

**SYNTHESIS AND CHARACTERIZATION OF PN MONOANIONIC LIGANDS
AND THEIR REACTIVITY WITH ACTINIDES**

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University of Missouri-Columbia

In Partial Fulfillment of the Requirements for the Degree of Master of Science

By

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The undersigned, appointed by the dean of the Graduate School, have examined the
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**SYNTHESIS AND CHARACTERIZATION OF PN MONOANIONIC LIGANDS
AND THEIR REACTIVITY WITH ACTINIDES**

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certify that, in their opinion, it is worthy of acceptance.

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DEDICATION

I dedicate this thesis to my amazing parents, Miranda and Arben Xhani.
None of this would be possible without your sacrifices, love, and support.

Ju dua shumë.

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I hope you know that your hard work has never gone unnoticed, on the contrary it has been nothing short of an inspiration and a true driving force for all I do. I can only hope that this accomplishment makes your sacrifices worth it.

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LIST OF ABBREVIATIONS

Actinides (An)

Lanthanides (Ln)

Nuclear Spent Fuel (NSF)

Hard Soft Acid Base Theory (HSAB)

Cyclopentadienyl ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)

Pentamethylcyclopentadienyl ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)

(N-(2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide (**NP**; bold represent anionic center)

[(TrippPH)-2-(C₆H₄)N(Me₂)], (**PN**; bold represent anionic center)

[(TrippPCl)-2-(C₆H₄)N(Me₂)], (**PN-Cl**; bold represent anionic center)

[(TrippAsCl)-2-(C₆H₄)N(Me₂)], (**AsN-Cl**; bold represent anionic center)

Nuclear Magnetic Resonance (NMR)

Fourier Transform Infrared Spectroscopy (FTIR)

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**SYNTHESIS AND CHARACTERIZATION OF PN MONOANIONIC LIGANDS
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ABSTRACT OF THESIS

Organoactinide complexes have gained much popularity in the recent decades particularly in the field of nuclear waste sequestration. With the increase of nuclear power along side other residual nuclear waste from power plants and testing and use of nuclear bombs, there has been a rapid increase in actinides in the environment. In an effort to sequester and separate actinides from other radioactive elements in the waste, understanding the unique reactivity of the actinides has been key. Actinides and lanthanides make up the f-block in the periodic table meaning they contain f-orbitals which affects its ligand bonding making their interaction more electrostatic versus covalent typically seen in d-block transition metals. The added radioactive properties also play a role in its environmental safety and half-life of the various elements in the actinide series. Utilizing already existing concepts and properties such as HSAB and the Relativistic Effects, have helped develop new ligands in the effort to further understand the reactivity of actinides and how it differs from other radio toxins.

In collaboration with Stephan Hohloch at the University of Innsbruck our group developed a new preliminary organoactinide complex, NP-Th containing the ligand (N-(2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide, short NP). The NP ligand has been extensively studied in its reactivity with lanthanide metals producing

numerous organolathanide complexes containing either one or two NP ligands. Thus far the only NP-actinide complex reported has been with uranium as observed in 2018 by Schelter and Mindiola et al. With the introduction of the preliminary NP-Th complex comparisons between the two organoactinide complexes can be determined.

In addition, a novel PN ligand was synthesized utilizing a phosphorous anionic center; [(TrippPH)-2-(C₆H₄)N(Me₂)], short as **PN**; *- bold shows the anionic reactivity site*; Tripp = 2,4,6- ⁱPr₃C₆H₂. Since the synthesis of the PN ligand required an intermediate complex, its precursor was also reported, [(TrippPCL)-2-(C₆H₄)N(Me₂)], along with its arsenic analogue; abbreviated as **EN-Cl** (E=P, As).

Nuclear magnetic resonance (¹H, ¹³C, and ³¹P) techniques were used in characterizing the purity of the NP-Th complex and the novel **PN** ligand and its precursor **EN**. The reactivity of the **PN** with any f-block metals have yet to be determined.

