ELSEVIER

Journal of Organometallic Chemistry 580 (1999) 137–144

Journal of Organometallic Chemistry

Bispentamethylcyclopentadienyl uranium(IV) thiolate compounds. Synthesis and reactions with CO_2 and CS_2

Christophe Lescop [a], Thérèse Arliguie [a], Monique Lance [b], Martine Nierlich [b], Michel Ephritikhine [a,*]

[a] *Laboratoire de Chimie de l'Uranium, Service de Chimie Moléculaire, CNRS URA 331, CEA Saclay, F-91191 Gif sur Yvette, France*
[b] *Laboratoire de Cristallochimie, Service de Chimie Moléculaire, CNRS URA 331, CEA Saclay, F-91191 Gif sur Yvette, France*

Received 1 September 1998

Abstract

The bisthiolate uranium complexes [U(Cp*)$_2$(SR)$_2$] (R = Me, ^{i}Pr, ^{t}Bu, Ph) were synthesized by treatment of [U(Cp*)$_2$(Cl)$_2$] with NaSR; the crystal structure of [U(Cp*)$_2$(SMe)$_2$] was determined. Their reactions with CO$_2$ or CS$_2$ gave the insertion derivatives [U(Cp*)$_2$(SR)(E$_2$CSR)] (E = O and R = ^{t}Bu; E = S and R = Me, ^{i}Pr or ^{t}Bu) and [U(Cp*)$_2$(E$_2$CSR)$_2$] (E = O and R = ^{t}Bu; E = S and R = Me or ^{t}Bu); [U(Cp*)$_2$(S^{t}Bu)(S$_2$CS^{t}Bu)] was characterized by its crystal structure. Treatment of this latter with CO$_2$ gave the mixed insertion complex [U(Cp*)$_2$(O$_2$CS^{t}Bu)(S$_2$CS^{t}Bu)]. Thermolysis of the insertion compounds led to the reverse elimination reaction of CO$_2$ and CS$_2$. Reduction of [U(Cp*)$_2$(O$_2$CS^{t}Bu)$_2$] with Na(Hg) afforded the corresponding U(III) anionic complex.

Keywords: Uranium(IV) thiolate compounds; Carbon dioxide; Carbon disulfide; Insertion reactions; Thiocarbonate compounds

---

1. Introduction

Uranium thiolates have been practically ignored for a long time, certainly because the U–S bond between a hard metal and a soft atom was reputed to be unstable. In fact, uranium exhibits a strong affinity for sulfur. In the organometallic series, we reported the synthesis and structure of the monocyclooctatetraenyl and triscyclopentadienyl complexes [U(COT)(SR)$_2$] (COT = η-C$_8$H$_8$) [1] and [U-(C$_5$H$_4$R')$_3$(SR)] (R' = H, ^{t}Bu, SiMe$_3$) [2]. The first studies on [U(Cp)$_3$(S^{i}Pr)] (Cp = η-C$_5$H$_5$) showed that the thiolate ligand could undergo substitution reactions and that unsaturated molecules could be inserted into the U–S bond. In particular, treatment of [U(Cp)$_3$(S^{i}Pr)] with carbon dioxide led to the formation of [U(Cp)$_3$(O$_2$CS^{i}Pr)], the first compound resulting from the insertion of CO$_2$ into a metal–sulfur bond [2]. However, this complex could not be isolated in a pure form because of the facile reverse decarboxylation reaction. With the aim of getting a better knowledge of such insertion complexes, we turned our attention to the family of bispentamethylcyclopentadienyl uranium thiolates; the [U(Cp*)$_2$(X)$_2$] compounds (Cp* = η-C$_5$Me$_5$) are regarded, for most of the X groups, as models in organouranium chemistry [3]. Here we present the synthesis and characterization of the [U(Cp*)$_2$(SR)$_2$] complexes and their CO$_2$ and CS$_2$ insertion derivatives [U(Cp*)$_2$(SR)(E$_2$CSR)], [U(Cp*)$_2$(E$_2$CS^{t}Bu)$_2$] (E = O or S) and [U(Cp*)$_2$(O$_2$CS^{t}Bu)(S$_2$CS^{t}Bu)], with the crystal structures of [U(Cp*)$_2$(SMe)$_2$] and [U(Cp*)$_2$(S^{t}Bu)(S$_2$CS^{t}Bu)]; we also describe some reactions of the insertion compounds.

---

[*] Corresponding author. Tel.: +33-1-69-08-64-36; fax: +33-1-69-08-66-40.
E-mail address: ephri@nanga.saclay.cea.fr (M. Ephritikhine)

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(98)01139-5

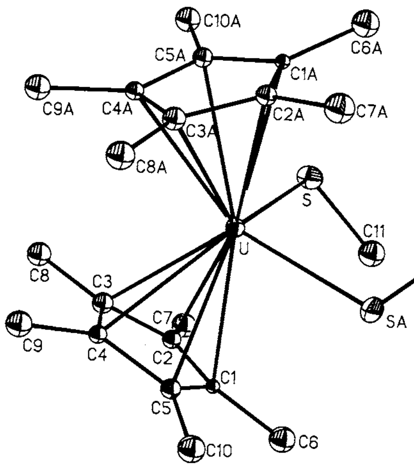


Fig. 1. X-ray crystal structure of **1a**.

