

Uranium complexes with amide, alkoxide and thiolate ligands

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Abstract

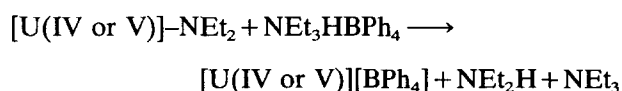
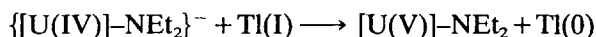
Alkoxide, hydroxide and μ -oxo complexes of U(IV) have been synthesized by (a) the reaction of alcohols, ketones and water with hydride or borohydride derivatives, (b) the coupling reaction of ketones with UCl_4 in the presence of sodium amalgam; (c) the reduction of CO_2 by $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$ or $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{H}]$; (d) the deoxygenation of CO by $[\text{U}(\text{C}_5\text{H}_5)_3\text{R}]$ complexes; and (e) condensation reactions of alkoxide and hydroxide compounds. Thiolate complexes were made by the treatment of uranium borohydride or hydride compounds with thiols. The reaction of UCl_4 with NaSR reagents afforded the homoleptic thiolate complexes $[(\text{THF})_3\text{Na}(\mu\text{-SR})_3\text{U}(\mu\text{-SR})_3\text{Na}(\text{THF})_3]$. Amide compounds, including U(V) derivatives, were prepared from $\text{U}(\text{NEt}_2)_4$.

1. Introduction

1956 is a crucial date in the history of uranium chemistry, since the first organo-metallic complex $[\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}]$ was synthesized then by Reynolds and Wilkinson [1], as were the first amide, alkoxide and thiolate compounds $\text{U}(\text{NEt}_2)_4$, $\text{U}(\text{OR})_4$ ($\text{R} \equiv \text{Me}, \text{Et}, t\text{-Bu}$) and $\text{U}(\text{SR})_4$ ($\text{R} \equiv \text{Et}, n\text{-Bu}$) by Gilman and coworkers [2]. These complexes do not seem to have attracted immediate attention and efforts to investigate them met with different amounts of success. The chemistry of the amide complexes has been developed regularly since the 1970s [3], whereas it is only during the last decade that our knowledge of the preparation, structure and reactions of the alkoxide compounds has been much improved [4]. In comparison with the NR_2 and OR groups, the SR ligand has been practically ignored in actinide chemistry.

2. Amide complexes

The new reactions depicted as follows represent efficient and convenient syntheses of pentavalent and cationic uranium complexes [5]:



At present, the only organo-uranium complexes in the +5 oxidation state are the imide derivatives $[\text{U}(\text{C}_5\text{H}_4\text{Me})_3(\text{NR})]$ ($\text{R} \equiv \text{SiMe}_3, \text{Ph}$), which were syn-

thesized by the oxidation of the trivalent compounds $[\text{U}(\text{C}_5\text{H}_4\text{Me})_3(\text{THF})]$ (THF, tetrahydrofuran) with the organic azide RN_3 [6]. However, the number of organo-actinide cations is rather limited and these have been prepared so far either by heterolytic cleavage of a metal-halogen bond or by protonolysis of a metal-carbon bond [7].

The treatment of $\text{U}(\text{NEt}_2)_4$ with $\text{NEt}_3\text{HBPh}_4$ in THF readily afforded $[\text{U}(\text{NEt}_2)_3(\text{THF})_3][\text{BPh}_4]$ (Fig. 1), which adopts a facial octahedral configuration in its crystalline form. This monocation was transformed into the dication $[\text{U}(\text{NEt}_2)_2(\text{THF})_3][\text{BPh}_4]_2$ using the same procedure. The addition of LiNEt_2 to $\text{U}(\text{NEt}_2)_4$ gave the anionic compound $[\text{Li}(\text{THF})][\text{U}(\text{NEt}_2)_5]$ and this, by treatment with TIBPh_4 , was oxidized into the pentavalent amide complex $[\text{U}(\text{NEt}_2)_5]$.

The same chemistry was applied to the monocyclo-octatetraenyl compound $[\text{U}(\text{COT})(\text{NEt}_2)_2]$ (Fig. 2), which was synthesized by treating UCl_4 with LiNEt_2 and K_2COT (COT, $\eta\text{-C}_8\text{H}_8$). The neutral compound $[\text{U}(\text{COT})(\text{NEt}_2)_3]$ is the first organo-uranium(V) complex to have been obtained from a tetravalent derivative, and $[\text{U}(\text{COT})(\text{NEt}_2)_2(\text{THF})][\text{BPh}_4]$ is the first organo-metallic cation of uranium in the +5 oxidation state.

