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Half-sandwich and mixed-ring uranium complexes

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Abstract

The monocyclooctatetraene uranium complex [U(COT)(I)$_2$(THF)$_2$] (COT=η-C_8H_8; THF=tetrahydrofuran), isolated from the reaction of bis(cyclooctatetraene)uranium with iodine, is a precursor for the synthesis of the alkyl derivatives [U(COT)(CH$_2$Ph)$_2$i (HMPA)$_2$], [U(COT)(CH$_2$SiMe$_3$)$_2$(HMPA)] (HMPA=hexamethyl phosphorous triamide) and [U(COT)(CH$_2$SiMe$_3$)$_3$] [Li(THF)$_3$] and of the mixed-ring compounds [U(COT)(η-C$_5$R$_5$)(I)] (R=H or Me). The last were used to prepare the amide and alkyl complexes [U(COT)(η-C$_5$H$_5$)(N{SiMe$_3$}$_2$)] and [U(COT)(η-C$_5$Me$_5$)(CH$_2$SiMe$_3$)].

Key words: Uranium; Cyclooctatetraene; Half-sandwiches; Mixed-ring complexes

1. Introduction

After the discovery in the late 1960s of bis(cyclooctatetraene)uranium and bis(cyclooctatetraene)thorium [An(COT)$_2$] (An = Th or U; COT = η-C_8H_8), which represent important milestones in organoactinide chemistry [1], many efforts were devoted to the synthesis of half-sandwich complexes of general formula [An(COT)(X)$_2$], expected to exhibit a much greater and more varied reactivity. These mono-COT actinide derivatives could undergo reactions similar to the [U(C$_5$Me$_5$)$_2$(X)$_2$] complexes, which were most useful for improving our knowledge of the fundamental and applied chemistry of the f elements [2]. The monocyclooctatetraenethorium compound [Th(COT)(Cl)$_2$(THF)$_2$] (THF = tetrahydrofuran) was obtained either by treatment of ThCl$_4$ with 1 equivalent of the cyclooctatetraene dianion or by a ligand exchange reaction between bis(cyclooctatetraene) and thorium tetrachloride [3]. The above methods are not applicable to the preparation of the analogous half-sandwich uranium compound [U(COT)(Cl)$_2$(THF)$_2$] which was isolated more recently by Streitwieser and coworkers [4], from the reaction of UCl$_4$ with cyclooctatetraene in the presence of sodium hydride. This dichloride complex has been used to synthesize the derivatives [U(COT)(acac)$_2$] (acac = $CH_3COCHCOCH_3$) [4] and [U(COT){N(SiMe$_3$)$_2$}$_2$] [5].

During the same period, alternative routes to monocyclooctatetraeneuranium complexes have been opened in our laboratory, with isolation of [U(COT)(BH$_4$)$_2$] and [U(COT)(I)$_2$(THF)$_2$] (**1**). The former, which was prepared by treatment of U(BH$_4$)$_4$ with cyclooctatetraene or bis(cyclooctatetraene)uranium [6], was transformed into the tris(borohydride) anion [U(COT)(BH$_4$)$_3$]$^-$ [7], the alkoxides [U(COT)(OR)$_2$] (R = Et, ^{i}Pr or ^{t}Bu) [7], the thiolates [U(COT)(SR)$_2$] (R = ^{n}Bu or ^{i}Pr) [8] and the mixed-ring cyclooctatetraene-cyclopentadienyl complexes [U(COT)(Cp)(BH$_4$)(L)] (Cp = η-C$_5$H$_5$; L = THF or OPPh$_3$) [6]. Here we describe the synthesis of the diiodide **1** and some of its derivatives, including alkyl and mixed-ring compounds [9]; these results emphasize the unusual reactivity of these mono-COT compounds.

