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Preparation of Heterobimetallic Ketimido-Actinide-Molybdenum Complexes

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Abstract

*During our attempts to prepare paddlewheel actinide-molybdenum complexes of the type $[(X)An(MesNPR_2)_3Mo(CO)_3]$ ($Mes = 2,4,6$ -trimethylphenyl; $X = Cl$ or I ; $An = U$ or Th ; $R = ^iPr$ or Ph) we have found that under certain conditions acetonitrile insertion reactions occur to give the hetero-bimetallic bridging ketimido species $[ClAn(\mu-MesNP^iPr_2)_2(\mu-MesNP^iPr_2\{\mu-NCMe\})Mo(CO)_3]$ ($An = U$, **1**; Th , **2**), $[ClAn(\mu-MesNPPh_2)_2(\mu-MesNPPh_2\{\mu-NCMe\})Mo(CO)_3]$ ($An = U$, **3**; $An = Th$, **4**), and $[IAn(\eta^2-MesNP^iPr_2)(\mu-MesNP^iPr_2)\{\mu-NC(Me)N(Mes)P^iPr_2\}Mo(CO)_3]$ ($An = U$, **5**; Th , **6**). Structural and spectroscopic data confirms the assignment of a ketimido ligand bridging $An(IV)$ and $Mo(0)$ centers. The isolation of **1-6** is in contrast to our previously reported preparations of $[(X)An(MesNPPh_2)_3Mo(CO)_3]$ ($An = U$ or Th ; $X = Cl$ or I ; *Chem. Commun.* **2018**, 54, 13515-13518) with the difference in reactivity being attributable to a combination of ancillary phosphino-amide, reaction solvent, and temperature variation. Complexes **1-5** represent the first examples of structurally characterized ketimido- bridged actinide-transition metal linkages, and demonstrate the profound differences in reaction outcomes that can occur from relatively minor experimental changes.*

Introduction

The area of metal-metal bonding continues to be an active area of endeavor.¹ Transition metal (TM) based hetero- and homo-bimetallic complexes historically dominate this area of research,² but more recently examples of s- and p- block metal-metal complexes have been reported,²⁻⁴ along with a recent surge in f-block examples.⁵⁻⁸ In particular for the actinide (An) elements uranium and thorium, structurally characterized examples are now known of unsupported or supported metal-metal bonds for U-Al,⁹ U-Ga,^{10,11} U-Sn,^{12,13} U-As,^{14,15} U-Sb,¹⁴ U-Bi,¹⁴ U-Mo,¹⁶ U-Re,¹⁷⁻¹⁹ U-Fe,²⁰⁻²² U-Ru,²³ U-Co,²⁴⁻²⁶ U-Rh,²⁸ U-Ni,²⁹ U-Pd,²⁹ U-Pt,²⁹ U-Ag,³⁰ Th-Sb,¹⁴ Th-As,^{14,31,32} Th-Te,³³ Th-Fe,³⁴ Th-Ru,³⁵ Th-Co,²⁶ Th-Ni,³⁶ Th-Pt,³⁷ Th-Cu.³⁸

We and others have recently reported examples of hetero-bimetallic An-TM linkages supported by bridging phosphino-amide linkages;^{16,25} ligands of this type have also been shown to stabilize a range of TM-TM linkages in recent years.³⁹⁻⁴² The ability of bimetallic species to effect unusual reactivity modes or catalysis is well documented,⁴³ with examples of naphthyridine-diamine stabilized Ni(I)-Ni(I) and Ru(II)-Ru(II) complexes being reported to effect the hydrosilylation of alkenes, dienes, alkynes and other unsaturated substrates for the former, and dehydrogenation of alcohols in the latter.^{44,45} Other examples include the *tris*(amidinate) Mo-Mo paddlewheel complexes which were reported to activate the C-Cl bond in CCl₄ across an alkene.⁴⁶ In particular hetero-bimetallic linkages have shown interesting reactivity modes towards small molecules, with the Ag-Ru species [(IMes)-AgRu(CO)₂] being reported to semi-hydrogenate alkynes,⁴⁷ and the heterolytic splitting of dihydrogen by the Pt-Sn bimetallic [Pt(SnBu₃)(COD)(H)] (COD = 1,5-cyclooctadiene).⁴⁸ We are unaware of any activation of acetonitrile or other nitriles by metal-metal linkages, but the activation of nitriles by other An complexes in general is well established. For example, the

insertion of acetonitrile into the U=C bond of $[\text{Cp}_3\text{U}=\text{CHPh}(\text{Ph})_2\text{Me}]$ was reported to afford $[\text{Cp}_3\text{UNC}(\text{Me})\text{CHPh}(\text{Ph})_2\text{Me}]$ where the newly formed U-N linkage was ascribed multiple bond character due to its very short distance.⁴⁹ More recently there have been many reports of insertion of nitriles into An-alkyl bonds to afford ketimido-type complexes,^{50–55} examples including the insertion of $^t\text{BuCN}$ into the U-C bonds in $[(\text{Cp}^*)_2\text{U}(\text{CCPh})_2]$ (Cp^* = pentamethylcyclopentadiene) to afford $[(\text{Cp}^*)_2\text{U}\{\text{NC}(^t\text{Bu})\text{CCPh}\}_2]$,⁵¹ the insertion of NCPhCN into the U-Me bond in $[(\text{R})_2\text{An}(\text{Me})_2]$ ($\text{R} = \text{Cp}^*$, $\text{An} = \text{Th}$, $\text{R} = \text{CpMe}_4\text{Et}$, $\text{An} = \text{U}$) to afford $[(\text{R})_2\text{An}\{\text{NC}(\text{Me})\text{PhCN}\}_2]$,⁵⁴ and the insertion of NCPh into $[(\text{Cp}^*)_2\text{An}(\text{R})_2]$ ($\text{An} = \text{Th}$, $\text{R} = \text{Ph}$, CH_2Ph , CH_3 , $\text{An} = \text{U}$, $\text{R} = \text{CH}_2\text{Ph}$ or CH_3) to afford $[(\text{Cp}^*)_2\text{An}\{\text{NC}(\text{R})(\text{Ph})\}_2]$.⁵⁵ Most recently, insertion of acetonitrile into a uranium-hydride linkage was reported to activate the nitrile to yield a bridging diuranium ketimido complex, namely $[\text{Cs}\{\text{U}[\text{OSi}(\text{O}^t\text{Bu})_3]\}_2(\mu\text{-NH})(\mu\text{-CH}_3\text{CHN})]$.⁵⁶

During our investigations towards preparing supported U-Mo linkages,¹⁶ we observed that under certain conditions (*vide infra*) our U-Mo linkages activate acetonitrile to afford An-ketimido systems, but the reaction conditions and ancillary ligands employed greatly affect the outcome of the reactions. Here, we provide an account of that work.