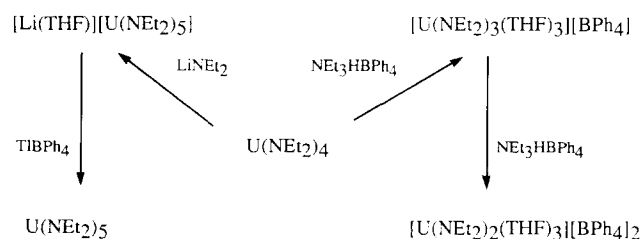
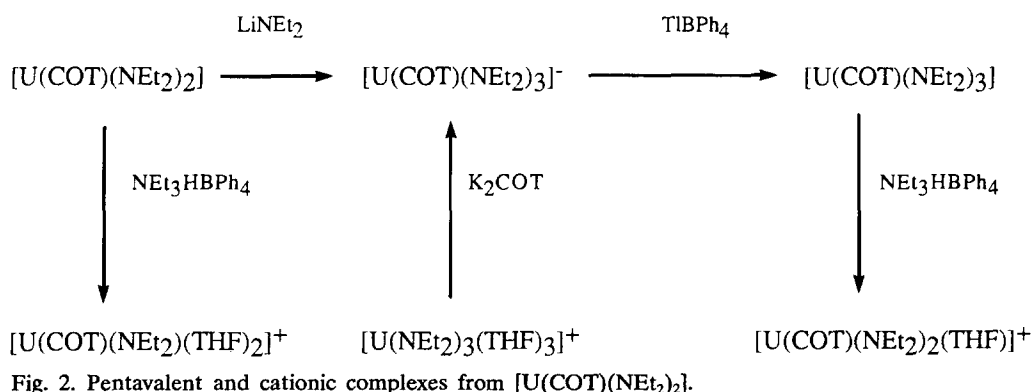
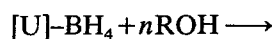


Fig. 1. Pentavalent and cationic complexes from $\text{U}(\text{NEt}_2)_4$.

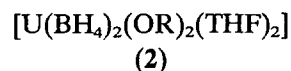
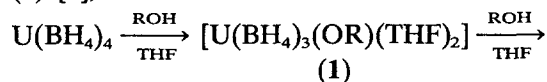


2. Alkoxide, hydroxide and μ -oxo complexes

Alcoholysis of uranium borohydrides constitutes a general route to alkoxide complexes, which can be depicted by



Thus, the treatment of $\text{U}(\text{BH}_4)_4$ with alcohols afforded successively the mono and bisalkoxide compounds $[\text{U}(\text{BH}_4)_3(\text{OR})(\text{THF})_2]$ (1) and $[\text{U}(\text{BH}_4)_2(\text{OR})_2(\text{THF})_2]$ (2) [8], *i.e.*



where $\text{R} \equiv \text{Et}$, *i*-Pr, *t*-Bu, *c*-C₆H₁₁, Ph₂CH.

Of special interest is the product $[\text{U}(\text{BH}_4)_3(\text{OC}-t\text{-Bu}_3)(\text{THF})]$ isolated from the reaction with tertibutyl methanol [9], which adopts a trigonal bipyramidal structure (Fig. 3(B)). The *t*-Bu₃CO group, called "tritox" by Wolczanski and coworkers [10], is a steric mimic of the ubiquitous cyclopentadienyl ligand (cp), while rendering the metal centre more electrophilic. This monotritox compound is very stable in coordinating solvents, whereas the tetrahedral complex $[\text{U}(\text{cp})(\text{BH}_4)_3]$ (see Fig. 3(A)) undergoes rapid rearrangement in the presence of such Lewis bases [11]. In contrast, the borohydride and chloride groups have similar cone angles, but chloride is less electron donating than BH_4 , and the species $[\text{U}(\text{cp})\text{Cl}_3]$ can be isolated

