Triscyclopentadienyl uranium thiolates and selenolates

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Abstract

Triscyclopentadienyl uranium (IV) thiolates were prepared by two principal methods namely (1) substitution of the chloride group of $[U(cp)_3(Cl)]$ (cp = η-C_5H_5) by SR^- and (2) oxidation of the trivalent precursors $[U(cp)_3(THF)]$ (THF = tetrahydrofuran), $[U(C_5H_4SiMe_3)_3]$ and $[U(C_5H_4{}^tBu)_3]$ with the disulfide RSSR (R = Me, Et, ${}^iPr$, ${}^tBu$ or Ph). Similar treatment with MeSeSeMe afforded $[U(cp)_3(SeMe)]$ and $[U(C_5H_4SiMe_3)_3(SeMe)]$. The crystal structure of $[U(cp)_3(SMe)]$ was determined. Several reactions of these complexes are described, namely cleavage of the U–S bond by acidic substrates or iodine, insertion of CS_2 and CO_2 into the U–S bond, and reduction into the corresponding U(III) anions. The synthesis, structure and reactivity of the thiolate compounds are compared with those of the alkoxide analogues.

Keywords: Uranium; Cyclopentadienyl; Thiolate; Selenolate; Crystal structure

1. Introduction

Organoactinide compounds with thiolate ligands are very scarce. The bispentamethylcyclopentadienyl complex $[Th(C_5Me_5)_2(S^nPr)_2]$ was isolated from the reaction of $[Th(C_5Me_5)_2(Me)_2]$ with ^nPrSH [1] and the cyclooctatetraene derivatives $[\{U(C_8H_8)(SR)_2\}_2]$ (R = ^nBu, ^iPr or ^tBu) were prepared by treating $[U(C_8H_8)\text{-}(BH_4)_2]$ with the corresponding thiol or NaSR reagent [2]; the studies of these bisthiolate complexes were limited to structural investigations. It is surprising that the triscyclopentadienyl monothiolates $[M(cp)_3(SR)]$ (M = Th or U; cp = η-C_5H_5) have not received much attention whereas the $[M(cp)_3(X)]$ compounds have commonly been regarded as useful models for a variety of X groups, [3]; the only report is of the oxidation of $[U(C_5H_4Me)_3(THF)]$ (THF = tetrahydrofuran) and $[U(C_5H_4{}^tBu)_3]$ with a thiol which afforded $[U(C_5H_4\text{-}Me)_3(S^iPr)]$ and $[U(C_5H_4{}^tBu)_3(SPh)]$ [4]. It seemed to us of interest to gain a better insight into the 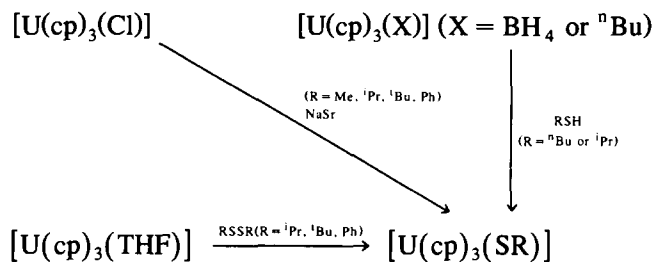preparation, characterization and reactions of such thiolate compounds. In this paper we first report several routes to the complexes $[U(C_5H_4R)_3(SR')]$ (R = H, $SiMe_3$ or ^tBu), starting from trivalent and tetravalent precursors. The features of these syntheses, the success of which was found to be greatly influenced by the nature of the ring substituent R, have been compared with those of the alkoxide analogues. The complexes were the subject of electrochemical and thermochemical studies [5]. The X-ray crystal structure of $[U(cp)_3(SMe)]$ has been determined. Some reactions of these compounds, in particular their reduction to give the first characterized U(III) thiolates, are described, and also the synthesis of the first selenolate compounds of a 5f element.

2. Results

2.1. Synthetic studies

The complexes $[U(cp)_3(SR)]$ (R = Me, ^iPr, ^tBu or Ph) were conveniently synthesized by treating $[U(cp)_3(Cl)]$ with the corresponding thiolate NaSR (Scheme 1); the reactions were performed in THF, toluene or diethyl ether, and the brown crystalline prod-

$[U(cp)_3(Cl)]$ $[U(cp)_3(X)]$ (X = BH$_4$ or ^{n}Bu)

(R = Me, ^{i}Pr, ^{t}Bu, Ph)
NaSr

RSH
(R = ^{n}Bu or ^{i}Pr)

$[U(cp)_3(THF)]$ $\xrightarrow{RSSR(R = ^iPr, ^tBu, Ph)}$ $[U(cp)_3(SR)]$

Scheme 1. Synthesis of the complexes [U(cp)$_3$(SR).

ucts were isolated with a 70–80% yield. Other methods of preparation are shown in Scheme 1; they involve thiolysis of the alkyl or borohydride derivatives $[U(cp)_3(X)]$ (X = BH$_4$ or ^{n}Bu) and oxidation of the trivalent precursor $[U(cp)_3(THF)]$ by the disulfide RSSR and afforded the desired compounds with almost quantitative yield (as indicated by NMR spectroscopy).

In contrast with $[U(cp)_3(Cl)]$, the ring substituted chlorides $[U(C_5H_4SiMe_3)_3(Cl)]$ and $[U(C_5H_4{}^tBu)_3(Cl)]$ were inert towards NaSR. In the presence of one equivalent of ^{n}BuSH or ^{i}PrSH, the hydride $[U(C_5H_4SiMe_3)_3$-(H)] was completely converted into the corresponding thiolate, but the complexes $[U(C_5H_4SiMe_3)_3(SR)]$ and $[U(C_5H_4{}^tBu)_3(SR)]$ (R = Et, ^{i}Pr or ^{t}Bu) were most easily prepared by oxidizing $[U(C_5H_4SiMe_3)_3]$ and $[U(C_5H_4{}^tBu)_3]$ with the disulfide RSSR in THF or toluene. These reactions were immediate and almost quantitative at room temperature, except for that of $[U(C_5H_4{}^tBu)_3]$ with ^{t}BuSS^{t}Bu which required 5 min at 50°C. Like the disulfides RSSR, the diselenide MeSeSeMe oxidized the trivalent complexes $[U(cp)_3$-(THF)] and $[U(C_5H_4SiMe_3)_3]$, with immediate formation of $[U(cp)_3(SeMe)]$ and $[U(C_5H_4SiMe_3)_3$-(SeMe)]; the latter was isolated as a pink oil with a 78% yield.

