

Conversion of Trivalent Uranium Anilido to Tetravalent Uranium Imido Species via Oxidative Deprotonation

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ABSTRACT: Two uranium(III) anilido complexes were synthesized, $\text{Tp}^*_2\text{U}(\text{NH}-\text{C}_6\text{H}_4\text{-}p\text{-terpyridine})$ (**2-terpy**) and $\text{Tp}^*_2\text{U}(\text{NH}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)$ (**2-ptol**), where Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate, by protonation of Tp^*_2UBn (**1-Bn**; Bn = benzyl) with 4-[2,6-di(pyridin-2-yl)pyridin-4-yl]benzenamine or *p*-toluidine, respectively. Conversion to the respective uranium(IV) imido species was possible by oxidation and deprotonation, forming $\text{Tp}^*_2\text{U}(\text{N}-\text{C}_6\text{H}_4\text{-}p\text{-terpyridine})$ (**3-terpy**) and $\text{Tp}^*_2\text{U}(\text{N}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)$ (**3-ptol**). These compounds were characterized by multinuclear NMR spectroscopy, IR spectroscopy, electronic absorption spectroscopy, and X-ray crystallography.

The synthesis of uranium imido species has been explored extensively over the last 2 decades because multiply bonded species have been at the center of the search for covalency in actinide chemistry.¹ Through these studies, a variety of nitrogen-containing reagents and synthetic pathways have been utilized. Redox neutral methods have been both popular and effective for building U–N multiple bonds. For example, Liddle and co-workers reported deprotonation of the uranium(IV) amide $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{NH}_2)]$ [$\text{Tren}^{\text{TIPS}} = \text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3$], with LiBu^t or $\text{MCH}_2\text{C}_6\text{H}_5$ ($\text{M} = \text{Na}-\text{Cs}$) in the presence of 15-crown-5 and yielding the terminal uranium(IV) parent imido $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{NH})][\text{K}(\text{15CS}_2)]$.² Boncella and co-workers synthesized uranium(IV) imido complexes by treating Lewis base adducts of UCl_4 with 2 equiv of LiNHdipp , furnishing $\text{U}(\text{NDipp})\text{Cl}_2(\text{L})_n$ ($\text{L} = \text{R}_2\text{bpy}$, $n = 2$; $\text{L} = \text{tppo}$, $n = 3$; $\text{R} = \text{Me}$, ^tBu ; $\text{bpy} = 4,4'$ -dialkyl-2,2'-bipyridine; $\text{tppo} = \text{triphenylphosphine oxide}$; $\text{dipp} = 2,6$ -diisopropylphenyl).³

Synthetic processes that rely on redox reactions at the U center have also been successful. Uranium(IV) imido species that rely on this method are less common because the starting material must be a stable, low-valent uranium species. Santos and co-workers demonstrated that this was possible with synthesis of the uranium(IV) bis(imido) $[\text{U}\{(\text{Bu}_2\text{OAr})_2\text{Me}_2\text{-cycclam}\}(\text{NPh})_2]$ [$\text{cycclam} = \text{hexadentate dianionic 1,4,8,11-tetraazacyclotetradecane-based bis(phenolate)}$] by the addition of 0.5 equiv of $\text{PhN}=\text{NPh}$ to trivalent $[\text{U}\{(\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cycclam}\}]\text{I}$.⁴ Boreen and Arnold reported a tetravalent uranium imido from the addition of 3 equiv of an organoazide, Terph-N_3 ($\text{Terph} = 2,6\text{-}(\text{C}_6\text{H}_4\text{-}4\text{-}^t\text{Bu})_2\text{C}_6\text{H}_3$), to $\text{UCl}_3(1,4\text{-dioxane})_{1.5}$, yielding $\text{K}\{[\text{N}(\text{Terph})]\{\kappa^3\text{-NH}[\text{Terph-2-(N}_3\text{-Terph)}]\}\text{U(I)-(THF)}\}$ ($\text{THF} = \text{tetrahydrofuran}$) in small quantities.⁵ Meyer and co-workers have demonstrated the utility of a reduction route, where the uranium(V) imido complex $[(\text{Np}^{\text{Me}}\text{ArO})_3\text{-tacn})\text{U}(\text{N-CPh}_3)]$ was treated with 1 equiv of KC_8 , producing the uranium(IV) imido anion K-

