C(12)	0.777(2)	1.102(2)	0.689(3)
C(13)	0.713(1)	1.035(2)	0.638(3)
C(14)	0.673(1)	1.035(2)	0.659(2)
C(15)	0.647(1)	1.063(2)	0.617(2)
C(16)	0.653(1)	1.085(2)	0.559(2)
C(17)	0.692(1)	1.092(2)	0.528(3)
C(18)	0.723(1)	1.064(2)	0.577(2)
C(19)	0.729(1)	0.973(2)	0.736(2)
C(20)	0.718(2)	0.997(3)	0.808(3)
C(21)	0.699(1)	0.955(2)	0.840(3)
C(22)	0.695(1)	0.910(2)	0.817(3)
C(23)	0.707(1)	0.890(2)	0.763(2)
C(24)	0.726(2)	0.915(2)	0.711(3)
C(25)	0.533(1)	0.975(2)	0.735(3)
C(26)	0.568(1)	0.973(2)	0.706(2)
C(27)	0.598(2)	0.950(2)	0.733(3)
C(28)	0.583(2)	0.922(2)	0.804(3)
C(29)	0.550(1)	0.930(2)	0.824(3)
C(30)	0.523(1)	0.950(2)	0.794(2)
C(31)	0.521(1)	1.048(2)	0.637(2)
C(32)	0.536(1)	1.030(2)	0.566(2)
C(33)	0.552(2)	1.071(2)	0.521(3)
C(34)	0.553(2)	1.120(2)	0.552(3)
C(35)	0.540(1)	1.133(2)	0.615(3)
C(36)	0.523(2)	1.090(2)	0.660(3)
C(37)	1.025(1)	0.955(2)	0.121(2)
C(38)	1.033(1)	0.974(2)	0.052(3)
C(39)	1.056(2)	0.934(3)	0.008(4)
C(40)	1.066(2)	0.887(3)	0.036(4)
C(41)	1.056(2)	0.861(3)	0.114(3)
C(42)	1.032(2)	0.912(3)	0.152(3)
C(43)	0.970(2)	0.963(2)	0.222(3)
C(44)	0.935(1)	0.960(2)	0.191(3)
C(45)	0.907(1)	0.938(2)	0.221(3)
C(46)	0.921(2)	0.912(2)	0.292(3)
C(47)	0.959(2)	0.927(2)	0.310(3)
C(48)	0.983(2)	0.947(2)	0.285(4)
C(100)	0.766(3)	0.750	0.999(6)
C(101)	0.764(2)	0.808(3)	1.037(4)
C(102)	0.970(3)	0.750	0.817(8)
C(103)	0.984(2)	0.790(3)	0.765(4)
C(111)	0.891(2)	0.956(2)	1.004(3)
C(112)	0.857(2)	0.881(3)	1.045(4)
C(121)	0.885(2)	0.964(3)	0.826(4)
C(122)	0.928(2)	0.902(2)	0.846(3)
C(131)	0.797(2)	0.880(2)	0.834(3)
C(132)	0.800(2)	0.945(3)	0.934(3)
C(141)	0.960(1)	0.841(2)	1.012(2)
C(142)	0.986(2)	0.787(3)	1.105(5)
C(151)	0.870(1)	0.799(2)	1.130(3)
C(161)	0.869(2)	0.831(2)	0.700(3)
C(162)	0.790(2)	0.815(3)	0.657(4)
C(171)	0.763(3)	0.750	0.662(6)
C(172)	0.761(3)	0.750	0.783(6)
C(201)	0.730(2)	0.750	1.453(4)
C(202)	0.755(2)	0.797(2)	1.453(3)
C(203)	0.516(3)	0.750	1.405(6)
C(204)	0.491(2)	0.702(3)	1.430(3)
C(211)	0.629(1)	0.962(2)	1.529(3)
C(212)	0.678(2)	0.897(2)	1.493(3)
C(221)	0.560(2)	0.882(2)	1.530(3)
C(222)	0.538(2)	0.926(3)	1.425(3)
C(231)	0.599(2)	0.882(2)	1.296(3)
C(232)	0.617(2)	0.955(3)	1.340(4)
C(241)	0.641(2)	0.830(3)	1.632(4)
C(242)	0.644(2)	0.769(3)	1.732(4)
C(251)	0.564(2)	0.814(3)	1.717(4)
C(252)	0.523(2)	0.750	1.609(5)
C(261)	0.701(1)	0.839(2)	1.301(3)
C(262)	0.683(2)	0.817(2)	1.170(3)
C(271)	0.649(4)	0.750	1.151(8)
C(272)	0.597(4)	0.750	1.201(7)
B(1)	0.748(2)	1.017(2)	0.675(5)
B(2)	0.500	1.000	0.676(3)
B(3)	1.000	1.000	0.161(5)