2.2. Crystal structure of [U(cp)₃(SMe)]

An ORTEP diagram [6] of the molecule is shown in Fig. 1; selected bond distances and angles are listed in Table 1. The complex adopts the pseudotetrahedral configuration that is familiar for $[U(cp)_3(X)]$ derivatives [3]. The U, S, C(1) and C(7) atoms lie in the plane of symmetry. The U–C(cp) bond distances range from 2.712(8) to 2.79(1) Å, averaging 2.74(2) Å. The U–S bond length of 2.695(4) Å is within the reported range found for uranium–S (thiolate) bond distances, which vary from 2.57(2) Å in $[U_3(S)(S^tBu)_{10}]$ [7] and 2.85(5) Å in $[\{U(C_8H_8)(S^iPr)_2\}_2]$ [2] or [Li(DME)]$_4$ [U-(SCH$_2$CH$_2$SMe)$_4$] [8]. The U–S–C(1) angle, 107.2(5)°, is similar to those in other uranium thiolates [7–10].

2.3. Reactivity studies

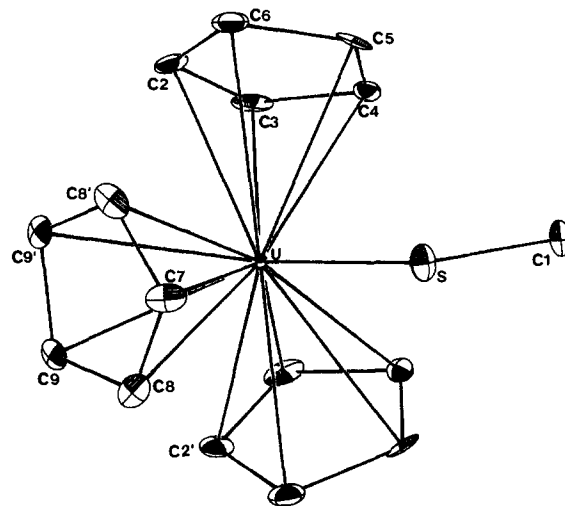Some reactions of $[U(cp)_3(S^iPr)]$ are summarized in Scheme 2. The U–S bond was readily cleaved by iodine

Fig. 1. ORTEP drawing of [U(cp)$_3$(SMe)]. Primed atoms are related to those unlabelled by the mirror plane passing through U, S, C(1) and C(7).

to give $[U(cp)_3(I)]$ and ^{i}PrSS^{i}Pr with a quantitative yield. Treatment with PPh$_3$HBr resulted in formation of equilibrium between $[U(cp)_3(S^iPr)]$ and $[U(cp)_3(Br)]$ and, not surprisingly, reaction of $[U(cp)_3(Cl)]$ with ^{i}PrSH gave a mixture of the chloride and thiolate compounds in similar proportions (80 : 20 in THF). Ethanolysis of $[U(cp)_3(S^iPr)]$ was not a clean reaction, as the product $[U(cp)_3(OEt)]$ reacted further with the alcohol to give $[U(cp)(OEt)_3]$ [11]. The thiolate group, which may be regarded as a pseudohalide, was displaced by the borohydride ligand. On exposure to carbon dioxide in THF (1 atm; 20°C), $[U(cp)_3(S^iPr)]$ was partly converted into a new derivative, presumably $[U(cp)_3(O_2CS^iPr)]$; this latter was not stable under vacuum, regenerating the thiolate complex. Reaction with CS$_2$ followed a different course, affording the trithiocarbonate $[U(cp)_2(S_2$-CS$^iPr)_2]$ and unidentified products. These compounds resulting from insertion of CO$_2$ and CS$_2$ into the U–S bond of $[U(cp)_3(S^iPr)]$ could not be isolated pure and

Table 1
Selected bond distances (Å) and angles (°) with estimated standard deviations for [U(cp)$_3$(SMe)]

Bond distances			
U–S	2.695(4)	U–C(2)	2.723(9)
U–C(3)	2.727(9)	U–C(4)	2.751(9)
U–C(5)	2.77(1)	U–C(6)	2.75(1)
U–C(7)	2.79(1)	U–C(8)	2.738(9)
U–C(9)	2.712(8)	S–C(1)	1.79(2)
U–1 [a]	2.48(1)	U–2 [a]	2.39(1)

Bond angles			
S–U–1	102.7(4)	S–U–2	95.6(4)
1–U–1	117.4(4)	1–U–2	116.5(4)
U–S–C(1)	107.2(5)		

[a] 1 and 2 are the centroids of the cyclopentadienyl rings containing C(2) and C(7) respectively.

Table 2

^{1}H NMR spectral data for the triscyclopentadienyl uranium thiolate and selenolate complexes [a]