Results

Synthesis

We previously reported the An-Mo paddlewheel complexes $[(\text{X})\text{An}(\text{MesNPPH}_2)_3\text{Mo}(\text{CO})_3]$ ($\text{X} = \text{Cl}$, $\text{An} = \text{U}$, **UCIMo**; $\text{X} = \text{I}$, $\text{An} = \text{U}$, **UIMo**; $\text{X} = \text{Cl}$, $\text{An} = \text{Th}$, **ThCIMo**; $\text{X} = \text{I}$, $\text{An} = \text{Th}$, **ThIMo**).¹⁶ In order to investigate any effects on the An-Mo linkages of these systems by variation of the ligand field, we targeted the preparation of a range of analogues by variation of the substituents on the phosphino-amide ligands, namely by using $\text{MesNP}^i\text{Pr}_2$, DippNPPH_2 , $\text{DippNP}^i\text{Pr}_2$, TripNPPH_2 and $\text{TripNP}^i\text{Pr}_2$ ($\text{Dipp} = 2,6\text{-diisopropylphenyl}$, $\text{Trip} = 2,4,6$

triisopropylphenyl) as supporting ligands rather than MesNPPh₂. Unfortunately, when *N*-substituents that are sterically more demanding than Mes are utilized we found that either the *tris*-phosphino-amides [XAn(R'NPR₂)₃] (R' = Dipp or Tripp; R = ⁱPr or Ph; An = Th or U; X = I or Cl) could not be obtained, and di-substituted species such as [Cl₃U(DippNPPh₂)₂][Li(THF)₄] and [Cl₃U(TrippNPPh₂)₂][Li(THF)₄] were isolated instead; presumably the steric bulk of those phosphino-amides prevents coordination of a third phosphino-amide to the actinide metal,⁵⁷ or in cases where a *tris*-phosphino-amide actinide halide was accessible, e.g [ClU(DippNPⁱPr₂)₃],⁵⁷ no further reactivity towards molybdenum carbonyl precursors was observed despite applying forcing thermolytic or photolytic conditions. Details of those pro-ligands, alkali metal ligand transfer reagents, and various metal-halide-phosphinoamide combinations are given in the Supporting Information (compounds **DippN(H)PⁱPr₂**, **TrippN(H)PⁱPr₂**, **TrippN(H)PPh₂**, and **S1-S14**).

In contrast, however, we were able to successfully isolate the MesNPⁱPr₂ derived *tris*-phosphino-amide actinide precursors [ClAn(MesNPⁱPr₂)₃] (An = U, **S8**; An = Th, **S9**) and their iodide substituted derivatives [IAn(MesNPⁱPr₂)₃] (An = U, **S10**; An = Th, **S11**).⁵⁷ Compound **S8** is initially isolated as a {ClLi(THF)₃} 'ate' complex but the occluded LiCl can be removed by extraction into toluene. With these compounds in hand, we targeted the preparation of more paddlewheel supported actinide-molybdenum complexes. However, in contrast to our previous preparation of **UCIMo** and **ThCIMo**, which proceeded *via* the reaction of [ClAn(MesNPPh₂)₃] with [Mo(CO)₃(NCMe)₃] in refluxing toluene, we find that no reaction is observed when [ClAn(MesNPⁱPr₂)₃] (An = U or Th) is used in place of [ClAn(MesNPPh₂)₃] under the same reaction conditions. In further attempts to prepare An-Mo complexes, we adjusted the reaction conditions and discovered that the reactions of [ClAn(MesNPⁱPr₂)₃] (An = U or Th) with [Mo(CO)₃(NCMe)₃] in dichloromethane (DCM)

proceeds under ambient conditions to afford the acetonitrile-inserted species $[\text{ClAn}(\mu\text{-MesNP}^i\text{Pr}_2)_2(\mu\text{-MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (An = U, **1**, 82%; M = Th, **2**, 61%), Scheme 1.

In order to assess the generality of this reaction we reacted $[\text{ClAn}(\text{MesNPPH}_2)_3]$ (An = U or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ in DCM affording $[\text{ClAn}(\mu\text{-MesNPPH}_2)_2(\mu\text{-MesNPPH}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (An = U, **3**, 52%; An = Th, **4**, 57%) and not **UCIMo/ThCIMo** as previously reported when refluxing toluene was used as the reaction solvent.¹⁶ In each case the acetonitrile can be considered to have been activated and converted into ketimido linkages that are reminiscent of previous reports of insertion of nitriles into uranium-alkyl bonds,^{51,54,55} whereas in this work it has the appearance of inserting into a putative An-Mo bond with concomitant Mo-P bond breaking. The synthesis of **3** and **4** in DCM versus the synthesis of **UCIMo/ThCIMo** in toluene, with $[\text{ClAn}(\text{MesNPPH}_2)_3]$ (An = U or Th) and $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ as the common starting materials in both cases, suggests that those reaction outcomes are purely a function of the solvent since the phosphino-amide is the same in both complexes. We therefore tentatively suggest that in both sets of reactions paddlewheel complexes are formed, but when DCM is used as the reaction solvent the increase in polarity of DCM vs toluene may lead the phosphine ligands being more labile which would make their *P*-lone pairs more available to attack the acetonitrile by-product of the reactions. Interestingly, the lack of reaction of $[\text{ClAn}(\text{MesNP}^i\text{Pr}_2)_3]$ (An = U or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ in toluene, even under refluxing conditions, suggests that a more polar solvent is necessary to activate the precursor complex for reactivity, and therefore under the conditions employed the proposed paddlewheel intermediate $[(\text{Cl})\text{An}(\text{MesNP}^i\text{Pr}_2)_3\text{Mo}(\text{CO})_3]$ is reactive towards acetonitrile and leads to the formation of **1-2**. As both *P*-Ph₂ and *P*-ⁱPr₂ derived phosphino-amide

paddlewheel complexes were observed to activate acetonitrile, it is not solely the ligand variation driving the reactivity, and so the reaction solvent is clearly playing a major role in the observed reactivity as demonstrated by the divergent preparations of **3/4** and **UCIMo/ThCIMo** when only the reaction solvent was varied.

To further ascertain the effect of ligand environment on the outcomes of these reactions, we reacted the iodide precursors $[\text{IAn}(\text{MesNP}^i\text{Pr}_2)_3]$ (An = U or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ in refluxing toluene, akin to our previous reports of **UIMo** and **ThIMo**.¹⁶ In contrast to our previous report, we found that once again acetonitrile is activated to afford $[\text{IAn}(\eta^2\text{-MesNP}^i\text{Pr}_2)(\mu\text{-MesNP}^i\text{Pr}_2)\{\mu\text{-NC(Me)N(Mes)P}^i\text{Pr}_2\}\text{Mo}(\text{CO})_3]$ (An = U, **5**, 57%; An = Th, **6**, 67%) (Scheme 1). Of note here is that the activation of acetonitrile in this case did not require a more polar solvent such as DCM, but proceeded in toluene solution; whether this is due to steric or electronic changes brought about by substituting Ph by ⁱPr is currently not clear. Interestingly, although the heterobimetallic formulation of **5** and **6** suggest that paddlewheel complexes may be formed which subsequently activate acetonitrile, this time the products are *N*- not *P*-inserted. To produce **5** and **6** the reaction mixtures are refluxed as no reaction occurs at room temperature, which is in contrast to the preparation of **1-4**, which proceed under ambient conditions, albeit in DCM not toluene. However, to eliminate that temperature is not a factor in converting from *P*- to *N*-inserted products we refluxed toluene solutions of **1-4** and did not find any evidence that these *P*-inserted compounds convert to the *N*-insertion congeners. Since covalent C-N and P-C bonds are formed during these reactions they are likely irreversible as supported by the thermolysis experiments.