2. Results and discussion

2.1. The iodide complexes

The diiodide [U(COT)(I)$_2$(THF)$_2$] (**1**) was prepared in almost quantitative yield by treating [U(COT)$_2$] with 1 equiv of iodine in tetrahydrofuran (Scheme 1). This reaction represents the first synthesis of a monocyclooctatetraeneuranium complex from bis(cycloocta-

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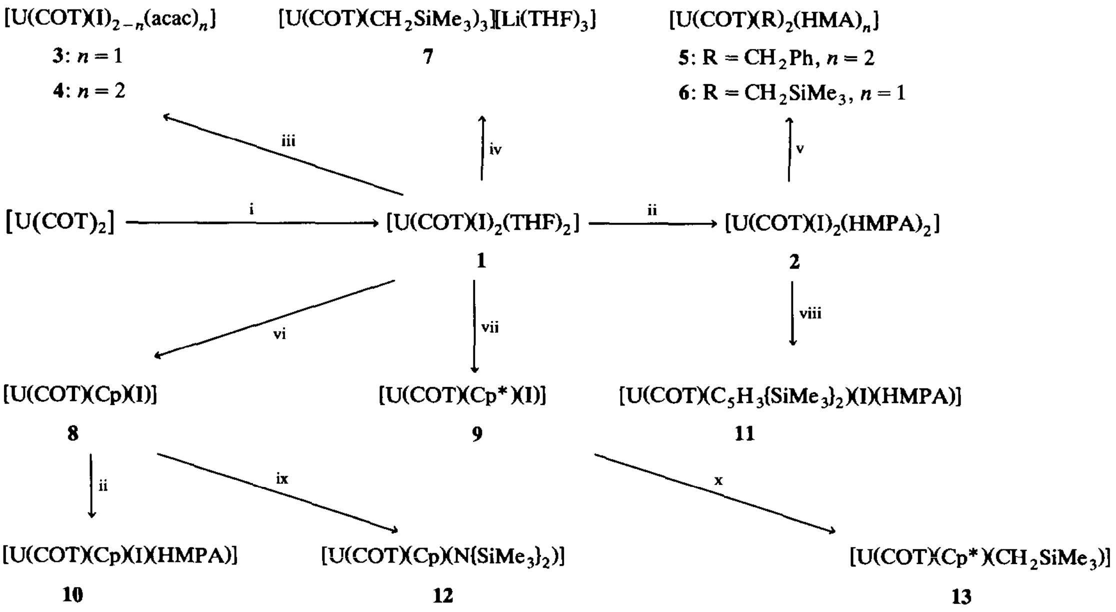

Scheme 1. Reagents and conditions: i, I_2, THF, 30 min; ii, HMPA, THF, 15 min; iii, Kacac, THF, 30 min; iv, LiCH$_2$SiMe$_3$, THF, 1.5 h; v, KCH$_2$Ph, toluene, 12 h, or LiCH$_2$SiMe$_3$, toluene, 30 min; vi, TlCp, THF, 45 min; vii, KCp*, THF, 10 h; viii, KC$_5$H$_3$(SiMe$_3$)$_2$, toluene, 1 h; ix, NaN(SiMe$_3$)$_2$, THF, 10 h; x, LiCH$_2$SiMe$_3$, THF, 10 h. All reactions at 20°C.

tetraene)uranium. However, such a displacement of COT has already been observed during the reduction of nitro compounds by [U(η-C$_8$H$_7^n$Bu)$_2$], leading to the corresponding azo products, with liberation of n-butylcyclooctatetraene [10]; it has been suggested that the oxo species [U(COT)(=O)] would be an intermediate in this transformation.

In contrast with [U(COT)(Cl)$_2$(THF)$_2$] which undergoes rapid desolvation [4,5], **1** is quite stable in the solid state and slowly loses THF in aromatic solvents. The THF of **1** can be displaced easily by stronger Lewis bases and the adducts [U(COT)(I)$_2$(THF)(HMPA)] and [U(COT)(I)$_2$(HMPA)$_2$] (**2**) were successively obtained in almost quantitative yield by treating **1** with the stoichiometric amount of hexamethyl phosphoroustriamide (HMPA) in tetrahydrofuran. By comparison with **1**, **2** is more soluble and much more stable in aromatic solvents. Such properties will be useful for the synthesis of some alkyl derivatives (see below). It is likely that the structures of **1** and **2** are similar to those of [U(COT)(Cl)$_2$(pyridine)$_2$] [4] and [Th(COT)(Cl)$_2$(THF)$_2$] [3], which adopt a four-legged piano stool configuration, with *trans* halogen atoms.