Compound	Solvent	δ (ppm)	
		Cyclopentadienyl ligand	SR or SeR ligand
[U(cp)$_3$(SMe)]	THF-d_8	− 4.61 (15H)	− 28.71(3H)
[U(cp)$_3$(S^{n}Bu)]	THF-d_8	− 4.82 (15H)	− 6.22 (3H), − 12.63, − 20.51, − 34.24 (2H × 3)
[U(cp)$_3$(S^{i}Pr)]	THF-d_8	− 4.80 (15H)	− 19.62 (6H, d, J = 6 Hz), − 45.15 (1H)
[U(cp)$_3$(S^{t}Bu)]	THF-d_8	− 5.33 (15H)	− 21.69 (9H)
[U(cp)$_3$(SPh)]	THF-d_8	− 4.33 (15H)	− 1.65 (3H), − 21.18 (2H)
[U(C$_5$H$_4$SiMe$_3$)$_3$(SEt)]	Toluene-d_8	− 0.71 (27H), 1.96 and − 14.77 (6H × 2)	− 18.81 (3H), − 32.23 (2H)
[U(C$_5$H$_4$SiMe$_3$)$_3$(S^{n}Bu)]	Toluene-d_8	− 0.65 (27H), 2.14 and − 14.82 (6H × 2)	− 6.21 (3H), − 12.50, − 20.11, − 31.73 (2H × 3)
[U(C$_5$H$_4$SiMe$_3$)$_3$(S^{i}Pr)]	THF-d_8	− 0.44 (27H), 1.14 and − 15.81 (6H × 2)	− 19.78 (6H, d, J = 6 Hz); − 44.82 (1H)
[U(C$_5$H$_4$SiMe$_3$)$_3$(S^{t}Bu)]	Toluene-d_8	0.72 (27H), 1.11 and − 17.27 (6H × 2)	− 20.91 (9H)
[U(C$_5$H$_4$^{t}Bu)$_3$(SEt)]	Benzene-d_6	− 1.30 (27H), 3.61 and − 15.64 (6H × 2)	− 17.40 (3H), − 28.31 (2H)
[U(C$_5$H$_4$^{t}Bu)$_3$(S^{i}Pr)]	Benzene-d_6	− 0.25 (27H), − 1.20 and − 19.31 (6H × 2)	− 18.59 (6H, d, J = 6 Hz), − 37.71 (1H)
[U(C$_5$H$_4$^{t}Bu)$_3$(S^{t}Bu)]	Benzene-d_6	0.51 (27H), 2.92 and − 17.90 (6H × 2)	− 19.49 (9H)
[U(cp)$_3$(SeMe)]	Benzene-d_6	− 5.04 (15H)	− 25.68 (3H)
[U(C$_5$H$_4$SiMe$_3$)$_3$(SeMe)]	Toluene-d_8	− 1.14 (27H), 1.17 and − 12.73 (6H × 2)	− 23.23 (3H)
Na[U(cp)$_3$(SMe)]	THF-d_8	− 14.81 (15H)	− 14.9 (3H)
Na[U(cp)$_3$(S^{i}Pr)]	THF-d_8	− 14.53 (15H)	− 10.42 (6H), − 16.09 (1H)
Na[U(cp)$_3$(S^{t}Bu)]	THF-d_8	− 14.37 (15H)	− 10.35 (9H)
Na[U(cp)$_3$(SPh)]	THF-d_8	− 14.41 (15H)	2.65 (1H), − 6.74 and − 18.12 (2H × 2)
Na[U(C$_5$H$_4$SiMe$_3$)(SeMe)]	THF-d_8	− 2.98 (27H), − 6.27 and − 16.30 (6H × 2)	− 11.72 (3H)

[a] At 30°C, δ relative to tetramethylsilane. When not specified, the signals are singlets with half-height widths of between 10 and 20 Hz.

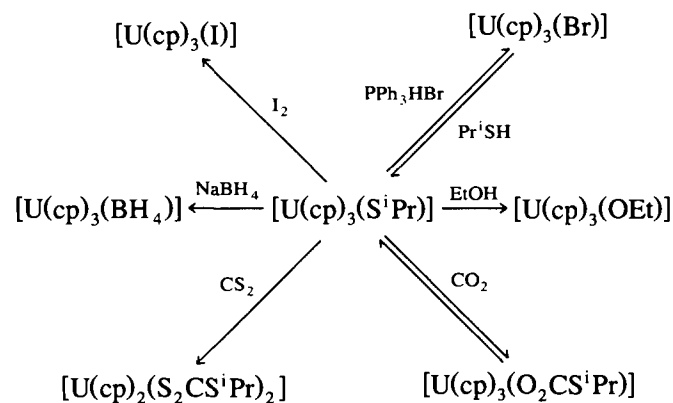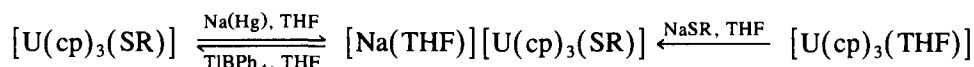were characterized only by their ^{1}H NMR spectra (Table 2).

Electrochemical studies showed that reversible reduction of [U(cp)$_3$(S^{i}Pr)] took place at a potential of − 2.03 V (vs. ferrocene–ferricinium) [12]. In keeping with this, the complexes [U(cp)$_3$(SR)] (R = Me, ^{i}Pr, ^{t}Bu or Ph) were reduced by use of sodium amalgam in THF to the corresponding trivalent anions, which were also made by addition of NaSR to [U(cp)$_3$(THF)]; dark-red microcrystals of [Na(THF)][U(cp)$_3$(S^{i}Pr)] were obtained with a 71% yield. The U(III) thiolate compounds were oxi-

dized back into their U(IV) precursors by TlBPh$_4$ (Scheme 3).

Reduction of [U(C$_5$H$_4$SiMe$_3$)$_3$(SeMe)] by Na(Hg) gave of the U(III) selenolate [Na(THF)][U(C$_5$H$_4$-SiMe$_3$)$_3$(SeMe)] (48% yield) as a red powder.