Spectroscopic Characterization

The ¹H NMR spectra of **1-4** are indicative of low-symmetry species in solution, consistent

with the insertion of acetonitrile breaking the C_3 -symmetry of the hypothetical paddlewheel precursors to these complexes, thus resulting in C_s symmetric species with two distinct phosphino-amide ligand environments. Although **1** and **3** are paramagnetic and **2** and **4** are diamagnetic, for a given pair broadly similar trends are observed in terms of the occurrence of unique proton environments in solution. For example, for **1**, four ^iPr -Me environments are observed, where two environments are Me-groups that are *endo* and *exo* to the ketimido linkage and the remaining two environments are Me-groups on the other two phosphino-amide ligands that are *endo* and *exo* to the former. Additionally, four mesityl-Me and two mesityl-CH environments are observed, again consistent with two NP-ligand environments. A similar picture emerges for **2**, except the diamagnetism of this complex results in sharper resonances than **1** resolving six and five individual ^iPr -Me and mesityl-Me environments, respectively. Similarly, the NMR spectra for **3-4** show two distinct NP-ligand environments with a lack of C_3 symmetry in solution. Overall the NMR spectroscopic data indicate that: a) two different NP-ligand types are present in each complex; b) the ^iPr -groups are diastereotopic; c) rotation of the mesityl-groups, and possibly the ^iPr -groups, is hindered producing unique environments from the approximate C_s symmetry of **1-4**; d) the solid state structures of these complexes is likely retained in solution. Although $^{31}\text{P}\{^1\text{H}\}$ NMR resonances could not be observed for paramagnetic **1** and **3**, those of diamagnetic **2** and **4** were observed and the presence of two resonances for each complex is again consistent with the presence of two types of NP-ligands, Table 1.

The ^1H NMR spectra of **5** and **6** are even more complex than those of **1-4**, which is in keeping with the highly asymmetric natures, and is in agreement with the three distinct coordination modes for the phosphino-amides observed in the solid state structures. For **5**, twelve methyl and three ^iPr -methine resonances are observed consistent with three different

ligand environments. Although **6** exhibits ten methyl resonances, as opposed to twelve, this is likely due to overlapping methyl resonances, as **6** exhibits three ^1Pr -methine resonances and also three resonances in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectra consistent with the three phosphino-amide ligands being inequivalent. The CH_3CN resonances for **1-6** span a narrow range, being observed at 1.97, 1.87 and 1.87 ppm for the thorium species **2**, **4**, and **6**, and at 4.77 and 3.53 ppm for the uranium species **1** and **3**, respectively. Unfortunately, no resonance for the acetonitrile derived methyl group could be assigned for complex **5**. The observed $^{13}\text{C}\{^1\text{H}\}$ NMR resonances for the Th-N=C group in **2** and **4** (172.5 and 166.5 ppm, respectively) are comparable to other reported thorium ketimides (range 157.9 - 181.1 ppm),^{53,58–62} and while we were unable to observe any U-N=C resonances for **1**, **3** or **5**, this is typical for uranium ketimides due to the quaternary nature of the carbon and the proximity to the paramagnetic uranium(IV) center. In fact, to our knowledge only four uranium ketimide complexes have reported observable resonances derived from the uranium ketimide center: $[(\text{Cp}^*)_2\text{U}(\text{N}=\text{CPh}_2)_2]$ (58.8 ppm); $[(\text{Cp}^*)_2\text{U}[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)\text{N}=\text{C}(1\text{-C}_{10}\text{H}_7)_2]]$ (44.9 ppm); $[(\text{Cp}^*)_2\text{U}\{\text{N}=\text{C}(\text{Ph})\{\text{C}_4(\text{SiMe}_3)_2\}\text{C}(\text{Ph})=\text{N}\}]$ (202.7 ppm); $[\text{Cs}\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-NH})(\mu\text{-CH}_3\text{CHN})]$ (128.7 ppm).^{56,63–65}

The FTIR spectra of **1-6** show that the $\text{C}\equiv\text{O}$ stretches are shifted to higher wavenumbers by $\sim 20\text{-}44\text{ cm}^{-1}$ for $\tilde{\nu}_1$ and $\sim 37\text{-}64\text{ cm}^{-1}$ for $\tilde{\nu}_2$ relative to *fac*- $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ (Table 1). These shifts are lower than those observed for **UCIMo/UIMo/ThCIMo/ThIMo** where shifts of $\sim 50\text{ cm}^{-1}$ for $\tilde{\nu}_1$ and $\sim 100\text{ cm}^{-1}$ for $\tilde{\nu}_2$ relative to *fac*- $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ were observed. This suggests that there is more Mo-CO backbonding present in **1-6** than **UCIMo/UIMo/ThCIMo/ThIMo** suggesting that the effective replacement of a phosphine and metal-metal linkage with the formally datively bound ketimido center leads to more electron-rich molybdenum centers in **1-6**. The C=N stretches of the ketimido linkage in **1-6**

are observed between 1594-1632 cm^{-1} , which, where data are available, is consistent with other reported actinide ketimido linkages (range 1579-1631 cm^{-1}),^{50,51,56,59–63,65–69} but they are otherwise unremarkable.

The UV/Vis/NIR spectra of **1**, **3**, and **5** were obtained, but in each case they are largely unremarkable, with only minor absorptions in the NIR region - consistent with f-f transitions of uranium(IV) - and charge transfer bands that extend into the UV region being observed.

Solid State Structures

The solid state structures of **1-5** were determined and are depicted in Figures 1-5 (see Tables S1-S5 in the Supporting Information). Unfortunately, despite repeated attempts single crystals of **6** suitable for X-ray diffraction studies could not be obtained. Complexes **1-4** show very similar motifs in the solid state so they are discussed together, but **5** is discussed separately (*vide infra*). In **1-4**, the insertion of acetonitrile into a putative Mo-P linkage is confirmed and leads to a five membered An-N(Mes)-P(R)₂-C(Me)-N(Mo)- chelate ring in each complex. In **1-4**, the An-Mo distances [**1**, 3.3150(5); **2**, 3.361(2); **3**, 3.3019(3); **4**, 3.4061(3) Å] are longer than the An-Mo distances in **UCIMo/ThCIMo/UIMo/ThIMo** [3.1682(4), 3.2986(11), 3.159(2), and 3.310(2) Å, respectively], and are greater than the sum of the covalent radii of U/Th and Mo of 3.08 and 3.12 Å, respectively.⁷⁰ This suggests that **1-4** should not be considered to exhibit any significant metal-metal bonding interactions. With this in mind, the actinide centers in **1-4** can be best considered as 5-coordinate, being coordinated by a halide, the ketimido-nitrogen and three nitrogens from the phopshino-amide ligands. Inspection of the metrical parameters about the metal centers reveals τ parameters of 0.43 (**1**), 0.39 (**2**), 0.45 (**3**) and 0.44(**4**) so assignment of trigonal-pyramidal vs square based pyramidal geometry is not appropriate as each structure sits between the two extremes.⁷¹ In each case the An-

