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Consecutive N₂ loss from a uranium diphosphazide complex†

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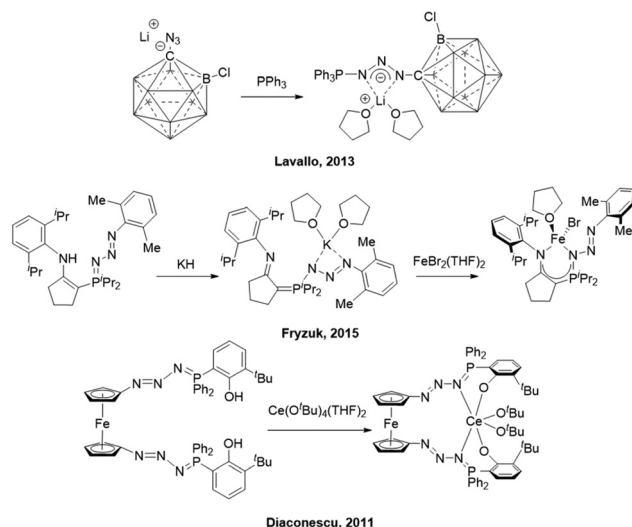
A new ‘diphosphazidosalen’ ligand was synthesized and successfully transferred to uranium using salt metathesis strategies. The resultant 8-coordinate uranium(IV) diphosphazide complex $[\kappa^6\text{-}1,2\text{-}\{(\text{N}_3)\text{PPh}_2(2\text{-O-C}_6\text{H}_4)\}_2\text{C}_6\text{H}_4]\text{UCl}_2$ (1) is unstable to consecutive N₂ loss, affording the asymmetric species $[\kappa^5\text{-}1\text{-}\{(\text{N}_3)\text{PPh}_2(2\text{-O-C}_6\text{H}_4)\}\text{-}2\text{-}\{(\text{N}=\text{PPh}_2(2\text{-O-C}_6\text{H}_4))\text{C}_6\text{H}_4\}]\text{UCl}_2$ (2), defined by a phosphazide-phosphinimine mixed-ligand framework, and ultimately, the uranium(IV) phosphasalen complex $[\kappa^4\text{-}1,2\text{-}\{(\text{N}=\text{PPh}_2(2\text{-O-C}_6\text{H}_4))\}_2\text{C}_6\text{H}_4]\text{UCl}_2(\text{THF})$ (3).

In forming ‘aza-ylides’ (iminophosphanes or phosphinimines) from organic azides and tertiary phosphines, the phosphazide intermediate, a neutral analogue of the triazenide (R-(N₃)⁻-R) moiety, has the potential for rich coordination chemistry as a $\kappa^2\text{-N}_2\text{N}$ or $\eta^3\text{-N}_2\text{N}_2\text{N}$ chelate, but is rarely isolated. Mechanistic studies have shown that the Staudinger reaction (PR₃ + R-N₃ → R₃P=N-R + N₂) proceeds through a *cis*-phosphazide (R₃P-(N₃)-R) intermediate, which readily eliminates dinitrogen gas and phosphinimine (R₃P=N-R).¹ However, the *trans*-isomer, which is resistant to N₂ loss, can be stabilized by H-bonding,² as well as coordination to main group Lewis acids³ and transition metals.^{1,4}

To date, there have only been two examples of phosphazides coordinated to group 1 metals: Lavallo and coworkers reported an anionic azido carboranyl cluster with a lithium counterion which, when reacted with PPh₃, produced a lithium stabilized phosphazide (Scheme 1, top).⁵ In the solid state, the lithium cation is bound by N_α and N_γ of the phosphazide and two THF molecules. Intriguingly, this species does not release N₂, even upon heating at 150 °C in C₆H₅F. In

addition, Fryzuk prepared a sterically encumbered organic azide supported by hydrogen bonding with a nearby NH group.^{4h} Upon NH deprotonation with KH, a potassium stabilized phosphazide can participate in a salt metathesis reaction with FeBr₂(THF)₂ to produce an iron(II) phosphazide (Scheme 1, middle). Interestingly, this species undergoes an unusual radical process when exposed to the hydride KBET₃H wherein nitrogen gas is liberated and an anionic phosphinimine generated. Notably, this is the only previously published example of intentional transfer of a stabilized phosphazide.