3. Discussion

The simplest and most straightforward synthetic route to transition metal thiolate complexes, that involving chloride displacement by the appropriate SR group [13], proved to be very satisfactory for the preparation of the derivatives [U(cp)$_3$(SR)] (R = Me, ^{i}Pr, ^{t}Bu or Ph). The alkoxide analogues [U(cp)$_3$(OR)] (R = Me, ^{i}Pr or ^{t}Bu) were prepared similarly by treatment of [U(cp)$_3$(Cl)] with NaOR [14]. However, the chlorides [U(C$_5$H$_4$-SiMe$_3$)$_3$(Cl)] and [U(C$_5$H$_4$^{t}Bu)$_3$(Cl)] could not be converted into the expected thiolates in this way, undoubtedly because of steric hindrance by the ring substituents; such kinetic factors also played a role in the difference between the reactivities of [Ce(C$_5$H$_4$Me)$_3$] and [Ce(C$_5$H$_4$^{t}Bu)$_3$] [4]. Another standard approach to thiolate compounds involves oxidation of low valence metal complexes with disulfides [13]. The trivalent pre-

Scheme 2. Some reactions of [U(cp)$_3$(S^{i}Pr)].

$$[U(cp)_3(SR)] \underset{\text{TlBPh}_4, \text{ THF}}{\overset{\text{Na(Hg), THF}}{\rightleftarrows}} [Na(THF)][U(cp)_3(SR)] \overset{\text{NaSR, THF}}{\longleftarrow} [U(cp)_3(THF)]$$

R = Me, ^{i}Pr, ^{t}Bu, Ph

Scheme 3. Synthesis of the U(III) thiolate complexes [Na(THF)][U(cp)$_3$(SR)].

cursors [U(C$_5$H$_4$SiMe$_3$)$_3$] and [U(C$_5$H$_4$^{t}Bu)$_3$], as well as [U(cp)$_3$(THF)], were transformed in this way to the desired triscyclopentadienyl U(IV) thiolates. Similar reactions with the diselenide MeSeSeMe afforded [U(cp)$_3$(SeMe)] and [U(C$_5$H$_4$SiMe$_3$)$_3$(SeMe)], the first selenolate compounds of a 5f element. It is note worthy that [U(C$_5$H$_4$SiMe$_3$)$_3$] was readily oxidized with ^{t}BuSS^{t}Bu, whereas [U(C$_5$H$_4$^{t}Bu)$_3$] was inert towards this disulfide at room temperature. This difference on reactivities, which is obviously not due to steric factors since the two substituted cyclopentadienyl ligands are isosteric, can be attributed to the greater ease of initial coordination of the disulfide to the less-electron-rich compound [U(C$_5$H$_4$SiMe$_3$)$_3$]; it is known that the latter gives a much more stable adduct with THF than does [U(C$_5$H$_4$^{t}Bu)$_3$] [15]. Nevertheless, if it is the electronic effects of the ring substituents that play a major role in the reactions of [U(C$_5$H$_4$SiMe$_3$)$_3$] and [U(C$_5$H$_4$^{t}Bu)$_3$] with ^{t}BuSS^{t}Bu, their steric influence is also important in these oxidative processes since the less bulky disulfides EtSSEt and ^{i}PrSS^{i}Pr immediately reacted with [U(C$_5$H$_4$^{t}Bu)$_3$] at 20°C; the reaction of [U(C$_5$H$_4$^{t}Bu)$_3$] with ^{t}BuSS^{t}Bu was thus disfavored by both steric and electronic factors. The different behaviours of [U(C$_5$H$_4$SiMe$_3$)$_3$] and [U(C$_5$H$_4$^{t}Bu)$_3$] were again observed during their reaction with ^{t}BuOO^{t}Bu and, moreover, oxidation of the U(III) complexes was much slower with the peroxide than with the disulfide; after 72 h at 50°C, formation of [U(C$_5$H$_4$SiMe$_3$)$_3$(O^{t}Bu)] was complete and 30% of [U(C$_5$H$_4$^{t}Bu)$_3$] were converted into the alkoxide. In agreement with the proposals of Andersen and coworkers [16] who demonstrated that the labile THF ligand of [U(C$_5$H$_4$Me)$_3$(THF)] could be readily displaced by tetrahydrothiophene, these facts can be attributed to the greater stability of the disulfide adduct [U(C$_5$H$_4$R)$_3$(^{t}BuSS^{t}Bu)], which reflects the relative softness of the uranium (III) center. The oxidation reactions of [U(C$_5$H$_4$SiMe$_3$)$_3$] with RSSR (R = Et or ^{t}Bu) were quite rapid and quantitative and were useful for determining the absolute U–S bond disruption enthalpies D(U–S), which were found to be 266 ± 9 kJ mol^{-1} and 158 ± 8 kJ mol^{-1} for [U(C$_5$H$_4$SiMe$_3$)$_3$(SEt)] and [U(C$_5$H$_4$SiMe$_3$)$_3$(S^{t}Bu)] respectively [5]. These energies are, not surprisingly, lower than the corresponding D(U–O) values for the alkoxide analogues [U(C$_5$H$_4$SiMe$_3$)$_3$(OR)] (324 ± 23 kJ mol^{-1} (R = Et) and 280 ± 8 kJ mol^{-1} (R =^{t}Bu)] [17]), whereas D(U–S) in [U(C$_5$H$_4$SiMe$_3$)$_3$(SEt)] is similar to D(U–H) (252 ± 5 kJ mol^{-1}) and D(U–I) (265 ± 5 kJ mol^{-1}) in [U(C$_5$H$_4$SiMe$_3$)$_3$(X)] (X = H or I) [18].

Other triscyclopentadienyl uranium(IV) thiolates, [U(C$_5$H$_4$Me)$_3$(S^{i}Pr)] and [U(C$_5$H$_4$^{t}Bu)$_3$(SPh)], were isolated by Andersen and coworkers [4] from the reactions of [U(C$_5$H$_4$Me)$_3$(THF)] and [U(C$_5$H$_4$^{t}Bu)$_3$] with the corresponding thiol. This method is less convenient than the oxidation by disulfide, since it requires the unpleasant use of RSH and gives the products with a low yield (about 35%); it was shown that [U(C$_5$H$_4$-^{t}Bu)$_3$(SPh)] resulted from the rearrangement of the U(III) complex [U(C$_5$H$_4$^{t}Bu)$_2$(SPh)], initially formed by protonolysis of a cyclopentadienyl ligand. Also less useful, although quantitative, were the syntheses of [U(cp)$_3$(SR)] (R =^{n}Bu or ^{i}Pr) and [U(C$_5$H$_4$SiMe$_3$)$_3$-(SR)] (R =^{n}Bu or ^{i}Pr) by thiolysis of [U(cp)$_3$(X)] (X = BH$_4$ or ^{n}Bu) and [U(C$_5$H$_4$SiMe$_3$)$_3$(H)]. It is, however, noteworthy that these proton transfer reactions were much slower with a thiol than with an alcohol, and that the thiolates were inert in the presence of an excess of RSH whereas ethanolysis of [U(cp)$_3$(S^{i}Pr)] gave [U(cp)$_3$(OEt)], which was further transformed into [U(cp)(OEt)$_3$] [11]. The difference between the reactivities of ROH and RSH, which is opposite to what would be expected from the acidity scale, could be tentatively attributed to intermediate formation of the adduct [U(cp)$_3$(X)(REH)] (E = O or S); such an associative rate determining step, which was found to occur during the reaction of nickelocene with thiols [19], would be more favored with the alcohol because of the stronger interaction between the less polarizable oxygen atom and the hard uranium(IV) center.

