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Reductive Elimination of Diphosphine from a Thorium−NHC−Bis(phosphido) Complex

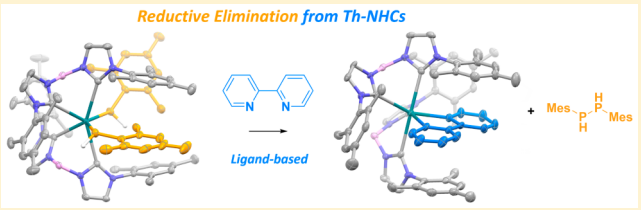
Mary E. Garner and John Arnold*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The synthesis, characterization, and reductive elimination reactivity of a bis(NHC)borate-supported thorium bis(phosphido) complex (2^{Mes}) is described. Treating 2^{Mes} with 2,2′-bipyridine leads to the reductive elimination of dimesityldiphosphine (**4**) and the formation of the previously reported NHC−thorium−bpy complex (**3**). The kinetics of the bpy-induced reductive elimination were studied by ^{31}P NMR and suggest the presence of an intermediate. Treatment with alternative oxidants also leads to diphosphine elimination, but the corresponding thorium species have not been isolated cleanly. Additional primary (2^{Ph}) and secondary (2^{PPh2}) Th−bis(phosphido) complexes were synthesized but do not demonstrate the same facile reductive elimination as 2^{Mes}.

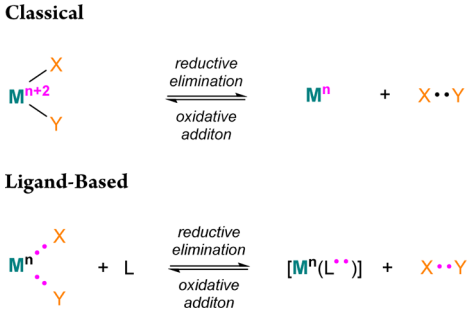


Oxidative addition and reductive elimination in organometallic chemistry and catalysis are fundamental steps for bond-making and -breaking reactions.[1,2] Mid to late transition metals are generally preferred for such transformations over early d- and f-block elements because they can accommodate changes in electron density through oxidation state changes at the metal. Yet, by using noninnocent supporting ligands as electron reservoirs, Heyduk and co-workers were able to extend this type of redox chemistry to early transition metals with formal d^0 electron counts.[3,4] In these systems, the ability of the supporting ligand to convert between its oxidized and reduced forms obviated the need for oxidation state changes at the metal center during the redox processes. Integrating noninnocent molecules into the organoactinide regime has been a useful endeavor as well.[5−20] In fact, a major advance for metals that are redox-active but have unstable reduced species came from the work of Bart and co-workers involving reductive elimination from a uranium(IV) benzyl complex.[12,15] While some uranium complexes perform metal-based oxidative addition and reductive elimination,[21] Bart and co-workers demonstrated how providing noninnocent molecules to attenuate electron richness at the metal center enabled cleaner, better-controlled redox transformations.

Unlike uranium, metal-based redox chemistry is impractical for most thorium compounds due to the very negative $Th^{IV/III}$ and $Th^{III/II}$ reduction potentials (−3.9 and −4.9 V vs NHE, respectively).[22−24] Therefore, our group[16,17] and others[6−9,19,20,25] have been exploring ligand-based ways to promote oxidative and reductive chemistry from thorium complexes. For example, we have shown that incorporating a reduced, noninnocent 2,2′-bipyridine (bpy) ligand into the coordination sphere of a bis(NHC)borate-supported (Bc^{Mes}) thorium compound affords a well-defined NHC−thorium−bpy complex (**3**) with potent reducing power. Utilizing its stored electrons, this complex mediates reductive transformations such as nitrene transfer from *p*-tolyl azide, coupling of carbonylated substrates, and well-defined C−N bond cleavage of alkyl isocyanides.[16,17]

Perhaps even more challenging than facilitating redox reactivity in these ways is promoting noninnocent reactivity from a complex that lacks both a redox-active supporting ligand and a redox-active metal center. Here we describe the reductive elimination of diphosphine from an NHC−Th−bis(phosphido) complex (2^{Mes}). Instead of relying on oxidation state changes at the metal center ("classical"), the reductive elimination involves redox changes entirely at the −HP(Mes) ligands and bpy ("ligand-based") (Scheme 1).

