Journal of Organometallic Chemistry xxx (2017) 1–4

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Promoting oxo functionalization in the uranyl ion by ligation to ketimides

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ARTICLE INFO

Article history:
Received 11 July 2017
Received in revised form
13 August 2017
Accepted 14 August 2017
Available online xxx

Dedicated to William J. Evans on the occasion of his 70th birthday.

Keywords:
Actinide
Uranyl
Ketimide
Oxo functionalization
Lithium

ABSTRACT

Reaction of $[UO_2Cl_2(THF)_2]_2$ with 8 equiv of $Li(N{=}C^tBuPh)$ or 6 equiv of $Li(N{=}C^tBu_2)$ affords the uranyl ketimide complexes, $[Li(THF)(Et_2O)]_2[UO_2(N{=}C^tBuPh)_4]$ (**1**) and $[Li(THF)(TMEDA)][UO_2(N{=}C^tBu_2)_3]$ (**2**), respectively. Complexes **1** and **2** have been fully characterized, including analysis by X-ray crystallography. Most importantly, both complexes feature dative interactions between their lithium counterions and the uranyl oxo ligands. These interactions are likely a consequence of their weaker UO bonds, which are caused by electrostatic repulsion between the anionic N donor atom of the strongly electron donating ketimide ligand and the oxo ligand of the uranyl fragment.

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1. Introduction

Uranyl (UO_2^{2+}) is the most ubiquitous fragment in actinide chemistry [1–3]. Yet, despite this ubiquity, uranyl complexes containing classic organometallic ligands, such as amide and alkyl, are still relatively rare. For example, only a handful of uranyl complexes with direct uranium-carbon bonds have been reported [4–12], including $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ [4], reported by us in 2013, and $Cp^*UO_2(^{Mes}PDI^{Me})$, reported by Bart and co-workers in 2015 [5]. Likewise, amide complexes of uranyl are also rare [13–18]. Notable examples include $[K(toluene)_2][UO_2(NAr^FPh)_4]$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) [14], which was reported by Schelter and co-workers in 2014, and the uranyl piperidide complex, $[\{Li(DME)\}_2Cl][Li(DME)][UO_2(NC_5H_{10})_3]_2$ [13], which was reported by us in 2010.

The rarity of uranyl complexes featuring these ligands can be partly ascribed to the highly reducing nature of these ligand types, which can result in facile reduction of the U(VI) center [19–23]. Intriguingly, these complexes also often feature weaker U=O bonds than typical uranyl complexes, on account of the electrostatic repulsion between the anionic donor atom (e.g., C, N) and the O^{2-} ligand [2,24,25]. As a result of this weakening, the uranyl oxo ligands in uranyl alkyl and amide complexes feature enhanced nucleophilicity, which can result in formation of dative interactions between the uranyl oxo ligands and alkali metals [2,4,13], as is found in the solid-state structures of $[\{Li(DME)\}_2Cl][Li(DME)][UO_2(NC_5H_{10})_3]_2$ and $[Li(DME)_{1.5}]_2[UO_2(CH_2SiMe_3)_4]$ [4,13].

In an effort to expand the chemistry of the uranyl ion bound to "organometallic-type" ligands we endeavoured to ligate the ketimide ligand, $[N{=}CR_2]^-$, to the uranyl fragment. Ketimides are known for their ability to stabilize high oxidation states in the d block metals, e.g., Mn(IV), Fe(IV) and Co(IV) [26–29]. Ketimides can also stabilize high oxidation states in the f elements. For example, our group reported the syntheses of the homoleptic U(VI) ketimide, $U(N{=}C^tBuPh)_6$, and the homoleptic U(V) ketimide, $U(N{=}C^tBu_2)_5$ [30,31], while Kiplinger and co-workers reported the synthesis of U(V) ketimide, $Cp^*_2U(NAr)(N{=}CPh_2)$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) [32]. Most importantly, the ketimide ligand is known to be strongly electron donating, and is comparable to the amide ligand in donating ability [33]. Accordingly, it should impart increased nucleophilicity to the uranyl oxo ligands. Herein, we reported the synthesis and structural characterization of the first uranyl ketimide complexes, $[Li(THF)(Et_2O)]_2[UO_2(N{=}C^tBuPh)_4]$ and $[Li(THF)(TMEDA)][UO_2(N{=}C^tBu_2)_3]$. Significantly, we observe

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http://dx.doi.org/10.1016/j.jorganchem.2017.08.007
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Please cite this article in press as: L.A. Seaman, et al., Journal of Organometallic Chemistry (2017), http://dx.doi.org/10.1016/j.jorganchem.2017.08.007

evidence for a marked increase in uranyl oxo ligand nucleophilicity in these complexes, as evidenced by formation of dative interactions between their lithium counterions and the uranyl oxo ligands.