Iodine was also found to cleave the U–S bond of [U(cp)$_3$(S^{i}Pr)]; such iodonolysis of metal–sulfur bonds was previously performed on the complexes [Os(η^2-S$_2$)(CO)$_2$(PPh$_3$)$_2$] [20] and [U(S^{i}Pr)$_4$] [11].

Most interesting are the insertion reactions into the U–S bond. Several examples of insertion of carbon disulfide into d transition metal–sulfur bonds have been described [21] and, in the case of element thiolates, Gilje and coworkers [8] reported that reaction of CS$_2$ with the anionic homoleptic compound [Li(DME)]$_4$[U-(SCH$_2$CH$_2$CH$_2$SMe)$_4$] gave [Li(DME)$_2$]$_2$[S$_2$CSCH$_2$-CH$_2$SCS$_2$] as an isolable product, but they could not decide whether the insertion took place at Li–S or U–S bonds. Although formation of [U(cp)$_2$(S$_2$CS^{i}Pr)$_2$] by treatment of [U(cp)$_3$(S^{i}Pr)] with CS$_2$ is difficult to explain mechanistically, it provides clear evidence of insertion of carbon disulfide into the uranium–sulfur bond. Reversible insertion of carbon dioxide into metal–oxygen and metal–nitrogen bonds is well documented [22], but [U(cp)$_3$(O$_2$CS^{i}Pr)] would be, to our knowledge, the first compound formed by insertion of CO$_2$ into a metal–sulfur bond; further studies of this new reaction are in progress.

The anionic compounds [Na(THF)][U(cp)$_3$(SR)] (R = Me, ^{i}Pr, ^{t}Bu or Ph) and [Na(THF)][U(C$_5$H$_4$SiMe$_3$)$_3$-(SeMe)], obtained by sodium amalgam reduction of the corresponding tetravalent precursors, are the first U(III) thiolates and selenolate to be isolated; the alkoxide analogues could not be made by this method. The reduction potentials of the complexes [U(cp)$_3$(S^{i}Pr)] and [U(cp)$_3$(O^{i}Pr)] were −2.03 and −2.38 V respectively (vs. ferrocene–ferricinium) [12], confirming that the

thiolate ligand is a much worse electron donor than is alkoxide [13]. The distinct electronic effects of the SR and OR groups were manifest in the reactions and structures of analogous thiolate and alkoxide compounds [2]. In particular, Marks and coworkers [1], when considering the geometrical parameters of $[Th(C_5Me_5)_2(S^nPr)_2]$, pointed out that the actinide thiolate bonding involves less ligand-to-metal π donation than does actinide alkoxide bonding. The same conclusion can be drawn from the crystal structure of $[U(cp)_3(SMe)]$. The U–S bond distance of 2.695(4) Å corresponds exactly to the sum of the two-coordinate sulfur covalent radius (1.04 Å) [24] and of the uranium covalent radius (1.66 Å), determined by substracting the sp^3 carbon covalent radius of 0.77 Å [24] from the U–C(sp^3) distance of 2.43 Å in $[U(cp)_3(^nBu)]$ [23]. A similar calculation yields a value of 2.3 Å for the U–O distance, but the observed distances are much shorter, ranging typically between 2.05 and 2.15 Å [25], and equal to 2.119(7) Å in $[U(cp)_3(OPh)]$ [26]; this difference reflects a more important π component in the metal–oxygen bonding. Also indicative of a weak π interaction in the U–S bond of $[U(cp)_3(SMe)]$ is the U–S–C angle of 107.2(5)°; in contrast the actinide–O–C angles in terminal alkoxides are close to linearity (159.4(5)° in $[U(cp)_3(OPh)]$).

4. Conclusion

Oxidation of the trivalent complexes $[U(cp)_3(THF)]$, $[U(C_5H_4S^iMe_3)_3]$ and $[U(C_5H_4^tBu)_3]$ with the disulfides RSSR provides an efficient route to the triscyclopentadienyl U(IV) thiolates. Only the compounds $[U(cp)_3(SR)]$ could be prepared from the corresponding chloride by the classical metathetical exchange reaction with NaSR. These reactions are quite sensitive to the steric and electronic effects of the ring substituents. The synthesis of $[U(cp)_3(SeMe)]$ and $[U(C_5H_4SiMe_3)_3-(SeMe)]$ provides an entry into the chemistry of the 5f element selenolates. The thiolate complexes were shown to be useful precursors for the preparation of new derivatives, in particular by insertion of heteroallenes into the U–S bond. The first uranium (III) thiolate compounds have been isolated. That the SR group is less electron donating than OR is evident from the distinct reactions and structures of analogous thiolate and alkoxide derivatives; the crystal structure of $[U(cp)_3(SMe)]$ revealed the absence of significant π interaction in the U–S bond. The different reactivities of sulfur and oxygen derivatives molecules (REH and REER with E = S or O) towards uranium compounds is not what would be expected from their acidic and oxidative properties but can be explained by the classification of the U(III) and U(IV) centres as soft and hard sites respectively.

5. Experimental details

5.1. General methods

All preparations and reactions were carried out under argon (less than 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.

Elemental analyses were performed by Analytische Laboratorien at Engelskirchen (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (Fourier transform) instrument and with the residual protio solvent resonances as references. The spectra are described in Table 2.

