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Communications

Uncommon η^3-(*N*,*C*,*C*′)-1-Azaallyl Bonding Mode for the Nacnac Ligand: A Bis(β-diketiminato)uranium(III) Iodide Complex

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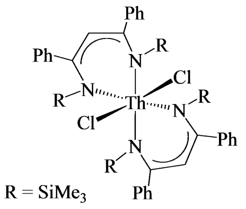
Summary: The reaction between 2 equiv of K(Nacnac) (Nacnac$^-$ *=* *[Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-*$^{i}Pr_2C_6H_3$*) and* $UI_3(THF)_4$ *in toluene affords* $(Nacnac)_2UI$ *(**4**), which features a β-diketiminate ligand bound to uranium(III) in an unusual* η^3*-(N,C,C′)-1-azaallyl mode and possesses close U···*C_{alkene} *contacts.*

β-Diketiminato ligands have found increasing utility as ancillary ligands for organometallic and nonaqueous coordination chemistry of main-group, d-block, and lanthanide metals.[1] Sterically encumbered ligands of this type have been shown to encourage low coordination numbers in transition-metal complexes and, therefore, have been used to prepare a variety of coordinatively and electronically unsaturated reactive compounds, polymerization catalysts, and structural models for the active sites in metalloproteins.[1] In contrast to the large number of transition-metal and lanthanide β-diketiminate complexes, only two β-diketiminato actinide derivatives have been reported: the thorium dichloride complex $(Nacnac)_2ThCl_2$ (**1**)[2] and the interesting mixed-valence $[\{U^{VI}\}_2][U^{III}]_2$ salt **2**,[3] prepared from the reaction of $ThCl_4$ and UCl_4 with Li(Nacnac) ($Nacnac^-$ = $[SiMe_3]NC(Ph)CHC(Ph)N[SiMe_3]$), respectively.



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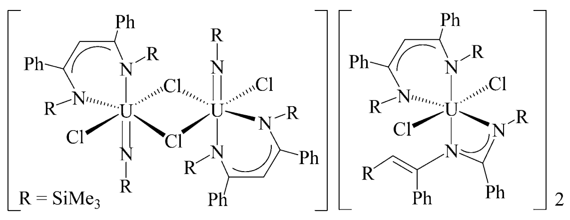

2

Since the β-diketiminate ligand basically combines the steric bulk and multihapticity of a cyclopentadienyl ligand and the "hardness" of an amide or alkoxide ligand, we rationalized that the appropriately tailored "Nacnac" ligand may serve as an excellent scaffold for

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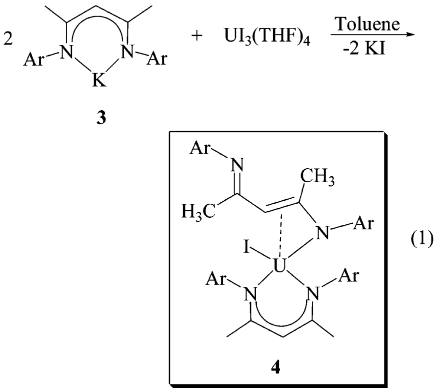
the stabilization of coordinatively unsaturated uranium(III) complexes. Herein we report a synthetic methodology, which accesses the first neutral, monometallic β-diketiminatouranium complex. This molecule features a β-diketiminate ligand bound to uranium(III) in an unusual η^3-(N,C,C')-1-azaallyl mode.

As illustrated in eq 1, reaction of $UI_3(THF)_4$[4] with 2 equiv of the sterically demanding K(Nacnac) (Nacnac$^-$ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-$^iPr_2C_6H_3$) (**3**)[5] in toluene solution at ambient temperature affords the bis(β-diketiminato)uranium(III) complex **4** as a dark blue crystalline solid in 42% isolated yield.[6] The ^1H NMR data are in accord with the compound's formulation as a monomeric uranium(III) derivative with two different β-diketiminate ligand environments.



(1)

The identity of complex **4** as a bis(β-diketiminato)uranium(III) iodide complex was confirmed by a single-crystal X-ray diffraction study (Figure 1).[7] The molecular structure of **4** reveals a six-coordinate uranium complex having C_1 symmetry with the metal bound to two β-diketiminate ligands and an iodide. One of the β-diketiminate ligands is coordinated to the metal center in a typical N,N′-chelating fashion; the uranium−nitrogen distances (U(1)−N(1) = 2.362(4) Å, U(1)−N(2) = 2.379(4) Å) and bite angle of 82.65(14)° compare favorably with those observed for the uranium β-diketiminate complex **2**.[3]