$[(\text{Np}^{\text{Me}}\text{ArO})_3\text{-tacn})\text{U}(\text{N-CPh}_3)]$ [$(\text{Np}^{\text{Me}}\text{ArO})_3\text{-tacn} = 1,4,7\text{-tris(2-hydroxy-5-methyl-3-neopentylbenzyl)-1,4,7-triazacyclononane}$].⁶

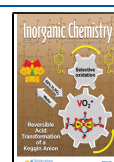
Our group has also achieved the synthesis of uranium(IV) imido species using a redox pathway. The addition of 1 equiv of an organoazide to trivalent Tp^*_2UBn (**1-Bn**; Bn = benzyl) resulted in formation of the uranium(IV) imido Tp^*_2UNR [$\text{R} = \text{benzyl}$, *p*-tolyl, 2,6-diethylphenyl (detp), 2,6-diisopropylphenyl (dipp), 2,4,6-trimethylphenyl (Mes), 1-adamantyl (Ad), and phenyl (Ph)]. Similarly, these molecules were accessible by treating $\text{Tp}^*_2\text{UI}^{7,8}$ with 1 equiv each of the organoazide and KC_8 .

We sought to understand whether the bis(Tp^*) uranium(III) system would be amenable to a deprotonation pathway. To test this, the reactivity of **1-Bn** with bulky 4-[2,6-di(pyridin-2-yl)pyridin-4-yl]benzenamine (terpy-aniline) and sterically smaller *p*-toluidine was explored. Herein, we report the synthesis of uranium(IV) imido species synthesized by oxidative deprotonation of the corresponding uranium(III) anilido species. Full characterization with multinuclear NMR spectroscopy, IR spectroscopy, and electronic absorption spectroscopy, as well as X-ray crystallography of these species, is reported, supporting formation of the desired imido compounds.

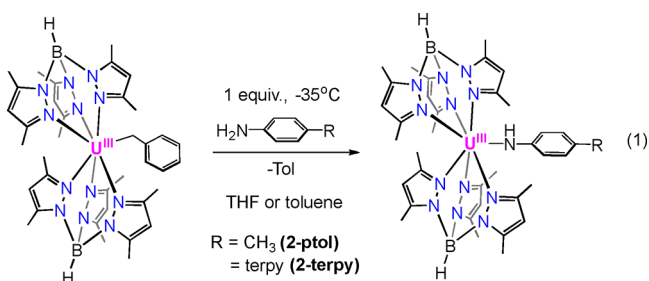
Results and Discussion. Trivalent Anilido Complexes. Initial experiments were aimed at the synthesis of uranium(III) anilido species because they could easily be accessed from the corresponding aniline. Treating **1-Bn** with 1 equiv of either terpy-aniline or *p*-toluidine produced $\text{Tp}^*_2\text{U}(\text{terpy-anilido})$

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(**2-terpy**) and $\text{Tp}^*_2\text{U}(\text{ptol-anilido})$ (**2-ptol**), respectively (eq 1). This synthetic method is convenient because the byproduct



is 1 equiv of toluene, which is easily removed in vacuo. The two uranium(III) anilidos were isolated as yellow-green and blue-green solids, respectively, in high yields and assigned as **2-terpy** (91%) and **2-ptol** (90%).