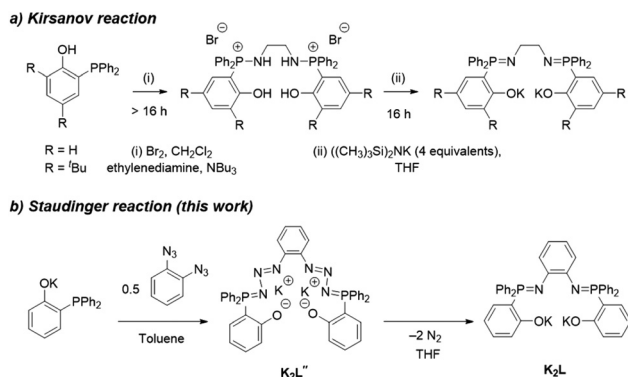
As potential chelating ligands, phosphazides provide an opportunity to introduce functionality and coordinative-flexibility to a variety of metals, yet are seldom discussed or targeted in coordination chemistry.^{1,6} Phosphinimines, in contrast, are established components in ligand design.⁷ Isostructural variants of the ubiquitous ‘salen’ ligand have recently been developed that feature phosphinimine donors in place of the conventional Schiff base (R₂C=N-R).⁸ These phos-



Scheme 1 Some examples of stabilized phosphazides.^{4h,5,10}

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† Electronic supplementary information (ESI) available: Experimental and crystallographic details, molecular structure of 3, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for 1, 2 and 4. CCDC 1533033-1533034, 1533036-1533037, 1942135. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04517a



Scheme 2 Comparison of phosphasalen ligand synthesis by the Kirsanov reaction (a)^{9a} and by the Staudinger reaction (this work) (b).

phasalen ligands, reported by Auffrant and Williams, have demonstrated exceptional stability when supporting reactive metals, notably serving as an ancillary scaffold for a highly-active ring-opening polymerization yttrium catalyst.⁹ The synthesis of such phosphasalen ligands has thus far been largely limited to the Kirsanov reaction,^{9a} which generates the phosphinimine fragment from triarylphosphine, Br₂, and diamine over a number of steps and days (Scheme 2a). Although diamine starting materials are attractive from a practical standpoint, diazides provide access to diphosphazides, species which are not accessible *via* the Kirsanov reaction.

To our knowledge, the Staudinger reaction has not been utilized for the preparation of entirely organic phosphasalen ligands. However, a ferrocene-based variant reported by Diaconescu and co-workers has been disclosed, whereby 1,1'-diazidoferrocene Fc(N₃)₂ was reacted with a bulky phosphinophenol.¹⁰ Notably, a cerium complex [Fc(N₆O₂)]Ce(O^tBu)₂ (Fc = 1,1'-ferrocenylene; Fc(N₆O₂) = κ⁴-1,1'-[(N₃)PPh₂(2-O-C^tBuC₆H₄)₂]) was isolated in the reaction, wherein the distal N atoms of a phosphazide ligand were bound to the cerium center (Scheme 1, bottom). Thus far, [Fc(N₆O₂)]Ce(O^tBu)₂ appears to be the only example of a ligand featuring two phosphazide subunits coordinated to a metal, and aside from thermally promoted N₂ loss, its reaction/coordination chemistry has not been studied.

Herein, we provide details on the one-step synthesis and characterization of new phosphasalen and phosphazidosalen ligands and describe the conversion of phosphazide to phosphinimine at a single uranium center.

A phosphasalen ligand featuring a rigid benzene backbone was targeted wherein 1,2-diazidobenzene would be reacted with an appropriate phosphine (Scheme 2b). Although the requisite 1,2-(N₃)₂-C₆H₄ was previously reported,¹¹ it had been generated *in situ* and used without characterization. In an effort to isolate this diazide, it was prepared by stepwise diazotization of 2-nitroaniline. Low-temperature analysis by an X-ray diffraction study (see ESI for details[†]) revealed a linear arrangement of the azide functional groups with extended conjugation in the aromatic bridge [N1–N2–N3 = 173.6(2)°, N4–N5–N6 = 171.7(2)°].

Initial attempts at reacting 1,2-diazidobenzene with Ph₂P[(2-OH)C₆H₄] produced insoluble byproducts, presumed

to be the result of acidic –OH protons interfering with phosphazide cyclization and subsequent N₂ loss. Therefore, to mitigate this issue, and to directly prepare phosphasalen salts suitable for subsequent salt metathesis reactions, the –OH group of Ph₂P[(2-OH)C₆H₄] was deprotonated with KH prior to reaction with 1,2-diazidobenzene.