Perusal of the uranium to ligand atom contacts (bonding distances to N(1) and N(2) and nonbonding distances to the three carbon atoms; $U-C_{av}$ = 3.101(5) Å) suggests that the ligand is symmetrically disposed about the uranium metal center; additionally, the five ligand atoms are virtually coplanar and the uranium metal dips out (~1.4 Å) of the plane defined by the N(1)−C(1)−C(2)−C(3)−N(2) atoms of the ligand backbone, possibly due to unfavorable steric interactions between the aryl isopropyl groups on the ligand and the other substituents on the metal.[8]

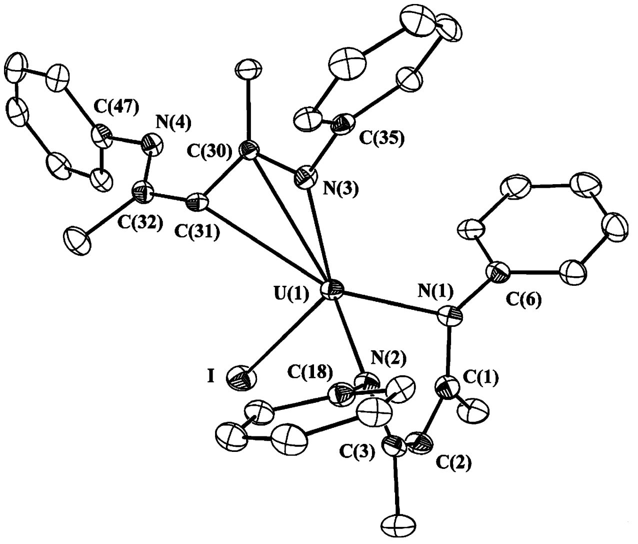


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and ^iPr groups on the β-diketiminate ligands have been removed for clarity. Selected bond distances (Å) and angles (deg): U(1)−N(1), 2.362(4); U(1)−N(2), 2.379(4); U(1)−N(3), 2.387(4); U(1)−C(30), 2.928(4); U(1)−C(31), 2.891(4); U(1)−I, 3.0665(8); N(1)−C(1), 1.349(7); N(2)−C(3), 1.341(7); C(1)−C(2), 1.399(8); C(2)−C(3), 1.413(7); N(3)−C(30), 1.372(6); C(30)−C(31), 1.385(7); C(31)−C(32), 1.452(7); C(32)−N(4), 1.297(7); N(1)−U(1)−N(2), 82.65(14); N(3)−U(1)−C(31), 51.52(13); N(3)−C(30)−C(31), 116.0(4); C(30)−U(1)−C(31), 27.53(13).

The most striking aspect of the structure is the second β-diketiminate ligand, which is bound to the uranium metal center in an unusual η^3-(N,C,C′) fashion.[9] This may be a result of unfavorable steric interactions at the metal center; however, electronic factors cannot be ruled out. The U(1)−N(3) bond distance of 2.387(4) Å is comparable to the other U−N(diketiminate) bond distances. The N(3)−C(30) (1.372(6) Å) and C(30)−C(31) (1.385(7) Å) fragments have bond lengths typical for N−C(sp^2) and C═C bonds.[10] These metrical parameters coupled with the acute C(31)−U(1)−N(3) bite angle of 51.52(13)° are consistent with the formulation of the ligand as a 1-azaallyl functional group.[2,11] To the best of our knowledge, there are no structurally characterized examples of uranium 1-azaallyl complexes and only one thorium 1-azaallyl derivative has been reported.[2]

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(1) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3065 and references therein.

(2) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Tian, S. *J. Organomet. Chem.* **1997**, *536−537*, 473−480.

(3) Hitchcock, P. B.; Lappert, M. F.; Liu, D. S. *J. Organomet. Chem.* **1995**, *488*, 241−248.

(4) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248−2256.

(5) Clegg, W.; Cope, E. K.; Edwards, A. J.; Mair, F. S. *Inorg. Chem.* **1998**, *37*, 2317−2319.

(6) In an inert-atmosphere (nitrogen) drybox, a 125 mL Erlenmeyer flask equipped with a stir bar was charged with K(Nacnac) (**3**;[5] 0.421 g, 0.917 mmol), $UI_3(THF)_4$[4] (0.411 g, 0.452 mmol), and toluene (20 mL). The resultant dark blue reaction mixture was stirred at ambient temperature for 16 h and filtered through a Celite-padded coarse frit. The filtrate was collected, and the volatiles were removed under reduced pressure to give crude **4** as a dark blue solid. Analytically pure samples of **4** were obtained by recrystallization from a concentrated hexanes solution at −30 °C (0.225 g, 0.187 mmol, 42%). Mp: 156.0−156.6 °C. Anal. Calcd for $C_{64}H_{96}IN_4U$ (mol wt 1286.38): C, 59.76; H, 7.30; N, 4.36. Found: C, 59.68; H, 7.52; N, 4.14.