Analysis of these species by ^1H NMR spectroscopy shows paramagnetically broadened and shifted spectra due to $\text{U}^{\text{III}} f^3$ ions (Figures S1 and S4). The spectra for **2-terpy** and **2-ptol** are analogous, with resonances for the anilido groups appearing in the range of 7.55–35.32 ppm. Broad resonances for the NH peaks are both downfield relative to the rest of the resonances, visible at 65.32 ppm for **2-terpy** and 77.88 ppm for **2-ptol**. Broad BH resonances for Tp^* ligands have similar chemical shifts for both compounds (**2-terpy**, 2.69 ppm; **2-ptol**, 2.71 ppm). The CH resonance for the pyrazole on Tp^* are only present in the spectrum for **2-ptol** (0.17 ppm); this resonance could not be located for **2-terpy**, likely because of the paramagnetic nature of the complex. As seen for other bis(Tp^*) derivatives,^{9,10} CH_3 resonances farthest from the U^{III} center are visible between -3 and 0 ppm; that for **2-terpy** appears at -1.83 ppm, whereas the one for **2-ptol** appears at -2.42 ppm. The other CH_3 that points toward the U^{III} ion is not visible in the spectra for either compound, likely because of broadness.

Previous studies from our group have shown that the ^{11}B NMR peak for Tp^* is sensitive to the electronic environment at the U center and that the chemical shift can be indicative of the oxidation state in these systems.¹¹ ^{11}B NMR spectroscopy shows resonances for **2-terpy** (-8.62 ppm) and **2-ptol** (-11.94 ppm) (Figures S5 and S2, respectively), which are shifted from the starting material, **1-Bn** (-15.39 ppm), indicating a change in the ligand environment from the benzyl to the anilido ligand. However, all of these data are consistent with previously reported trivalent Tp^*_2U compounds.¹¹

IR spectroscopic data for **2-terpy** and **2-ptol** show two $\nu_{\text{B-H}}$ stretches [$(2556\text{ cm}^{-1}, 2526\text{ cm}^{-1})$ and $(2552\text{ cm}^{-1}, 2527\text{ cm}^{-1})$, respectively] similar to those for previously reported Tp^*_2U complexes, further confirming that both Tp^* ligands were maintained during the reaction (Figures S3 and S6). An absorption for the N–H bond was visible at 3334 cm^{-1} for **2-terpy** and 3359 cm^{-1} for **2-ptol**, confirming the formulation as anilido species.

To evaluate the structural properties of these new compounds, single crystals of each were grown from concentrated solutions of diethyl ether at -35°C and analyzed by X-ray crystallography (Figure 1, left and center). Refinement of data collected for Tp^*_2U anilido complexes displayed analogous seven-coordinate U centers with distorted pentagonal bipyramidal U ions that feature two $\kappa^3\text{-Tp}^*$ ligands per U center, with $\text{U}-\text{N}_{\text{pyrazole}}$ distances ranging from 2.531(2) to 2.704(2) Å for **2-terpy** and from 2.565(4) to 2.712(4) Å for **2-ptol** (Table 1). These distances are consistent with other

Table 1. Select Angles (deg) and Distances (Å) for **2-ptol**, **2-terpy**, and **3-terpy**

	2-ptol	2-terpy	3-terpy
U1–N1	2.352(4)	2.371(2)	2.010(6)
U1–N7	2.708(4)	2.688(2)	2.601(6)
U1–N5	2.574(4)	2.563(2)	2.541(6)
U1–N2	2.630(4)	2.655(2)	2.702(6)
U1–N8	2.712(4)	2.704(2)	2.669(7)
U1–N10	2.565(4)	2.531(2)	2.547(6)
U1–N12	2.651(4)	2.617(2)	2.616(6)
U1–N1–C1	145.6(4)	144.8(2)	166.8(5)