center is close to the plane defined by the three paddlewheel nitrogens [**1**, 0.139(3); **2**, 0.071(12); **3**, 0.1405(18); **4**, 0.238(2) Å]. In **1-4**, the molybdenum centers adopts a slightly distorted octahedral geometries, with the three carbonyls adopting a *fac* arrangement. The most informative aspect of the solid state structures is the bond distances about the 5-membered An-N(Mes)-P(R)₂-C(Me)-N(Mo) ring as these can confirm the ketimido assignment in these complexes. For example in **1**, the endocyclic U-N(Mes), N(Mes)-P(R)₂, P(R)₂-C(Me), C(Me)-N(Mo) and N(Mo)-U distances are 2.436(5), 1.637(5), 1.853(6), 1.265(8) and 2.288(5) Å, respectively. The U-N(Mes) distance in the endocyclic ring is ca 0.15 Å longer than the other U-N distances involving the PN paddlewheel ligands within the same structure [2.278(4), 2.305(5) Å] and in **UIMo/UCIMo** suggesting a loss of amide character with this distance being more akin to uranium-amine distances [range: 2.465(5)-2.989(2) Å].⁷² Similarly, the U-N(Mo) distance of 2.288(5) Å is shorter than expected for a purely dative interaction and is suggestive of a formal bond between the nitrogen and actinide center. Comparing the metrical parameters of **1** to the sum of the respective radii (Pyykkö's formal single and double bond data⁷⁰ as follows: C-N = 1.46; C=N = 1.27; P-C = 1.86; P=C = 1.69; P-N = 1.82; P=N = 1.62 Å) leads to an assignment of a P=N double bond, P-C single bond, and C=N double bond about the endocyclic ring (Scheme 1). This suggests that the P-N paddlewheel linkage is now bound to the uranium center as an iminophosphorane and the nitrogen that is derived from acetonitrile is a ketimide C=N⁻ linkage. Even though it is bridging, the U-N(Mo) distance of 2.288(5) Å is short, reflecting the electron-rich nature of ketimides, and indeed the U-N(Mo) distance is within the range of reported bridging actinide-metal ketimido linkages (2.228 - 2.480 Å; mean 2.299 Å).^{56,72,73} The strong donation of the ketimide to uranium appears to come at the expense of its interaction with the molybdenum center, with the Mo1-N4 distance in **1** of 2.249(4) Å being longer than the sum of the covalent radii of molybdenum and nitrogen (2.09 Å) and longer than molybdenum ketimides

generally, e.g. $[\text{Mo}(\text{CO})_2(\text{Cp})\{\text{N}=\text{C}(\text{tBu})_2\}]$ (1.892(5) Å) and $[\text{Mo}\{\text{N}=\text{C}(\text{tBu})_2\}_4]$ (1.880(5)-1.885(2) Å).⁷⁴⁻⁷⁵ Complexes **2-4** show similar bond distances about the endocyclic ring, but with the Th-N distances being longer, as expected due to the larger covalent radius of Th (1.75 Å) compared to uranium (1.70 Å), but these are in agreement with an assignment of an iminophosphorane and ketimido-type linkages to the metal centers.

The solid state structure of **5** confirms that acetonitrile has been incorporated into the uranium-molybdenum structure, but in this case has inserted into a putative U-N linkage rather than the Mo-P linkage as in **1-4**, leading again to a 5-membered endocyclic ring, but with a different conformation, namely Mo-P(R)₂-N(Mes)-C(Me)-N(U). Interestingly in **5**, the CO ligands adopt a *mer* arrangement rather than *fac*, as in **1-4**, while the absence of a U-Mo linkage is suggested by the long U-Mo distance of 3.3145(8) Å. Assessment of the metrical parameters about the endocyclic ring again suggests that the acetonitrile has been transformed into a ketimide anion but, in this case, the assignment of single or double bond character to the bonds about the endocyclic ring are not as clear cut as in **1-4**, suggesting delocalization of charge about the ring with the expected C=N bond being 1.311(12) Å (cf 1.27 Å for a formal C=N) and the P-N bond distance of 1.730(9) Å being intermediate to formal P=N and P-N bonds (1.62 and 1.82 Å, respectively). The ketimide center is again bridging the two metals resulting in U-N and Mo-N distances of 2.235(7) and 2.237(7) Å, respectively, which are each similar to those observed in **1-4**. The Mo-P distances in **5** (2.495(3) and 2.449(3) Å) are shorter than those observed in **1-4** (ca 2.61 Å), which is likely due to a *trans* effect as they are mutually *trans* to one another in **5**, whereas in **1-4** they are each *trans* to carbonyl groups.

Magnetism

Complexes **2**, **4**, and **6** exhibit NMR spectra in the normal diamagnetic range consistent with

the Th(IV) oxidation state possessing a 1S_0 ground state and are indicative of molybdenum being an, albeit distorted, octahedral low spin Mo(0) $4d^6$ center in each case. The uranium species **1**, **3** and **5** each exhibit NMR spectra with resonances paramagnetically shifted over ~50 ppm spectral windows, in-line with their uranium(IV) $5f^2$ assignments. The effective magnetic moment of solution samples of **1**, **3** and **5** in benzene at 298 K were determined using the Evans method⁷⁶ to be 2.41, 2.49 and 2.91 μ_B , respectively, which are each within the range for reported uranium(IV) complexes.^{77,78} Confirmation of the uranium(IV) assignments was obtained by variable temperature SQUID magnetometry (Figure 6) of **1**, **3** and **5** dispersed in eicosane. We find magnetic moments at 300 K of 2.68, 2.55 and 2.65 μ_B for **1**, **3** and **5** respectively, which are consistent with a 3H_4 ground state for U(IV) $5f^2$ centers.^{77,78} For all three compounds the value of μ_{eff} decreases smoothly as the temperature is lowered from 300 K to ~30 K, where it begins to decrease more sharply and at 1.8 K the respective magnetic moments for **1**, **3** and **5** are 0.63, 0.66 and 0.66 μ_B . The magnetization traces tend to zero at this temperature, which is consistent with the presence of a 3H_4 uranium(IV) ion that is a magnetic singlet subject to temperature independent paramagnetism at low temperature.