2. Results and discussion

2.1. Synthesis of $[U(Cp^*)_2(SR)_2]$ 1 and the X-ray crystal structure of $[U(Cp^*)_2(SMe)_2]$

The first actinide thiolates, the homoleptic compounds $[U(SR)_4]$ (R = Et, ^{n}Bu) [4] and the organometallic derivatives $[Th(Cp^*)_2(S^nPr)_2]$ [5] and $[U(Cp)_2(S^tBu)_2]$ [6] were made by protonolysis of methyl or amide precursors with RSH. After the successful synthesis of the complexes $[U(COT)(SR)_2]$ [1] and $[U(Cp)_3(SR)]$ [2], the compounds $[U(Cp^*)_2(SR)_2]$ **1** (R = Me, **1a**; R = ^{i}Pr, **1b**; R = ^{t}Bu, **1c** and R = Ph, **1d**) were prepared by treating $[U(Cp^*)_2(Cl)_2]$ with a slight excess of the corresponding thiolate NaSR. The reactions were performed in THF or toluene and the red crystalline products were isolated in a 75–85% yield. The chlorothiolate compounds $[U(Cp^*)_2(Cl)(SR)]$, which were intermediates in the formation of **1**, could not be isolated in pure form, being in equilibrium with **1** and $[U(Cp^*)_2(Cl)_2]$. Thus, the same mixture of $[U(Cp^*)_2(Cl)(S^iPr)]$, $[U(Cp^*)_2(Cl)_2]$ and **1b** in the proportions 90:5:5 was formed either by the reaction of $[U(Cp^*)_2(Cl)_2]$ and one equivalent of NaS^{i}Pr or by comproportionation of $[U(Cp^*)_2(Cl)_2]$ and **1b** (NMR experiments).

The X-ray crystal structure of **1a** is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The U atom lies on the 2-fold axis of symmetry. The mononuclear molecule is found in the familiar pseudo tetrahedral bent sandwich configuration; the geometry of the UCp_2^* fragment is unexceptional. The U–S bond distance of 2.639(3) Å and the U–S–C(11) angle of 108.1(4)° are similar to those found in other uranium thiolates, in particular $[U(Cp)_3(SMe)]$ where U–S = 2.695(4) Å and U–S–C = 107.2(1)° [2]; in the thorium complex $[Th(Cp^*)_2(S^nBu)_2]$, these values are equal to 2.718(3) Å and 108.3(5)° [5].

2.2. Synthesis of the CO_2 and CS_2 insertion compounds. Crystal structure of $[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$

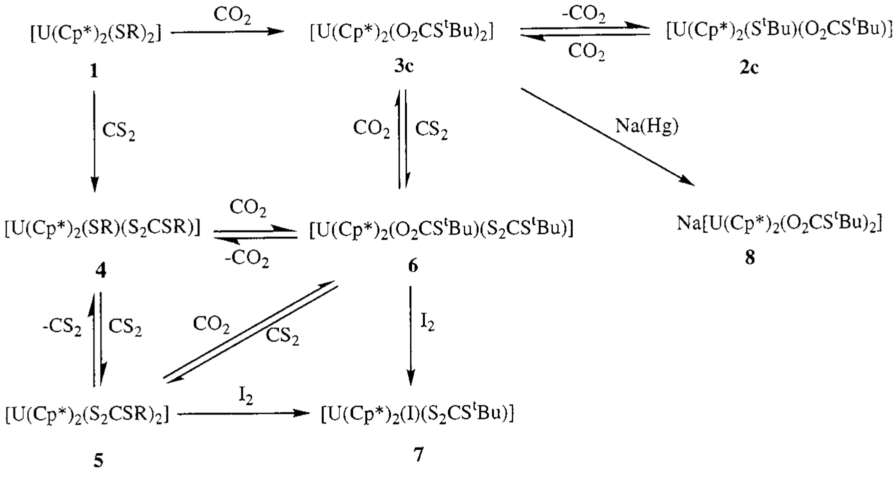
Reactions of the alkylthiolates **1** are summarized in Scheme 1. Treatment of **1a** or **1b** with CO_2 in THF (1 atm., 20°C) led to a mixture of unidentified products. On exposure to carbon dioxide, **1c** was cleanly transformed into $[U(Cp^*)_2(O_2CS^tBu)_2]$ **3c** which was obtained as a red microcrystalline powder in an almost quantitative yield, after evaporation of the THF solu-

Table 1
Selected bond distances (Å) and angles (°) with estimated standard deviations for $[U(Cp^*)_2(SMe)_2]$ **1a** and $[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**

$[U(Cp^*)_2(SMe)_2]$ **1a**					
U–S	2.639(3)	U–C(1)	2.77(1)	U–C(2)	2.71(1)
U–C(3)	2.71(1)	U–C(4)	2.73(1)	U–C(5)	2.75(1)
U–1[a]	2.47(2)	S–C(11)	1.81(1)		
S–U–1	109.9(4)	S–U–1A[b]	98.0(3)	S–U–SA	97.2(4)
1–U–1A	137.6(4)	U–S–C(11)	108.1(5)		
$[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**					
U–S(1)	2.643(4)	U–S(2)	2.885(4)	U–S(3)	2.821(5)
U–C(1)	2.74(1)	U–C(2)	2.76(2)	U–C(3)	2.75(2)
U–C(4)	2.73(2)	U–C(5)	2.72(2)	U–C(11)	2.76(2)
U–C(12)	2.78(2)	U–C(13)	2.80(2)	U–C(14)	2.71(2)
U–C(15)	2.75(1)	U–1[a]	2.47(2)	U–2[a]	2.49(2)
S(1)–C(21)	1.83(2)	S(2)–C(25)	1.66(2)	S(3)–C(25)	1.72(1)
S(4)–C(25)	1.73(2)	S(4)–C(26)	1.82(2)		
S(1)–U–S(3)	78.2(1)	S(2)–U–S(3)	62.0(1)	S(1)–U–1	101.3(2)
S(1)–U–2	101.5(3)	S(2)–U–1	95.5(2)	S(2)–U–2	92.4(1)
S(3)–U–1	108.6(3)	S(3)–U–2	115.7(3)	1–U–2	133.3(3)
U–S(1)–C(21)	139.8(2)				

[a] 1 and 2 are the centroids of the Cp rings.