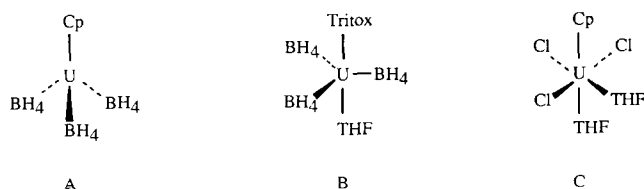


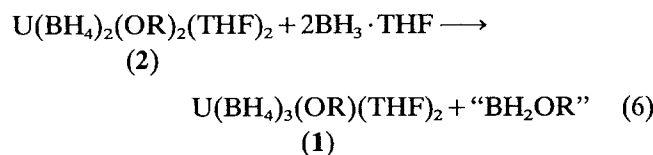
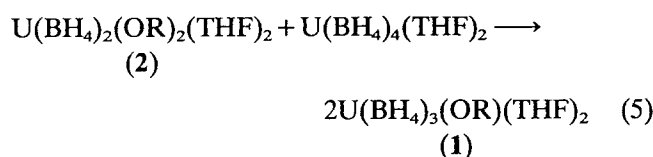
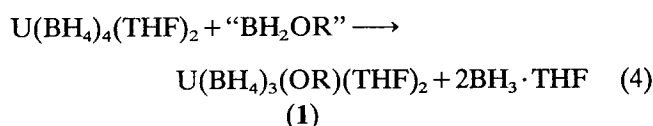
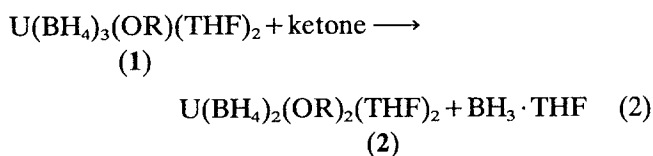
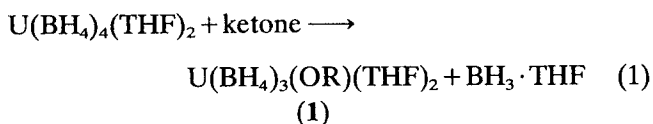
Fig. 3. Coordination chemistry of the isosteric units $[\text{U}(\text{cp})(\text{BH}_4)_3]$, $[\text{U}(\text{tritox})(\text{BH}_4)_3]$ and $[\text{U}(\text{cp})\text{Cl}_3]$.

only in the form of octahedral bis adducts (Fig 3(C)) with oxygen or nitrogen donor ligands [12].

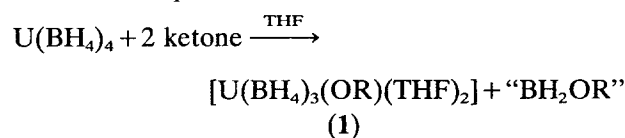
The coordination geometry of the complexes in Fig. 3 is clearly not determined by steric factors and can be accounted for by the distinct electron-donating ability of the ligands, with the electron richness of the isosteric units following the order $[\text{U}(\text{cp})(\text{BH}_4)_3] > [\text{U}(\text{tritox})(\text{BH}_4)_3] > [\text{U}(\text{cp})\text{Cl}_3]$. These results indicate that, contrary to accepted ideas, steric parameters are not the unique factors which must be considered to explain and predict the structure and stability of actinide compounds [13]. It is evident that the electron density on the metal plays a determining role and should not exceed an upper limit. An important consequence of this result is that synthesis of sterically unsaturated species should be favoured by the use of electron-donating ligands. It is also noteworthy that $[\text{U}(\text{C}_4\text{Me}_4\text{P})_3\text{X}]$ complexes were easily prepared, whereas no $[\text{U}(\text{C}_5\text{Me}_5)_3\text{X}]$ compound has been isolated so far. The tetramethylphosphoryl and pentamethylcyclopentadienyl ligands are isosteric but $\text{C}_4\text{Me}_4\text{P}$ is much less electron donating than C_5Me_5 ; therefore, the trispentamethylcyclopentadienyl actinide complexes should be difficult to synthesize, not because they are sterically saturated but because they are too electron rich [14].

In comparison with the metathesis reaction of uranium chlorides with LiOR or NaOR reagents, the alcoholysis of uranium borohydrides has the advantage of avoiding the formation of "double alkoxide" salts. For example, the monocyclooctatetraenyl alkoxides $[\text{U}(\text{COT})(\text{OR})_2]$, which could not be prepared from $[\text{U}(\text{COT})\text{Cl}_2]$ [15], were obtained by alcoholysis of $[\text{U}(\text{COT})(\text{BH}_4)_2]$, by the intermediacy of the mixed alkoxyborohydrides $[\text{U}(\text{COT})(\text{BH}_4)(\text{OR})]$ [16].