Discussion

The isolation of **1-4** in contrast to our previous reports of **UCIMo/UIMo/ThClMo/ThIMo** show that these reaction pathways are not predictable and highlight the inherent instability of these actinide-molybdenum linkages. Further to this, the replacement of either a *P*-substituent group or the change of reaction solvent can lead to a different outcome on the reaction routes observed highlighting the importance of fine tuning the reaction conditions when attempting to prepare novel and unstable metal-metal linkages, even when stabilized by bridging ligands. We postulate that in the preparation of **1-4** the targeted paddlewheel complexes of the general formula $[(X)An(MesNPR_2)_3Mo(CO)_3]$ are formed, but that these are unstable towards the

acetonitrile which is eliminated during the reaction and react to yield the more thermodynamically stable **1-4** (Scheme 2). Whilst it can be reasoned that a $P\text{-}^i\text{Pr}_2$ variant will give a $[(X)\text{An}(\text{MesNP}^i\text{Pr}_2)_3\text{Mo}(\text{CO})_3]$ intermediate that is more susceptible to reaction with acetonitrile compared to a $P\text{-Ph}_2$ one, the choice of reaction solvent also has a significant influence on the reaction outcome. Reaction of $[\text{ClAn}(\text{MesNPPH}_2)_3]$ ($\text{An} = \text{U}$ or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ in refluxing toluene affords **UCIMo** and **ThCIMo**, whereas reaction in DCM under ambient conditions leads to **3** and **4**, which suggests that a more polar solvent such as DCM is required for **UCIMo** or **ThCIMo** to activate acetonitrile when no reactivity towards acetonitrile is observed in a toluene solution, even under forcing conditions (Scheme 1). However, the steric bulk of the P -substituents does influence the reaction outcome when iodide precursors are used, with the reaction of $[\text{IAn}(\text{MesNPPH}_2)_3]$ ($\text{An} = \text{U}$ or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ affording the stable **UIMo** and **ThIMo**, whereas when the ^iPr substituted congener is used in the reaction of $[\text{IAn}(\text{MesNP}^i\text{Pr}_2)_3]$ ($\text{An} = \text{U}$ or Th) with $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ the acetonitrile activated products **5** and **6** were isolated under the same reaction conditions. This shows that the reaction outcome in these systems is nuanced and has a large number of contributory factors. The spectroscopic data for **1-4** show that the overall geometry is the same in each case with the acetonitrile inserted into the putative intermediate An-Mo and Mo-P linkage of $[(\text{Cl})\text{An}(\text{MesNR}_2)_3\text{Mo}(\text{CO})_3]$ to afford a 5-membered metallocyclic ring. Inspection of the metrical parameters of each of **1-4** confirms an assignment of a ketimido motif, leading to formal $\text{P}=\text{NMes}$ and $\text{R}_2\text{C}=\text{N}^-$ ligand linkages across the metallocycle which bind to the metal centers in dative and mono-anionic modes, respectively. The molybdenum ketimido bond distances of ca 2.24 Å are outside the sum of the respective single bond covalent radii (2.09 Å) whereas the actinide-ketimido distances are short (**1**, 2.288(5); **2**, 2.39(2); **3**, 2.312(3); **4**, 2.377(3) Å] when compared to the sum of covalent radii ($\text{U-N} = 2.41$; $\text{Th-N} = 2.46$ Å)⁷⁰ leading to the assignment of a formal U-N ionic

bond and a Mo-N dative bond. It follows that the molybdenum center is coordinated by 6 donor ligands, namely the ketimide, two phosphines and three carbonyls leading to a formal low-spin Mo(0) assignment which is commensurate with the diamagnetism of **2** and **4**. The magnetic data indicate that the uranium and thorium centers are in the (IV) oxidation state, being coordinated by two amides, the ketimido-, a halide, and completing the coordination sphere is a formal iminophosphorane, which is bound datively. Analysis of the metrical parameters about the An-N-Mo linkage in **5** leads to the same conclusions, as here there is a short An-N and long N-Mo distance commensurate with a U(IV) and Mo(0) assignment, only in this case the uranium is bound by a phosphine of the paddlewheel in place of an iminophosphorane as in **1-4**, but each are bound datively. Of note, there are three examples of bridging ketimido-type linkages between two uranium metals but to our knowledge **1-5** represent the first structurally characterized examples of complexes containing a ketimido-type ligand bridging between an actinide and a transition metal.⁷² The activation of acetonitrile and other nitriles to afford ketimides by An-X bonds is not unprecedented,^{50-55,58,61,79} but somewhat surprisingly the An-N bond distances in **1-4** and **5** are comparable to terminal actinide(IV)-ketimide distances, e.g. [U{N=C(^tBu)₂}₅{μ-Li(THF)}] (2.233-2.256 Å) and [U(Cp*)₂{N=C(Ph)(CH₂Ph)}₂] (2.184 Å)^{54,66} despite adopting a bridging motif. The isolation of **5-6** in contrast to **1-4** is interesting, but the cause is not certain. A potential cause is that during the reaction an intermediate of the form [(I)An(MesNPⁱPr₂)(μ-MesNPⁱPr₂)₂Mo(NCMe)(CO)₃] (**5'** or **6'**) (Scheme 3) is formed which in the case of **1-4**, reacts by displacing NCMe to give the *tris*-paddlewheel structures which then react intermolecularly with NCMe to afford **1-4**. However in the case of the iodide derivatives, it is possible that before the NCMe is dissociated from the molybdenum center and the third paddlewheel linkage is formed, the acetonitrile undergoes nucleophilic attack by the amide of a bridging phosphino-amide rather than the phosphine lone pair, as in **1-4**. This would lead

to three different PN environments as observed in the solid state structures and NMR spectroscopic data, and formally would be a result of an intramolecular reaction. Unfortunately, we were unable to observe any reaction intermediates via variable temperature NMR spectroscopy suggesting that insertion of the acetonitrile into the An-Mo linkage is fast relative to the NMR time-scale.

Conclusions

To conclude, we have reported the preparation of a range of actinide phosphino-amide halide precursors along with our attempts to prepare actinide-molybdenum paddlewheel complexes, which under certain reaction conditions results in insertion of acetonitrile into the putative An-Mo or An-N linkages depending on the solvent conditions and ancillary ligands utilized. The activation of acetonitrile in this fashion leads to U(IV)-N(=CR₂)-Mo(0) linkages in each case, which represent the first examples of a bridging ketimido ligand between an actinide and a transition metal. In each case, the phosphino-amide ligand undergoes a shift to an iminophosphorano motif as a result of the insertion of the acetonitrile group. The exact mechanism for the divergent reactivity modes that lead to the isolation of **1-4** vs **5-6** vs **UCIMo/ThCIMo/UIMo/ThIMo** is uncertain, but the variety of reactivity modes observed shows the importance of tuning the ancillary ligand systems and the reaction conditions when attempting to prepare heterobimetallic actinide-metal bonds, particularly with the earlier transition metals. This report also suggests that An-metal linkages may be suitable precursors for unusual bonding motifs in actinide chemistry.

Experimental

General experimental details

All manipulations were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen or argon. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors except for ethers, which were stored over activated 4 Å sieves. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. The compounds UCl_4 ,⁸⁰ $\text{ThCl}_4(\text{DME})_2$,⁸¹ MesN(H)PPh_2 ,¹⁶ $\text{MesN(H)P}^i\text{Pr}_2$,⁴⁰ DippN(H)PPh_2 ,⁸² and $[\text{ClAn}(\text{MesNPPh}_2)_3]$ (An= U or Th)¹⁶ were prepared as described previously. All other items were purchased from commercial sources and used as received. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^7\text{Li}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.1, 100.6, 79.5, 162.0 and 155.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^1H , ^{13}C ^{29}Si), 85%, H_3PO_4 (^{31}P) and 1.0M LiCl (^7Li). FTIR spectra were recorded on a Bruker Alpha spectrometer with a Platinum-ATR module in the glovebox. UV/Vis/NIR spectra were recorded on a Perkin Elmer L M DTM 750 spectrometer. Data were collected in a 1mm path-length cuvette loaded in an MBraun glovebox and were run versus the appropriate solvent. Elemental microanalyses were carried out by Dr Tong Liu at the School of Chemistry, The University of Nottingham. All other chemicals were purchased and dried prior to use.