[b] Symmetry code A: −x, y, −z.



Scheme 1. Formation and reactions of the CO_2 and CS_2 insertion compounds.

tion at room temperature (r.t.). To our knowledge, **3c** is the first complex isolated from the insertion of carbon dioxide into a metal–sulfur bond. In the triscyclopentadienyl series, $[U(Cp)_3(O_2CS^iPr)]$ was formed in a quantitative yield from $[U(Cp)_3(S^iPr)]$ but could not be obtained in pure crystalline form because of its easy decarboxylation at 20°C under vacuum [2]. Formation of **3c** was very rapid at 20°C, being achieved in a few minutes, and the monoinsertion compound $[U(Cp^*)_2(S^tBu)(O_2CS^tBu)]$ **2c**, which is a likely intermediate, was not observed by NMR. However, an equilibrating mixture of **2c**, **1c** and **3c** in the proportions of 80:10:10 was formed by comproportionation of **1c** and **3c** (NMR experiments).

Insertion of carbon disulfide into d-transition metal–sulfur bonds has already been reported [7]. In the case of f-element thiolates, it was found that CS_2 reacted with the homoleptic uranium thiolate $[Li(DME)]_4[U(SCH_2CH_2S)_4]$ (DME = dimethoxyethane) to give $[Li(DME)_2]_2[S_2CSCH_2CH_2SCS_2]$ as an isolable product, but it was not possible to discover whether the insertion took place at the Li–S or U–S bonds [8]. Although difficult to explain mechanistically, formation of $[U(Cp)_2(S_2CS^iPr)_2]$ by treatment of $[U(Cp)_3(S^iPr)]$ with CS_2 provided clear evidence of insertion of carbon disulfide into the U–S bond; however, the trithiocarbonate compound was not obtained in pure form [2].

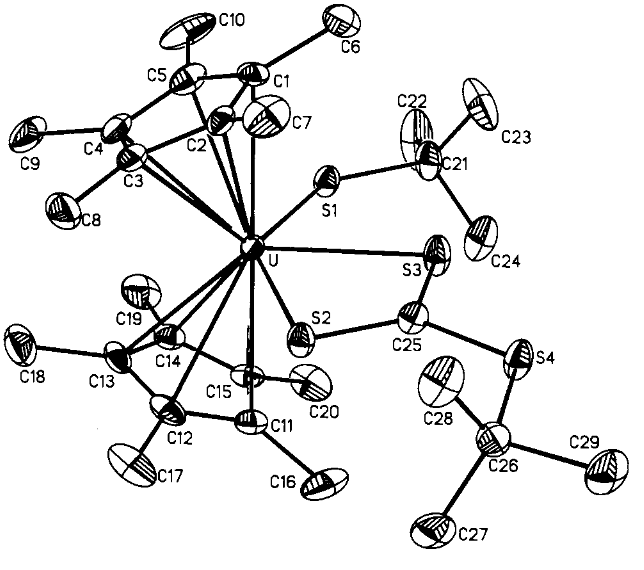


Fig. 2. X-ray crystal structure of **4c**.

Complexes **1** reacted with a slight excess of CS_2 in toluene to give the monoinsertion derivatives $[U(Cp^*)_2(SR)(S_2CSR)]$ **4**. The rate of this reaction was strongly dependent on the size of the R group: formation of **4a** (R = Me) and **4b** (R = ^{i}Pr) was achieved after a few hours at 70°C whereas synthesis of **4c** (R = ^{t}Bu) required 2 days to proceed to completion. Dark brown crystals of **4c** were isolated in an 89% yield; **4c** is the first uranium trithiocarbonate to have been crystallographically characterized (Fig. 2, Table 1). The molecule adopts the classical bent sandwich structure of the $[M(Cp^*)_2(X)_2(Y)]$ compounds. The U, C(21), C(25), S(1), S(2) and S(4) atoms are coplanar within ± 0.04 Å and this plane is almost perpendicular [91(1)°] to that defined by U and the two centroids of the Cp* rings. The U–S(1) bond distance of 2.643(4) Å is similar to those determined in other uranium thiolates whereas the U–S(2) and U–S(3) bond lengths are longer, 2.885(4) and 2.821(5) Å, respectively and can be compared with the distances of ca. 2.81 Å found in uranium dithiocarbamate complexes [9]. The C(25)–S bond lengths of the trithiocarbonate ligand are almost identical, with an average value of 1.70(4) Å, and are shorter than the C(21)–S(1) and C(26)–S(4) distances [1.83(2) and 1.82(2) Å].

