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# Backbonding in Thorium(IV) and Uranium(IV) Diarsenido Complexes with <sup>t</sup>BuNC and CO

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**Abstract:** The coordination of <sup>t</sup>BuNC and CO with the diarsenido complexes, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), An = Th, U, has been investigated. For the first time, a comparison between isostructural complexes of Th(IV) and U(IV) has been possible with CO, indicating an appreciable amount of π backbonding which originates from charge transfer from an actinide-arsenic sigma bond according to density functional calculations. The calculated CO stretching frequencies in the Th(IV) and U(IV) diarsenido complexes are consistent with the experimental measurements, both with large red shifts. We demonstrate that the π backbonding is crucial in explaining the red shifts of CO frequency upon An(IV) complex formation. Interestingly, this interaction essentially correlates to the parallel orientation of π\*(C-O) orbitals relative to the An-As bond.

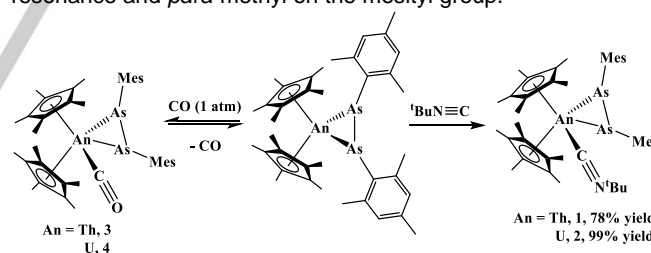
For over three decades, attempts to understand actinide-ligand bonding have been at the forefront of synthetic and computational studies.<sup>1-4</sup> This is driven by the effort to investigate the role of the valence 5f and 6d orbitals in influencing the structure, bonding, and reactivity of the actinides, which provides insight into advanced separation methods as well as improving our fundamental knowledge of these understudied metals. Actinide chemistry is enriched by the metal (5f)-ligand (ηp) orbital energetics that may lead to varying degrees of covalent bonding.<sup>5-6</sup>

Transition metal carbonyl complexes afford insight into the electronic environment about the metal center, since they are amenable to significant amounts of backbonding between the occupied metal d-orbitals and the π\* orbitals of CO. This scenario does not usually occur with the f elements, and therefore there are only four U(III)<sup>7-11</sup> and one Th(IV)<sup>12-15</sup> complex with coordinated carbonyl ligands reported thus far. Due to the Th(IV/III) redox couple measured at -2.96 V to -3.32 V vs. (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sup>+0</sup>,<sup>16</sup> it is not possible for Th(III) carbonyl complexes to be synthesized and compared to their U(III) counterparts. Until now, no U(IV) carbonyl complexes have been reported, and therefore no direct comparisons could be made between two

structurally similar actinide carbonyl species. However, carbonyl complexes are valuable as they directly probe metal-ligand interaction, one of the grand challenges in f element chemistry.

Recently, we reported the diarsenido complexes, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), An = Th, U, which result from loss of H<sub>2</sub> from the bis(arsenido) complexes, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An[As(H)Me<sub>2</sub>]<sub>2</sub>.<sup>17</sup> The exploration of actinide complexes with phosphorus and arsenic ligands has produced unusual reactivity with substrates such as <sup>t</sup>BuNC and CO,<sup>18-21</sup> and we sought to examine this unique diarsenido moiety in more detail. Herein, we report the coordination of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>) with the isoelectronic, unsaturated substrates <sup>t</sup>BuNC and CO. The IR stretching frequencies of the N≡C and C≡O show that these complexes exhibit significant backbonding, similar to those observed in tris(cyclopentadienyl)uranium(III) complexes, but the donation is achieved through charge transfer from an actinide-arsenic σ-bond.

The reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>) with <sup>t</sup>BuNC, Scheme 1, results in a color change from dark green to light orange. The <sup>1</sup>H NMR spectrum exhibits a (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> resonance at 2.05 ppm, shifted from the 1.92 ppm in the starting material. With analogous uranium reaction, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>) and <sup>t</sup>BuNC, the (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> resonance shifted from 7.57 ppm in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>) to 6.39 ppm. Similar to the parent compound, the only visible resonances in the <sup>1</sup>H NMR spectrum are for the (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> resonance and *para*-methyl on the mesityl group.



**Scheme 1.** Reactivity of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), An = Th, U, with <sup>t</sup>BuNC and CO.

Each complex has a characteristic absorption at 2152 cm<sup>-1</sup> (for Th) and 2131 cm<sup>-1</sup> (for U) in the IR spectrum which is attributed to the asymmetric CN stretch, compared to free <sup>t</sup>BuNC at 2132-2134 cm<sup>-1</sup>.<sup>9, 22-23</sup> There are few thorium complexes with alkyl substituted isocyanide ligands for comparison, Table 1, and their CN stretching frequencies range from 2176-2188 cm<sup>-1</sup>.<sup>24-26</sup> Therefore, the thorium isocyanide complex is red-shifted 20-30 cm<sup>-1</sup> from previously reported Th(IV) compounds. The stretching frequency observed in the uranium complex can be compared to the U(III) complexes, Table 1, (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>U(CN<sup>t</sup>Bu),<sup>9</sup> (1,3-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)<sub>3</sub>U(CN<sup>t</sup>Bu),<sup>27</sup> [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(CN<sup>t</sup>Bu)(μ-CN)]<sub>3</sub>,<sup>28</sup> and (C<sub>5</sub><sup>i</sup>Pr<sub>4</sub>H)<sub>2</sub>U(CN<sup>t</sup>Bu)(I)<sup>29</sup> which show ν<sub>CN</sub> of 2127, 2140, 2143, and 2166 cm<sup>-1</sup>, respectively. For a more direct comparison, U(IV)