The commercial thiols, disulfides and MeSeSeMe (Aldrich and Janssen) were dried over molecular sieves. The NaSR reagents were obtained as white powders by reaction of sodium will a slight excess (1.1 equivalent) of the corresponding thiol in THF. TlBPh$_4$ was made by mixing TlNO$_3$ with NaBPh$_4$ in water. PPh$_3$HBr [27], $[U(cp)_3(Cl)]$ [28], $[U(cp)_3(BH_4)]$ [29], $[U(cp)_3(^nBu)]$ [30], $[U(cp)_3(THF)]$ [31], $[U(C_5H_4SiMe_3)_3(Cl)]$ [32], $[U(C_5H_4^tBu)_3(Cl)]$ [33], $[U(C_5H_4SiMe_3)_3(H)]$ [15], $[U(C_5H_4SiMe_3)_3]$ [32], $[U(C_5H_4^tBu)_3]$ [4] were prepared by published methods.

5.2. Synthesis of the complexes $[U(cp)_3(SR)]$ (R = Me, ^iPr, ^tBu or Ph) from $[U(cp)_3(Cl)]$

In a typical experiment, a 50 ml round-bottomed flask was charged with $[U(cp)_3(Cl)]$ (100 mg, 0.21 mmol) and 1.0 equivalent of NaSR and THF (20 ml) was condensed in under vacuum at −78°C. The mixture was stirred for 2 h at 20°C and then filtered; the filtrate was evaporated to dryness and the residue was extracted with diethyl ether (20 ml). The solvent was evaporated from the extract to leave brown microcrystals of the product (yield, 70–80%). Anal. For R = Me. Found: C, 39.64; H, 3.91; S, 6.49. $C_{16}H_{18}SU$ Calc.: C, 40.00, H, 3.78; S, 6.67%. For R = ^iPr. Found: C, 42.18; H, 4.09; S, 6.14. $C_{18}H_{22}SU$ Calc.: C, 42.52, H, 4.36; S, 6.31%. For R = ^tBu. Found: C, 43.42; H, 4.51; S, 5.99. $C_{19}H_{24}SU$ Calc.: C, 43.68, H, 4.63; S, 6.14%. For R = Ph. Found: C, 46.13; H, 3.75; S, 5.99. $C_{21}H_{20}SU$ Calc.: C, 46.50, H, 3.72; S, 5.91%.

5.3. Reactions of $[U(cp)_3(THF)]$ with the disulfides RSSR (R = ^iPr, ^nBu or Ph)

In a typical experiment, an NMR tube was charged with $[U(cp)_3(THF)]$ (5 mg, 0.01 mmol) and 0.5 equivalent of RSSR in THF-d_8 (0.3 ml). After 5 min at 20°C, the spectrum of the red solution showed that the triva-

lent complex had been totally converted into [U(cp)$_3$(SR)].

5.4. Reactions of [U(cp)$_3$(X)] (X = BH$_4$ or ^{n}Bu) with RSH

(a) An NMR tube was charged with [U(cp)$_3$(BH$_4$)] (10 mg, 0.02 mmol) in THF-d_8 (0.3 ml) and ^{i}PrSH (8.3 μl, 0.09 mmol) was introduced from a microsyringe. After 8 h at 60°C, the spectrum of the red solution showed that the borohydride complex had been converted into [U(cp)$_3$(S^{i}Pr)].

(b) An NMR tube was charged with [U(cp)$_3$(^{n}Bu)] (5 mg, 0.01 mmol) in THF-d_8 (0.3 ml) and 1.0 equivalent of RSH (R =^{n}Bu or ^{i}Pr) was introduced from a microsyringe. After 24 h at 60°C, the spectrum of the red solution showed that the alkyl complex had been totally converted into the corresponding thiolate.

5.5. Reactions of [U(C$_5$H$_4$SiMe$_3$)$_3$] and [U(C$_5$H$_4$^{t}Bu)$_3$] with the disulfides RSSR (R = Et or ^{t}Bu)

(a) An NMR tube was charged with [U(C$_5$H$_4$-SiMe$_3$)$_3$] (8 mg, 0.012 mmol) in THF-d_8 or toluene-d_8 (0.3 ml) and 0.5 equivalent of RSSR was introduced from a microsyringe. The green solution immediately turned red and the spectrum showed that the U(III) complex had been totally converted into the corresponding U(IV) thiolate.

(b) An NMR tube was charged with [U(C$_5$H$_4$^{t}Bu)$_3$] (8 mg, 0.013 mmol) in THF-d_8 or toluene-d_8 (0.3 ml) and EtSSEt (0.9 μl, 0.007 mmol) was introduced from a microsyringe. The green solution immediately turned red and the spectrum showed that the U(III) complex had been totally converted into [U(C$_5$H$_4$^{t}Bu)$_3$(SEt)].

(c) An NMR tube was charged with [U(C$_5$H$_4$^{t}Bu)$_3$] (8 mg, 0.013 mmol) in THF-d_8 or toluene-d_8 (0.3 ml) and ^{t}BuSS^{t}Bu (1.5 μl, 0.007 mmol) was introduced from a microsyringe. No reaction was observed at 20°C. After 5 min at 50°C, the spectrum of the red solution indicated complete formation of [U(C$_5$H$_4$^{t}Bu)$_3$(S^{t}Bu)].

5.6. Synthesis of [U(C$_5$H$_4$SiMe$_3$)$_3$(S^{i}Pr)]

A 100 ml round-bottomed flask was charged with [U(C$_5$H$_4$SiMe$_3$)$_3$] (300 mg, 0.46 mmol) in pentane (60 ml) and ^{i}PrSS^{i}Pr (35 mg, 0.23 mmol) was added from a syringe. The green solution immediately turned red. The solution was filtered and evaporated to dryness to give the product as a red powder (300 mg (90%)). Anal. Found: C, 44.61; H, 6.35; S, 4.23. C$_{27}$H$_{46}$Si$_3$SU Calc.: C, 44.73; H, 6.40; S, 4.42%.