Scheme 1. Classical (Top) and Ligand-Based (Bottom) Reductive Elimination and Oxidative Addition Reactions



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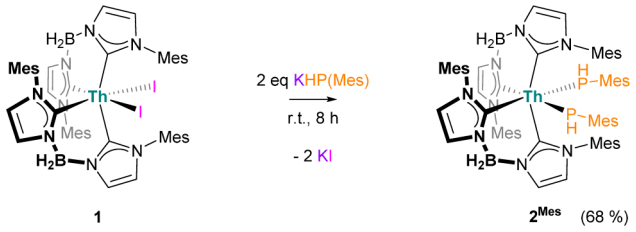
Treatment of the bis(iodo) complex Th(Bc^{Mes})$_2$I$_2$ (**1**) with 2 equiv of KHP(Mes) (Mes = 2,4,6-trimethylphenyl) affords the bright orange bis(phosphido) complex Th(Bc^{Mes})$_2$[HP(Mes)]$_2$ (**2**^{Mes}) in 68% yield (Scheme 2).

Scheme 2. Synthesis of Th(Bc^{Mes})$_2$[HP(Mes)]$_2$ (2^{Mes})



The ^{1}H NMR spectrum of **2**^{Mes} in C_6D_6 supports the assignment of a C_2-symmetric bis(phosphido) complex. The set of peaks corresponding to the two bis(NHC)borate ligands and those attributable to the two −PH(Mes) ligands are present in a 1:1 ratio. Notably, the two ^{31}P nuclei in **2**^{Mes} are magnetically nonequivalent and as a result the atoms comprising the H−P bond exhibit virtual coupling (J = 238.0, 16.1 Hz) in the ^{1}H NMR (+4.16 ppm) and ^{31}P NMR (+21.7 ppm) spectra (Figures S5 and S11 in the Supporting Information). These resonances collapse to singlets upon selective ^{31}P and ^{1}H decoupling (Figures S20 and S14 in the Supporting Information, respectively).

Red-orange crystals of **2**^{Mes} deposit from a vapor diffusion of hexanes into a concentrated benzene solution after storage for 48 h at room temperature. Single-crystal X-ray diffraction studies confirm that **2**^{Mes} is a rare example of a primary bis(phosphido)−thorium complex.[26,27] The compound maintains C_2 symmetry in the solid state and crystallizes in the monoclinic space group $P2_1/n$ (Figure 1). A 2-fold rotation axis runs through the thorium center bisecting the two −HP(Mes) ligands.

Similar to the Th−bis(phosphido) complexes previously reported by Walensky and co-workers,[26,27] **2**^{Mes} is highly sensitive to air and moisture but can be stored as a solid for several months at room temperature under an atmosphere of dry nitrogen. Solutions of **2**^{Mes} are stable at room temperature for 1 week and can be heated to 60 °C with no signs of decomposition. Unlike the case for the metallocene-supported thorium−bis(phosphido) complex,[26] heating solutions of **2**^{Mes} above 60 °C fails to form an isolable phosphinidene (=PR^{2-}) but instead generates 1 equiv of free H_2P(Mes) and an unidentified phosphorus-containing product. Lewis bases such as DMAP, pyridine, and THF do not form adducts[28] with **2**^{Mes}, and ^{t}BuNC does not react cleanly to form a phosphaazaallene.[27]

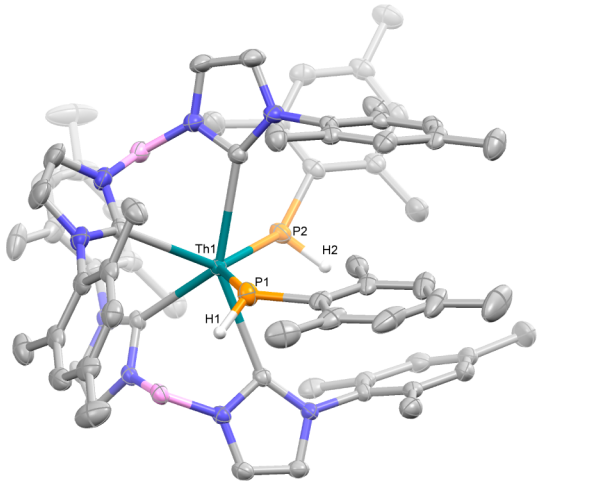
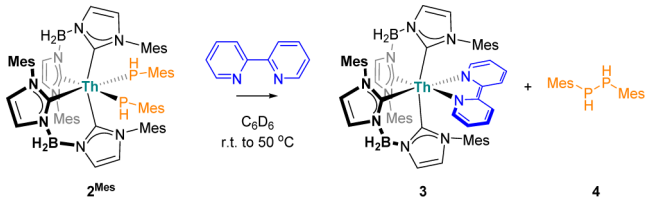


Figure 1. Molecular structure of **2**^{Mes} (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms, excluding those bound to phosphorus, are omitted for clarity. Selected bond distances (Å) and angles (deg): Th1−P1, 2.855(5); Th1−P2, 2.938(6); P1−Th1−P2, 137.01(2).