Reactions of ketones with uranium borohydrides also provide an efficient synthesis of alkoxide derivatives [8], and the alkoxyborohydride compounds 1 and 2 were prepared in this way from $\text{U}(\text{BH}_4)_4$. The mechanism of these reactions is rather complicated and can be described by six competitive elemental steps:



The feasibility of each independent process has been demonstrated by separate experiments. According to the overall equation



the reaction of two equivalents of 2-methylcyclohexanone, 4-tertbutylcyclohexanone or norcamphor with $\text{U}(\text{BH}_4)_4$ gave an equimolar mixture of complexes 1 and alkoxyborane species “ BH_2OR ”. These two products have been separated and, after hydrolysis, afforded the corresponding epimeric alcohols in different proportions. Similar results were obtained when the uranium tetraborohydride was replaced by a 1:4 mixture of UCl_4 and LiBH_4 . The reduction of ketones by such a combination of LiBH_4 or NaBH_4 with a transition metal compound is obviously one of the most important transformations in organic synthesis [17], and these results clearly show that these complex mixtures contain a number of active species which may react with their own selectivity. In many cases, the stereoselectivity of the reduction of ketones by means of a complex reducing reagent is determined after hydrolysis of the crude reaction mixture; in fact, this stereoselectivity should be the result of several independent processes.

A second example of the formation of uranium alkoxides from ketones is provided by the reaction of

benzophenone with UCl_4 in the presence of sodium amalgam, which gives the uranium pinacolates $(\text{Ph}_4\text{C}_2\text{O}_2)\text{UCl}_2$ and $(\text{Ph}_4\text{C}_2\text{O}_2)_2\text{U}(\text{THF})_2$ [18]. Hydrolysis of these complexes gave benzopinacol and their treatment with $\text{Na}(\text{Hg})$ afforded tetraphenylethylene. Thus, for the first time, metallapinacols were shown to be intermediates in the reductive coupling of ketones into α diols or alkenes – a useful reaction which is generally mediated by low-valent titanium species (McMurry alkene synthesis [19]).

The complexes $[\text{U}(\text{C}_5\text{H}_4\text{R})_3\text{H}]$ ($\text{R} \equiv \text{SiMe}_3$, **3**, *t*-Bu), which are unique examples of stable U(IV) hydrides [20], were transformed into the isopropoxide derivative $[\text{U}(\text{C}_5\text{H}_4\text{R})_3(\text{O}-i\text{-Pr})]$ by treatment with isopropanol or acetone (Fig. 4) [21]. More interesting is the reaction of **3** with CO_2 , which afforded the monodentate formate complex **4**. This insertion reaction is classical, and is considered as a first, crucial step in the catalytic reduction of CO_2 . It was proposed that this reduction should involve a binuclear species with an O-CH₂-O bridge, resulting from the addition of a metal hydride to the metalloformate complex which is initially formed. Indeed, such a reaction between **3** and **4** afforded the dioxymethylene complex **5**.

The uranium hydrides **3** were also useful in preparing the first organo-actinide hydroxide complexes $[\text{U}(\text{C}_5\text{H}_4\text{R})_3\text{OH}]$ ($\text{R} \equiv \text{SiMe}_3$, **7**, *t*-Bu) [22]. The oxo-bridged complex **6** was readily obtained by oxidation of the triscyclopentadienyl compound $[\text{U}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$ with CO_2 or nitrous oxide [23]. The two reactions of CO_2 described in Fig. 4 represent the first examples of the reduction of this molecule by f element complexes. Compound **6** was formed when **7** was heated in toluene in the presence of **3**; such a reaction between a metal hydride and a metal hydroxide is, to our knowledge, unprecedented. The trinuclear complex **8** was synthesized from **7** by thermolysis or treatment with sodium hydride.

The trinuclear compound $[\{\text{U}(\text{C}_5\text{H}_4-t\text{-Bu})_2(\mu\text{-O})\}_3]$ was obtained by rearrangement in THF of the acyl derivative $[\text{U}(\text{C}_5\text{H}_4-t\text{-Bu})_3(\text{COMe})]$, which also gave a mixture of meta- and para-tertbutyl toluene. More generally, transformation of the η^2 acyl complexes $[\text{U}(\text{cp})_3(\text{COR})]$ afforded the alkyl benzene molecules $\text{C}_6\text{H}_5\text{R}$, via deoxygenation of the acyl ligand and ring enlargement of a cyclopentadienyl ligand [24].