5.7. Synthesis of [U(C$_5$H$_4$^{t}Bu)$_3$(S^{i}Pr)]

A 100 ml round-bottomed flask was charged with [U(C$_5$H$_4$SiMe$_3$)$_3$] (300 mg, 0.5 mmol) in toluene (40

ml) and ^{i}PrSS^{i}Pr (37 mg, 0.25 mmol) was added from a syringe. The green solution immediately turned red. The solution was filtered and evaporated to dryness to give the product as a red powder (285 mg (84%)). Anal. Found: C, 53.15; H, 6.95; S, 4.59. C$_{30}$H$_{46}$SU Calc.: C, 53.24; H, 6.85; S, 4.74%.

5.8. Reactions of [U(C$_5$H$_4$SiMe$_3$)$_3$] and [U(C$_5$H$_4$^{t}Bu)$_3$] with ^{t}BuOO^{t}Bu

An NMR tube was charged with the U(III) complex (8 mg) and 0.5 equivalent of ^{t}BuOO^{t}Bu in THF-d_8 (0.3 ml). After 3 days at 50°C, the spectrum showed that [U(C$_5$H$_4$SiMe$_3$)$_3$] had been completely converted into [U(C$_5$H$_4$SiMe$_3$)$_3$(O^{t}Bu)]. ^{1}H NMR: δ −0.26 (27H, SiMe$_3$), −19.98 and −21.63 (2 × 6H, ring H) and −24.34 (9H, O^{t}Bu) ppm. Under the same conditions, 30% of [U(C$_5$H$_4$^{t}Bu)$_3$] were converted into [U(C$_5$H$_4$-^{t}Bu)$_3$(O^{t}Bu)]. ^{1}H NMR: δ 24.83 (6H, ring H), −1.26 (27H, ^{t}Bu), −5.32 (9H, O^{t}Bu) and −24.12 (6H, ring H).

5.9. Reactions of [U(C$_5$H$_4$SiMe$_3$)$_3$(H)] with ^{n}BuSH and ^{i}PrSH

An NMR tube was charged with [U(C$_5$H$_4$SiMe$_3$)$_3$(H)] (7 mg, 0.01 mmol) in toluene-d_8 (0.3 ml) and 1.0 equivalent of RSH was introduced from a microsyringe. After 24 h at 20°C, the spectrum showed that the hydride had been completely converted into the thiolate derivative.

5.10. Synthesis of the selenolate compounds [U(cp)$_3$(SeMe)] and [U(C$_5$H$_4$SiMe$_3$)$_3$(SeMe)]

(a) An NMR tube was charged with [U(cp)$_3$(THF)] (5 mg, 0.01 mmol) in THF-d_8 or toluene-d_8 (0.3 ml) and MeSeSeMe (0.5 μl, 0.005 mmol) was introduced from a microsyringe. The red solution immediately turned pink, and the spectrum revealed the formation of [U(cp)$_3$(SeMe)], which eventually separated out.

(b) A 100 ml round-bottomed flask was charged with [U(C$_5$H$_4$SiMe$_3$)$_3$] (100 mg, 0.16 mmol) in pentane (40 ml) and MeSeSeMe (15.4 mg, 0.08 mmol) was added from a syringe. The solution, which turned pink immediately, was filtered and evaporated to dryness, to give the product as a red oil (95 mg (78%)). Anal. Found: C, 40.50; H, 5.82; Se, 10.30; Si, 11.05. C$_{25}$H$_{42}$Si$_3$SeU Calc.: C, 40.37; H, 5.69; Se, 10.61; Si, 11.33%.

5.11. Reactions of [U(cp)$_3$(S^{i}Pr)]

The products [U(cp)$_3$(X)] of these reactions were identified by comparison of their NMR spectra with those of authentical samples.

(a) With I$_2$: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (10 mg, 0.02 mmol) and I$_2$ (2.5 mg, 0.01

mmol) in THF-d_8 (0.3 ml). After 5 min at 20°C, the spectrum showed that the thiolate had been completely converted into an equimolar mixture of [U(cp)$_3$(I)] [34] and ^{i}PrSS^{i}Pr.

(b) With PPh$_3$HBr: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (5 mg, 0.01 mmol) and PPh$_3$HBr (3.4 mg, 0.01 mmol) in THF-d_8 (0.3 ml). After 5 min at 20°C, the spectrum showed the presence of [U(cp)$_3$(S^{i}Pr)] and [U(cp)$_3$(Br)] [34] in a ratio of 20 : 80. A similar mixture of [U(cp)$_3$(S^{i}Pr)] and [U(cp)$_3$(Cl)] was obtained when the latter was treated with 1.0 equivalent of ^{i}PrSH.

(c) With EtOH: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (5 mg, 0.01 mmol) and EtOH (0.6 μl, 0.01 mmol) in THF-d_8 (0.3 ml). After 3 days at 20°C, the spectrum showed the presence of [U(cp)$_3$(S^{i}Pr)], [U(cp)$_3$(OEt)] and [U(cp)(OEt)$_3$] [11] in a ratio of 30 : 60 : 10.

(d) With NaBH$_4$: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (15 mg, 0.03 mmol) and NaBH$_4$ (1.2 mg, 0.03 mmol) in THF-d_8 (0.3 ml). After 5 min at 20°C, the spectrum showed that the thiolate had been completely converted into [U(cp)$_3$(BH$_4$)] [29].

(e) With CO$_2$: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (5 mg, 0.01 mmol) in THF-d_8 (0.3 ml) and filled with CO$_2$ (1 atm). After 10 min at 20°C, the spectrum showed that 20% of the thiolate compound had been converted into a new derivative, presumably [U(cp)$_3$(O$_2$CS^{i}Pr)]. ^{1}H NMR: δ −2.84 (15H, cp), −6.19 (6H, d, J = 6 Hz, CHMe_2) and −10.58 (1H, CHMe$_2$) ppm. Under vacuum the latter underwent reconversion to [U(cp)$_3$(S^{i}Pr)].