Preparation of $[\text{UCl}(\text{MesNP}^i\text{Pr}_2)_2(\text{MesNP}^i\text{Pr}_2\{\mu\text{-NCMe}\})\text{Mo}(\text{CO})_3]$ (1)

DCM (30 ml) was added slowly to a cold ($-78\text{ }^\circ\text{C}$) stirring mixture of $[\text{ClU}(\text{MesNP}^i\text{Pr}_2)_3]$ (1.02 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol) and the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 5 ml and stored at $9\text{ }^\circ\text{C}$

for 24 hours to yield **1** as red crystals suitable for a single crystal X-ray diffraction study. Yield 1.02 g, 82 %. Anal. Calc'd for: C₅₀H₇₈ClMoN₄O₃P₃U: C, 48.22; H, 6.31; N, 4.50 %. Found: C, 48.17; H, 6.45; N, 4.30 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) - 27.64 (6H, s, br, ⁱPr-CH₃), -16.17 (6H, s, br, ⁱPr-CH₃), -12.29 (12H, s, br, ⁱPr-CH₃), - 5.80 (12H, s, br, ⁱPr-CH₃), -2.16 (6H, s, br, Mes-CH₃), -0.97 (12H, s, br, Mes-CH₃), - 0.05 (6H, s, Mes-CH₃), 0.27 (3H, s, Mes-CH₃), 4.61 (6H, s, br, ⁱPr-CH), 4.77 (3H, s, br, CH₃CN) 13.57 (2H, s, Ar-CH) 18.66 (4H, s, Ar-CH). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 500 (w), 539 (w), 588 (w), 647 (w), 671 (w), 765 (w), 854 (m), 878 (w), 934 (w), 965 (w), 1142 (m), 1198 (m), 1261 (w), 1303 (w), 1549 (w) 1631 (w, C=N) 1833 (s, C≡O), 1926 (s, C≡O). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.41 \mu_{\text{B}}$.

Preparation of [ThCl(MesNPⁱPr)₂]₂(MesNPⁱPr)₂{ μ -NCMe}Mo(CO)₃] (2)

DCM (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ClTh(MesNPⁱPr)₃] (1.01 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 5 ml and stored at 9 °C for 24 hours to yield **2** as red crystals suitable for a single crystal X-ray diffraction study. Yield 0.75 g, 61 %. Anal. Calc'd for: C₅₀H₇₈ClMoN₄O₃P₃Th: C, 48.45; H, 6.34; N, 4.52 %. Found: C, 47.67; H, 6.30; N, 3.95 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 0.73 (6H, q, ²J_{HH} = 6 Hz, ⁱPr-CH₃), 0.83 (6H, q, ²J_{HH} = 6 Hz, ⁱPr-CH₃), 1.17 (6H, m, ⁱPr-CH₃), 1.31 (6H, q, ²J_H = 6 Hz, ⁱPr-CH₃) 1.35 (6H, m, ⁱPr-CH₃), 1.68 (6H, q, ²J_{HH} = 6 Hz, ⁱPr-CH₃), 1.97 (3H, s, CH₃CN), 2.04 (6H, m, ⁱPr-CH), 2.14 (6H, s, Mes-CH₃), 2.20 (6H, s, Mes-CH₃), 2.41 (6H, s, Mes-CH₃), 2.60 (3H, d, ²J_{HH} = 6 Hz, Mes-CH₃), 2.72 (6H, s, Mes-CH₃), 6.43 (2H, s, Ar-CH), 6.83 (4H, s, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 17.32 (ⁱPr-CH₃), 17.81 (ⁱPr-CH₃), 19.96 (Mes-CH₃), 20.21

(Mes-CH₃), 20.44 (Mes-CH₃), 21.59 (Mes-CH₃), 22.92 (CNCH₃), 32.04 (ⁱPr-CH), 32.68 (ⁱPr-CH₃), 127.69 (Ar-C), 129.51 (Ar-CH), 129.99 (Ar-CH), 132.51 (Ar-C), 133.23 (Ar-C), 133.98 (Ar-C), 141.84 (Ar-C), 141.93 (Ar-C), 172.5 (C=N). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 66.27 (s), 70.67 (s). FTIR (Nujol): $\tilde{\nu}$ (cm⁻¹) 647 (w), 682 (w), 718 (w), 766 (w), 855 (m), 933 (w), 964 (w), 1143 (m), 1199 (m), 1261 (w), 1303 (w), 1560 (2), 1607 (w, C=N), 1827 (s, C≡O), 1925 (s, C≡O).

Preparation of [UCl(MesNPPPh₂)₂(MesNPPPh₂{μ-NCMe})Mo(CO)₃] (3)

DCM (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ClU(MesNPPPh₂)₃] (1.24 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol), the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 10 ml and stored at -30 °C for 24 hours to yield **3** as red crystals suitable for a single crystal X-ray diffraction study. Yield 0.76 g, 52%. Anal. Calc'd for: C₆₈H₆₆ClMoN₄O₃P₃U: C, 56.34; H, 4.59; N, 3.86 %. Found: C, 57.13; H, 4.78; N, 3.32 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) -31.07 (6H, s, Mes-CH₃), -17.34 (4H, s, Ar-CH), -5.35 (6H, s, Mes-CH₃), -2.36 (4H, s, Ar-CH), -1.94 (2H, s, Ar-CH), -0.55 (2H, s, Ar-CH), -0.40 (3H, s, Mes-CH₃) 0.84 (3H, s, Mes-CH₃), 2.35 (4H, s, Ar-CH), 2.49 (2H, s, Ar-CH), 3.48 (4H, s, Ar-CH), 3.53 (3H, s, CH₃CN), 4.13 (2H, s, Ar-CH), 6.40 (6H, s, Mes-CH₃), 8.08 (4H, s, Ar-CH), 12.80 (4H, s, Ar-CH), 13.39 (4H, s, Ar-CH), 18.89 (3H, s, Mes-CH₃). FTIR Nujol): $\tilde{\nu}$ (cm⁻¹) 597 (m), 625 (m), 658 (w), 667 (w), 696 (m), 728 (m), 748 (w), 767 (m), 853 (m), 893 (m), 938 (w), 970 (w), 1027 (w), 1089 (m), 1151 (m), 1208 (m), 1434 (s), 1594 (w, C=N), 1823 (s), 1854 (s, C≡O), 1933 (s, C≡O). Magnetic moment (Evans method, C₆D₆, 298 K): $\mu_{\text{eff}} = 2.49 \mu_{\text{B}}$.