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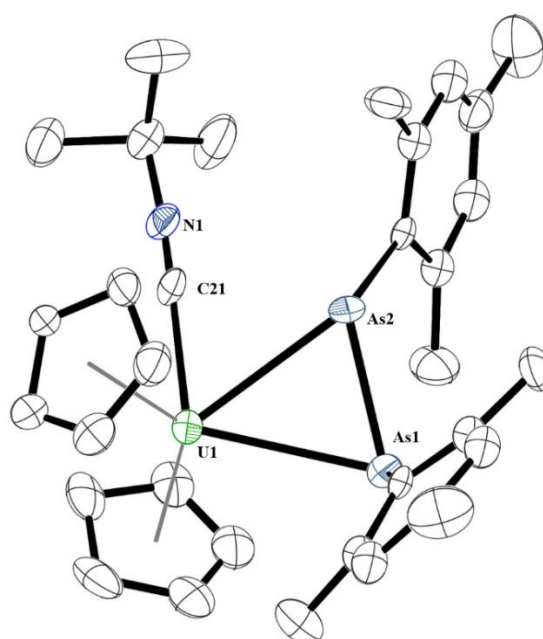
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complexes with <sup>t</sup>BuNC have <sup>29 29 30 25, 31</sup>  $\nu_{\text{NC}}$  range from 2165–2182  $\text{cm}^{-1}$ , Table 1. Thus, the Th(IV) complex displays a CN stretching frequency lower than known U(IV) complexes, while those with U(IV) complex are similar to those seen with U(III) ions. This indicates an appreciable amount of backbonding rarely seen in actinide isocyanide complexes, especially in the tetravalent oxidation state.

**Table 1.** The actinide-carbon distance (Å) and NC stretching frequency ( $\text{cm}^{-1}$ ) of previously reported Th(IV), U(III), and U(IV) complexes with coordinated isocyanide ligands as well as **1** and **2** are shown. Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; Tipp = 2,4,6-<sup>t</sup>-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

Compound	An-C Bond Distance, Å	IR, $\nu \text{ cm}^{-1}$	Ref
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡N <sup>t</sup> Bu), <b>1</b>	2.570(5)	2152	
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡N <sup>t</sup> Bu), <b>2</b>	2.46(2)	2131	
( $\eta^8$ -C <sub>8</sub> H <sub>8</sub> ) <sub>2</sub> Th(CN <sup>t</sup> Bu)	2.701(2)	2176	24
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th(CN <sup>t</sup> Bu)( <sup>t</sup> BuNC=PPh)	2.650(8)	2188	25
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th(CN <sup>t</sup> Bu)( <sup>t</sup> BuNC=PMes)	---	2186	26
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th(CN <sup>t</sup> Bu)( <sup>t</sup> BuNC=PTipp)	2.643(6)	2181	26
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th(CN <sup>t</sup> Bu)( <sup>t</sup> BuNC=AsTipp)	2.638(6)	2182	26
(C <sub>5</sub> Me <sub>4</sub> H) <sub>3</sub> U(CN <sup>t</sup> Bu)	---	2127	9
(1,3-(Me <sub>3</sub> Si) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ) <sub>3</sub> U(CN <sup>t</sup> Bu)	---	2140	27
[(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U(CN <sup>t</sup> Bu)( $\mu$ -CN)] <sub>3</sub>	2.62(2)	2143	28
(C <sub>5</sub> <sup>i</sup> Pr <sub>4</sub> H) <sub>2</sub> U(CN <sup>t</sup> Bu)(I)	2.602(8)	2166	29
[(C <sub>5</sub> <sup>i</sup> Pr <sub>4</sub> H) <sub>2</sub> U(CN <sup>t</sup> Bu) <sub>2</sub> (I)][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	2.584(4)	2176	29
[(C <sub>5</sub> <sup>i</sup> Pr <sub>4</sub> H) <sub>2</sub> U(CN <sup>t</sup> Bu) <sub>4</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	2.635(9)	2182	29
[(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U(NMe <sub>2</sub> )(CN <sup>t</sup> Bu) <sub>2</sub> ][BPh <sub>4</sub> ]	2.60(1)	2181	30
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U(CN <sup>t</sup> Bu)( $\eta^2$ -N( <sup>t</sup> Bu)C=PPh)	2.568(3)	2171	25
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U(CN <sup>t</sup> Bu)( $\eta^2$ -N( <sup>t</sup> Bu)C=PMes)	2.554(4)	2165	31

The solid-state structure of each complex was determined by X-ray crystallography to reveal the anticipated complexes, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An( $\eta^2$ -As<sub>2</sub>Mes<sub>2</sub>)(CN<sup>t</sup>Bu) An = Th, **1**; U, **2** (Figure 1). While some disordered positions for thorium and arsenic were found in **1**, there is no sign of systematic errors in the distances of the main moiety. Complex **1** has Th-As bond distances of 2.9842(7) and 3.0283(8) Å, Table 2, longer than the 2.923(2) and 2.971(3) in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th( $\eta^2$ -As<sub>2</sub>Mes<sub>2</sub>). The Th-C(isocyanide) bond distance is 2.570(5) Å, much shorter than the 2.650(8) Å and 2.643(6) Å in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(CN<sup>t</sup>Bu)( $\eta^2$ -<sup>t</sup>BuNC=PR), R = Ph<sup>25</sup> or Tipp,<sup>26</sup> respectively. Complex **2** has U-As bond distances of 2.913(2) and 2.960(2) Å which have elongated from 2.8914(11) and 2.9231(9) Å in the parent uranium diarsenido complex. It is noteworthy that the shorter U-As bond distance is in As2, which is adjacent to the <sup>t</sup>BuNC. The As-As bond distance in **2** is 2.390(3) Å with an As-U-As bond angle of 48.02(6)°. However, the U-C distance of 2.46(2) Å is identical to the 2.464(4) Å in the U(III) complex, (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>U(CNC<sub>6</sub>H<sub>4</sub>-4-OMe),<sup>9</sup> which also shows a large amount of backbonding, but significantly shorter than the 2.584(4) and 2.613(4) Å in the U(IV), [(C<sub>5</sub><sup>i</sup>Pr<sub>4</sub>H)<sub>2</sub>U(I)(CN<sup>t</sup>Bu)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or the 2.59(2) Å in (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U(OTf)(CN<sup>t</sup>Bu).<sup>32</sup> Hence, the IR spectroscopy and crystallographic data both suggest that the diarsenido ligand donates a substantial amount of electron density to the metal center, similar to the amount that is observed with U(III), not U(IV).