$\text{Tp}^*_2\text{U}^{\text{III}}$ complexes including **1-Bn** [$\text{U}-\text{N}_{\text{pyrazole}}$: 2.538(10)–2.734(12) Å],⁹ Tp^*_2UI [$\text{U}-\text{N}_{\text{pyrazole}}$: 2.510(6)–2.807(5) Å],¹⁰ $\text{Tp}^*_2\text{U}(\kappa^2\text{-O}_2\text{CCH}_2\text{Ph})$ [$\text{U}-\text{N}_{\text{pyrazole}}$: 2.570(8)–2.726(8) Å],⁹ and $\text{Tp}^*_2\text{U}(\text{N}(\text{SiMe}_3)_2)$ [$\text{U}-\text{N}_{\text{pyrazole}}$: 2.542(5)–2.802(6) Å].¹² The $\text{U}-\text{N}_{\text{anilido}}$ distances for **2-terpy** of 2.371(2) Å and for **2-ptol** of 2.352(4) Å (Table 1) are about 0.1 Å shorter than other seven-coordinate $\text{Tp}^*_2\text{U}^{\text{III}}$ amide compounds, including $\text{Tp}^*_2\text{U}(\text{N}(\text{C}_6\text{H}_5)_2)$ [2.489(9) Å]¹² and $\text{Tp}^*_2\text{U}(\text{N}(\text{SiMe}_3)_2)$ [2.480(6) Å],¹² likely because of the reduced steric hindrance from the primary amide ligands. The $\text{U1}-\text{N}_{\text{anilido}}-\text{C}$ bond angles for **2-terpy** [$144.8(2)^\circ$] and **2-ptol** [$145.6(4)^\circ$] (Table 1) are in the range of other uranium(III) amides because of sp^3 hybridization of the N atom, including $[\text{Li}(12\text{-crown-4})_2][\text{U}(\text{NHCPH}_3)(\text{N}(\text{SiMe}_3)_2)_3]$ [$151.2(3)^\circ$],¹³ $[\text{K}(\text{THF})_2][\text{U}$

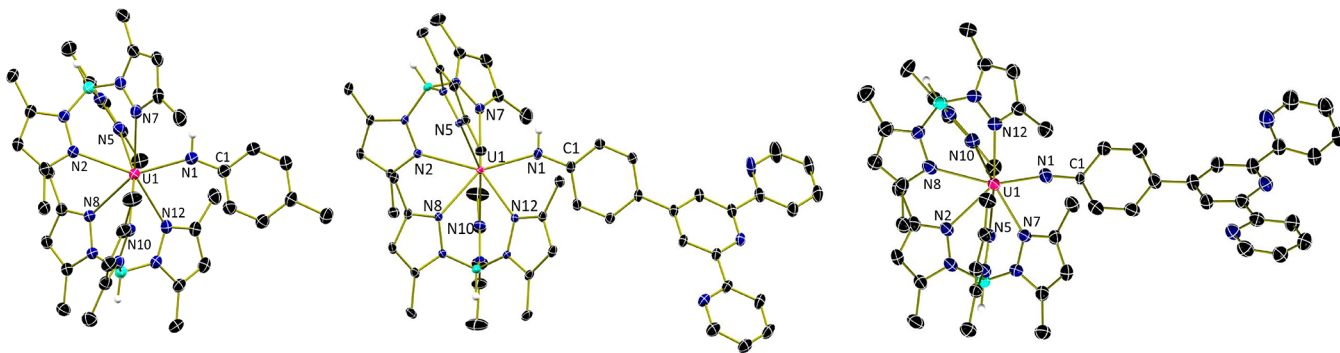
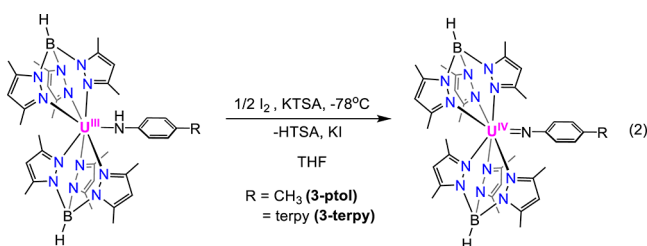


Figure 1. Molecular structures of **2-ptol**, **2-terpy**, and **3-terpy** (left to right), displayed with 30% probability ellipsoids. Selected H atoms and cocrystallized solvent molecules have been omitted for clarity.

(NH₂,6-ⁱPr₂C₆H₃)₅] [141(2)–156(2)°],¹⁴ and [U(NH(2,6-(2,4,6-ⁱPr₃C₆H₂)₂C₆H₃))₂] [137(2) and 135.6(2)°].¹⁵ The steric effects of the terpy ligand have little effect on the U–N_{anilido} distances because that in **2-terpy** [2.371(2) Å] is similar to that in **2-ptol** [2.352(4) Å].