Metathesis of **1** with potassium acetylacetonate (Kacac) in THF gave the acac derivatives [U(COT)(I)(acac)] (**3**) and [U(COT)(acac)$_2$] (**4**) with 87% and 60% yields, respectively. Compound **4** was synthesized independently by Streitwieser and coworkers [4] from [U(COT)(Cl)$_2$(THF)$_2$] and was crystallographically characterized.

2.2. *The alkyl complexes*

As also observed with [U(COT)(Cl)$_2$(THF)$_2$] [4,5], treatment of **1** with 2 equivalents of alkyllithium or Grignard reagents did not produce any stable alkyl derivatives. Decomposition of the alkylation products was much more rapid with the less sterically demanding alkyl groups (Me or ^{n}Bu) and was also accelerated in non-coordinating solvents, such as toluene. When R = CH$_2$Ph or CH$_2$SiMe$_3$, the complexes [U(COT)(R)$_2$(THF)$_x$] (or the anions [U(COT)(I)(R)$_2$]$^-$) were observed by NMR spectroscopy (see experimental section), but after a few hours in THF, they were transformed into bis(cyclooctatetraene)uranium and unidentified compounds. These observations suggested that stabilization of such mono(COT)uranium alkyl complexes could be achieved by filling the coordination sphere and/or by using more robust Lewis base adducts. The more sterically saturated derivatives [U(COT)(CH$_2$Ph)$_2$(HMPA)$_2$] (**5**) and [U(COT)(CH$_2$SiMe$_3$)$_2$(HMPA)] (**6**) were synthesized in toluene from **2** and were isolated as microcrystalline powders with 38% and 46% yields respectively. However, treatment of **2** with other alkylating reagents (LiMe, Li^{n}Bu, Li^{t}Bu or Mg(allyl)Br) invariably led to the formation of bis(cyclooctatetraene)uranium.

It is known that f-element halide compounds can be transformed easily into anionic polyalkyl derivatives which are, in many cases, more stable than the corresponding neutral complexes, as a consequence of the greater steric and electronic saturation of the metallic centre [2]. In particular, reaction of [{Ln(COT)(μ-Cl)(THF)}$_2$] with LiCH(SiMe$_3$)$_2$ did not yield the neutral compound [Ln(COT)(CH{SiMe$_3$}$_2$)(THF)] but gave the anion [Ln(COT)(CH{SiMe$_3$}$_2$)$_2$]$^-$ (Ln = Y, Sm or La) [11]. In this context, it was not surprising that **1** reacted with 3 equivalents of LiCH$_2$SiMe$_3$ to afford readily the stable anionic trisalkyl complex [U(COT)(CH$_2$SiMe$_3$)$_3$] [Li(THF)$_3$] (**7**), isolated as an orange oil with 40% yield. This was also obtained by reaction of **6** with LiCH$_2$SiMe$_3$. Nevertheless, all attempts to prepare other [U(COT)(R)$_3$]$^-$ anions (R = Me, ^{n}Bu, allyl or CH$_2$Ph) were unsuccessful and, here again, led to the formation of green crystals of bis(cyclooctatetraene)uranium and unidentified products and even though the benzyl derivative was stable for several days in THF, it readily decomposed in toluene.

From the above results, it would appear that the mono(COT)uranium alkyl compounds are generally not stable towards decomposition to bis(cyclooctatetraene) uranium, since only in the case of R = CH$_2$SiMe$_3$ could complexes [U(COT)(R)$_2$(HMPA)] and [U(COT)(R)$_3$][Li(THF)$_3$] be isolated. The stabilizing effect of the polarizable α-silicon atom has been widely used and is well documented [12]. However, it is also conceivable that the lack of success in isolating these alkyl compounds is due to their mode of preparation rather than to their inherent instability. It has been demonstrated that the stable bisalkoxide complexes [U(COT)(OR)$_2$], which were easily synthesized by alcoholysis of [U(COT)(BH$_4$)$_2$] [7], could not be prepared by reaction of [U(COT)(X)$_2$(THF)$_2$] (X = Cl or I) with alkali metal alkoxide reagents [4], certainly because of rapid rearrangement of the plausible intermediates [U(COT)(X)$_2$(OR)]$^-$. Similarly, it is possible that ligand exchange reactions of the anions [U(COT)(X)$_2$(R)]$^-$ or [U(COT)(X)(R)$_2$]$^-$ prevent the synthesis of the alkyl compounds.