Chapter 1

INTRODUCTION

1.1 f-Block Elements

Lanthanides (Ln) and actinides (An) are found in the 6th and 7th row of the periodic table spanning with atomic numbers 57-71 and 89-103, respectively. This series of elements are referred to as the “f-block” due to having f-orbitals with Ln occupying the 4f and An the 5f.

Although containing similar characteristics to An, apart from promethium, Ln are non-radioactive metals with a preferred trivalent oxidation state. Actinides on the other hand are radioactive typically alpha emitters with varying ranges of oxidation states^[1]. Actinium (Ac), thorium (Th), protactinium (Pa), and uranium (U) are naturally occurring at any significant quantities and are found in the earth’s crust. Elements with atomic number greater than that of U ($Z= 92$) are manmade and referred to as the transuranic or the minor-actinides. Neptunium (Np) through curium (Cm) are produced by neutron capture of ²³⁸U inside a nuclear reactor while berkelium (Bk) through lawrencium (Lr) are synthesized in higher neutron fluxes under specially designed conditions^[2-4].

1.2 Environmental Increase of Actinide and its Consequences

1.2.1 Actinide Contamination and its Waste Separation

In an effort to reduce greenhouse gases, the use of nuclear power has increased in the last century. Consequently, global inventory of nuclear waste disposal has also increased, and its long-term management, separation, and storage has been a topic of recent research^[1,5]. Although elements Ac through U in the An series are naturally occurring, their increase amongst other An in the environment can be attributed to human

activity such as nuclear reactor accidents, use and testing of nuclear weapons, and the generation of nuclear waste. Spent Nuclear Fuel (SNF) is the byproduct of fission produced by nuclear power plants. During this process of neutron capture occurring in the reactor, U and Pu are used as fuel^[6,11] and are then recycled leaving a mixture of waste predominantly consisting of lanthanides (III), (>98.5 wt%) and minor-actinides (III) such as Np, Cm, and Am, (approx. 1 wt%)^[1,6]. Though An occupy a small percentage of the NSF, they along with their daughter isotopes are typically long-lived ($t_{1/2} = 10^3 - 10^6$ years) alpha emitters and considered to be radiotoxins^[8]. While Ln on the other hand pose less environmental threats^[1]. This alone has caused environmental concerns regarding the storage of these long-lived isotopes and the repercussions of a potential waste spill^[6].

Initial separation attempts involved the transmutation^[1] of An isotope to produce a short-lived product nuclei with a fraction of the original half-life. This can be achieved by neutron irradiation of the desired An isotope resulting in the half-life decreasing to a more manageable time frame, as short as $t_{1/2} = 10^1$ years^[1,8], making its storage less of an environmental burden. Lanthanides in the waste are considered ‘neutron poisons’ due to having a higher cross section inhibiting the irradiation of the An isotope, ultimately hindering the separation process more difficult and less effective^[6,9-11].

Therefore, understanding the difference between the two series can provide more insight into the electronics and reactivity characteristics unique to the An.