Dropwise addition of 0.5 equivalents of 1,2-(N₃)₂-C₆H₄ to a stirring solution of Ph₂P[(2-OK)C₆H₄] in toluene resulted in immediate precipitation of a bright yellow solid that exhibits a ³¹P NMR resonance at δ 28.4 in [D₈]THF. When combined with UCl₄ a rapid change from yellow to orange was observed, along with a new signal in the ³¹P NMR spectrum at δ 49.6. An X-ray crystallographic study confirmed the reaction product to be L''UCl₂, (L'' = κ⁶-1,2-[(N₃)PPh₂(2-O-C₆H₄)₂])₂C₆H₄ (**1**), a uranium dichloride complex supported by a symmetric diphosphazide ligand. Both of the phosphazide P(N₃) units coordinate to the metal center *via* a κ²-N,N bonding mode, with anionic phenoxide-O and Cl ligands completing the coordination sphere of the paramagnetic uranium(IV) center (Fig. 1). Notably, the N–N–N angles in the phosphazide subunits [103.7(2) and 104.1(2)°] are substantially smaller than those observed in a previously reported metal-free phosphazide [116.55(14)°].^{4d} The geometry about the eight-coordinate uranium center is best described as distorted hexagonal bipyramidal with a Cl1–U–Cl2 angle of 163.08(3)°. The diphosphazide ligand is remarkably planar, with only the O2 atom sitting out of the plane defined by U1–O1–N1–N3–N6–N4 (by 0.545 Å). In addition, the phosphazides coordinate in a markedly different manner (κ²-N,N) than those in the cerium diphosphazide complex [Fc(N₆O₂)]Ce(O^tBu)₂, wherein each phosphazide unit adopts an η¹-N bonding mode.¹⁰ When heated, two equivalents of N₂ were liberated from [Fc(N₆O₂)]Ce(O^tBu)₂, along with quantitative conversion to the analogous phosphinimine-bound complex. Similar to [Fc(N₆O₂)]Ce(O^tBu)₂, both phosphazide donors in **1** display a *trans*-configuration with varying N–N bond lengths [N1–N2 = 1.356(4), N2–N3 = 1.266(3), N5–N6 = 1.273(3), N4–N5 = 1.358(3) Å]. Complex **1** is the first example of the phosphazide functionality bound to an actinide metal; as uranium can accommodate high coordination numbers, it is an ideal candidate for supporting multiple phosphazide groups.

Complex **1** is unstable to slow elimination of 1 equivalent of N₂ at ambient temperature in THF. After 12 hours, two new ³¹P NMR resonances of equal intensity (δ 104.1 and 71.2) had completely supplanted the resonance attributed to complex **1** (δ 49.6). X-ray quality crystals grown from a concentrated benzene solution at ambient temperature permitted a study that identified the asymmetric decomposition product as L'UCl₂, (L' = κ⁵-1-[(N₃)PPh₂(2-O-C₆H₄)]-2-[N=PPh₂(2-O-C₆H₄)]C₆H₄) (**2**), the result of singular N₂ loss from the diphosphazide ligand in **1** (Fig. 1). Intriguingly, one P(N₃) phosphazide unit, which remains κ² bound to uranium, was conserved. The new phosphinimine donor is also coordinated to the metal, resulting in distorted pentagonal bipyramidal geometry at the seven-coordinate uranium(IV) center. Upon monitoring by ³¹P NMR spectroscopy, a [D₈]THF solution of **2**, heated at