(f) With CS$_2$: an NMR tube was charged with [U(cp)$_3$(S^{i}Pr)] (5 mg, 0.01 mmol) in THF-d_8 (0.3 ml) and CS$_2$ (1.8 μl, 0.03 mmol) was introduced from a microsyringe. After 3 days at 20°C, an unidentified red powder had precipitated out, and the spectrum revealed the formation of [U(cp)$_2$(S$_2$CS^{i}Pr)$_2$]. ^{1}H NMR: δ 8.15 (10H, cp), −2.25 (12H, CHMe_2) and −4.36 (2H, CHMe$_2$) ppm.

5.12. Reduction of the complexes [U(cp)$_3$(SR)] with sodium amalgam

An NMR tube was charged with [U(cp)$_3$(SR)] (5 mg) and 2% Na(Hg) (2.0 equivalents) in THF-d_8 (0.3 ml) and was immersed in an ultrasound bath (60 W; 40 kHz). After 1 h at 20°C, the spectrum indicated quantitative formation of Na[U(cp)$_3$(SR)] (R = Me, ^{i}Pr, ^{t}Bu or Ph). The latter was immediately oxidized back to the U(IV) thiolate upon addition of TlBPh$_4$ (1.0 equivalent); a black precipitate of metallic thallium was observed.

5.13. Reactions of [U(cp)$_3$(THF)] with NaSR

An NMR tube was charged with [U(cp)$_3$(THF)] (5 mg) and NaSR (1.0 equivalent) in THF-d_8 (0.3 ml).

Table 3
Crystallographic data and details of refinement for [U(cp)$_3$(SMe)]

Crystal data	
Formula	C$_{16}$H$_{18}$SU
M	480.42
Crystal dimensions (mm)	0.70×0.25×0.20
Colour	Brown
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	15.631(4)
b (Å)	11.366(3)
c (Å)	8.275(2)
V (Å^3)	1470(1)
Z	4
D_{calc} (g cm^{-3})	2.170
μ(Mo Kα) (cm^{-1})	105.87
F(000)	888
Data collection	
θ limits (°)	1, 21
Scan type	ω−2θ
Scan width	0.8 + 0.35 tan θ
Range of absorption transmission	0.551, 0.998
Range of h, k, l	0–8, 0–11, 0–15
Number of reflections collected	
Unique	841
With $I > 3\sigma(I)$	719
Number of parameters	88
$R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$	0.025
$R_w = [\Sigma_w \| |F_o| - |F_c| \|^2 / \Sigma_w (|F_o|)^2]^{1/2}$	0.034
Maximum residual electron density (electrons Å^{-3})	0.68

After 1 h at 20°C, the spectrum revealed the quantitative formation of Na[U(cp)$_3$(SR)] (R = Me, ^{t}Bu or Ph).

5.14. Synthesis of [Na(THF)][U(cp)$_3$(S^{i}Pr)]

A 100 ml round-bottomed flask was charged with [U(cp)$_3$(THF)] (200 mg, 0.4 mmol) and NaS^{i}Pr (41 mg, 0.4 mmol) in THF (40 ml). The mixture was stirred for 1 h at 20°C and the solution then filtered. The solvent was evaporated off, to leave the product as a red

Table 4
Fractional atomic coordinates, thermal parameters and their estimated standard deviations for [U(cp)$_3$(SMe)]

	x	y	z	B_{eq}
U	0.11394(2)	0.250	0.16233(4)	1.811(9) [a]
S	−0.0583(2)	0.250	0.1796(4)	4.91(9) [a]
C(1)	−0.0863(9)	0.250	0.390(2)	5.4(4) [a]
C(2)	0.2085(7)	0.4486(8)	0.206(1)	5.1(2) [a]
C(3)	0.2140(7)	0.3892(8)	0.353(1)	4.9(2) [a]
C(4)	0.1340(6)	0.3951(8)	0.426(1)	4.2(2) [a]
C(5)	0.0796(7)	0.4581(9)	0.323(1)	4.5(2) [a]
C(6)	0.1279(6)	0.490(1)	0.189(1)	4.8(3) [a]
C(7)	0.045(1)	0.250	−0.148(1)	5.7(4) [a]
C(8)	0.0976(6)	0.152(1)	−0.138(1)	4.7(3) [a]
C(9)	0.1820(6)	0.1879(8)	−0.127(1)	4.1(2) [a]

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} a_i a_j$.

microcrystalline powder (170 mg (71%)). Anal. Found: C, 43.53; H, 4.87; S, 5.53. $C_{22}H_{30}NaOSU$ Calc.: C, 43.78; H, 5.01; S, 5.31%.

5.15. Synthesis of [Na(THF)][U(C₅H₄SiMe₃)₃(SeMe)]

A 100 ml round-bottomed flask was charged with [U(C₅H₄SiMe₃)₃(SeMe)] (64 mg, 0.09 mmol) and 2% Na(Hg) (410 mg, 0.35 mmol Na) in THF (40 ml). The mixture was stirred for 12 h at 20°C and then filtered. The solvent was evaporated from the filtrate to leave the product as a dark-red powder (35 mg (48%)). Anal. Found: C, 41.31; H, 5.90; Se, 9.25. $C_{29}H_{50}NaOSeSi_3U$ Calc.: C, 41.52; H, 6.01; Se, 9.41%.

5.16. X-ray crystal structure of [U(cp)₃(SMe)]

A selected single crystal was introduced into a thin-walled Lindeman glass tube in the glove-box. Data were collected on an Enraf–Nonius diffractometer equipped with a graphite monochromator (λ(Mo Kα) = 0.700 73 Å). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after every hour; a decay was observed (3% in 11 h) and linearly corrected. The data were corrected for Lorentz–polarization effects and absorption [35]. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method on F with anisotropic thermal parameters. The U, S, C(1) and C(7) atoms lie in the mirror plane; H atoms were not included. All calculations were performed on a Vax 4200 computer with the Enraf–Nonius MolEN system [36]. Analytical scattering factors for neutral atoms were corrected for both Δf and $\Delta f''$ components of anomalous dispersion [37]. Crystallographic data are given in Table 3 and final positional parameters in Table 4. A table of thermal parameters and a complete list of bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgment

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