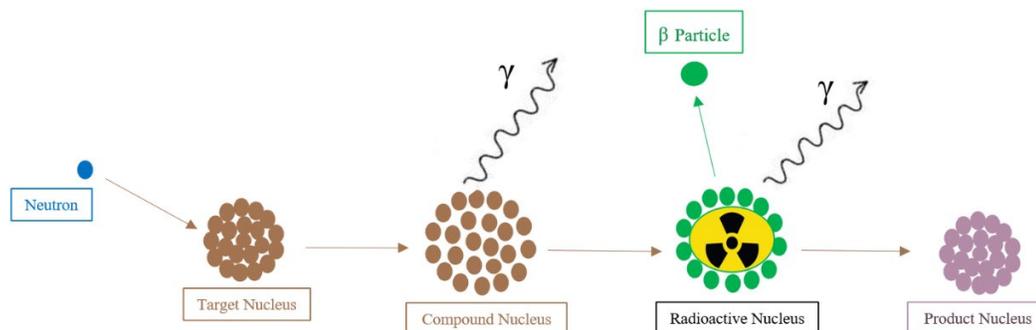


Figure 1-1 A general reaction steps of a transmutation process

1.3 Actinide Covalency

1.3.1 Ln vs An: Electronics and Periodic Trends

Understanding the fundamental differences between the Ln vs An is key to the separation success. One common trend is the decreasing size of atomic radii as the atomic number increases, as shown in **Figure 1-1**. This is due to the poor shielding effect of the f-orbitals causing the lanthanide and actinide contraction^[2,13]. In comparison to transition metals that experience covalent bonding through orbital overlap with main group ligands, f-elements don't experience the same level of orbital overlap therefore preferring an electrostatic interactions^[2].

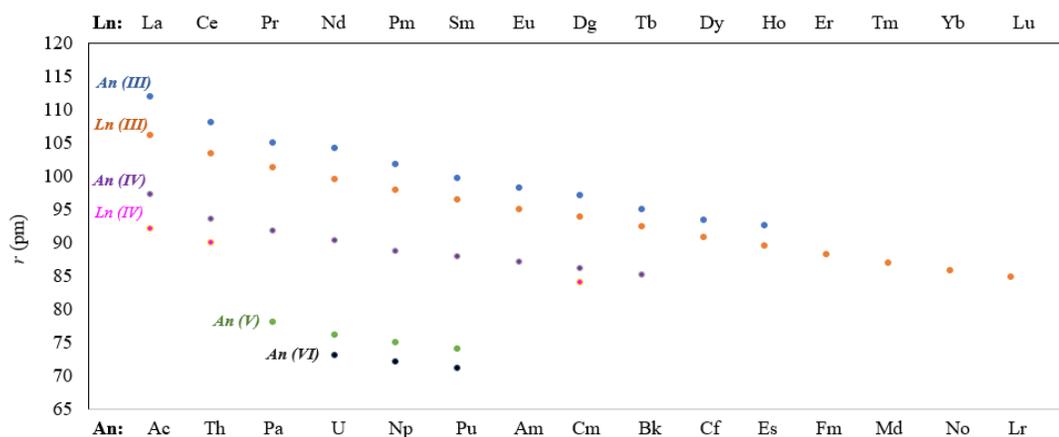


Figure 1-2 The similar trends of Ln and An atomic radii decreasing as the atomic number increases. Image is adapted from Liddle et al.^[2] and data reported by Abraham et al.^[12]

The differences between Ln and An are very minute, but a closer look reveals that An tend to have a more covalent nature in ligand bonding compared to Ln. This fundamental difference is attributed to the Relativistic Effect and its effect on the 5f-orbital of An. This has shifted the research interest towards understanding the covalent properties of An and ligand design to target specific An in the quest to sequester them from nuclear waste^[2, 13].

1.3.2 Relativistic Effects

Relativistic effects are a physical property that is observed throughout all of the elements in the period table, but only plays a major role in heavier atoms typically platinum and onward. The Relativistic effects can be described by Einstein's Theory of Relativity, stating that an object traveling near the speed of light will gain mass proportionately to that of the kinetic energy and mass^[13]. At the atomic level, this concept can be observed in inner shell electrons gaining mass as they are being pulled closer towards the nucleus causing a contraction of the 1s and its proceeding s-orbitals. Also, a similar effect can be observed in the p-orbitals, consequently causing the d and f orbitals to experience a radial expansion, see **Figure 1-2**, due to the increase in shielding from the effective nuclear charge. For An the increase in shielding results in the 5f orbitals to extend outward towards the valence^[14] region increasing its covalent character in actinide-ligand bonding.