Tetravalent Imido Complexes. With the uranium(III) anilido species in hand, conversion to the uranium(IV) imido species was targeted through oxidation and deprotonation. This was first attempted with **2-ptol** because the imido analogue of this, Tp*₂UNptol (**3-ptol**), has been previously reported.⁷ In the previous synthesis, **1-Bn** was treated with *p*-tolylazide, forming **3-ptol** with extrusion of bibenzyl. In this case, **2-ptol** was treated with 0.5 equiv of oxidant, I₂, and 1 equiv of base, potassium *tert*-butyl(dimethylsilyl)amide (KTSA), followed by filtration to remove KI and drying in vacuo to afford a red solid in 96% yield (eq 2). A comparison of the spectroscopic data for **3-ptol** matched those previously established.⁷



With this successful synthesis, the procedure was repeated with **2-terpy**, which produced Tp*₂U(terpy-imido) (**3-terpy**) as a red solid in high yield (96%). Analysis of **3-terpy** by IR spectroscopy showed two ν_{B-H} stretches at 2556 and 2522 cm^{−1} (Figure S9) similar to the previously reported ν_{B-H} stretches of **3-ptol** at 2559 and 2515 cm^{−1}, confirming the presence of two Tp* ligands.⁷ Importantly, N–H absorption was missing from the spectrum for **3-terpy**, supporting formation of the corresponding imido species.

Analysis of both of these species by ¹H NMR spectroscopy shows paramagnetically broadened and shifted spectra, with similarities for **3-ptol**⁷ and **3-terpy** (Figure S7). Resonances for the imido groups range between 9 and 79 ppm for both compounds, whereas the broad BH resonances from Tp* are almost identical (**3-terpy**, −21.34 ppm; **3-ptol**, −21.21 ppm). The resonances assignable to the CH protons from Tp* can be found at 5.76 ppm for **3-terpy** and 5.48 ppm for **3-ptol**. The CH₃ resonances closest to the U^{III} center are in the range of 2–3 ppm (**3-terpy**, 2.69 ppm; **3-ptol**, 2.81 ppm), while the CH₃ resonances furthest from the U^{III} center are analogous in the range of −6 to −7 ppm (**3-terpy**, −6.86 ppm; **3-ptol**, −6.89 ppm).

In contrast to **2-ptol** and **2-terpy**, the ¹¹B NMR spectroscopic data show resonances for **3-terpy** at −66.7 ppm (Figure S8) and for **3-ptol** at −66.6 ppm. These chemical shifts are consistent with the values previously reported for **3-ptol**, as well as other Tp*₂U^{IV} imido compounds.^{7,11} Both resonances are indicative of an oxidation state change from U^{III} to U^{IV} as expected.

Because **3-ptol** has previously been characterized in the solid state, single crystals of **3-terpy** grown from a concentrated diethyl ether solution at −35 °C were analyzed by X-ray crystallography to evaluate and compare their structural properties (Figure 1, right). Refinement of these data displayed a seven-coordinate U center with distorted pentagonal

bipyramidal geometry that features two κ^3 -Tp* ligands on the U center. The U–N_{pyrazole} distances range from 2.541(6) to 2.702(6) Å (Table 1), consistent with those of other Tp*₂U^{IV} imido complexes including **3-ptol** [2.526(6)–2.786(6) Å], Tp*₂UNBn [2.533(2)–2.737(2) Å], Tp*₂UNdetp [2.511(9)–2.727(10) Å], and Tp*₂UNDipp [2.533(6)–2.681(6) Å].⁷ The U=N_{imido} distance of **3-terpy** [2.010(6) Å] (Table 1) is consistent with those of other Tp*₂U^{IV} imido complexes including **3-ptol** [2.011(9) Å], Tp*₂UNBn [1.972(2) Å], Tp*₂UNdetp [2.004(12) Å], and Tp*₂UNDipp [2.003(7) Å].⁷ The U–N_{imido} bond distances are the same within error for **3-terpy** [2.010(6) Å] and **3-ptol** [2.011(9) Å], despite the larger steric profile of the terpy ligand. The U1–N_{imido}–C bond angle for **3-terpy** [166.8(5)°] (Table 1) is consistent with other bond angles observed for other Tp*₂U^{IV} imido complexes including **3-ptol** [163.6(9)°], Tp*₂UNBn [165.7(2)°], Tp*₂UNdetp [173.8(9)°], and Tp*₂UNDipp [180.0°] because of sp² hybridization of the N atom.⁷