Table 2
Elemental analyses of the compounds

Compound	Analyses % found (calc.)		
	C	H	S
$[U(Cp^*)_2(SMe)_2]$ **1a**	43.58 (43.84)	5.87 (6.02)	10.35 (10.64)
$[U(Cp^*)_2(S^iPr)_2]$ **1b**	47.26 (47.40)	6.87 (6.73)	9.47 (9.73)
$[U(Cp^*)_2(S^tBu)_2]$ **1c**	48.72 (48.96)	6.88 (7.04)	9.13 (9.34)
$[U(Cp^*)_2(SPh)_2]$ **1d**	52.63 (52.88)	5.43 (5.55)	8.58 (8.82)
$[U(Cp^*)_2(O_2CS^tBu)_2]$ **3c**	46.77 (46.50)	6.24 (6.24)	8.07 (8.28)
$[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**	45.38 (45.65)	6.21 (6.34)	16.64 (16.81)
$[U(Cp^*)_2(S_2CSMe)_2]$ **5a**	37.92 (38.18)	4.76 (4.81)	25.60 (25.48)
$[U(Cp^*)_2(S_2CS^tBu)_2]$ **5c**	42.61 (42.94)	5.61 (5.77)	22.83 (22.93)
$[U(Cp^*)_2(O_2CS^tBu)(S_2CS^tBu)]$ **6**	44.51 (44.65)	5.95 (6.00)	15.72 (15.89)
$[U(Cp^*)_2(I)(S_2CS^tBu)]$ **7**	37.39 (37.50)	4.79 (4.91)	11.82 (12.01)
$Na[U(Cp^*)_2(O_2CS^tBu)_2]$ **8**	45.26 (45.16)	6.22 (6.06)	7.84 (8.04)

Table 3
^{1}H-NMR spectra of the compounds[a]

Compounds	Solvent	Cp* groups[b]	SR groups
$[U(Cp^*)_2(SMe)_2]$ **1a**	Benzene d_6	10.9	−20.7 (6 H)
$[U(Cp^*)_2(S^iPr)_2]$ **1b**	Benzene d_6	11.8	−18.1 (12 H), −33.7 (2 H)
$[U(Cp^*)_2(S^tBu)_2]$ **1c**	Benzene d_6	12.2	−17.7 (18 H)
$[U(Cp^*)_2(SPh)_2]$ **1d**	Benzene d_6	13.3	1.32 (2 H, t, $J = 7$ Hz, *p*-Ph), 0.4 (4 H, *m*-Ph), −33.6 (4 H, *o*-Ph)
$[U(Cp^*)_2(Cl)(SMe)]$[c]	THF-d_8	12.25	−45.2 (3 H)
$[U(Cp^*)_2(Cl)(S^iPr)]$[c]	Benzene d_6	12.4	−23 (6 H), −61 (1 H)
$[U(Cp^*)_2(Cl)(S^tBu)]$[c]	THF-d_8	13.3	−21.7 (9 H)
$[U(Cp^*)_2(S^tBu)(O_2CS^tBu)]$ **2c**	THF-d_8	10.6	−10.3 (9 H), −12.1 (9 H)
$[U(Cp^*)_2(O_2CS^tBu)_2]$ **3c**	Benzene d_6	6.9	−4.9 (18 H)
$[U(Cp^*)_2(SMe)(S_2CSMe)]$ **4a**	THF-d_8	10.8	−1.0 (3 H), −12.2 (3 H)
$[U(Cp^*)_2(S^iPr)(S_2CS^iPr)]$ **4b**	THF-d_8	10.8	−3.7 (6 H), −7.1 (6 H) −16.8 (1 H), −21.1 (1 H)
$[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**	THF-d_8	11.7	−5.0 (9 H), −7.6 (9 H)
$[U(Cp^*)_2(S_2CSMe)_2]$ **5a**	THF-d_8	18.6	−9.5 (6 H)
$[U(Cp^*)_2(S_2CS^tBu)_2]$ **5c**	THF-d_8	17.8	−3.9 (18 H)
$[U(Cp^*)_2(O_2CS^tBu)(S_2CS^tBu)]$ **6**	THF-d_8	6.5	5.5 (9 H), −4.7 (9 H)
$[U(Cp^*)_2(I)(S_2CS^tBu)]$ **7**	THF-d_8	16.3	−9.7 (9 H)
$Na[U(Cp^*)_2(O_2CS^tBu)_2]$ **8**	THF-d_8	−5.2	−3.9 (18 H)
$[U(Cp^*)_2(I)(O_2CS^tBu)]$	THF-d_8	14.4	−12.4 (9 H)

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

[b] Integrates for 30 H.

[c] In a mixture of $[U(Cp^*)_2(Cl)_2]$ and $[U(Cp^*)_2(SR)_2]$.

Once complex **4** was formed, further insertion of CS_2 into the remaining U–S thiolate bond was rather difficult and required much more drastic conditions. The dark red bis trithiocarbonates $[U(Cp^*)_2(S_2CSMe)_2]$ **5a** and $[U(Cp^*)_2(S_2CS^tBu)_2]$ **5c** were synthesized in an 88 and 51% yield, respectively, by refluxing a CS_2 solution of **4a** for 3 days and a solution of **4c** in a 1:1 mixture of THF and CS_2 for 30 days.

Reactions of **1c** with CO_2, which gave **2c** and **3c**, thus appeared much more rapid than reactions with CS_2, leading to **4c** and **5c**. Insertion of CO_2 into the U–S thiolate bond of **4c** was also much faster than the CS_2 insertion and was complete after 30 min under normal conditions; the mixed insertion complex $[U(Cp^*)_2(O_2CS^tBu)(S_2CS^tBu)]$ **6** was isolated as a dark red powder in a 95% yield. This distinct reactivity of CO_2 and CS_2 is possibly related to the oxophilic character of uranium which would favour initial coordination of carbon dioxide onto the metal centre, before migration of the SR group [10].