2.3. The mixed-ring complexes

The first-mixed ring actinide compound [Th(COT)(Cp*)(Cl)] (Cp* = η-C$_5$Me$_5$) was prepared by Sattelberger and coworkers [13] by treatment of [Th(COT)(Cl)$_2$(THF)$_2$] with the Grignard reagent Cp*MgCl · THF. Similarly, reactions of **1** with 1 equivalent of TlCp or KCp* gave [U(COT)(Cp)(I)] (**8**) and

TABLE 1. Elemental analyses

Compound	Analyses, found (calc.) (%)				
	C	H	N	I	Si
[U(COT)(I)$_2$(THF)$_2$] (**1**)	25.70	3.12		34.44	
	(25.96)	(3.26)		(34.29)	
[U(COT)(I)$_2$(HMPA)$_2$] (**2**)	24.98	4.48	8.68	26.64	
	(25.17)	(4.64)	(8.80)	(26.59)	
[U(COT)(I)(acac)] (**3**)	27.32	2.52		22.55	
	(27.48)	(2.66)		(22.53)	
[U(COT)(acac)$_2$] (**4**)	40.02	3.98			
	(40.00)	(4.10)			
[U(COT)(CH$_2$Ph)$_2$(HMPA)$_2$] (**5**)	45.97	6.48	9.30		
	(46.25)	(6.62)	(9.52)		
[U(COT)(CH$_2$SiMe$_3$)$_2$(HMPA)] (**6**)	37.74	6.81	6.06		
	(37.97)	(6.95)	(6.04)		
[U(COT)(CH$_2$SiMe$_3$)$_3$][Li(THF)$_3$] (**7**)	46.20	7.65			9.90
	(46.47)	(7.32)			(10.18)
[U(COT)(Cp)(I)] (**8**)	29.04	2.35		23.85	
	(29.23)	(2.45)		(23.75)	
[U(COT)(Cp*)(I)] (**9**)	35.54	3.67		20.94	
	(35.77)	(3.83)		(21.00)	
[U(COT)(Cp)(I)(HMPA)] (**10**)	31.75	4.39	6.03	17.64	
	(31.99)	(4.38)	(5.89)	(17.79)	
[U(COT)(C$_5$H$_3${SiMe$_3$}$_2$)(I)(HMPA)] (**11**)	35.18	5.43			6.37
	(35.00)	(5.52)			(6.55)
[U(COT)(Cp)(N{SiMe$_3$}$_2$)] (**12**)	39.85	5.28	2.35		9.64
	(40.20)	(5.50)	(2.46)		(9.89)
[U(COT)(Cp*)(CH$_2$SiMe$_3$)] (**13**)	46.60	5.86			5.06
	(46.80)	(6.07)			(4.97)

TABLE 2. ^{1}H NMR spectra of the complexes **1–13** at 30°C, in toluene d_8, except for **1–3** in THF d_8 and **7**, **11** and **13** in benzene d_6