mg, 1.06 mmol) in thf (40 cm^3). The reaction mixture was heated at 60 °C for 1 h and the red solution was evaporated to dryness. Recrystallization from pentane gave red crystals which were filtered off and dried under vacuum (362 mg, 75%).

$[U(SPr^i)_2(hmpa)_4][BPh_4]_2$ **6**.—A round-bottom flask (100 cm^3) was charged with complex **5** (152 mg, 0.17 mmol), $[NEt_3H][BPh_4]$ (142 mg, 0.34 mmol) and hmpa (61 mg, 0.34 mmol) in thf (40 cm^3). The reaction mixture was stirred at 20 °C for 48 h and a light green powder precipitated; this was filtered off, washed with pentane (3 × 20 cm^3) and dried under vacuum (244 mg, 83%). A similar reaction in [$^2H_8$]thf was monitored by NMR; the spectrum showed the formation of two equivalents of Pr^iSH. Similar treatment of complex **5** with one equivalent of $[NEt_3H][BPh_4]$ gave a mixture of **6** and unreacted **5**.

Reactions of $U(SPr^i)_4$ *with Iodine*.—An NMR tube was charged with compound **4** (10 mg, 0.018 mmol) and I_2 (4.5 mg, 0.018 mmol) in [$^2H_5$]pyridine (0.25 cm^3). After 2 h at 60 °C, the spectrum showed the formation of an equimolar mixture

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for $[U(SPr^i)_2I_2(py)_3]$

Atom	*x*	*y*	*z*
U	0.388 1(2)	0.000	0.250
I	0.395 5(3)	−0.063 5(3)	0.331 58(8)
S	0.331 8(9)	−0.120 0(9)	0.210 0(3)
N(1)	0.506(3)	0.000	0.250
N(2)	0.315(3)	0.049(3)	0.217 0(9)
C(1)	0.516(3)	−0.041(3)	0.224 1(9)
C(2)	0.569(3)	−0.053(3)	0.223(1)
C(3)	0.635(5)	0.000	0.250
C(4)	0.265(4)	0.006(4)	0.185(1)
C(5)	0.226(3)	0.030(3)	0.168(1)
C(6)	0.222(5)	0.089(4)	0.181(1)
C(7)	0.276(5)	0.135(6)	0.213(1)
C(8)	0.300(5)	0.097(4)	0.232(1)
C(9)	0.293(5)	−0.201(5)	0.239(1)
C(10)	0.349(4)	−0.212(4)	0.247(1)
C(11)	0.230(6)	−0.251(6)	0.225(2)

of $[U(SPr^i)_2I_2(py)_x]$ and Pr^iSSPr^i; integration of the spectrum by using the residual protio resonances of $[^2H_5]$pyridine as an internal reference showed that the yield was almost quantitative. Similar treatment of compound **4** with 0.5 equivalents of I_2 gave a mixture of unreacted **4**, $[U(SPr^i)_3I(py)_x]$ and $[U(SPr^i)_2I_2(py)_x]$ in the ratio 12:76:12; the same mixture was obtained from equimolar quantities of **4** and **7**. In the ^1H NMR spectrum ($[^2H_5]$pyridine, 30 °C), the two signals at δ 51.82 (s, 1 H, CH) and 23.62 (s, 6 H, Me) were attributed to the monoiodide. Reaction of compound **4** with 1.5 equivalents of I_2 gave $[U(SPr^i)I_3(py)_x]$, characterized by its NMR spectrum, δ 83.44 (s, 1 H, CH) and 37.89 (s, 6 H, Me).