Bart and co-workers have shown that treating homoleptic uranium(IV) benzyl complexes with noninnocent moieties circumvents the formation of unstable uranium(II) species during the elimination of bibenzyl.[12,15] Curious as to how these types of outer-sphere moieties would affect our redox-inactive thorium system, we turned our attention to the interaction of **2**^{Mes} and bpy. Although addition of 1 equiv of bpy to a C_6D_6 solution of **2**^{Mes} causes a dramatic color change from bright red-orange to brown within seconds, the ^{1}H and ^{31}P NMR spectra taken after 5 min were unchanged. However, after several hours at room temperature, the reaction mixture became dark green and resonances corresponding to the previously described direduced Th−NHC−bpy complex[16] **3** were clearly visible in the ^{1}H NMR spectrum (Figure S3 in the Supporting Information), along with signals attributable to both isomers of the oxidatively coupled dimesityldiphosphine product **4** in the ^{31}P NMR spectrum (Figure S4 in the Supporting Information).[29] The transformation is clean and proceeds to completion with mild heating (50 °C); only trace amounts of free H_2P(Mes) side product are detected.

While the synthesis of direduced Th−bpy complexes is precedented, this is a rare example where the reduced bpy ligand is installed without the use of a strong reductant.[7,9,16,18,25] This overall two-electron redox transformation (Scheme 3) mimics that of reductive elimination by mid to late transition metals, but instead of occurring at the metal, the redox process involves only the ligands (−HP(Mes) and bpy). Performing a control reaction between the potassium phosphide salt [KHP(Mes)] and bpy in benzene does not afford a measurable amount of diphopshine **4**. Instead, the major product is free H_2P(Mes), likely arising from H atom abstraction from the solvent.

Scheme 3. Reductive Elimination Reactivity of 2^{Mes} on Treatment with bpy



Alternative outer-sphere redox mediators also induce the reductive elimination of **4**. Treatment of **2**^{Mes} with 1 equiv of iodine leads to the controlled formation of **4** along with the known thorium−bis(iodo) complex **1**.[16] In contrast, the reaction of iodine with KHPMes does not proceed cleanly to a single product but instead leads to a mixture of **4** and other unidentified phosphorus-containing species. Interaction of **2**^{Mes} with other oxidants such as *p*-tolyl azide, white phosphorus,

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1,10-phenanthroline, and acenaphthenequinone all lead to the formation of **4**, but despite our efforts no thorium-containing products have been isolated cleanly from these reactions. Still, our group is currently focused on utilizing this unique ligand-based reductive elimination of diphosphine as a potential strategy to access rare, or unknown, thorium compounds.

The kinetics of the elimination reaction by complex $\mathbf{2}^{\mathbf{Mes}}$ on treatment with bpy (Scheme 3) were studied by ^{31}P NMR spectroscopy. An initial rate investigation confirms that the disappearance of $\mathbf{2}^{\mathbf{Mes}}$ is first order, with no observable intermediates. The observed rate of **4** formation displays saturation behavior as the initial concentration of bpy is increased from 0.01 to 0.77 M (Figure 2).

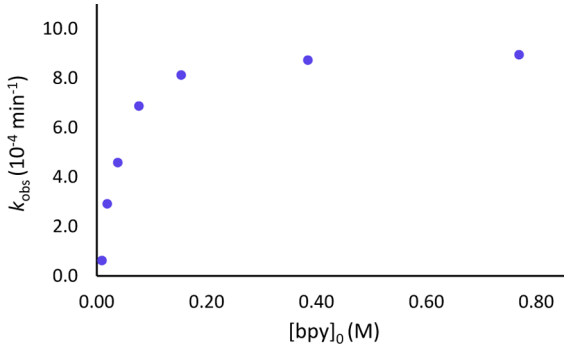
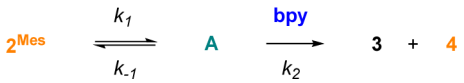


Figure 2. Variation in the observed rate of formation of **4** as a function of the initial concentration of bpy.