Compound	δ [a] (ppm)	
	COT [b]	Other ligands
$[\mathrm{U(COT)(I)_2(THF)_2}]$ (**1**)	-35.43	
$[\mathrm{U(COT)(I)_2(HMPA)_2}]$ (**2**)	-32.31	5.36 (36H, d, $J = 10$ Hz, HMPA)
$[\mathrm{U(COT)(I)(acac)}]$ (**3**)	-31.37	42.84 (1H, CH); 6.30 (6H, Me)
$[\mathrm{U(COT)(acac)_2}]$ (**4**)	-29.18	10.32 (2H, CH); -9.83 (12H, Me)
$[\mathrm{U(COT)(CH_2Ph)_2(HMPA)_2}]$ (**5**)	-27.95	3.02 (4H, t, $J = 8$ Hz, *m*-Ph); 1.28 (40H, d, $J = 10$ Hz, HMPA + $\mathrm{CH_2}$); -0.62 (2H, t, $J = 8$ Hz, *p*-Ph); -8.46 (4H, d, $J = 8$ Hz, *o*-Ph)
$[\mathrm{U(COT)(CH_2SiMe_3)_2(HMPA)}]$ (**6**)	-26.57	16.57 (4H, $\mathrm{CH_2}$); -1.82 (18H, d, $J = 10$ Hz, HMPA); -5.21 (18H, $\mathrm{Me_3Si}$)
$[\mathrm{U(COT)(CH_2SiMe_3)_3}][\mathrm{Li(THF)_3}]$ (**7**)	-19.96	10.77 (12H, α-THF); 4.83 (12H, β-THF); -4.71 (27H, $\mathrm{Me_3Si}$); -26.04 (6H, $\mathrm{CH_2}$)
$[\mathrm{U(COT)(Cp)(I)}]$ (**8**)	-33.97	20.96 (5H, Cp)
$[\mathrm{U(COT)(Cp^*)(I)}]$ (**9**)	-38.50	12.08 (15H, Cp*)
$[\mathrm{U(COT)(Cp)(I)(HMPA)}]$ (**10**)	-31.36	6.03 (5H, Cp); -1.44 (18H, d, $J = 10$ Hz, HMPA)
$[\mathrm{U(COT)(C_5H_3\{SiMe_3\}_2)(I)(HMPA)}]$ (**11**)	-31.45	68.34; 55.07 and -33.97 (3 × 1H, cyclopentadienyl H); 1.23 (18H, d, $J = 10$ Hz, HMPA), -9.32 and -10.50 (2 × 9H, $\mathrm{Me_3Si}$)
$[\mathrm{U(COT)(Cp)(N\{SiMe_3\}_2)}]$ (**12**)	-34.23	-18.48 (5H, Cp); -6.75 (18H, $\mathrm{Me_3Si}$)
$[\mathrm{U(COT)(Cp^*)(CH_2SiMe_3)}]$ (**13**)	-35.07	26.60 (2H, $\mathrm{CH_2}$); 0.17 (15H, Cp*); -5.63 (9H, $\mathrm{Me_3Si}$)

[a] δ relative to tetramethylsilane (intensity, multiplicity, J or half-height width, assignment); when not specified, the signal is a singlet with $w_{1/2} = 10$–30 Hz.

[b] The COT signal integrates for 8H.

$[\mathrm{U(COT)(Cp^*)(I)}]$ (**9**) with 83% and 60% yield, respectively. Burns and coworkers [14] have recently prepared **9** by a quite different route, namely oxidation of the U(III) compound $[\mathrm{U(COT)(Cp^*)(THF)}]$, which was itself obtained by treating $[\mathrm{U(Cp^*)(I)_2(THF)_3}]$ with the potassium salt of the cyclooctatetraene dianion with iodine. The crystal structure of **9** consists of infinite chains with bridging iodide groups [14] and it is likely that **8** also adopts such a polymeric form in the solid state. Addition of HMPA to a THF solution of **8** afforded the adduct $[\mathrm{U(COT)(Cp)(I)(HMPA)}]$ (**10**), which was prepared alternatively in almost quantitative yield by reaction of **2** with TlCp. Similar treatment of **2** with $\mathrm{KC_5H_3(SiMe_3)_2}$ gave $[\mathrm{U(COT)(\eta\text{-}C_5H_3\{SiMe_3\}_2)(I)(HMPA)}]$ (**11**). These results indicate that **8** and **9** are sterically and electronically unsaturated species.