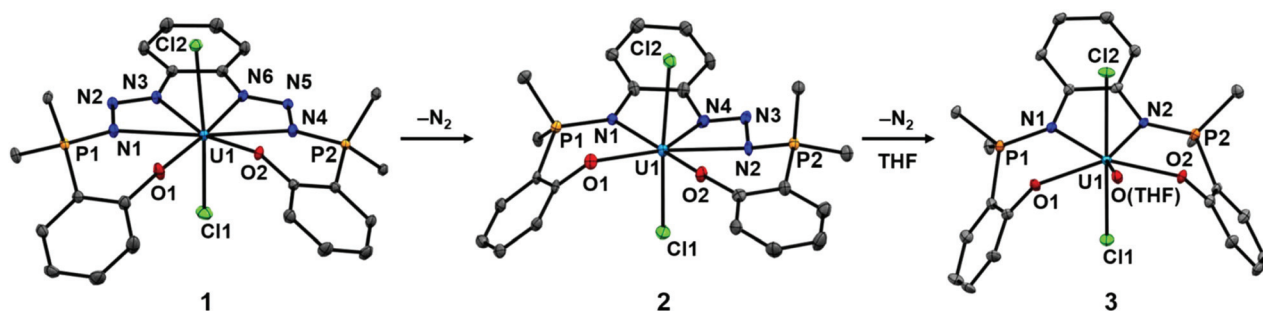


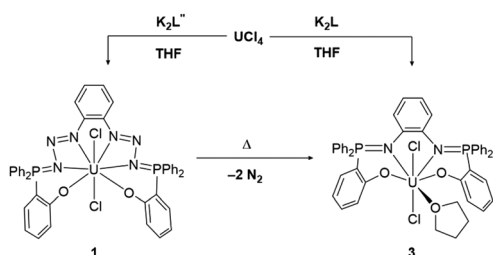
Fig. 1 X-ray crystal structures of **1–3** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms, P-phenyl groups, except for the *ipso* carbons, coordinated THF C atoms and solvent molecules of recrystallization (benzene, THF) are omitted for clarity. Selected bond distances (Å) and angles (°): **1**: U–N1 = 2.589(3), U–N3 = 2.586(2), U–N4 = 2.641(2), U–N6 = 2.613(2), U–O1 = 2.203(2), U–O2 = 2.221(2), U–Cl1 = 2.6424(8); Cl1–U–Cl2 = 163.08(3), O1–U–O2 = 79.68(8), N1–N2–N3 = 103.7(2), N4–N5–N6 = 104.1(2); P1–N1–N2–N3 = 175.1(2), P2–N4–N5–N6 = –173.8(2); **2**: U–N1 = 2.55(1), U–N2 = 2.52(1), U–N4 = 2.44(1), U–O1 = 2.18(1), U–O2 = 2.185(9), U–Cl1 = 2.640(3), U–Cl2 = 2.603(5), P1–N1 = 1.61(1); Cl1–U–Cl2 = 168.1(1), O1–U–O2 = 99.1(4), N2–N3–N4 = 104(1); P2–N2–N3–N4 = 165(1); **3**: connectivity structure of **3**.

135 °C for 5 days, was observed to gradually convert into a single product (**3**; $\delta = -56.4$) with C_s or C_{2v} symmetry.

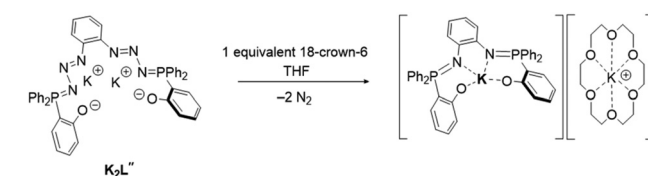
To confirm the identity of complex **3** as the product of a second consecutive N_2 elimination from **1**, the putative phosphasalen complex was targeted for independent synthesis by reaction of K_2L ($K_2L = 1,2-[N=PPh_2(2-OK-C_6H_4)]_2C_6H_4$) with UCl_4 . To generate K_2L , $1,2-(N_3)_2-C_6H_4$ was added to an *in situ* generated THF solution of $(2-OK-C_6H_4)PPh_2$. Immediate yellow colouration occurred, followed by formation of a fine suspension, and ultimately, after one hour, a clear yellow solution. The $^{31}P\{^1H\}$ NMR spectrum of K_2L in $[D_8]THF$ exhibits a broad peak at δ 11.4, a considerable upfield shift compared to the phosphazidosalen ligand (δ 28.4), thus suggesting formation of the desired phosphasalen ligand (Scheme 2b). When K_2L was combined with UCl_4 , a resonance was observed at $\delta -56.4$ in the ^{31}P NMR spectrum, which is consistent with that obtained when complex **2** was heated (Scheme 3, right). Crystals grown from THF provided a low-quality X-ray structure that served to establish atom connectivity within the THF-coordinated uranium phosphasalen complex $LUCl_2(THF)$, ($L = \kappa^4-1,2-[N=PPh_2(2-O-C_6H_4)]_2C_6H_4$) (**3**) (Fig. 1). To the best of our knowledge, the only other phosphasalen-supported actinide complexes were reported by the Auffrant group,¹² rounding out diverse coordination chemistry involving transition, rare earth, and actinide metals.^{8a,9,13} Notably, in the work by Auffrant, the phosphasalen ligand possessed a pyridine backbone and sterically demanding *tert*-butyl groups.

