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Synthesis and reactions of U(III) complexes with tripodal nitrogen and oxygen donor ligands

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Abstract

Reaction of $UI_3(THF)_4$ (where THF is tetrahydrofuran) with sodium or potassium hydrotris(3,5-dimethylpyrazolyl)borate ligand ($(HBpz_3{}^{*})^-$) in 1:1 and 1:2 ratios gives the corresponding $U(HBpz_3{}^*)I_2(THF)_2$ (**1**) and $U(HBpz_3{}^*)_2I$ (**2**) complexes in excellent yields. Iodide abstraction from **2** with $TlBPh_4$ results in the formation of the cationic complex $[U(HBpz_3{}^*)_2(THF)]BPh_4$ (**3**). The solid state structures of **1**, **2** and **3** have been determined. Similar reactions with the anionic tripodal oxygen donor ligand $[(\eta^5-C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$ (L_{OEt}) proceeded via oxidation of U^{3+} to U^{4+} and fragmentation of the ligand. The structures of some key compounds were established by X-ray crystallography. $U(HBpz_3{}^*)I_2(THF)_2$ readily reacts with two equivalents of KH_2Bpz (pz ≡ pyrazolyl) to give $U(HBpz_3{}^*)(H_2Bpz_2)_2$, but attempted substitution with other ligands led to mixtures or, in one case, displacement of the $(HBpz_3{}^*)^-$ ligand.

1. Introduction

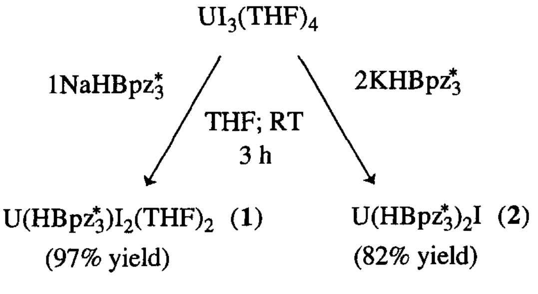
The organo-metallic chemistry of the actinide metals is dominated by complexes containing the ubiquitous cyclopentadienyl and modified cyclopentadienyl ligand systems, although the use of alternative ligands has recently been receiving increased attention [1]. As a result of the large size of the metal ions, it is not surprising that the bulky pentamethylcyclopentadienyl (C_5Me_5) and related $SiMe_3$ substituted ligands provide some of the highest coordinative unsaturation and, hence, high and unusual reactivity for the complexes formed.

The hydrotris(pyrazolyl)borates ($HBpz_3{}^-$, where pz is unsubstituted and substituted pyrazole; "Trofimenko's ligands" [2]) offer attractive alternatives. By virtue of the wide range of available substituents, these allow for fine tuning the steric size of the ligands and thereby the coordination environment of the metal center. Since Bagnall first reported an actinide polypyrazolylborate complex [3], we have joined the quest [4] and, in particular, the group of Pires de Matos has recently made numerous interesting discoveries [5]. The attention of the research has largely focused on the +4 oxidation state. With the disclosure of a convenient preparation of $UI_3(THF)_4$ (where THF is tetrahydrofuran) [6], it is time to begin exploring the polypyrazolylborate chemistry of low valent uranium.

The reactions between $UI_3(THF)_4$ and Na/KHB(3,5-$Me_2pz)_3$ (Na/$KHBpz_3{}^*$) in various ratios have been carried out. To compare the behavior of a related tripodal oxygen donor ligand, the analogous reactions with $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$ (L_{OEt}, "Kläui's ligand") [7] were also investigated. Early results on the derivative, substitution chemistry are also presented [8]. U(III) pyrazolylborate complexes and their chemistry are also being studied by Santos [8].

2. Reactions with $MHBpz_3{}^*$ (M ≡ Na, K)

The reactions proceed readily at room temperature. Depending on the reaction stoichiometry, eqn. (1).



(1)

1:1 and 1:2 complexes are obtained as dark-blue crystals in excellent yield following routine work up.

The structures of both complexes **1** and **2** have been determined by X-ray crystallography [9]. Compound **1**

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contains an η^3-HBpz$_3$* ligand; the uranium center is seven coordinated; and the coordination geometry is best described as distorted capped octahedral, similar to the structure of U(HBpz$_3$*)Cl$_3$(THF) [10]. The structure of **2** is highly unusual, in that it contains an η^3-HBpz$_3$* and an η^2-HBpz$_3$* ligand in addition to the U–I covalent bond. However, the η^2-HBpz$_3$* ligand is also involved in unprecedented, secondary π-type interactions with the uranium center. The ^{1}H NMR (nuclear magnetic resonance) spectra of the complexes are deceptively simple, and indicate a fluxional solution behavior.

The congested nature of complex **2** is shown by the facility of iodide abstraction from it. The result is the cationic compound given by

$$\mathrm{U(HBpz_3^*)_2I} \xrightarrow[\mathrm{THF;\ RT}]{\mathrm{TlBPh_4}} [\mathrm{U(HBpz_3^*)_2(THF)]BPh_4} + \mathrm{TlI} \quad (2)$$

(**3**) (turquoise crystals; 65% yield)

It is interesting to note that I$^-$ abstraction is accompanied by the recoordination of nitrogen, both HBpz$_3$* ligands becoming η^3 bonded, and the coordination of a THF molecule.