The amide complex $[\mathrm{U(COT)(Cp)(N\{SiMe_3\}_2)}]$ (**12**) was synthesized with 48% yield by treating **8** with $\mathrm{NaN(SiMe_3)_2}$. Alkyl derivatives of general formula $[\mathrm{U(COT)(Cp)(R)}]$ (R = Me, allyl, $\mathrm{CH_2Ph}$ or $\mathrm{CH_2SiMe_3}$) could not be isolated from the reactions of **8** with alkylating agents. It is possible that the addition products $[\mathrm{U(COT)(Cp)(I)(R)}]^-$ which are initially formed undergo further rearrangement into bis(cyclooctatetraene)uranium and unidentified compounds. This decomposition is also suggested by the behaviour of $[\mathrm{Th(COT)(Cp^*)(Cl)(THF)_x}]$ which did not react cleanly with alkyllithium reagents but gave the 'Grignard adduct' $[\mathrm{Th(COT)(Cp^*)(\mu\text{-}Cl)_2\,Mg(CH_2CMe_3)(THF)}]$ with $\mathrm{Me_3CCH_2MgCl}$ [13]. Metathesis of **9** with $\mathrm{LiCH_2SiMe_3}$ led to $[\mathrm{U(COT)(Cp^*)(CH_2SiMe_3)}]$ (**13**), isolated as a red powder with 52% yield.

Complexes **1–13** have been characterized by their elemental analyses (Table 1) and their ^{1}H NMR spectra (Table 2).

3. Conclusion

The syntheses of $[\mathrm{U(COT)(I)_2(THF)_2}]$, $[\mathrm{U(COT)(Cl)_2(THF)_2}]$ [4] and $[\mathrm{U(COT)(BH_4)_2}]$ [6] provide useful precursors to monocyclooctatetraene complexes of uranium. However, as observed by Streitwieser and coworkers [4], by Sattelberger and coworkers [5] and by ourselves, the formation of half-sandwich and mixed-ring derivatives from the $[\mathrm{U(COT)(X)_2}]$ and $[\mathrm{U(COT)(Cp^*)(X)}]$ is not always straightforward, in contrast with the easy preparation of triscyclopentadienyl and bispentamethylcyclopentadienyl compounds from $[\mathrm{U(cp)_3(Cl)}]$ and $[\mathrm{U(Cp^*)_2(Cl)_2}]$ [2]. It is not obvious that the lack of success in isolating a greater variety of mono(COT) or mixed-ring uranium alkyl complexes is due to their intrinsic instability. Alternative methods of preparation of these derivatives can be envisaged from other precursors. The U(III) compound $[\mathrm{U(COT)(Cp^*)}]$ [14] or the cationic complex $[\mathrm{U(COT)(Cp^*)}][\mathrm{BPh_4}]$ [15] would be good candidates.

4. Experimental details

4.1. General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (Germany). The ^{1}H NMR spectra were recorded on a Bruker W 60 (FT) spectrometer; deuterated solvents were dried over

Na–K alloy. The chemical shifts are relative to tetramethylsilane ($\delta = 0$).

All experiments were carried out under argon (less than 5 ppm O_2 and water) in Schlenk-type glassware on a high vacuum line or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and were distilled immediately before use. Kacac was prepared by treating acacH with potassium and KC_5H_3 $(SiMe_3)_2$ was isolated from the reaction of $C_5H_4(SiMe_3)_2$ (Aldrich) with KH. [U(COT)$_2$] [1], NaN(SiMe$_3$)$_2$ [16], KCH$_2$Ph [17], LiCH$_2$SiMe$_3$ [18], TlCp [19] and KCp* [20] were prepared by the published methods.

4.2. Synthesis of the monocyclooctatetraeneuranium complexes 1–4

4.2.1. [U(COT)(I)$_2$(THF)$_2$] (1)

A 100 ml round-bottomed flask was charged with [U(COT)$_2$] (1000 mg, 2.24 mmol), and THF (30 ml) was condensed into it under vacuum at −78°C. A solution of I_2 (568 mg, 2.24 mmol) in THF (20 ml) was slowly added at 20°C. The reaction mixture was stirred for 30 min and the solvent was evaporated off. The red microcrystalline powder of **1** was washed with pentane (2 × 10 ml) and dried under vacuum (1605 mg (97%)).

4.2.2. [U(COT)(I)$_2$(HMPA)$_2$] (2) and [U(COT)(I)$_2$(THF)(HMPA)]

(a) A 50 ml round-bottomed flask was charged with **1** (150 mg, 0.2 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. HMPA (72 μl, 0.4 mmol) was introduced via a gas-tight microsyringe. **Caution**: HMPA is toxic. The reaction mixture was stirred for 15 min at 20°C, the dark solution was evaporated to dryness and the residue extracted with toluene (20 ml). After evaporation, the brown–red powder of **2** was washed with pentane (2 × 10 ml) and dried under vacuum (190 mg (98%)).