The potassiumated diposphazide ligand K_2L'' was postulated to contain $N \cdots K$ interactions that prevent *trans*–*cis* isomerization. To confirm this formulation, 1 equivalent of 18-crown-6 was added to sequester K^+ ions, resulting in immediate dissolution of the yellow solid along with concomitant production of a clear yellow solution and gas evolution (Scheme 4). The appearance of a new resonance at δ 4.25 in the $^{31}P\{^1H\}$ NMR spectrum accompanied this visible change; an asymmetric intermediate with two peaks at δ 12.79 and $\delta -13.45$ (1 : 1) was also observed (see ESI† for solid state structure of the product $[KL][K(18-crown-6)]$). Rapid N_2 loss upon addition of 18-crown-6 suggests that the phosphazide subunits in K_2L'' are indeed stabilized by coordination to the large K ions.

When complex **1** was heated in THF during the preparation of **3**, and the product extracted into benzene, a small amount of highly crystalline impurity (**4**) was obtained. A uranium(IV) complex $(H)L'UCl_3$ (**4**) bearing three chloride ligands and a protonated phosphinimine, which presumably formed *via* reaction of K_2L'' with THF solvent or trace quantities of adventitious moisture, was identified by X-ray diffraction studies. The presence of a $R_3P=NH^+$ was supported by the elongated P–N distance of 1.641(3) Å which is in agreement with similar species in the literature (Fig. 2).¹⁴ Solution state NMR spectroscopy identified an asymmetric complex with ^{31}P chemical shifts of δ 88.9 and $\delta -38.2$, and 17 paramagnetically shifted 1H resonances ranging from δ 61.6 to $\delta -21.3$. In the solid-state, the protonated phosphinimine nitrogen sits 4.319(3) Å from the uranium(IV) center. The phosphazide unit, in contrast to 7-coordinate complex **2**, is κ^1 bound. Complex **4**, while only



Scheme 3 Synthesis of uranium complexes **1** and **3**.



Scheme 4 Reaction of phosphazidosalen ligand K_2L'' with 18-crown-6.

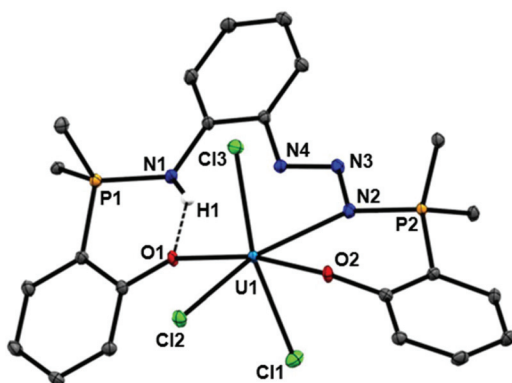


Fig. 2 Solid-state structure of complex 4 with thermal ellipsoids shown at 30% probability. Hydrogen atoms except for H1, $\text{P}(\text{C}_5\text{H}_5)_2$ groups excluding *ipso*-C, and solvent molecules of recrystallization (benzene) are omitted for clarity. The position of H1 was located directly in the difference map. Selected bond distances (Å) and angles (°) are given: U–N2 = 2.479(3), U–O1 = 2.214(2), U–O2 = 2.214(2), U–Cl1 = 2.6465(9), U–Cl2 = 2.6547(9), U–Cl3 = 2.6517(9), P1–N1 = 1.641(3), H1...O1 = 2.18(6); N2–N3–N4 = 109.9(3).

isolable in small amounts, demonstrates the variable coordination of the phosphazide group in this system. The remaining phosphazide unit is coordinated through only the α -N of the phosphazide, similar to the η^1 -N bonding mode in Diaconescu's cerium diphosphazide.¹⁰

As demonstrated, the Staudinger reaction, in combination with appropriate choice of solvent, provides convenient and selective routes to phosphazidosalen and phosphasalen ligands. The corresponding group 1 phosphazidosalen species affords a unique opportunity to explore phosphazides as a ligand in coordination chemistry using simple and versatile salt metathesis strategies. The ease with which pendant groups can be fine-tuned, the observed coordinative versatility, and the ability for intentional conversion into phosphinimines, suggest that phosphazides offer great potential as ligands in inorganic chemistry and homogeneous catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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