Preparation of [ThCl(MesNPPPh₂)₂(MesNPPPh₂{μ-NCMe})Mo(CO)₃] (4)

DCM (30 ml) was added slowly to a cold (-78 °C) stirring mixture of [ClTh(MesNPPPh₂)₃] (1.24 g, 1.0 mmol) and [Mo(NCMe)₃(CO)₃] (0.30 g, 1.0 mmol), and the resultant mixture was allowed to warm to room temperature slowly and stirred over 16 hours. The resulting red solution was concentrated to 10 ml and stored at -30 °C for 24 hours to yield **4** as red crystals suitable for a single crystal X-ray diffraction study. Yield 0.82 g, 57%. Anal. Calc'd for: C₆₈H₆₆ClMoN₄O₃P₃Th: C, 55.84; H, 4.42; N, 3.61 %. Found: C, 52.43; H, 4.42; N, 3.61 %. ¹H NMR (C₆D₆, 295 K): δ (ppm) 1.48 (6H, s, Mes-CH₃), 1.87 (3H, s, CH₃CN), 1.98 (6H, s, Mes-CH₃), 2.10 (6H, s, Mes-CH₃), 2.59 (6H, s, Mes-CH₃), 2.77 (3H, s, Mes-CH₃), 6.26 (2H, s, Mes-CH), 6.62 (2H, s, Mes-CH), 6.76 (2H, s, Mes-CH), 6.97 (8H, s, Ar-CH), 7.01 (2H, m, Ar-CH), 7.05 (8H, m, Ar-CH), 7.48 (4H, m, Ar-CH), 7.83 (4H, m, Ar-CH), 7.90 (4H, m, Ar-CH). ¹³C{¹H} NMR (C₆D₆, 295 K): δ (ppm) 20.21 (Mes-CH₃), 20.50 (Mes-CH₃), 23.12 (d, ³J_{PC} = 68.0 Hz, CH₃CN), 29.32 (Mes-CH₃), 29.82 (Mes-CH₃), 127.06 (Ar-CH), 127.25 (Ar-CH), 127.69 (Ar-CH), 128.85 (Ar-CH), 129.56 (Ar-CH), 129.85 (Ar-CH), 130.22 (Ar-CH), 132.95 (Ar-C), 133.31 (Ar-C), 133.31 (Ar-C), 133.65 (Ar-C), 134.22 (Ar-C), 134.72, (Ar-C) 140.98 (Ar-C), 141.27 (Ar-C), 143.15 (Ar-C), 143.48 (Ar-C), 166.5 (m, C=N). ³¹P{¹H} NMR (C₆D₆, 295 K): δ (ppm) 44.87 (s), 47.08 (s). FTIR (Nujol): ν̄ (cm⁻¹) 596 (m), 624 (m), 658 (w), 667 (w), 695 (m), 728 (m), 748 (w), 768 (m), 853 (m), 895 (m), 938 (w), 970 (w), 1027 (w), 1092 (m), 1152 (m), 1208 (m), 1434 (s), 1571 (w), 1587 (w), 1607 (w), 1632 (w, C=N), 1822 (s), 1854 (s, C≡O), 1934 (s, C≡O).

Preparation of $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{UI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (5)

Toluene (30 ml) was added to a stirring mixture of $[\text{IU}(\text{MesNP}^i\text{Pr}_2)_3]$ (1.12 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting red solid was washed with hexanes (3 x 10 ml) to yield **5** as an analytically pure powder. Red crystals suitable for a single crystal X-ray diffraction study were grown from the storage of a concentrated toluene solution of **5** at room temperature over 24 hours. Yield 0.77 g, 57 %. $\text{C}_{50}\text{H}_{78}\text{IMoN}_4\text{O}_3\text{P}_3\text{U}$: C, 44.92; H, 5.88; N, 4.19 %. Found: C, 44.68; H, 5.56; N, 4.09 %. ^1H NMR (C_6D_6 , 295 K): δ (ppm) -9.44 (6H, m-br, CH_3), -8.81 (6H, m-br, CH_3), -3.31 (12H, m-br, CH_3), -1.11 (6H, s, CH_3), 0.44 (6H, s, CH_3), 0.80 (3H, s, CH_3), 1.84 (3H, sr, CH_3), 1.97 (3H, s-br, CH_3), 2.04 (3H, s, CH_3), 2.11 (6H, s, CH_3), 12.11 (6H, s, CH_3), 12.81 (2H, s, Ar-CH), 13.82 (6H, s-br, CH_3), 17.70 (2H, s-br, Ar-CH), 18.46 (2H, s-br, Ar-CH). One set of ^iPr methyl hydrogens were not observed. FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 500 (w), 529 (w), 560 (m), 615 (w), 675 (m), 729 (w), 763 (w), 850 (m), 878 (m), 1038 (m), 1153 (m), 1205 (m), 1304 (w), 1542 (m), 1606 (w), 1632 (w, C=N), 1840 (s, C $\equiv$ O), 1949 (s, C $\equiv$ O). Magnetic moment (Evans method, C_6D_6 , 298 K): $\mu_{\text{eff}} = 2.91 \mu_{\text{B}}$.

Preparation of $[(\eta^2\text{-MesNP}^i\text{Pr}_2)\text{ThI}(\text{MesNP}^i\text{Pr}_2)(\{\mu\text{-NCMe}\}\text{MesNP}^i\text{Pr}_2)\text{Mo}(\text{CO})_3]$ (6)

Toluene (30 ml) was added to a stirring mixture of $[\text{ITh}(\text{MesNP}^i\text{Pr}_2)_3]$ (1.11 g, 1.0 mmol) and $[\text{Mo}(\text{NCMe})_3(\text{CO})_3]$ (0.30 g, 1.0 mmol). The resulting brown solution was slowly heated to reflux for 16 hours. Volatiles were removed *in vacuo* and the resulting yellow solid was washed with hexanes (3 x 10 ml) to yield **6** as an analytically pure powder. Yield 0.89, 67 %. $\text{C}_{50}\text{H}_{78}\text{IMoN}_4\text{O}_3\text{P}_3\text{Th}$ 0.4(C_7H_8): C, 46.36;

H, 5.98; N, 4.10 %. Found: C, 46.28; H, 5.92; N, 3.97 %. ^1H NMR (C_6D_6 , 295 K): δ (ppm) 0.54 (3H, m, $^i\text{Pr-CH}_3$), 0.73 (3H, m, $^i\text{Pr-CH}_3$), 0.93 (6H, m, $^i\text{Pr-CH}_3$), 1.16 (6H, m, $^i\text{Pr-CH}_3$), 1.47 (12H, m, $^i\text{Pr-CH}_3$), 1.73 (6H, m, $^i\text{Pr-CH}_3$), 1.87 (3H, s, CH_3CN), 2.22 (12H, m, Mes- CH_3), 2.44 (6H, s, Mes- CH_3), 2.46 (3H, s, Mes- CH_3), 2.52 (6H, s, Mes- CH_3), 2.67 (2H, m, $^i\text{Pr-CH}$), 2.85 (2H, m, $^i\text{Pr-CH}$), 3.07 (2H, s, $^i\text{Pr-CH}$), 6.70-7.00 (6H, m, Mes- CH). Due to the low solubility of **6** no resonances could be observed via ^{13}C NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 295 K): δ (ppm) 59.64 (s), 89.47 (s), 154.27 (s). FTIR (Nujol): $\tilde{\nu}$ (cm^{-1}) 595 (m), 615 (m), 671 (m), 685 (m), 729 (m), 764 (m), 851 (m), 860 (w), 883 (m), 1036 (m), 1156 (m), 1206 (m), 1213 (w) 1304 (w), 1549 (m), 1606 (w), 1631 (w, C=N), 1838 (s, C=O), 1949 (s, C $\equiv$ O).