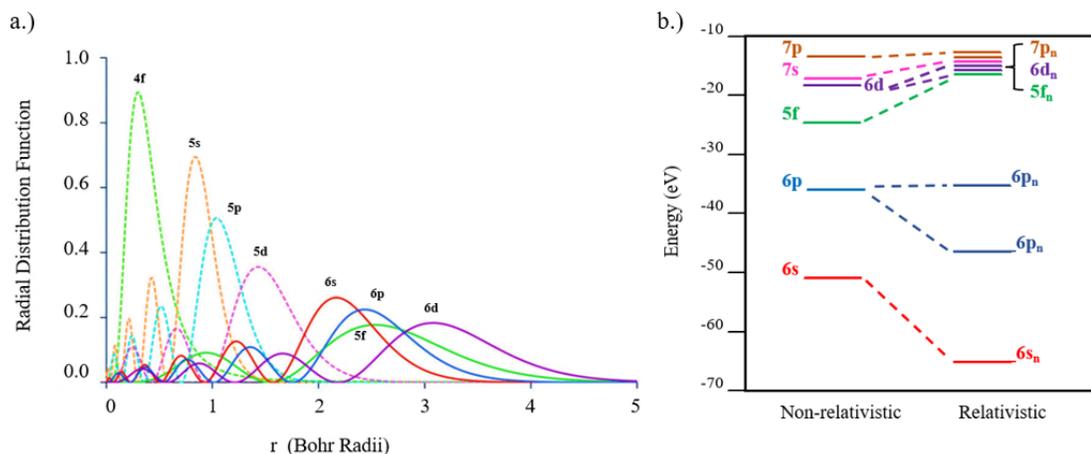


Figure 1-3 The effects of the Relativistic Effect and spin coupling (n) on the inner s and p electrons being pulled closer toward the nucleus center resulting in the radial expansion of the outer shell d and f orbitals. Image is adapted from Liddle et al. [2]

Researchers have tried to understand the nature and amount of covalency between An and main group elements specifically soft donor elements^[15]. Typically, in transition metal chemistry, one can predict the interaction type between the metal and ligand given certain trends, one of which is the HSAB.

1.3.3 HSAB Theory

Originally introduced by Ralph Pearson in 1963, the concept of Hard Soft Acid Base (HSAB) Theory, also referred to as the Pearson Acid-Base Concept, was first proposed to predict chemical reactions by understanding dominant factors that favor one reaction over another. Pearson characterized chemical species into two categories: Hard or Soft (Lewis) Acids or Bases. Typically, “hard” species refer to those that are small, high charge or oxidation state, and are weakly polarizable. The opposite is true for “soft” species. The basis of the theory is that hard acids bond stronger to hard or nonpolarizable bases, while soft acids bond stronger to soft or polarizable bases^[16].

Predicting metal and ligand interactions can provide an idea of the practicality of a reaction. Actinides are highly electropositive and large in size and are therefore deemed as hard acids. Hard acids typically have a strong affinity for hard bases such as nitrogen or oxygen which are considered to be small electronegative species^[17]. In contrast the further down on any given column on the Periodic Table, the more polarizable the elements. This increase polarizability weakens the interaction between the An and soft-donor ligands such as phosphorus or sulfur^[15]. Regardless, recent research shows that the increase in covalency found in An can exhibit stronger interaction in organoactinide complexes bearing soft-donor ligands than previously expected^[6,18]. This concept was first observed in 1950 from Street and Seaborg who studied the interaction of Cl⁻ and Am relative to promethium (Pr) resulting in Am preferring a covalent interaction compared to Pr^[19]. The degree of covalency exhibited from the An 5f-orbital vs the p-orbital from the soft base is still a major topic of discussion in the field.

1.4 Impact of the Cp Motifs and Alternative Ligands in Organoactinide

1.4.1 Cp Ligand and its Impact in Organoactinide Chemistry

Ligands play a large role in understanding the coordination of the complexes and behaviors of the metals they coordinate to. Organoactinide complexes are no different with the use of the cyclopentadienyl (Cp = η^5 -C₅H₅) ligand and its derivatives being considered the most significant and well understood ligands in the field^[20, 21].