Discussion of Anilido and Imido Complexes. The optical properties of **2-ptol**, **2-terpy**, and **3-terpy** were examined by electronic absorption spectroscopy. Data for these compounds were recorded in THF over the range 300–1600 nm at ambient temperature (Figure 2). For **2-ptol** and **2-terpy**, their

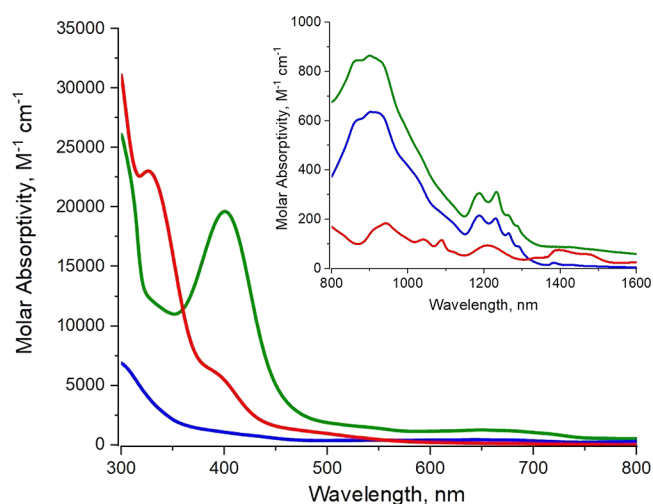


Figure 2. Electronic absorption spectra of **2-ptol** (blue), **2-terpy** (green), and **3-terpy** (red) recorded from 300 to 1600 nm in THF at 25 °C.

spectra exhibit almost identical weak and broad *f*–*f* transitions in the near-IR range (800–1600 nm), consistent with previously reported uranium(III) compounds.^{13,15,16} In the visible region, the broad color-producing band is present at 644 nm for **2-ptol** and 401 nm for **2-terpy**. For **3-terpy**, the spectra exhibit much weaker and broader *f*–*f* transitions in the near-IR range (800–1800 nm) compared to the uranium(III) complexes, which is signature for uranium(IV) compounds.⁷ In the visible region, the broad color-producing band is present at 515 nm.

As anticipated, the KTSA base serves to deprotonate the anilido species in each case, furnishing the corresponding imido. A base this strong could have also acted as a reductant, which in combination with I₂ would have produced an outcome that appeared as “no reaction”. Alternately, Tp* ligand dissociation could also have occurred, in favor of the formation of U–TSA and KTp*. The formation of **3-terpy** and

3-ptol by this route shows the robust nature of the bis(Tp*) ligand framework for supporting imido species under reducing conditions.

In summation, the synthesis of uranium(IV) imido compounds **3-terpy** and **3-ptol** by deprotonation and one-electron oxidation from the parent uranium(III) anilido compounds **2-terpy** and **2-ptol** has been achieved. Structural studies reveal that the bulky terpy group has little effect on the coordination chemistry, likely because of the fact that steric bulk is in the *p*-aryl position, moving it from the face of the Tp* ligand. Interestingly, these studies demonstrate the robust nature of this system because side reactions, such as reduction, were not observed. Deprotonation of an anilido is advantageous because it obviates the need for potentially explosive organoazides. It is worth noting that the terpyridine portion of **2-terpy** and **3-terpy** is well-known for its ability to coordinate transition metals, lanthanides, and other cations.^{17–21} Further studies will be aimed at coordinating Lewis acids in the terpy tridentate coordination site to evaluate how those interactions could affect the core U–N interactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01704>.

Synthetic procedures, spectroscopic data, and crystallographic details (PDF)

Accession Codes

CCDC 1998751, 1998752, and 1998754 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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