Conflicts of interest

There are no conflicts to declare.

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Supporting Information

Experimental and characterization data for proligands, ligand transfer reagents, and some resulting actinide-phosphinoamide complexes. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1899457-1899474.

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Figures and Schemes

Scheme 1. Preparation of 1-6.

Scheme 2. Contrasting stability of UCIMo/ThCIMo in toluene vs DCM.

Scheme 3. Proposed intermediate towards the synthesis of 5-6.

Table 1. IR frequencies for the C≡O and C=N stretches for compounds 1 – 6 and Mo(CH₃CN)₃(CO)₃ and ³¹P{¹H} NMR data for compounds 2, 4 and 6.

Compound	$\tilde{\nu}_1(\text{C}\equiv\text{O})^{[a]}$	$\tilde{\nu}_2(\text{C}\equiv\text{O})^{[a]}$	$\tilde{\nu}(\text{C}=\text{N})^{[a]}$	³¹ P{ ¹ H} NMR ^[b]
1	1926 (s)	1833 (s)	1631	not detected
2	1925 (s)	1827 (s)	1607	66.27 (s), 70.67 (s)
3	1933 (s)	1854 (s)	1594	not detected
4	1934 (s)	1854 (s)	1632	44.87 (s), 47.08 (s)
5	1949 (s)	1840 (s)	1632	not detected
6	1949 (s)	1838 (s)	1631	59.64 (s), 89.47 (s), 154.27 (s)
	1915 (s) ^{81[c]}	1783 (s) ^{81[c]}	n/a	n/a
Mo(CH ₃ CN) ₃ (CO) ₃	1905 (s) ^[d]	1790 (s, br) ^[d]		n/a
	1921 (s) ^[e]	1793 (vs) ^[e]		n/a

[a] $\tilde{\nu}$ in (cm⁻¹) [b] NMR shifts in ppm (C₆D₆, 295 K) [c] nujol mull⁸³ [d] KBr disk⁸⁴ [e] CH₃CN solution.⁸⁵

Figure 1. Solid state structure of complexes **1** at 120K. Thermal ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: U1-Mo1 3.3150(5), U1-Cl1 2.6272(15), U1-P1 3.1535(14), U1-P2 3.2800(14), U1-N1 2.278(4), U1-N2 2.305(5), U1-N3 2.436(5), U1-N4 2.288(5), Mo1-P1 2.6185(16), Mo1-P2 2.6142(16), Mo1-N4 2.249(4), Mo1-C48 1.968(6), Mo1-C49 1.966(7), Mo1-C50 1.966(7), O1-C48 1.165(8), O2-C49 1.160(8), O3-C50 1.165(8), N4-C46 1.265(8), C46-C47 1.516(8), P3-C46 1.853(6), N4-C46-P3 114.8(4), N4-C46-C47 124.7(5), C47-C46-P3 120.5(4).

Figure 2. Solid state structure of **2** at 120K. Thermal ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] Th1-Mo1 3.361(2), Th1-Cl1 2.705(6), Th1-N1 2.32(2), Th1-N2 2.35(2), Th1-N3 2.62(2), Th1-N4 2.39(2), Mo1-P1 2.665(7), Mo1-P2 2.618(6), Mo1-N4 2.23(2), Mo1-C48 1.87(3), Mo1-C49 1.98(3), Mo1-C50 1.97(3), O1-C48 1.26(3), O2-C49 1.17(3), O3-C50 1.17(3), N4-C46 1.29(3), C46-C47 1.48(4), P3-C46 1.83(3), N4-C46-P3 114(2), N4-C46-C47 126(2), C47-C46-P3 120.6(18).

Figure 3. Solid state structure of **3** at 120K. Thermal ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: U1-Mo1 3.3019(3), U1-Cl1 2.6260(9), U1-P1 3.2756(9), U1-P2 3.1782(9), U1-N1 2.307(3), U1-N2 2.271(3), U1-N3 2.473(3), U1-N4 2.312(3), Mo1-P1 2.5956(9), Mo1-P2 2.5454(9), Mo1-N4 2.227(3), Mo1-C66 1.995(4), Mo1-C67 1.978(4), Mo1-C68 1.972(4), O1-C66 1.151(6), O2-C67 1.160(5), O3-C68 1.153(5), N4-C64 1.280(5), C64-C65 1.499(5), P3-C64 1.835(4), N4-C64-P3 114.4(3), N4-C64-C65 127.0(3), C65-C64-P3 118.3(3).

Figure 4. Solid state structure of **4** at 120K. Thermal ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Th1-Mo1 3.4061(3), Th1-Cl1 2.6960(9), Th1-P1 3.3618(10), Th1-P2 3.2420(9), Th1-N1 2.345(3), Th1-N2 2.325(3), Th1-N3 2.502(3), Th1-N4 2.377(3), Mo1-P1 2.5970(10), Mo1-P2 2.5504(10), Mo1-N4 2.246(3), Mo1-C66 1.968(4), Mo1-C67 1.980(5), Mo1-C68 1.986(4), O1-C66 1.173(5), O2-C67 1.147(6), O3-C68 1.156(6), P3-C64 1.848(4), N4-C64 1.269(5), C64-C65 1.513(6), N4-C64-P3 114.9(3), N4-C64-C65 127.9(3), C65-C64-P3 116.9(3).

Figure 5. Solid state structure of complex **5** at 120K. Thermal ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: U1-I1 3.0211(8), U1-Mo1 3.3145(8), U1-P1 2.873(3), U1-N1 2.262(7), U1-N2 2.221(7), U1-N4 2.235(7), Mo1-P2 2.495(3), Mo1-P3 2.449(3), Mo1-N4 2.237(7), Mo1-C48 2.053(14), Mo1-C49 1.978(13), Mo1-C50 2.038(12), N3-C46 1.435(12), N4-C46 1.311(12), C46-C47 1.438(14), N3-C46-C47 116.0(9), N4-C46-N3 117.6(9), N4-C46-C47 126.4(9).

Figure 6. Temperature-dependent magnetic susceptibility plotted as $\mu_{\text{eff}} (\mu_B)$ vs temperature (K) for **1**, **3** and **5**. Square = **1**, circle = **3**, triangle = **5**. Lines are a guide to the eye only.

ToC Entry

The preparation of heterobimetallic ketimido-actinide-molybdenum complexes resulting from acetonitrile activation and insertion reactions is described.