$[U(SPr^i)_2I_2(py)_3]$ **7**.—Diiodine (94 mg, 0.37 mmol) was added to a solution of compound **4** (200 mg, 0.37 mmol) in pyridine (30 cm^3). The reaction mixture was heated for 2 h at 60 °C and by cooling at 20 °C a yellow powder precipitated; this was filtered off, washed with pentane (3 × 20 cm^3) and dried under vacuum (243 mg, 74%).

Reaction of $U(SPr^i)_4$ *with Carbon Disulfide*.—A round-bottom flask (50 cm^3) was charged with compound **4** (200 mg, 0.37 mmol) in CS_2 (20 cm^3). The mixture was stirred for two weeks at room temperature; the green powder of **4** slowly disappeared and a red solution was obtained. Evaporation to dryness gave a red oil from which were sublimed (10^{-3} mm Hg, *ca.* 0.133 Pa, 20 °C, 8 h) yellow crystals of $(Pr^iS)_2C{=}S$ (65 mg, 90%) (Found: C, 43.15; H, 7.35; S, 49.25. $C_7H_{14}S_3$ requires C, 43.3; H, 7.2; S, 49.5%), m.p. 34 °C. ^1H NMR (60 MHz, $[^2H_6]$benzene, 30 °C): δ 4.23 (spt, 1 H, *J* 7, C*H*Me$_2$), 1.15 (d, 6 H, *J* 7 Hz, CH*Me*$_2$). Mass spectrum: $M^+ = 194$.

Crystal Structure Determinations of $[U(SPr^i)_2(hmpa)_4][BPh_4]_2$ **6** *and* $[U(SPr^i)_2I_2(py)_3]$ **7**.—Complexes **6** and **7** were recrystallized from pyridine–thf and pyridine respectively. Selected single crystals were introduced into thin-walled Lindeman glass tubes in a glove box. Data were collected on an Enraf–Nonius diffractometer equipped with a graphite monochromator (λ = 0.710 73 Å). The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured each hour; a decay was observed (32% in 53 h for **6** and 40% in 26 h for **7**) and was linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[39] The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic factors for the U and S atoms in **6** and only for the U atom in **7**. The hydrogen atoms were not introduced. One hmpa ligand in one of the two independent cations of **6** [which contains U(2)] was found to be disordered. The P(22) atom is linked to three N atoms, none of these being in a particular position; they were assigned an occupancy factor of 0.5. The N(241) atom shares the C(241) and C(251) atoms with N(24) and N(25) respectively. All calculations were performed on a Vax 4000-200 computer with the Enraf–Nonius MOLEN system.[40] Analytical scattering factors for neutral atoms[41] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3 and final positional parameters in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

References

1 R. G. Jones, G. Karmas, G. A. Martin, jun. and H. Gilman, *J. Am. Chem. Soc.*, 1956, **78**, 4285.

2 K. Tatsumi, T. Amemiya, H. Kawaguchi and K. Tani, *J. Chem. Soc., Chem. Commun.*, 1993, 773.

3 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.

4 K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, R. E. Cramer, G. J. Tagoshi, J. A. Golen and J. W. Gilje, *Inorg. Chem.*, 1990, **29**, 4928.

5 P. C. Leverd, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1993, 2251.

6 P. C. Leverd, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1994, 3563.

7 P. C. Leverd, T. Arliguie, M. Ephritikhine, M. Nierlich, M. Lance and J. Vigner, *New J. Chem.*, 1993, **17**, 769.

8 L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248.

9 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

10 J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni and A. L. Rogers, *Inorg. Chim. Acta*, 1978, **27**, 181.

11 K. W. Bagnall, F. Benetollo, G. Bombieri and G. De Paoli, *J. Chem. Soc., Dalton Trans.*, 1984, 67.

12 T. R. Boussie, R. M. Moore, A. Streitwieser, A. Zalkin, J. Brennan and K. A. Smith, *Organometallics*, 1990, **9**, 2010.