2.3. Reactions of the CO_2 and CS_2 insertion compounds

The bis insertion compounds **3c** and **5c** were quite stable in solution and in the solid state at 20°C but their thermolysis led to elimination of CO_2 and CS_2. Sealed NMR tubes containing THF solutions of these compounds were heated at 65°C and after 10 h, 54% of **3c** was converted into **2c** whereas 10% of **5c** was trans-

Table 4
Crystallographic data and experimental details for $[U(Cp^*)_2(SMe)_2]$ **1a** and $[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**

	$[U(Cp^*)_2(SMe)_2]$	$[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$
Crystal data		
Empirical formula	$C_{22}H_{36}S_2U$	$C_{29}H_{48}S_4U$
M	602.69	762.99
Crystal dimensions (mm^3)	0.50 × 0.35 × 0.25	0.55 × 0.50 × 0.50
Colour	Dark red	Dark brown
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	$P2_1/n$
a (Å)	14.230(3)	12.822(4)
b (Å)	9.585(3)	16.982(3)
c (Å)	16.422(4)	15.263(4)
β (°)		102.22(5)
V (Å^3)	2240(2)	3248(3)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.787	1.56
μ(Mo–K$_\alpha$) (cm^{-1})	70.54	50.01
F(000)	1168	1512
Data collection		
Temperature (K)	213	294
θ limits (°)	1, 25	1, 22
Scan type	*ω*, 2*θ*	*ω*, 2*θ*
Scan width	0.8 + 0.35 tan *θ*	0.8 + 0.35 tan *θ*
Range of abs. trans.	0.670, 0.999	0.783, 0.999
Range of *h*, *k*, *l*	0 to 11, 0 to 17, 0 to −19	0 to 13, 0 to 17, −16 to 16
Reflections collected		
Total	2359	4585
Unique	1980	3977
with $I>3\sigma(I)$	1084	2834
Number of parameters	59	307
$R=\Sigma\Vert F_o\vert-\vert F_c\Vert/\Sigma\vert F_o\vert$	0.030	0.042
$Rw=[\Sigma w\Vert F_o\vert-\vert F_c\Vert^2/\Sigma w(\vert F_o\vert)^2]^{1/2}$	0.053	0.054
$w=1/(\sigma F)^2=4F^2/[\sigma I^2+(pF^2)^2]^{1/2}$	$w=1$	$w=1$
Max. residual electron density (e Å^{-3})	0.934	0.899

formed into **4c**; upon cooling at r.t., **3c** was entirely recovered, following re-insertion of CO_2 into the U–S bond of **2c**. From these results, it was not surprising to observe the interconversion of complexes **3c**, **5c** and **6** in the presence of an excess of CO_2 or CS_2.

Table 5
Fractional atomic coordinates, thermal parameters and their estimated standard deviations for $[U(Cp^*)_2(SMe)_2]$ **1a**

Atom	*x*	*y*	*z*	B(A2)
U	0.000	−0.18127(5)	0.250	1.702(9)*
S	−0.1389(2)	−0.3633(3)	0.2436(2)	3.16(6)*
C(1)	0.0339(7)	−0.201(1)	0.4160(6)	1.0(2)
C(2)	−0.0494(8)	−0.147(1)	0.4083(7)	1.7(2)
C(3)	−0.0522(8)	−0.013(1)	0.3752(7)	2.3(2)
C(4)	0.0440(8)	0.020(1)	0.3615(6)	1.5(2)
C(5)	0.0973(8)	−0.099(1)	0.3863(6)	2.0(2)
C(6)	0.060(1)	−0.334(1)	0.4561(8)	3.7(3)
C(7)	−0.141(1)	−0.210(1)	0.4406(9)	3.7(3)
C(8)	−0.1328(9)	0.085(1)	0.3657(7)	2.9(2)
C(9)	0.080(1)	0.161(1)	0.3383(8)	3.3(3)
C(10)	0.2021(8)	−0.103(1)	0.3886(7)	3.2(3)
C(11)	−0.113(1)	−0.504(1)	0.3136(9)	3.9(3)

* $B_{eq}=(4/3)\Sigma_i\Sigma_j\beta ij a_i a_j$.

Treatment of **4c** with 0.5 equivalents of I_2 gave the iodo-trithiocarbonate complex $[U(Cp^*)_2(I)(S_2CS^tBu)]$ **7** which was alternatively synthesized by iodonolysis of the bis insertion compound **5c**, and isolated as red microcrystals in a 82% yield. After the synthesis of $[U(Cp)_3(I)]$ from $[U(Cp)_3(S^iPr)]$ [2] and $[U(I)_2(S^iPr)_2(NC_5H_5)_3]$ from $[U(S^iPr)_4]$ [11], these reactions provide further examples of the cleavage of U–S bonds with iodine. The O_2CS^tBu ligand of the mixed insertion compound **6** was selectively displaced by I_2, giving **7**, and $[U(Cp^*)_2(I)(O_2CS^tBu)]$ was obtained from **3c** (NMR experiments).

Reduction of **4c** and **5c** by means of sodium amalgam was not straightforward, leading to the formation of unidentified products. In contrast, **3c** cleanly reacted with Na(Hg) to give the corresponding anionic U(III) complex $Na[U(Cp^*)_2(O_2CS^tBu)_2]$ **8**, which was isolated as brown microcrystals in a 65% yield.