(b) [U(COT)(I)$_2$(THF)(HMPA)] was obtained either from an equimolar mixture of **1** (10 mg, 13.5 μmol) and **2** (12.9 mg, 13.5 μmol) in THF-d_8 (0.4 ml) or by addition of HMPA (2.3 μl, 13.5 μmol) to a solution of **1** (10 mg, 13.5 μmol) in THF-d_8 (0.4 ml). NMR (THF-d_8, 30°C): δ − 34.05 (8H, s, COT), 13.85 (18H, d, $J = 10$ Hz, HMPA).

4.2.3. [U(COT)(I)(acac)] (3)

A 50 ml round-bottomed flask was charged with **1** (150 mg, 0.2 mmol) and Kacac (28 mg, 0.2 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 30 min at 20°C and the solvent was evaporated off. The residue was extracted with toluene (25 ml), and after evaporation, the red microcrystalline powder of **3** was washed with pentane (2 × 10 ml) and dried under vacuum (100 mg (87%)).

4.2.4. [U(COT)(acac)$_2$] (4)

A 50 ml round-bottomed flask was charged with **1** (250 mg, 0.34 mmol) and Kacac (93 mg, 0.68 mmol), and THF (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 30 min at 20°C and the solvent was evaporated off. The residue was dried under vacuum and then extracted with toluene (20 ml). The solution was filtered and reduced to about 10 ml. After slow addition of pentane (40 ml), the red microcrystalline powder of **4** which precipitated was filtered off and dried under vacuum (111 mg (61%)). Formation of [U(acac)$_4$] [21] was observed when using an excess of Kacac.

4.3. Synthesis of the mono(COT) uranium alkyl complexes

4.3.1. Reactions of 1 with 2 equivalents of KCH$_2$Ph or LiCH$_2$SiMe$_3$

An NMR tube was charged with **1** (about 10 mg) and 2 equivalents of KCH$_2$Ph or LiCH$_2$SiMe$_3$ in THF-d_8 (0.4 ml). The spectrum showed the immediate formation of [U(COT)(R)$_2$(THF)$_x$] or [U(COT)(R)$_2$(I)]$^-$. NMR (THF-d_8, 30°C): δR=CH$_2$Ph: −31.09 (8H, s, COT); −11.27 (4H, s, o-Ph); −1.94 (2H, t, $J = 8$ Hz, p-Ph); 1.7 (masked by the THF signal, m-Ph); 46.70 (4H, s, CH$_2$); R=CH$_2$SiMe$_3$: −28.21 (8H, s, COT); −1.29 (18H, s, SiMe$_3$); 39.75 (4H, s, CH$_2$). Decomposition of these products and precipitation of [U(COT)$_2$] were observed after 4–5 h at 20°C.

4.3.2. [U(COT)(CH$_2$Ph)$_2$(HMPA)$_2$](5)

A 50 ml round-bottomed flask was charged with **2** (200 mg, 0.21 mmol) and KCH$_2$Ph (54.6 mg, 0.42 mmol), and toluene (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 12 h at 20°C. The solution was filtered and evaporated to dryness. The oily residue was washed with pentane (2 × 10 ml) and was transformed into a red powder when dried under vacuum (72 mg (38%)).

4.3.3. [U(COT)(CH$_2$SiMe$_3$)$_2$(HMPA)] (6)

A 50 ml round-bottomed flask was charged with **2** (300 mg, 0.31 mmol) and LiCH$_2$SiMe$_3$ (59.2 mg, 0.62 mmol) and toluene (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 30 min at 20°C and the solvent was evaporated off. The residue was extracted with pentane (20 ml) and evaporation gave an orange microcrystalline powder. This operation was repeated three times to obtain **6** free of LiI (102 mg, (46%)).