In 1956 Reynolds and Wilkinson synthesized the first Cp supported An(IV) complex, Cp₃UCl^[22], following the synthesis of the tetrakis(cyclopentadienyl), Cp₄An (An = Th, U), complexes reported in 1962^[23]. Soon after, the first U(III) Cp supported complex was reported in 1970^[25], following the introduction of the influential

pentamethylcyclopentadienyl ligand ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). The Cp^* ligand has become a staple due to its electron richness and higher degree of coordination stabilizing An at various oxidation states. Currently there are two major cyclopentadienyl structural motifs commonly used in organoactinide chemistry: the Z_3AnX and Z_2AnX_2 , ($\text{Z} = \text{Cp}^n\text{-C}_5\text{R}_n$)^[20, 25].

Organoactinide chemistry is still considered to be in its infancy in comparison to transition metal or main group chemistry. Regardless, there has been numerous findings which have revealed the degree of An covalency, its magnetism, and potential use in catalysis. Many of these complexes involve the use of the Cp ligand or one its analogues but in recent years the interest in exploring alternative supporting ligands has increased^[26].

1.4.2 Alternative Ligands

The shift in developing alternative spectator ligand dates back to the 1980s with ligands such as the PNP, NPN, and P_2N_2 first synthesized by Fryzuk and coworkers^[27-34]. Since then, variations of these soft-donor alternatives have been explored by Izod and coworkers in 2006^[35], and Hohloch et al. in 2020 who utilizes the NP (*bold signifies anionic center*) motif^[26]. The chemistry of these ligands has been extensively studied in coordination to transition metal and lanthanides though only a fraction of the studies involve An-complexes. In 2018 Schelter and Mendiola et al., isolated a terminal uranium(IV) complex utilizing the NP ligand from the Hohloch group^[39].

In this study a new Th(IV) complex been synthesized using the NP (d (N- (2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide) ligand provided by our collaborator Stephan Hohloch at the University of Innsbruck, Austria^[26]. Furthermore, a

new **PN** (*bold signifies the anionic center*) ligand has also been determined alongside its **AsN-Cl** precursor, adding to the small but in-progress library of An soft-donor ligands complexes.