Table 6
Fractional atomic coordinates, thermal parameters and their estimated standard deviations for $[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ **4c**

Atom	x	y	z	B(A2)*
U	0.09927(4)	0.13580(3)	0.27331(4)	2.72(1)
S(1)	−0.0275(3)	0.2546(3)	0.2915(3)	4.15(9)
S(2)	0.3197(3)	0.1053(2)	0.2699(3)	3.72(9)
S(3)	0.2458(3)	0.2612(3)	0.3143(4)	5.0(1)
S(4)	0.4647(3)	0.2477(3)	0.3000(3)	4.8(1)
C(1)	0.120(1)	0.1184(9)	0.4547(8)	3.5(4)
C(2)	0.194(1)	0.0663(9)	0.434(1)	3.8(4)
C(3)	0.138(1)	0.0048(9)	0.381(1)	4.1(4)
C(4)	0.029(1)	0.022(1)	0.373(1)	4.8(4)
C(5)	0.018(1)	0.091(1)	0.417(1)	4.8(4)
C(6)	0.150(2)	0.188(1)	0.515(1)	7.0(6)
C(7)	0.310(1)	0.064(1)	0.476(1)	6.6(6)
C(8)	0.185(2)	−0.067(1)	0.350(1)	6.2(5)
C(9)	−0.064(1)	−0.033(1)	0.337(1)	8.5(5)
C(10)	−0.083(1)	0.123(2)	0.436(1)	9.9(7)
C(11)	0.113(1)	0.141(1)	0.095(1)	4.4(4)
C(12)	0.111(1)	0.0594(9)	0.115(1)	4.2(4)
C(13)	0.010(1)	0.041(1)	0.127(1)	4.2(4)
C(14)	−0.049(1)	0.109(1)	0.121(1)	4.1(4)
C(15)	0.010(1)	0.172(1)	0.0975(9)	3.8(4)
C(16)	0.199(1)	0.186(1)	0.064(1)	7.3(6)
C(17)	0.194(2)	0.001(1)	0.104(1)	7.2(5)
C(18)	−0.030(2)	−0.043(1)	0.131(1)	8.1(7)
C(19)	−0.165(1)	0.115(1)	0.122(1)	7.8(6)
C(20)	−0.025(2)	0.252(1)	0.068(1)	8.0(6)
C(21)	−0.021(1)	0.361(1)	0.314(1)	5.6(5)
C(22)	−0.128(1)	0.392(1)	0.300(2)	10.4(9)
C(23)	0.049(2)	0.382(1)	0.394(2)	10.9(9)
C(24)	0.033(2)	0.402(1)	0.244(1)	7.8(6)
C(25)	0.345(1)	0.1995(9)	0.294(1)	3.2(3)
C(26)	0.568(1)	0.1822(9)	0.277(1)	3.8(4)
C(27)	0.538(1)	0.147(1)	0.182(1)	6.5(5)
C(28)	0.594(1)	0.117(1)	0.346(1)	6.3(5)
C(29)	0.661(1)	0.237(1)	0.285(1)	6.3(5)

* $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta ij a_i a_j$.

3. Conclusion

The synthesis of the complexes $[U(Cp^*)_2(SR)_2]$ permitted the study of the insertion reactions of CO_2 and CS_2 into the U–S bond. The thiocarboxylate products were much more stable than in the triscyclopentadienyl series and could be isolated and characterized. The crystal structure of $[U(Cp^*)_2(S^tBu)(S_2CS^tBu)]$ was determined; $[U(Cp^*)_2(O_2CS^tBu)_2]$ is the first complex isolated from the insertion of carbon dioxide into a metal–sulfur bond. Insertion of CS_2 was much slower than insertion of CO_2; both reactions were reversible.

4. Experimental

4.1. 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. Deuterated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H-NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to TMS (δ 0). Analytical and NMR data are given in Tables 2 and 3.

The commercial thiols (Aldrich and Janssen) were dried over molecular sieves. The NaSR reagents were obtained as white powders by reaction of sodium with a slight excess (1.1 equivalents) of the corresponding thiol in THF. The complex $[U(Cp^*)_2(Cl)_2]$ was prepared as described in Ref. [12].

*4.2. Synthesis of $[U(Cp^*)_2(SMe)_2]$ **1a***

A round-bottomed flask was charged with $[U(Cp^*)_2(Cl)_2]$ (662 mg, 1.14 mmol) and NaSMe (240 mg, 3.42 mmol) and toluene (50 ml) was condensed into the mixture at −78°C under vacuum. The reaction mixture was stirred for 3 days at 60°C and, after filtration, the solution was evaporated to dryness, leaving a dark red microcrystalline powder of **1a** (548 mg, 80%).

*4.3. Synthesis of $[U(Cp^*)_2(SR)_2]$ ($R = {}^iPr$, **1b**; $R = {}^tBu$, **1c**; $R = Ph$, **1d**)*

*4.3.1. **1b***

A round-bottomed flask was charged with $[U(Cp^*)_2(Cl)_2]$ (428 mg, 0.74 mmol) and NaS^iPr (145 mg, 1.48 mmol) and THF (50 ml) was condensed into the mixture at −78°C under vacuum. The reaction mixture was stirred for 10 h at 20°C. The solvent was evaporated off and **1b** was extracted in pentane (50 ml) and isolated as a dark red microcrystalline powder after drying under vacuum (386 mg, 79%).

*4.3.2. **1c***

By following the same procedure, the reaction of $[U(Cp^*)_2(Cl)_2]$ (803 mg, 1.39 mmol) and NaS^tBu (465 mg, 4.15 mmol) gave **1c** (813 mg, 85%).