4.3.4. Reaction of 1 with 3 equivalents of KCH_2Ph

An NMR tube was charged with **1** (10 mg, 13.5 μmol) and KCH_2Ph (5.3 mg, 40.5 μmol) in THF-d_8. The spectrum showed the immediate formation of the anion $[U(COT)(CH_2Ph)_3]^-$. NMR (THF-d_8, 30°C): δ −27.31 (8H, s, COT); −10.62 (6H, s, *o*-Ph); −10.18 (6H, s, CH_2); −1.12 (3H, t, $J = 8$ Hz, *p*-Ph); 1.6 (masked by the THF signal, *m*-Ph). The product was stable for 3 days in THF but decomposed in toluene with formation of $[U(COT)_2]$.

4.3.5. $[U(COT)(CH_2SiMe_3)_3][Li(THF)_3]$ (7)

A 50 ml round-bottomed flask was charged with **1** (150 mg, 0.20 mmol) and $LiCH_2SiMe_3$ (57.2 mg, 0.60 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 1.5 h at 20°C. The solvent was evaporated off and the oily residue was extracted with pentane (30 ml). After evaporation to dryness, **7** was obtained as an orange oil (67 mg (40%)). The complex was also formed in almost quantitative yield when **6** (10 mg, 14.3 μmol) was treated with $LiCH_2SiMe_3$ (1.3 mg, 14.3 μmol) in THF-d_8 (0.3 ml). The NMR spectrum also showed the signals corresponding to 1 equivalent of free HMPA.

4.4. Synthesis of the mixed-ring compounds

4.4.1. [U(COT)(Cp)(I)] (8)

A 50 ml round-bottomed flask was charged with **1** (500 mg, 0.67 mmol) and TlCp (182 mg, 0.67 mmol), and THF (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 45 min at 20°C. The solution was filtered and evaporated to dryness, and the red powder of **8** was washed with pentane (20 ml) and dried under vacuum (302 mg, 83%).

4.4.2. [U(COT)(Cp)(I)] (9)*

A 50 ml round-bottomed flask was charged with **1** (2000 mg, 2.7 mmol) and KCp* (520 mg, 3.0 mmol), and THF (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 10 h at 20°C. The solvent was evaporated off and the residue was extracted with toluene (25 ml). The solution was reduced to 10 ml and, after addition of pentane (25 ml), a red microcrystalline powder of **9** deposited, was filtered off and was dried under vacuum (979 mg (60%)).

4.4.3. [U(COT)(Cp)(I)(HMPA)] (10)

A 50 ml round-bottomed flask was charged with **8** (150 mg, 0.28 mmol) and HMPA (48.8 μl, 0.28 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. After 15 min at 20°C, the solvent was evaporated off and the residue extracted with toluene (10 ml). Crystals of **10** deposited upon addition of pentane (35 ml). These were filtered off and dried under vacuum (19.6 mg (98%)). Compound **10** was also formed in almost quantitative yield by treating **2** (10 mg, 10.5 μmol) with TlCp (2.8 mg, 10.5 μmol) in THF-d_8 (0.3 ml).

4.4.4. $[U(COT)(C_5H_3\{SiMe_3\}_2)(I)(HMPA)]$ (11)

A 50 ml round-bottomed flask was charged with **2** (302.4 mg, 0.32 mmol) and $KC_5H_3(SiMe_3)_2$ (79 mg, 0.32 mmol), and toluene (15 ml) was condensed into it under vacuum at −78°C. After 1 h at 20°C, the solvent was evaporated off and the residue extracted with toluene (10 ml). The brown powder of **11** which deposited upon addition of pentane (40 ml) was filtered off and dried under vacuum (121 mg (44%)).

4.4.5. $[U(COT)(Cp)(N\{SiMe_3\}_2)]$ (12)

A 50 ml round-bottomed flask was charged with **8** (200 mg, 0.37 mmol) and $NaN(SiMe_3)_2$ (68.7 mg, 0.37 mmol), and THF (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 10 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (20 ml). This operation was repeated three times to obtain an orange microcrystalline powder of **12**, free of NaI (102 mg (48%)).

4.4.6. $[U(COT)(Cp^*)(CH_2SiMe_3)]$ (13)

A 50 ml round-bottomed flask was charged with **9** (180 mg, 0.30 mmol) and $LiCH_2SiMe_3$ (28 mg, 0.30 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 10 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (20 ml); evaporation gave a red powder of **13** (86 mg (52%)).

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