**Figure 1.** Thermal ellipsoid plot of **2** shown at the 50% probability level. The methyl groups of the (C<sub>5</sub>Me<sub>5</sub>)<sup>+</sup> ligands and hydrogen atoms have been omitted for clarity.

**Table 2.** Selected bond distances and IR stretching frequencies.

Compound	U-As Bond Distance, Å	IR, $\nu \text{ cm}^{-1}$	
		Expt	Calc
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡N <sup>t</sup> Bu), <b>1</b>	2.9842(7), 3.0283(8)	2152	
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡O), <b>3</b>	---	1979	1954
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> Th( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )( <sup>13</sup> C≡O)	---	1937	---
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡N <sup>t</sup> Bu), <b>2</b>	2.962(3), 2.913(2)	2131	
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )(C≡O), <b>4</b>	---	1939	1919
(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U( $\eta^2$ -As <sub>2</sub> Mes <sub>2</sub> )( <sup>13</sup> C≡O)	---	1898	---

Based on the results with <sup>t</sup>BuNC, we attempted the reaction with isoelectronic CO. Reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An( $\eta^2$ -As<sub>2</sub>Mes<sub>2</sub>) with 1 atm of CO, Scheme 1, also results in immediate color changes with both thorium and uranium as well as changes in the <sup>1</sup>H NMR spectra. However, within a minute of removing the atmosphere of CO blanketing the reaction vessel, the solution changes back to the color of the parent (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An( $\eta^2$ -As<sub>2</sub>Mes<sub>2</sub>) complexes. Many attempts were made to crystallize the product under a CO atmosphere but did not result in crystals suitable for X-ray diffraction analysis.

Liquid IR spectroscopy was performed to determine if CO was coordinating to each actinide(IV) metal center. Indeed, each complex showed a strong absorption for coordinated carbonyl at 1979  $\text{cm}^{-1}$  (for Th) and 1939  $\text{cm}^{-1}$  (for U). Addition of <sup>13</sup>CO to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An( $\eta^2$ -As<sub>2</sub>Mes<sub>2</sub>) was also conducted and absorptions at 1937 and 1898  $\text{cm}^{-1}$  were observed for Th and U, respectively. The <sup>13</sup>CO frequency shifts match the expected values from the quantum harmonic oscillator model for the effective mass change which are 1935  $\text{cm}^{-1}$  and 1895  $\text{cm}^{-1}$  for Th and U, respectively. This is in good agreement with those obtained experimentally. In addition, a resonance at 244.4 ppm in the <sup>13</sup>C NMR spectrum was found with the thorium complex. The correlation of <sup>13</sup>C NMR

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resonance and IR absorption for the Th(IV) carbonyl compound fit well with the data assembled for Zr carbonyl complexes.<sup>33</sup> Hence, we formulate these complexes as  $(C_5Me_5)_2An(CO)(\eta^2-As_2Mes_2)$ , An = Th, **3**; U, **4**.

The only other Th CO complex reported,  $[(C_5Me_5)_3Th(CO)][BPh_4]$ , showed a stretching frequency at 2131  $cm^{-1}$ , close to 2143  $cm^{-1}$  for free CO. In addition, this complex also displayed a  $^{13}C$  NMR resonance at 200.4 ppm. Hence, complex **3** shows significantly more interaction based on these metrics. For further comparison, nearly all carbonyl complexes with  $d^0$  metals fall into the range of 1980–2200  $cm^{-1}$  for their observed CO stretching frequencies.<sup>34–39</sup> For example,  $(C_5Me_5)_2Zr(\eta^2-E_2)(CO)$  show stretching frequencies of 2057 (E = S), 2037 (E = Se), and 2006 (E = Te)  $cm^{-1}$ .<sup>33</sup> One notable exception is  $(C_5H_5)_2Zr(\eta^2-Me_2Si=N^tBu)(CO)$  with  $\nu_{CO}$  of 1797  $cm^{-1}$ ,<sup>40–41</sup> which showed an unusual interaction between the silicon and carbonyl.

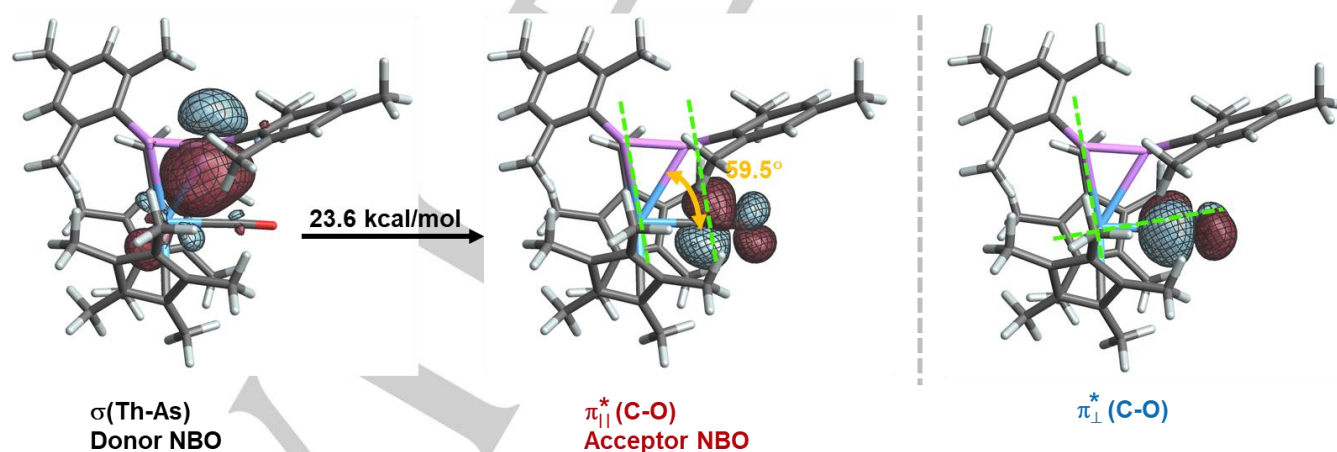
There are four CO complexes known with U, all of them U(III):  $(C_5H_4SiMe_3)_3U(CO)$ ,<sup>7</sup>  $(C_5Me_5)_3U(CO)$ ,<sup>10</sup>  $[C_8H_6(1,4-SiMe_3)_2(C_5Me_5)_2U(CO)]$ ,<sup>11</sup> and  $(C_5Me_4H)_3U(CO)^8$  with  $\nu_{CO}$  of 1976, 1922, 1920, and 1880  $cm^{-1}$ , respectively. Therefore, like the isocyanide complex, **2**, the amount of backbonding observed in **4** with CO is in the range found with U(III) carbonyl complexes. This question of how Th(IV),  $d^0$ , and U(IV),  $d^0f^2$ , could have similar backbonding interactions was explored using density functional calculations.