*4.3.3. **1d***

By following the same procedure, the reaction of $[U(Cp^*)_2(Cl)_2]$ (503 mg, 0.87 mmol) and NaSPh (304 mg, 2.30 mmol) gave **1d** (491 mg, 78%).

The above reactions were monitored by NMR and the complexes $[U(Cp^*)_2(Cl)(SR)]$ were found to be intermediates.

4.4. Formation of [U(Cp*)$_2$(Cl)(S^{i}Pr)]

4.4.1. Procedure (a)

An NMR tube was charged with [U(Cp*)$_2$(Cl)$_2$] (14.8 mg, 25.5 μmol) and NaS^{i}Pr (2.5 mg, 25.5 μmol) in THF-d_8 (0.35 ml). After 30 min at 20°C the spectrum showed the presence of [U(Cp*)$_2$(Cl)(S^{i}Pr)], [U(Cp*)$_2$(Cl)$_2$] and **1b** in the proportions 90:5:5.

4.4.2. Procedure (b)

An NMR tube was charged with [U(Cp*)$_2$(Cl)$_2$] (4.8 mg, 8.3 μmol) and **1b** (5.5 mg, 8.3 μmol) in THF-d_8 (0.35 ml). After 30 min at 20°C the spectrum showed the presence of the same mixture as in (a).

4.5. Synthesis of [U(Cp*)$_2$(O$_2$CS^{t}Bu)$_2$] 3c

A round-bottomed flask was charged with **1c** (176.4 mg, 0.25 mmol) and THF (20 ml) was condensed into it at −78°C under vacuum; the flask was pressurised with CO$_2$ (1 atm.). The solution was stirred for 30 min at 20°C and after evaporation to dryness at 20°C, **3c** was isolated as a red–orange powder (195 mg, 98%).IR (nujol): 1311, 1162, 848 cm^{-1}.

4.6. Formation of [U(Cp*)$_2$(S^{t}Bu)(O$_2$CS^{t}Bu)] 2c

An NMR tube was charged with **1c** (7.8 mg, 11 μmol) and **3c** (8.8 mg, 11 μmol) in THF-d_8 (0.35 ml). After 30 min at 20°C, the spectrum showed the presence of **2c**, **1c** and **3c** in the proportions of 80:10:10.

4.7. Reactions of 1a and 1b with CS$_2$

An NMR tube was charged with **1a** or **1b** (ca. 10 mg) and 1.5 equivalents of CS$_2$ in toluene-d_8 (0.3 ml). After 5 h at 70°C the spectrum showed that **1a** and **1b** were completely transformed into **4a** and **4b**, respectively.

4.8. Synthesis of [U(Cp*)$_2$(S^{t}Bu)(S$_2$CS^{t}Bu)] 4c

A round-bottomed flask was charged with **1c** (607 mg, 0.88 mmol) and CS$_2$ (69 μl, 1.15 mmol) and toluene (100 ml) was condensed into the mixture at −78°C under vacuum. The mixture was stirred for 48 h at 65°C. The solution was filtered and evaporated, leaving **4c** as a dark brown microcrystalline powder (596 mg, 89%).

4.9. Synthesis of [U(Cp*)$_2$(S$_2$CSMe)$_2$] 5a and [U(Cp*)$_2$(S$_2$CS^{t}Bu)$_2$] 5c

4.9.1. 5a

A round-bottomed flask was charged with **1a** (192 mg, 0.3 mmol) in CS$_2$ (3.2 ml). After refluxing for 3 days, THF (30 ml) was added; the solution was filtered, evaporated to dryness, and the dark red microcrystalline powder of **5a** was washed with pentane (10 ml) and dried under vacuum (135 mg, 88%).

4.9.2. 5c

A round-bottomed flask was charged with **1c** (300 mg, 0.43 mmol) in a mixture of CS$_2$ (3.2 ml) and THF (4 ml). After stirring for 30 days at 65°C, THF (30 ml) was added; the solution was filtered, evaporated to dryness, and the dark brown microcrystalline powder of **5c** was washed with pentane (20 ml) and dried under vacuum (185 mg, 51%). IR (nujol): 1024, 994, 863 cm^{-1}.

4.10. Synthesis of [U(Cp*)$_2$(O$_2$CS^{t}Bu)(S$_2$CS^{t}Bu)] 6

A round-bottomed flask was charged with **4c** (209 mg, 0.27 mmol) and THF (30 ml) was condensed into the mixture at −78°C under vacuum; the flask was pressurised with CO$_2$ (1 atm). The solution was stirred for 30 min at 20°C and after evaporation to dryness, **6** was isolated as a red orange powder (210 mg, 95%).

4.11. Thermolysis of 3c and 5c

4.11.1. 3c

An NMR tube was charged with **3c** (ca. 10 mg, 13 μmol) in THF-d_8 (0.35 ml) and heated for 2 h under vigorous reflux. Immediate spectrum showed that 54% of **3c** was transformed into **2c**; upon cooling at 30°C **3c** was completely recovered.

4.11.2. 5c

An NMR tube charged with **5c** (ca. 10 mg, 12 μmol) in THF-d_8 (0.35 ml) was heated at 65°C. After 10 h, the spectrum showed that 10% of **5c** was converted into **4c**.