3. Reactions with Kläui's ligand

Reactions of UI$_3$(THF)$_4$ with (L$_{\mathrm{OEt}}$)$^-$ proved complicated. No pure compounds could be isolated from the 1:1 reaction. The crude reaction product from the 1:2 reaction displayed a complex ^{1}H NMR spectrum, indicating either a mixture of products or a compound with a low degree of molecular symmetry. Furthermore, the reactions were accompanied by a color change from the deep blue of UI$_3$(THF)$_4$ to green, possibly indicating an oxidation to U^{4+}. Since the conversion of **2** to the cationic complex **3** occurred readily, we reasoned that similar iodide abstraction would allow for easier isolation of a cationic "U-Kläui" complex, and perhaps shed light on the course of the above-mentioned reactions. The reaction

$$\mathrm{UI_3(THF)_4} \xrightarrow[\mathrm{(2)\ 1TlBPh_4}]{\mathrm{(1)\ 2NaL_{OEt}}} [\mathrm{U(L_{OEt})_2(THF)_2](BPh_4)_2} + \ldots \quad (3)$$

(**4**)

was carried out in toluene and gave grass-green crystals of **4** in a 28% yield. The ^{1}H NMR spectrum of **4** was simple but revealed the presence of two BPh$_4^-$ anions per uranium. The X-ray structure corroborated the formulation [11], so establishing that these reactions are accompanied by the oxidation of U^{3+} to U^{4+}.

Re-examination of the 1:2 reactions showed that the product formation depends on whether the hydrated or anhydrous Kläui's ligand is used:

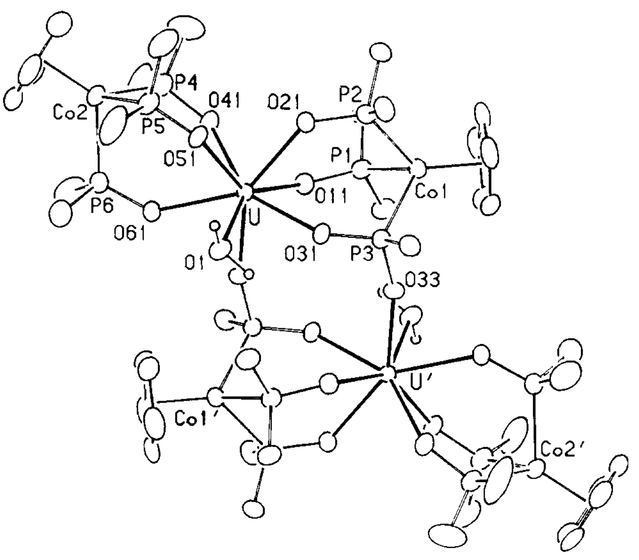

Fig. 1. A schematic view of the dimeric compound **5**.

$$\mathrm{UI_3(THF)_4} \xrightarrow[\mathrm{THF;\ RT}]{\mathrm{2NaL_{OEt}\cdot H_2O}} [\mathrm{(L_{OEt})U[CpCo\{P(O)(OEt)_2\}_2} \times \mathrm{\{P(=O)(OEt)(O)\}](H_2O)]_2I_2} + \ldots \quad (4)$$

(**5**) (green crystals; 31% yield)

$$\mathrm{UI_3(THF)_4} \xrightarrow[\mathrm{THF;\ RT}]{\mathrm{2NaL_{OEt}}} \underset{(\mathbf{6})}{\mathrm{U(L_{OEt})_2I_2}} + \underset{(\mathbf{7})}{\mathrm{U(L_{OEt})_2(OEt)I}} + \ldots \quad (5)$$

A schematic view of the dimeric compound **5** is shown in Fig. 1. Dealkylation of L$_{\mathrm{OEt}}$ and the formation of a Y dimer was seen by Nolan [12], but that reaction is not accompanied by redox behavior. Cleavage of the P–OEt bonds and the formation of compound **7** is more unusual.

In view of the ready oxidation of U(III) by Kläui's ligand, the effect of the donor atom (N *vs.* O) on the behavior of U(III) could not be assessed.

4. Derivative chemistry of compounds 1 and 2

Although complex **1** reacts readily and cleanly with two equivalents of KH$_2$Bpz$_2$ to give U(HBpz$_3$*)(H$_2$Bpz$_2$)$_2$, the reaction with the bidentate ligand Kdpm (dpm = *t*-BuC(O)CHC(O)-*t*-Bu, dipyvaloylmethanide) proceeds with displacement of the pyrazolylborate ligand as well, and yields U(dpm)$_3$. Reactions of **1** and **2** with other potential ligands (c.f. alkoxide) have so far led to products which are difficult to characterize. The discovery of suitable synthetic strategies is a major challenge in this area.

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