Similar to Figure 1, we labeled the As atom away from the small ligand (CO) as As1. As2 is adjacent to CO. For both complexes, the optimized average An-As and An-C distances (Table S1) are similar to those measured in **1** and **2**. As shown in Table 2, the calculated CO stretching frequencies for **3** and **4** are very close to the experimental data (within 25  $cm^{-1}$ ), and they nearly quantitatively reproduce the frequency difference between **3** and **4**. Compared to free CO (2143  $cm^{-1}$ ), the frequency reduction by 164  $cm^{-1}$  and 204  $cm^{-1}$ , respectively, in the experiment (Calc.: 189

$cm^{-1}$  and 224  $cm^{-1}$ ), indicates pronounced backbonding interactions.

NBO (Natural Bond Orbital) analysis corroborates the presence of an interesting  $\pi$  backbonding interaction. For **3**, as seen in Table S2, the  $\sigma(Th-As_2)$  NBO has an occupation much below 2. Most of the missing occupation, 0.31 e, is in  $\pi^*(C-O)$ . This means the back-donation to CO comes mainly from the As2-U bond and goes into one of the CO  $\pi^*$  orbitals, viz. the ‘parallel’ one in the same plane (Figure 2). The strong donor-acceptor interaction is quantified via the second-order perturbation energy in the NBO calculation, and calculated to be 24 kcal/mol. By comparison, the  $\sigma(Th-As_1)$  bond has a negligible contribution towards stabilization of the system by donor-acceptor interaction, and the ‘perpendicular’  $\pi^*(C-O)$  likewise is not an important acceptor.

The ground state of **4** is calculated to be a spin triplet, as expected. According to the NBO analysis, there is a slightly larger charge transfer (by  $\sim 0.01$ – $0.03$ ) from  $\sigma(An-As_2)$  to the ‘parallel’  $\pi^*(C-O)$  for **4** vs. **3** (Table S3). Accordingly, the combined donor-acceptor stabilization energy for alpha and beta spin orbitals in **4** is greater by 5 kcal/mol than that in **3**. This enhanced energetic stabilization also goes along with stronger covalency of the An-C(CO) bond as evidenced by the Wiberg bond orders of 0.84 for U-C vs. 0.73 for Th-C. The NBO compositions (Table S4) further show that  $\sigma(Th-As_2)$  (29% Th) has less metal contribution than the  $\sigma(U-As_2)$  (33% U). The contributing metal shells in  $\sigma(An-As_2)$  are 74/15% 6d/5f for **3**, and 64/25% 6d/5f (spin-averaged) for **4**. Overall, these comparative computational analyses provide detailed insight into the electronic structure and the presence of unusual backbonding in the carbonyl complexes. We note that the backbonding in tris(substituted cyclopentadienyl)U(III) carbonyl complexes has been shown to involve cyclopentadienyl-based orbitals of  $\pi$ -symmetry;<sup>42</sup> however, in this case, an An-As  $\sigma$ -bond is responsible for the observed backbonding.



**Figure 2.** Isosurface ( $\pm 0.03$  a.u.) plots of the  $\sigma(Th-As_2)$  orbital and two  $\pi^*(C-O)$  orbitals (roughly parallel and perpendicular to the As-U-As plane) in **3**. The stabilizing energy associated with the donor-acceptor interaction is indicated above the arrow. (Color code for atoms: Th blue, As purple, C dark gray, O red, H white.)

In summary, isostructural Th(IV) and U(IV) complexes of isocyanide and, for the first time, carbonyl complexes have been examined. Each complex shows a pronounced red shift in the IR spectrum, indicating strong backbonding between the actinide and isocyanide or carbonyl. Quantum mechanical calculations

show that charge transfer from an An-As  $\sigma$ -bond to the  $\pi^*$  orbital of the carbonyl ligand is responsible for the strong donor-acceptor interaction. While this type of bonding has been described with  $d^0$  metals, it is rare, and the first time this phenomenon has emanated from a non-cyclopentadienyl ligand. This is also an

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unusual case where a soft donor ligand (As) is so strongly donating to a hard Lewis acid (Th, U). We are currently investigating this further.