2. Results and discussion

Addition of 8 equiv of Li(N=C^{t}BuPh) to a THF solution of $[UO_2Cl_2(THF)_2]_2$ affords the uranyl ketimide complex, [Li(THF)(Et$_2$O)]$_2$[UO$_2$(N=C^{t}BuPh)$_4$] (**1**), which can be isolated dark red crystalline solid in 58% yield after work-up (Scheme 1). Complex **1** is highly soluble in Et$_2$O, THF, and aromatic solvents. Its ^{1}H NMR spectrum in C_6D_6 exhibits resonances at 7.47 ppm, 7.20 ppm, and 7.04 ppm assignable to the *ortho*, *meta*, and *para* protons of the phenyl ring, respectively. Additionally, a resonance at 1.52 ppm is assignable to the methyl protons of the ^{t}Bu groups. Complex **1** exhibits a single resonance at 1.31 ppm in its ^{7}Li{^{1}H} NMR spectrum, while its ^{13}C{^{1}H} NMR spectrum exhibits a resonance at 175.7 ppm, corresponding to the N=C carbon of the ketimide ligand. This resonance is in-line with those reported for other metal ketimide complexes [34].

Complex **1** crystallizes in the monoclinic space group, $P2_1/c$, as a Et$_2$O solvate, **1**·0.5C$_4$H$_{10}$O (Fig. 1). Complex **1**·0.5C$_4$H$_{10}$O exhibits an octahedral geometry about the uranium center, and features four ketimide ligands within the equatorial plane. Two of these ligands are bound only to uranium, while two are bound to uranium and lithium. Each lithium cation is also coordinated by a uranyl oxo ligand, a THF molecule, and a Et$_2$O molecule, in an overall pseudotetrahedral arrangement. The U-N distance for the terminal ketimide ligands (2.230(5) Å) is significantly shorter than those of the bridging ketimide ligands (2.416(5) Å), but is comparable to the U-N distances found in uranyl amide complexes (ca. 2.25 Å) [13]. Notably, though, this distance is longer than those observed for the homoleptic U(VI) ketimide, U(N=C^{t}BuPh)$_6$ (ca. 2.17 Å) [30]. The U=O bond length (1.838(4) Å) is slightly longer than those normally observed for uranyl [1], but it is similar to those reported for the uranyl amide complex, [{Li(DME)}$_2$Cl][Li(DME)][UO$_2$(NC$_5$H$_{10}$)$_3$]$_2$ (1.827(5) Å and 1.847(5) Å) [13], as well as the uranyl alkyl complex, [Li(DME)$_{1.5}$]$_2$[UO$_2$(CH$_2$SiMe$_3$)$_4$] (1.885(4) Å) [4]. The lengthening of the U=O distance in **1** is due, in part, to the coordination of the strongly electron-donating ketimide ligand to the uranyl equatorial plane, which weakens the U=O bond. This interaction also enhances the oxo ligand basicity [2,24,25]. In this regard, the Li-O distance (1.97(1) Å) is within the range of those observed previously for other U^{VI}=O···Li interactions [2,4,35,36]. Finally, the U-N-C bond angle of the terminal ketimide ligands (175.3(5)°) is suggestive of sp hybridization at nitrogen, and may indicate some amount of π-donation to the uranium center [26,28,29,33].