3. Thiolate complexes

The homoleptic U(IV) thiolates $[\text{U}(\text{Set})_4]$ and $[\text{U}(\text{S}-n\text{-Bu})_4]$, which are insoluble in common organic solvents, were not well characterized [2]. These complexes were found to form adducts with strong Lewis bases [25]; in particular, the *trans* octahedral compound

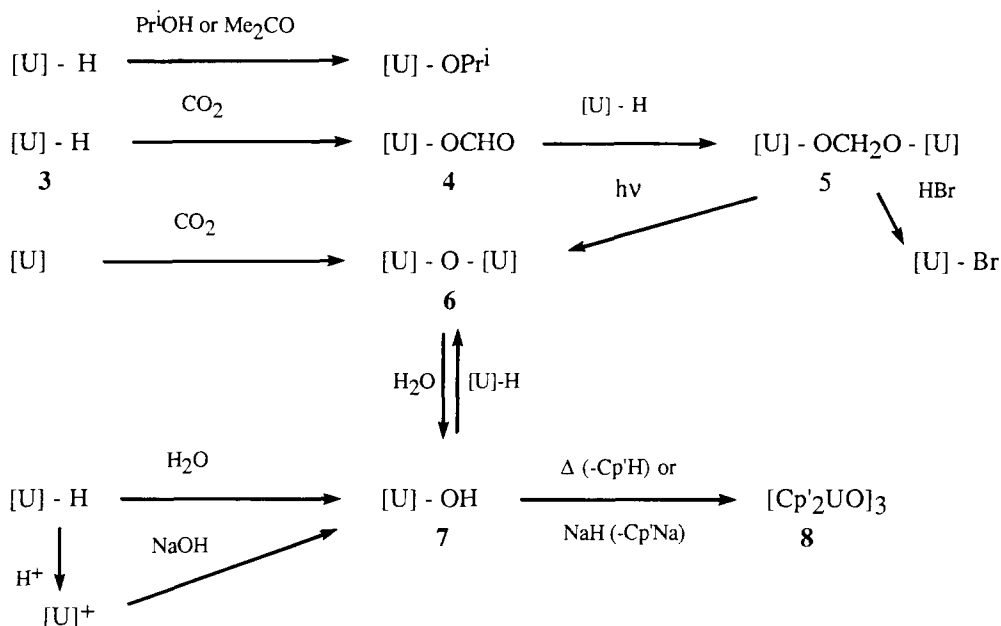


Fig. 4. Cyclopentadienyl U(IV) alkoxides, hydroxide and oxide complexes, where $[U] \equiv (C_5H_4SiMe_3)_3U$.

$[U(S-i-Pr)_4(HMPA)_2]$ (HMPA, hexamethylphosphoramide) is the first U(IV) tetrathiolate to have been crystallographically characterized. Attempts to prepare $[U(S-t-Bu)_4]$ in a manner identical to that of $[U(S-n-Bu)_4]$, by the reaction of $U(NEt_2)_4$ with $t-BuSH$, led to the trinuclear compound $[U_3(\mu_3-S)(\mu_3-S-t-Bu)(\mu_2-S-t-Bu)_3(S-t-Bu)_6]$, which is the first U-S cluster. The reaction of uranium tetrachloride with 6 equivalents of NaSR reagents ($R \equiv n-Bu, i-Pr, t-Bu, Ph$) in THF afforded the hexathiolate compounds $[(THF)_3Na(\mu-SR)_3U(\mu-SR)_3Na(THF)_3]$ [26].

These reactions of UCl_4 with NaSR reagents, leading to anionic thiolate complexes [27], are in contrast to those with NaOR reagents, which give neutral tetraalkoxide compounds. This difference suggests that a $[U]-SR$ entity, being less electron rich than its alkoxide analogue, would have a tendency to increase the charge density around the metal by forming the anion $[U](SR)_2^-$. That a thiolate ligand is less electron donating than an alkoxide group was indicated by the reduction potentials of the compounds $[U(cp)_3(O-i-Pr)]$ and $[U(cp)_3(S-i-Pr)]$. $[Na(THF)][U(cp)_3(S-i-Pr)]$ is a unique example of a U(III) thiolate complex.

A further illustration of the distinct structural features between analogous thiolate and alkoxide uranium complexes is provided by the dimeric monocyclooctatetraenyl compounds $\{[U(COT)(O-i-Pr)(\mu-O-i-Pr)]_2\}$ and $\{[U(COT)(\mu-S-i-Pr)_2]_2\}$, which are respectively bridged by two O- $i-Pr$ and four S- $i-Pr$ groups [28].

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