## Experimental Section

**Experimental Details.** All reactions were performed under an inert atmosphere of dry N<sub>2</sub> inside of a glovebox. (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), An = Th, U, were prepared according to literature procedures. Solvents were dried via activated alumina, and dispensed through a solvent-purification system, MBRAUN, USA. C<sub>6</sub>D<sub>6</sub> (Cambridge Isotope Laboratories) was subjected to three freeze-pump-thaw cycles and dried over activated 4 Å molecular sieves for 72 h prior to use. All <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR experiments were performed on a 500 or 600 MHz Bruker NMR spectrometer. Spectra were referenced to residual C<sub>6</sub>D<sub>6</sub>H at 7.16 ppm (<sup>1</sup>H) and 128.06 ppm (<sup>13</sup>C{<sup>1</sup>H}), respectively. IR spectra were collected from samples prepared as KBr plates with a Nicolet Summit PRO FTIR Spectrometer. Elemental analyses were performed by the Microanalytical Facility, University of California, Berkeley, USA.

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(CN<sup>t</sup>Bu), 1.** A toluene solution of <sup>t</sup>BuNC (1 molar equivalent, 0.5 M) was added to a stirring, dark green, Et<sub>2</sub>O slurry of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>). The color progressed quickly from dark green, to dark red, to light red orange, with concomitant precipitation of a bright orange powder. The mixture was stirred for 30 min at room temperature, then filtered over a M-porosity fritted glass funnel to collect the precipitate. The precipitate was rinsed with ~2 mL Et<sub>2</sub>O, then stripped of volatiles under vacuum, 103 mg, 78%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25 °C): δ 7.00-6.92 (m, 4H, *m*-H), 2.98 (s, 12H *o*-CH<sub>3</sub>), 2.31 (s, 6 H, *p*-CH<sub>3</sub>), 2.05 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 0.80 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150 MHz, 25 °C): δ 145.85 (s, *quat*-C<sub>aryl</sub>), 143.80 (s, *quat*-C<sub>aryl</sub>), 132.6 (m, *p*-*quat*-C<sub>aryl</sub>), 128.34 (s, *m*-CH), 123.21 (s, C<sub>5</sub>Me<sub>5</sub>), 29.28 (s, *p*-CH<sub>3</sub>), 28.73 (s, *o*-CH<sub>3</sub>), 12.29 (s, C<sub>5</sub>Me<sub>5</sub>). IR (cm<sup>-1</sup>): 2976 (m), 2947 (m), 2907 (s), 2858 (m), 2722 (w), 2152 (s), 1597 (w), 1452 (s), 1425 (m), 1371 (m), 1261 (w), 1234 (w), 1187 (m), 1086 (m), 1022 (m), 1009 (m), 948 (m), 845 (m), 801 (w), 706 (w), 543 (w), 463 (w). Elemental analysis calculated for (C<sub>43</sub>H<sub>61</sub>NAs<sub>2</sub>Th) (973.83 g/mol): C, 53.03%; H, 6.31%; N, 1.44%. Found: C, 53.15%; H, 6.44%; N, 1.53%.

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(CN<sup>t</sup>Bu), 2.** Complex **2** was prepared in analogous manner to that of **1**, 99%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25 °C): δ 8.48 (s, 2H, *m*-H), 6.39 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 5.30 (s, 3H, *p*-Me), 4.46 (s, 6H, *o*-Me), 3.79 (s, 6H, *o*-Me), -3.52 (s, 2H, *m*-H), -12.19 (s, 9H, <sup>t</sup>Bu). IR (cm<sup>-1</sup>): 2977 (s), 2948 (s), 2906 (s), 2860 (s), 2721 (w), 2131 (s), 1713 (w), 1597 (w), 1452 (s), 1370 (s), 1184 (s), 1085 (s), 1024 (s), 948 (w), 846 (s), 799 (w), 706 (w), 542 (w), 461 (s). Elemental analysis calculated for C<sub>43</sub>H<sub>61</sub>NAs<sub>2</sub>U (979.82 g/mol): C, 52.71%; H, 6.27%; N, 1.43%. Found: C, 52.35%; H, 6.49%; N, 1.35%.

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(CO), 3.** A J. Young tube was charged with a ~1.5 mL C<sub>6</sub>D<sub>6</sub> solution of 25 mg (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), the solution frozen with liquid N<sub>2</sub>, and the N<sub>2</sub> atmosphere in the headspace replaced with 1 atm CO. The color of the solution immediately changed from dark brown to dark red, and was complete (by <sup>1</sup>H NMR spectroscopy) by 10 min at room temperature. The CO ligand is labile enough to disassociate quickly upon removal of the CO atmosphere, so solid-state characterization methods could not be performed. An IR spectrum was collected by quickly transferring a toluene solution to a liquid-IR cell, where the compound was stable enough for the spectrum to be collected. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25 °C): δ 6.96 (s, 4H, *m*-H), 2.84 (s, 12H, *o*-CH<sub>3</sub>), 2.29 (s, 6H, *p*-CH<sub>3</sub>), 1.87 (s, 30H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 150 MHz, 25 °C): δ 244.4 (CO), 182.7, 142.9, 140.0, 133.8, 129.0, 124.5, 28.01, 20.95, 15.60, 14.28, 11.50. IR (cm<sup>-1</sup>): 2997 (w), 2953 (m), 2913 (s), 2858 (m), 2728 (w),

1979 (s), 1453 (s), 1378 (m), 1293 (m), 1243 (m), 1189 (m), 1144 (w), 1021 (m), 948 (w), 848 (w), 707 (w), 544 (m).

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(<sup>13</sup>CO).** A preparative procedure identical to that of **3** was performed, using <sup>13</sup>CO. All spectra were identical with the exception of the IR absorption corresponding to the CO stretching mode, at 1937 cm<sup>-1</sup>.

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(CO), 4.** A J. Young tube was charged with a ~1.5 mL C<sub>6</sub>D<sub>6</sub> solution of 25 mg (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>), the solution frozen with liquid N<sub>2</sub>, and the N<sub>2</sub> atmosphere in the headspace replaced with 1 atm CO. The color of the solution immediately changed from dark brown to dark red, and was complete (by <sup>1</sup>H NMR spectroscopy) by 10 min at room temperature. The CO ligand is labile enough to disassociate quickly upon removal of the CO atmosphere, so solid-state characterization methods could not be performed. An IR spectrum was collected by quickly transferring a toluene solution to a liquid-IR cell, where the compound was stable enough for the spectrum to be collected. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600 MHz, 25 °C): δ 5.73 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 3.35 (s, 6H, *p*-Me). IR (cm<sup>-1</sup>): 2965 (w), 2987 (w), 1939 (s), 1434 (w), 1374 (w), 1020 (w), 847 (w), 727 (s), 470 (m).

**Synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(η<sup>2</sup>-As<sub>2</sub>Me<sub>2</sub>)(<sup>13</sup>CO).** A preparative procedure identical to that of **4** was performed, using <sup>13</sup>CO instead. All spectra were identical with the exception of the IR absorption corresponding to the CO stretching mode, at 1898 cm<sup>-1</sup>.

## Computational Section

**Computational Details.** Density Functional Theory calculations for **3** and **4** were performed with the hybrid B3LYP<sup>43-44</sup> exchange-correlation functional. Small-core Stuttgart energy-consistent relativistic pseudopotentials, ECP60MWB for Th and U, were used with matching valence basis sets.<sup>45</sup> The 6-31G(d) basis set was used for As, O, C, and H atoms.<sup>46</sup> Vibrational frequency analysis was carried out at the same level of theory. Additional calculations were performed to test the reliability of the calculations, as described in the SI. Calculated vibrational frequencies were scaled by 0.967. The calculations and bonding analysis employed the Gaussian 16 and NBO 6.0 programs.<sup>47-48</sup>

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**Keywords:** actinide, backbonding, carbonyl, isocyanide, synthesis

## References

1. Pepper, M.; Bursten, B. E. The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry. *Chem. Rev.* **1991**, *91*, 719-741.
2. Cantat, T.; Graves, C. R.; Jantunen, K. C.; Burns, C. J.; Scott, B. L.; Schelter, E. J.; Morris, D. E.; Hay, P. J.; Kiplinger, J. L. Evidence for the Involvement of 5f Orbitals in the Bonding and Reactivity of Organometallic Actinide Compounds: Thorium(IV) and Uranium(IV) Bis(hydrazonato) Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 17537-17551.
3. Neidig, M. L.; Clark, D. L.; Martin, R. L. Covalency in f-element complexes. *Coord. Chem. Rev.* **2013**, *257*, 394-406.