4.12. Interconversion of 3c, 5c and 6 in the presence of CO$_2$ or CS$_2$

4.12.1. Procedure (a)

An NMR tube was charged with **3c** (ca. 10 mg, 13 μmol) in a mixture of CS$_2$ (0.2 ml) and THF-d_8 (0.2 ml). After 10 h at 65°C, the spectrum showed the presence of **4c** (6%), **5c** (14%) and **6** (56%) plus 24% of unidentified products.

4.12.2. Procedure (b)

An NMR tube was charged with **5c** (ca. 10 mg, 12 μmol) in THF-d_8 (0.35 ml) and pressurised with CO$_2$. After 10 h at 65°C, the spectrum showed the presence of **3c** (35%) and **6** (65%).

4.13. Synthesis of [U(Cp*)$_2$(I)(S$_2$CS^{t}Bu)] **7**

A round-bottomed flask was charged with **4c** (231.7 mg, 0.30 mmol) and I_2 (39 mg, 0.15 mmol) and THF (50 ml) was condensed into it at − 78°C under vacuum. The reaction mixture was stirred for 24 h at 20°C. After filtration, the solution was evaporated to dryness and **7** was isolated as a red microcrystalline powder (209 mg, 86%).

4.14. Reactions of **3c**, **5c** and **6** with I_2

4.14.1. Reaction of **3c**

An NMR tube was charged with **3c** (6.0 mg, 7.7 μmol) and I_2 (1.0 mg, 3.9 μmol) in THF-d_8 (0.35 ml). After 1 h at 20°C, the spectrum showed that **3c** had completely transformed into [U(Cp*)$_2$(I)(O$_2$CS^{t}Bu)].

4.14.2. Reaction of **5c**

An NMR tube was charged with **5c** (8 mg, 9.5 μmol) and I_2 (1.2 mg, 4.7 μmol) in THF-d_8 (0.35 ml). After 1 h at 20°C, the spectrum showed that **7** had formed in an almost quantitative yield.

4.14.3. Reaction of **6**

An NMR tube was charged with **6** (10 mg, 12.4 μmol) and I_2 (1.6 mg, 6.3 μmol) in THF-d_8 (0.35 ml). After 1 h at 20°C, the spectrum showed that **7** had formed in an almost quantitative yield.

4.15. Synthesis of Na[U(Cp*)$_2$(O$_2$CS^{t}Bu)$_2$] **8**

A round-bottomed flask was charged with **3c** (248 mg, 0.32 mmol) and 1% Na(Hg) (375 mg, 0.32 mmol of Na) and THF was condensed into the mixture at − 78°C under vacuum. The reaction mixture was stirred for 10 h at 20°C and the solution was filtered and evaporated to dryness, leaving **8** as a dark brown microcrystalline powder (168 mg, 65%).

4.16. X-ray crystal structures of **1a** and **4c**

Crystals of **1a** and **4c** were obtained by crystallization from pentane. Selected single crystals were introduced into thin-walled Lindemann glass tubes in the glove box. Data were collected on an Enraf-Nonoius CAD-4 diffractometer equipped with a graphite monochromator [λ(Mo–K$_\alpha$) = 0.71073 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 (25% in 25 h for **1a** and 39% in 72 h for **4c**) and linearly corrected. The data were corrected for Lorentz polarization effects and absorption [13]. The structure was solved by the heavy-atom method and refined by full matrix least squares on F with anisotropic thermal parameters (U and S atoms for **1a** and all atoms for **4c**); H atoms were introduced at calculated positions (C–H = 0.95 Å, B = 6 Å^2) and constrained to ride on their parent carbon atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf–Nonius MolEN system [14]. Molecular graphics were made with the SHELXTL package [15]. Analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion [16]. Crystallographic data are given in Table 4 and final positional parameters in Tables 5 and 6.

References

[1] P.C. Leverd, T. Arliguie, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1994) 501.

[2] P.C. Leverd, M. Ephritikhine, M. Lance, J. Vigner, M. Nierlich, J. Organomet. Chem. 507 (1996) 229.

[3] F.T. Edelmann, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1995, p. 11.

[4] (a) R.G. Jones, G. Karmas, G.A. Martin, jun., H. Gilman, J. Am. Chem. Soc. 78 (1956) 4285. (b) P.C. Leverd, M. Lance, J. Vigner, M. Nierlich, M. Ephritikhine, J. Chem. Soc. Dalton Trans. (1995) 237.

[5] Z. Lin, C.P. Brock, T.J. Marks, Inorg. Chim Acta 141 (1998) 145.

[6] J.D. Jamerson, J. Takats, J. Organomet. Chem. 78 (1974) c23.

[7] I.S. Butler, A.E. Fenster, J. Organomet. Chem. 66 (1974) 161.

[8] K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, R.E. Cramer, G.J. Tagoshi, J.A. Golen, J.W. Gilje, Inorg. Chem. 29 (1990) 4928.

[9] C. Boisson, J.C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J. Organomet. Chem. 522 (1996) 249.

[10] N. Kano, N. Tokitoh, R. Okazaki, Organometallics 17 (1998) 1241.

[11] P.C. Leverd, M. Lance, J. Vigner, M. Nierlich, M. Ephritihine, J. Chem. Soc. Dalton Trans. (1995) 237.

[12] P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6650.

[13] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A24 (1968) 351.

[14] MolEN, An Interactive Structure Solution Procedure, Enraf–Nonius, Delft, 1990.

[15] SHELXTL, Version 5.03, Bruker, Madison, 1997.

[16] International Tables for X-ray Crystallography. Vol. IV, Kynoch Press, Birmingham, 1974 (present distributor: Academic Publishers, Dordrecht).