13 J. G. H. du Preez, B. Zeelie, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 1987, **129**, 289.

14 J. G. H. du Preez, L. Gouws, H. Rohwer, B. J. A. M. van Brecht, B. Zeelie, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1991, 2585.

15 C. Baudin, D. Baudry, M. Ephritikhine, M. Lance, A. Navaza, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, 1991, **415**, 59; R. Adam, C. Villiers, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *New J. Chem.*, 1993, **17**, 455.

16 D. C. Bradley, M. A. Saad and W. Wardlaw, *J. Chem. Soc.*, 1954, 1091, 3488; D. C. Bradley, A. K. Chatterjee and W. Wardlaw, *J. Chem. Soc.*, 1956, 2260, 3469.

17 M. T. Vilhena, A. M. T. S. Domingos and A. Pires de Matos, *Inorg. Chim. Acta*, 1984, **95**, 11.

18 W. G. Van Der Sluys, J. C. Huffman, D. S. Ehler and N. N. Sauer, *Inorg. Chem.*, 1992, **31**, 1318.

19 R. H. Holm, R. B. King and F. G. A. Stone, *Inorg. Chem.*, 1963, **2**, 219; P. Zanella, R. Ros and M. Graziani *Inorg. Chem.*, 1973, **12**, 2736; K. T. Aye, J. J. Vittal and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1993, 1835; L. Y. Goh, M. Tay, T. C. W. Mak and R. J. Wang, *Organometallics*, 1992, **11**, 1711.

20 L. Que, jun., M. A. Bobrik, J. A. Ibers and R. H. Holm, *J. Am. Chem. Soc.*, 1974, **96**, 4168; F. G. Bordwell and D. L. Hughes, *J. Org. Chem.*, 1982, **47**, 3224.

21 B. Delavaux-Nicot and M. Ephritikhine, *J. Organomet. Chem.*, 1990, **399**, 77; unpublished work.

22 A. Müller and E. Diemann, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 515.

23 S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 1623.

24 F. A. Cotton, D. O. Marler and W. Schwotzer, *Inorg. Chim. Acta*, 1984, **95**, 207.

25 D. Coucouvanis, A. Hadjikyriacou and M. G. Kanatzidis, *J. Chem. Soc., Chem. Commun.*, 1985, 1224.

26 W. J. Evans, T. F. Deming, J. M. Olofson and J. W. Ziller, *Inorg. Chem.*, 1989, **28**, 4027.
27 W. G. Van Der Sluys, A. P. Sattelberger and M. W. McElfresh, *Polyhedron*, 1990, **9**, 1843.
28 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
29 W. E. Piers, L. Koch, D. S. Ridge, L. R. MacGillivray and M. Zaworotko, *Organometallics*, 1992, **11**, 3148.
30 M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 3572.
31 M. J. Carney, P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1992, **11**, 761.
32 P. M. Boorman, K. A. Kerr and V. D. Patel, *J. Chem. Soc., Dalton Trans.*, 1981, 506.
33 I. K. Adzumi, D. L. Nosco and E. Deutsch, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1364.
34 W. F. Liaw, C. Kim, M. Y. Darensbourg and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 3591.
35 D. H. Farrar, K. R. Grudy, N. C. Payne, W. R. Roper and A. Walker, *J. Am. Chem. Soc.*, 1979, **101**, 6577.
36 I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 1974, **66**, 161.
37 J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein and L. K. Templeton, *Inorg. Chem.*, 1976, **15**, 2498.
38 V. V. Volkov and K. G. Myakishev, *Radiokhimiya*, 1980, **22**, 745.
39 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
40 MOLEN, An Interactive Structure Solution Procedure, Enraf–Nonius, Delft, 1990.
41 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham (present distributor: Academic Publishers, Dordrecht), 1974, vol. 4.

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