4. Vitova, T.; Pidchenko, I.; Fellhauer, D.; Bagus, P. S.; Joly, Y.; Pruessmann, T.; Bahl, S.; Gonzalez-Robles, E.; Rothe, J.; Altmair, M.; Denecke, M. A.; Geckeis, H. The role of the 5f valence orbitals of early actinides in chemical bonding. *Nat. Commun.* **2017**, *8*, 16053.
5. Walensky, J. R.; Martin, R. L.; Ziller, J. W.; Evans, W. J. Importance of Energy Level Matching for Bonding in Th<sup>3+</sup>-Am<sup>3+</sup> Actinide Metallocene Amidinates, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>[PrNC(Me)NPr]An. *Inorg. Chem.* **2010**, *49*, 10007-10012.
6. Su, J.; Batista, E. R.; Boland, K. S.; Bone, S. E.; Bradley, J. A.; Cary, S. K.; Clark, D. L.; Conradson, S. D.; Ditter, A. S.; Kaltsoyannis, N.; Keith, J. M.; Kerridge, A.; Kozimor, S. A.; Löble, M. W.; Martin, R. L.; Minasian, S. G.; Mocko, V.; La Pierre, H. S.; Seidler, G. T.; Shuh, D. K.; Wilkerson, M. P.; Wolfsberg, L. E.; Yang, P. Energy-Degeneracy-Driven Covalency in Actinide Bonding. *J. Am. Chem. Soc.* **2018**, *140*, 17977-17984.
7. Brennan, J. G.; Andersen, R. A.; Robbins, J. L. Preparation of the first molecular carbon monoxide complex of uranium, (Me<sub>3</sub>SiC<sub>3</sub>H<sub>4</sub>)<sub>3</sub>UCO. *J. Am. Chem. Soc.* **1986**, *108*, 335-336.
8. Parry, J.; Carmona, E.; Coles, S.; Hursthouse, M. Synthesis and Single Crystal X-ray Diffraction Study on the First Isolable Carbonyl Complex of an Actinide, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U(CO). *J. Am. Chem. Soc.* **1995**, *117*, 2649-2650.
9. del Mar Conejo, M.; Parry, J. S.; Carmona, E.; Schultz, M.; Brenmann, J. G.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. B. Carbon Monoxide and Isocyanide Complexes of Trivalent Uranium Metallocenes. *Chem. Eur. J.* **1999**, *5*, 3000-3009.
10. Evans, W. J.; Kozimor, S. A.; Nyce, G. W.; Ziller, J. W. Comparative Reactivity of Sterically Crowded nf<sup>3</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Nd and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex. *J. Am. Chem. Soc.* **2003**, *125*, 13831-13835.
11. Frey, A. S.; Cloke, F. G. N.; Hitchcock, P. B.; Day, I. J.; Green, J. C.; Aitken, G. Mechanistic Studies on the Reductive Cyclooligomerisation of CO by U(III) Mixed Sandwich Complexes; the Molecular Structure of [(U(η-C<sub>8</sub>H<sub>8</sub>(Si<sup>i</sup>Pr<sub>3</sub>-1,4)<sub>2</sub>)(η-Cp\*))<sub>2</sub>(μ-η<sup>1</sup>-C<sub>2</sub>O<sub>2</sub>)]. *J. Am. Chem. Soc.* **2008**, *130*, 13816-13817.
12. Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. Reactions of Th Atoms with CO: The First Thorium Carbonyl Complex and an Unprecedented Bent Triplet Insertion Product. *J. Am. Chem. Soc.* **1999**, *121*, 12188-12189.
13. Li, J.; Bursten, B. E.; Zhou, M.; Andrews, L. A Combined Theoretical and Experimental Study of the Reaction Products of Laser-Ablated Thorium Atoms with CO: First Identification of the CThO, CThO<sup>+</sup>, OThCCO, OTh(η<sup>3</sup>-CCO), and Th(CO)<sub>n</sub> (n = 1-6) Molecules. *Inorg. Chem.* **2001**, *40*, 5448-5460.
14. Andrews, L.; Liang, B.; Li, J.; Bursten, B. E. Noble Gas-Actinide Complexes of the CUO Molecule with Multiple Ar, Kr, and Xe Atoms in Noble-Gas Matrices. *J. Am. Chem. Soc.* **2003**, *125*, 3126-3139.
15. Langeslay, R. R.; Chen, G. P.; Windorff, C. J.; Chan, A. K.; Ziller, J. W.; Furche, F.; Evans, W. J. Synthesis, Structure, and Reactivity of the Sterically Crowded Th<sup>3+</sup> Complex (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Th Including Formation of the Thorium Carbonyl, [(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Th(CO)](BPh<sub>4</sub>). *J. Am. Chem. Soc.* **2017**, *139*, 3387-3398.
16. Inman, C. J.; Cloke, F. G. N. The experimental determination of Th(IV)/Th(III) redox potentials in organometallic thorium complexes. *Dalton Trans.* **2019**, *48*, 10782-10784.
17. Tarlton, M. L.; Fajen, O. J.; Kelley, S. P.; Kerridge, A.; Malcomson, T.; Morrison, T. L.; Shores, M. P.; Xhani, X.; Walensky, J. R. Systematic Investigation of the Molecular and Electronic Structure of Thorium and Uranium Phosphorus and Arsenic Complexes. *Inorg. Chem.* **2021**, *60*, 10614-10630.
18. Vilanova, S. P.; del Rosal, I.; Tarlton, M. L.; Maron, L.; Walensky, J. R. Functionalization of Carbon Monoxide and *tert*-Butyl Nitrile by Intramolecular Proton Transfer in a Bis(Phosphido) Thorium Complex. *Angew. Chem. Int. Ed.* **2018**, *57*, 16748-16753.
19. Zhang, C.; Hou, G.; Zi, G.; Ding, W.; Walter, M. D. A Base-Free Terminal Actinide Phosphinidene Metallocene: Synthesis, Structure, Reactivity, and Computational Studies. *J. Am. Chem. Soc.* **2018**, *140*, 14511-14525.
20. Ward, R. J.; Rungthanaphatsophon, P.; Rosal, I. d.; Kelley, S. P.; Maron, L.; Walensky, J. R. Divergent uranium- versus phosphorus-based reduction of Me<sub>3</sub>SiN<sub>3</sub> with steric modification of phosphido ligands. *Chem. Sci.* **2020**, *11*, 5830-5835.
21. Wang, D.; Ding, W.; Hou, G.; Zi, G.; Walter, M. D. Experimental and Computational Studies on a Base-Free Terminal Uranium Phosphinidene Metallocene. *Chem. Eur. J.* **2020**, *26*, 16888-16899.
22. Ugi, I.; Meyr, R., Isonitrile, I. Darstellung von Isonitrilen aus monosubstituierten Formamiden durch Wasserabspaltung. *Chem. Ber.* **1960**, *93*, 239-248.
23. Tsoureas, N.; Kilpatrick, A. F. R.; Inman, C. J.; Cloke, F. G. N. Steric control of redox events in organo-uranium chemistry: synthesis and characterisation of U(v) oxo and nitrido complexes. *Chem. Sci.* **2016**, *7*, 4624-4632.
24. Berthet, J.-C.; Thuéry, P.; Garin, N.; Dognon, J.-P.; Cantat, T.; Ephritikhine, M. Revisiting the Chemistry of the Actinocenes [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>An] (An = U, Th) with Neutral Lewis Bases. Access to the Bent Sandwich Complexes [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>An(L)] with Thorium (L = py, 4,4'-bipy, <sup>t</sup>BuNC, R<sub>4</sub>phen). *J. Am. Chem. Soc.* **2013**, *135*, 10003-10006.
25. Rungthanaphatsophon, P.; Fajen, O. J.; Kelley, S. P.; Walensky, J. R. Thorium(IV) and Uranium(IV) Phosphaazaallenes. *Inorganics* **2019**, *7*, 105.
26. Behrle, A. C.; Walensky, J. R. Insertion of <sup>t</sup>BuNC into thorium-phosphorus and thorium-arsenic bonds: phosphaazaallene and arsaazaallene moieties in f element chemistry. *Dalton Trans.* **2016**, *45*, 10042-10049.
27. Lukens, W. W.; Speldrich, M.; Yang, P.; Duignan, T. J.; Autschbach, J.; Kögerler, P. The roles of 4f- and 5f-orbitals in bonding: a magnetochemical, crystal field, density functional theory, and multi-reference wavefunction study. *Dalton Trans.* **2016**, *45*, 11508-11521.
28. Evans, W. J.; Mueller, T. J.; Ziller, J. W. Lanthanide versus Actinide Reactivity in the Formation of Sterically Crowded [(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ML<sub>n</sub>] Nitrile and Isocyanide Complexes. *Chem. Eur. J.* **2010**, *16*, 964-975.
29. Boreen, M. A.; Groß, O. A.; Hohloch, S.; Arnold, J. Isocyanide adducts of tri- and tetravalent uranium metallocenes supported by tetra(isopropyl)cyclopentadienyl ligands. *Dalton Trans.* **2020**, *49*, 11971-11977.
30. Boisson, C.; Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. Reactivity of the cationic uranium amide compound [U(η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(NMe<sub>2</sub>)(OC<sub>4</sub>H<sub>8</sub>)](BPh<sub>4</sub>). *J. Organomet. Chem.* **1997**, *548*, 9-16.
31. Tarlton, M. L.; Del Rosal, I.; Vilanova, S. P.; Kelley, S. P.; Maron, L.; Walensky, J. R. Comparative Insertion Reactivity of CO, CO<sub>2</sub>, <sup>t</sup>BuCN, and <sup>t</sup>BuNC into Thorium- and Uranium-Phosphorus Bonds. *Organometallics* **2020**, *39*, 2152-2161.
32. Claude Berthet, J.; Ephritikhine, M.; Claude Berthet, J.; Lance, M.; Nierlich, M. First uranium(IV) triflates. *Chem. Commun.* **1998**, 1373-1374.
33. Howard, W. A.; Parkin, G.; Rheingold, A. L. Non-classical carbonyl complexes of zirconium: The syntheses, characterization, and reactivities of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(η<sup>2</sup>-E<sub>2</sub>)(CO) (E = S, Se, Te). *Polyhedron* **1995**, *14*, 25-44.
34. Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. Low-temperature infrared study of d<sup>0</sup> carbonyl complexes. *J. Am. Chem. Soc.* **1980**, *102*, 7244-7246.
35. Guo, Z.; Swenson, D. C.; Guram, A. S.; Jordan, R. F. Isolable Zirconium(IV) Carbonyl Complexes. Synthesis and Characterization of (C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>Zr(η<sup>2</sup>-COCH<sub>3</sub>)(CO)<sup>+</sup> Species (R = Me, H). *Organometallics* **1994**, *13*, 766-773.
36. Guram, A. S.; Swenson, D. C.; Jordan, R. F. Synthesis and characterization of Cp<sub>2</sub>Zr(CH{Me}{6-ethylpyrid-2-yl})(CO)<sup>+</sup>, a d<sup>0</sup> metal alkyl carbonyl complex. Coordination chemistry of the four-membered azazirconacycle Cp<sub>2</sub>Zr(η<sup>2</sup>-C,N-CH{Me}{6-ethylpyrid-2-yl})<sup>+</sup>. *J. Am. Chem. Soc.* **1992**, *114*, 8991-8996.
37. Antonelli, D. M.; Tjaden, E. B.; Stryker, J. M. A Thermally Stable Carbonyl Complex of Zirconium(IV). Structure and Reactivity Ramifications of Strong σ-donation. *Organometallics* **1994**, *13*, 763-765.
38. Burckhardt, U.; Tilley, T. D. Carbonylation Chemistry of the Tantalum Silyl Hydride Cp\*(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)Ta[Si(SiMe<sub>3</sub>)<sub>3</sub>]H: The Unexpected Formation of a Ta(V) Carbonyl Complex and the Complete Reduction of CO. *J. Am. Chem. Soc.* **1999**, *121*, 6328-6329.
39. La Pierre, H. S.; Arnold, J.; Bergman, R. G.; Toste, F. D. Carbon Monoxide, Isocyanide, and Nitrile Complexes of Cationic, d<sup>0</sup> Vanadium Bisimides: π-Back Bonding Derived from the π