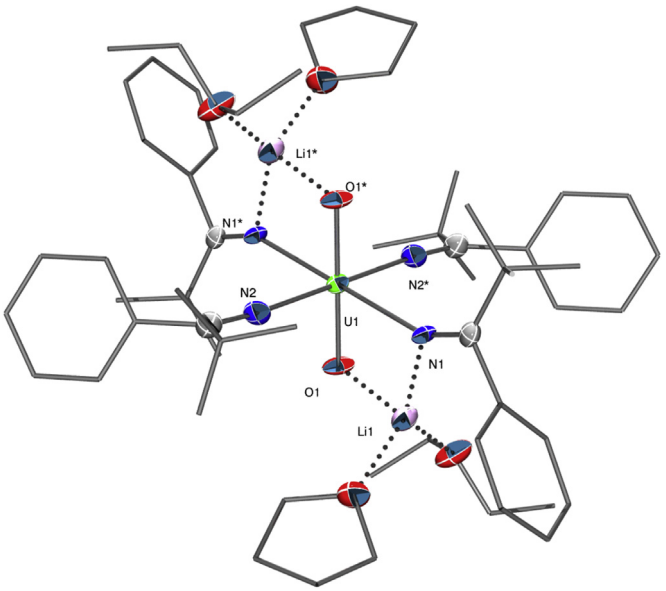
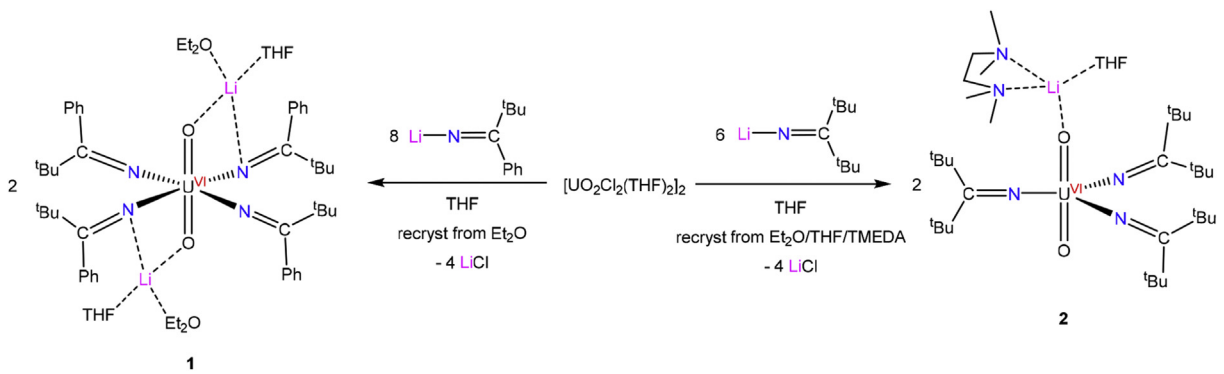


Fig. 1. ORTEP diagram of [Li(THF)(Et$_2$O)]$_2$[UO$_2$(N=C^{t}BuPh)$_4$]·0.5C$_4$H$_{10}$O (**1**·0.5C$_4$H$_{10}$O), shown with 50% ellipsoids. Carbon atoms (with the exception of the N=C carbons) shown in wire frame. Selected bond lengths (Å) and angles (deg): U1-N1 = 2.416(5), U1-N2 = 2.230(5), U1-O1 = 1.838(4), O1-Li1 = 1.97(1), O1-U1-O1* = 180, U1-N1-C1 = 153.5(5), U1-N2-C12 = 175.3(5).

Addition of 6 equiv of Li(N=C^{t}Bu$_2$) to $[UO_2Cl_2(THF)_2]_2$ in THF affords the uranyl ketimide complex, [Li(THF)(TMEDA)][UO$_2$(N=C^{t}Bu$_2$)$_3$] (**2**), which can be isolated as a dark brown crystalline solid in 16% yield after work-up (Scheme 1). We attribute the low yield of **2** to the challenge of cleanly separating it from the LiCl by-product, as they have similar solubilities. Note that complex **2** is formed even upon addition of 8 equiv of Li(N=C^{t}Bu$_2$) to $[UO_2Cl_2(THF)_2]_2$. The inability to coordinate four [N=C^{t}Bu$_2$]$^-$ ligands to the uranium center in this case is likely a consequence of its increased steric bulk relative to [N=C^{t}BuPh]$^-$.

Complex **2** is insoluble in hexane, very slightly soluble in toluene and Et$_2$O, and highly soluble in THF. Its ^{1}H NMR spectrum in THF-d_8 exhibits a singlet at 1.43 ppm corresponding to the CH$_3$ groups of the ketimide ligand, while its ^{7}Li{^{1}H} NMR spectrum features a single resonance at −1.98 ppm. Additionally, its ^{13}C{^{1}H} NMR spectrum in THF-d_8 features a resonance at 176.9 ppm, which is assignable to the N=C carbon of the ketimide ligand. This chemical shift is essentially identical to that observed for complex **1**.

Complex **2** crystallizes in the monoclinic space group $P2_1/n$, as the THF solvate, **2**·THF, and its solid-state molecular structure is



Scheme 1.

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