(7) Crystal data for a dark blue crystal of **4**: $C_{64}H_{96}N_4IU$, M_r = 1286.38, triclinic, $P\bar{1}$, Z = 2, a = 12.225(3) Å, b = 14.361(3) Å, c = 19.449(5) Å, α = 71.585(4)°, β = 75.007(5)°, γ = 83.868(4)°, V = 3128.3(13) $Å^3$, T = 203(2) K, $R(I > 2\sigma)$ = 0.0470, and GOF = 1.323.

(8) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533−2544.

(9) There is one report of a bimetallic tris(β-diketiminato)barium complex that features a delocalized η^3-(N,C,C')-1-azaallyl bonding interaction between a barium metal center and a β-diketiminate ligand: Clegg, W.; Coles, S. J.; Cope, E. K.; Mair, F. S. *Angew. Chem., Int. Ed.* **1998**, *37*, 796−798.

(10) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(11) Cui, C.; Hao, H.; Noltemeyer, M.; Schmidt, H. G.; Roesky, H. W. *Polyhedron* **2000**, *19*, 471−474 and references therein.

The electrophilic nature of the low-coordinate uranium(III) center is reflected in the structure of **4** by the close U⋯C_{alkene} contacts of 2.928(4) and 2.891(4) Å. In addition, the U−I distance of 3.0665(8) Å is considerably shorter than those observed for other uranium(III) iodide complexes (3.103(2)−3.267(10) Å).[4,12] The U⋯C_{alkene} interactions fall within the sum of the van der Waals radii of the two atoms and suggest that complex **4** is a rare example of a crystallographically characterized uranium(III)−alkene π-complex.[13] The U⋯C_{alkene} distances are ca. 0.4 Å longer than the U−C bond lengths (2.48(2) Å) reported for the only structurally characterized uranium(III) alkyl complex, U[CH$(SiMe_3)_2]_3$;[14] however, they are well within the range of the U⋯C contacts reported for other monometallic uranium(III)−arene π-complexes (∼2.85−2.97 Å).[15]

In summary, we have shown that voluminous β-diketiminate ligands can support a low-coordinate uranium(III) complex. In this case, a β-diketiminate ligand is bound to the uranium metal center in a rare η^3-(N,C,C')-1-azaallyl fashion. The close U⋯C_{alkene} contacts observed are consistent with the formulation of this complex as a uranium(III)−alkene π-complex. We are currently exploring the chemistry of complex **4** and developing the chemistry of other actinide β-diketiminate complexes.

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Supporting Information Available: Tables with bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structure of **4**; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] For example, see the following: (a) $[UI_2\{H(\mu\text{-}H)B(3\text{-}^tBu\text{-}5\text{-}Me\text{-}pz)_2\}(THF)_2]$, U−I = 3.104(2), 3.131(2) Å: Maria, L.; Campello, M. P.; Domingos, A.; Santos, I.; Andersen, R. *J. Chem. Soc., Dalton Trans.* **1999**, 2015−2020. (b) $(C_5Me_5)UI_2(THF)_3$, U−I = 3.161(1), 3.162(1) Å, and $(C_5Me_5)UI_2(py)_3$, U−I = 3.182(4) Å: Avens, L. R.; Burns, C. J.; Butcher, R. J.; Clark, D. L.; Gordon, J. C.; Schake, A. R.; Scott, B. L.; Watkin, J. G.; Zwick, B. D. *Organometallics* **2000**, *19*, 451−457. (c) $UI_3(bipy)_2(py)$, U−I_{av} = 3.22(3) Å: Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. *Inorg. Chem.* **2001**, *40*, 4428−4435. (d) U(tpza)-I_3(MeCN), U−I = 3.1632(10)−3.2637(10) Å: Mazzanti, M.; Wietzke, R.; Pécaut, J.; Latour, J. M.; Maldivi, P.; Remy, M. *Inorg. Chem.* **2002**, *41*, 2389−2399.

[13] For a Th(IV) example, see: Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549−561.

[14] Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. *Organometallics* **1989**, *8*, 855−857.

[15] For example: (a) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439−444. (b) Cotton, F. A.; Schwotzer, W. *Organometallics* **1987**, *6*, 1275−1280. (c) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 155−162. (d) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836−5837. (e) Evans, W. J.; Nyce, G. W.; Forrestal, K. J.; Ziller, J. W. *Organometallics* **2002**, *21*, 1050−1055.