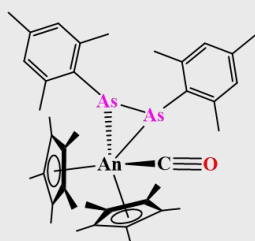
## COMMUNICATION

Symmetry, Bonding Metal Bisimido Ligand Orbitals. *Inorg. Chem.* **2012**, *51*, 13334-13344.

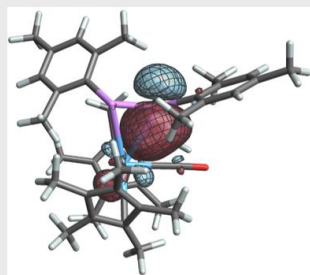
40. Procopio, L. J.; Carroll, P. J.; Berry, D. H.,  $\eta^2$ -Silanimine complexes of zirconocene: synthesis, structure, and reactivity of  $\text{Cp}_2\text{Zr}(\eta^2\text{-SiMe}_2\text{=N-}t\text{-Bu})(\text{PMe}_3)$ . *J. Am. Chem. Soc.* **1991**, *113*, 1870-1872.
41. Procopio, L. J.; Carroll, P. J.; Berry, D. H., Structure and reactivity of  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_2\text{Si=N}^i\text{Bu})(\text{CO})$ : An unusual silanimine carbonyl complex with extensive  $\sigma\text{-}\pi^*$  back-bonding. *Polyhedron* **1995**, *14*, 45-55.
42. Maron, L.; Eisenstein, O.; Andersen, R. A. The Bond between CO and  $\text{Cp}'_3\text{U}$  in  $\text{Cp}'_3\text{U}(\text{CO})$  Involves Back-bonding from the  $\text{Cp}'_3\text{U}$  Ligand-Based Orbitals of  $\pi$ -Symmetry, where  $\text{Cp}'$  Represents a Substituted Cyclopentadienyl Ligand. *Organometallics* **2009**, *28*, 3629-3635.
43. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785-789.
44. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
45. Cao, X.; Dolg, M. Valence basis sets for relativistic energy-consistent small-core lanthanide pseudopotentials. *J. Chem. Phys.* **2001**, *115*, 7348-7355.
46. Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. 6-31G\* basis set for atoms K through Zn. *J. Chem. Phys.* **1998**, *109*, 1223-1229.
47. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, Gaussian 16, Revision A. 03; Gaussian Inc.: Wallingford CT, 2016.
48. Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6.0: Natural bond orbital analysis program. *J. Comput. Chem.* **2013**, *34*, 1429-1437.

## Entry for the Table of Contents

## COMMUNICATION



An = Th,  $\nu(\text{CO})$ : 1979  $\text{cm}^{-1}$   
U,  $\nu(\text{CO})$ : 1939  $\text{cm}^{-1}$



$\sigma(\text{Th-As})$   
Donor NBO

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Backbonding in Thorium(IV) and Uranium(IV) Diarsenido Complexes with <sup>t</sup>BuNC and CO