Such saturation behavior points to a pre-equilibrium in the mechanism and suggests that bpy is involved after this equilibrium is reached (Scheme 4).[30] Applying the steady-

Scheme 4. Proposed Mechanism for the Formation of 4



state approximation to the concentration of intermediate **A** leads to the rate expression described by Scheme 4 and given in eq 1 (see the Supporting Information for derivation). This expression is consistent with the experimentally observed dependences on [$\mathbf{2}^{\mathbf{Mes}}$] and [bpy] and is also confirmed by bpy flooding experiments ([bpy]$_0$:[$\mathbf{2}^{\mathbf{Mes}}$]$_0$ > 10:1). As predicted from eq 1, the formation of **4** demonstrates a zero-order dependence on the concentration of bpy when large excesses of bpy are used. The identity of **A** is unknown at this time; however, a mono(phosphido)−thorium complex is likely.

$$\frac{d[4]}{dt} = \frac{k_1 k_2 [2^{Mes}][bpy]}{k_{-1} + k_2 [bpy]} \quad (1)$$

Syntheses of the additional primary bis(phosphido)−Th−NHC complex $\mathbf{2}^{\mathbf{Ph}}$ and the secondary bis(phosphido)−Th−NHC complex $\mathbf{2}^{\mathbf{PPh2}}$ offer more information about the scope of the elimination reaction. Unlike $\mathbf{2}^{\mathbf{Mes}}$, treating $\mathbf{2}^{\mathbf{Ph}}$ with bpy does not lead to the formation of diphenyldiphosphine (**5**) (Scheme S3 in the Supporting Information), despite extended reaction times and/or heating. In the case of the secondary bis(phosphido) complex $\mathbf{2}^{\mathbf{PPh2}}$, reductive elimination of tetraphenyldiphosphine (**6**) can be achieved by heating to 70 °C but is accompanied by competing thermal decomposition of $\mathbf{2}^{\mathbf{PPh2}}$ (Scheme S4 in the Supporting Information).

Investigating the thermodynamics of these phosphorus−phosphorus bond-forming reactions at the DFT level shows that the formations of **3** and **4**, **5**, or **6** from bpy and $\mathbf{2}^{\mathbf{Mes}}$, $\mathbf{2}^{\mathbf{Ph}}$, or $\mathbf{2}^{\mathbf{PPh2}}$, respectively, are each very energetically favorable with nearly equal ΔG_{rxn} values (−19.1, −19.7, and −20.2 kcal/mol, respectively). The reason for the difference in reductive elimination reactivity between the bis(phosphido) compounds is unclear and is currently being explored. However, crossover experiments involving $\mathbf{2}^{\mathbf{Mes}}$ and $\mathbf{2}^{\mathbf{Ph}}$ expose the lability of the Th−P bond and demonstrate that the phosphido ligands can be readily exchanged (Figures S21−S23 in the Supporting Information).

To summarize, we have described an NHC−Th−bis(phosphido) complex that reductively eliminates diphosphine on treatment with bpy and other outer-sphere redox-active substrates. Installing the mesityl-substituted phosphido ligand affords a convenient model complex ($\mathbf{2}^{\mathbf{Mes}}$) amenable to kinetics investigations. The rate of formation of **4** shows a first-order dependence on [$\mathbf{2}^{\mathbf{Mes}}$] but displays saturation behavior in [bpy], which is confirmed by flooding experiments. Computational studies reveal that changes to phosphido ligands do not alter the thermodynamics of the elimination reaction significantly; however, experimentally the ease and cleanliness of the reaction are greatly affected. Performing this reductive elimination chemistry with a redox-inactive thorium center demonstrates how the overall redox changes occur entirely at the −HP(Mes) ligands and bpy. Efforts to define and expand the scope of this reductive elimination reactivity with other NHC−thorium complexes are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00301.

NMR, FT-IR, and UV−vis spectra of new compounds, computational details, and crystallographic data of compounds $\mathbf{2}^{\mathbf{Mes}}$, $\mathbf{2}^{\mathbf{Ph}}$, and $\mathbf{2}^{\mathbf{PPh2}}$ (PDF)

Accession Codes

CCDC 1517847−1517849 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for J.A.: arnold@berkeley.edu.

ORCID

Mary E. Garner: 0000-0002-4630-0661

John Arnold: 0000-0001-9671-227X

Notes

The authors declare no competing financial interest.

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