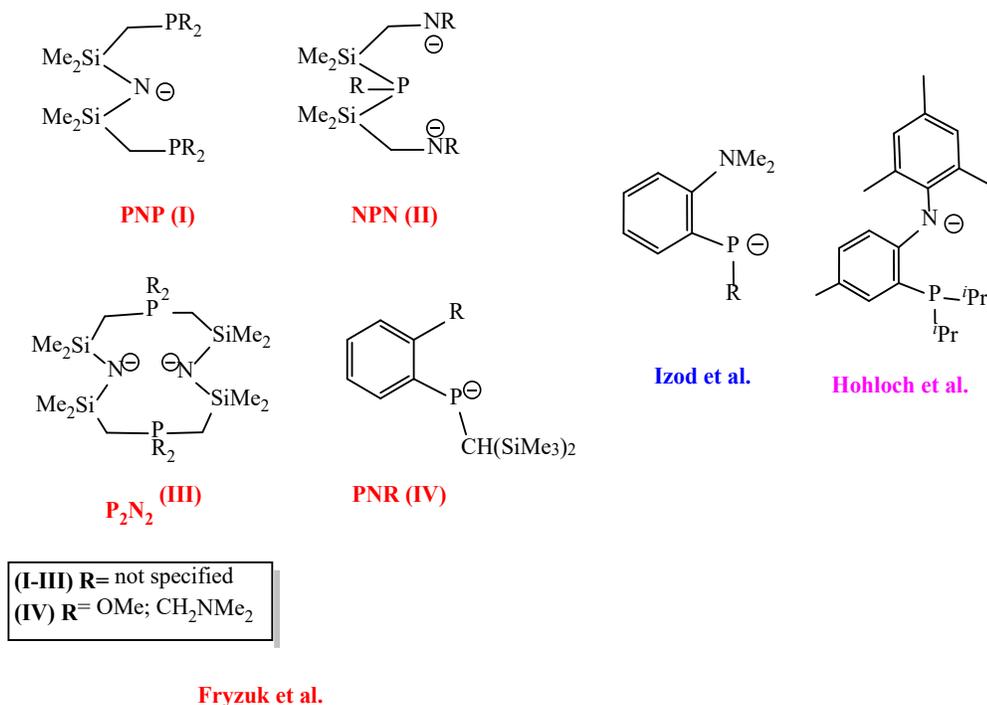


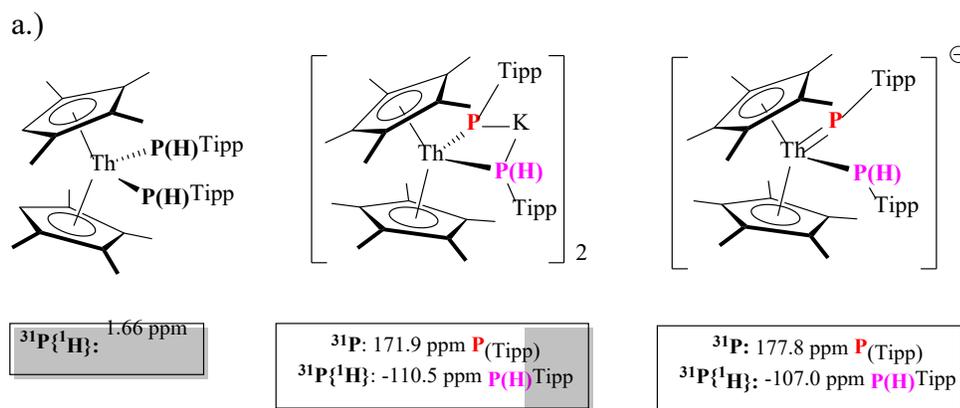
Figure 1-4 Previously reported PN⁻ motifs. Patrial image adapted from Fryzuk et al. [40]

1.5 NMR Spectroscopy

Ever since its invention in 1930, nuclear magnetic resonance (NMR) spectroscopy has been a useful tool in characterizing organic molecules. In most cases NMR can be used as a signature in confirming certain characteristics of the product. The most common NMR handle is the ¹H which is 100% abundant and used as a primary interpretation and sometimes diagnostic tool given the molecule^[41].

Another prominent NMR handle is the phosphorous-31 nuclei, ³¹P, which has a nuclear spin (I) of ½ and abundance of 100%. ³¹P is typically used in conjunction with a ¹H, and to further diagnose the compound. For P-P coupling a splitting in the ³¹P

spectrum can be observed while for any P-H present there is a doublet in the ^1H spectrum in which its coupling constant can be determined^[41]. The P-H bond can also be used as tool to show any deprotonation, given that the H is acidic and when removed by a base the ^{31}P NMR peak shifts significantly as shown in **Figure 1-3**. Lastly, carbon-13 NMR, ^{13}C , can also be used, but with only 1.1% abundance it is mainly used as a final confirmation^[42].



b.) ^{31}P NMR Chemical Shifts

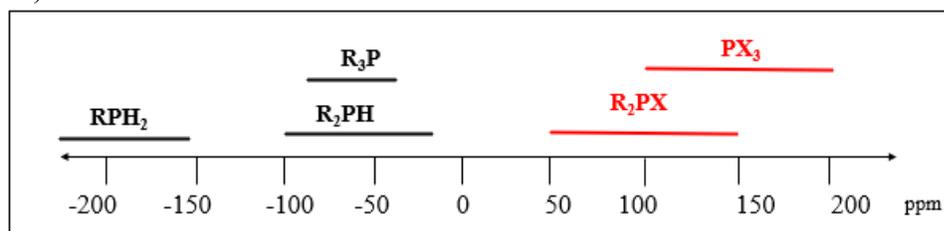


Figure 1-5 a.) Example of change in ^{31}P NMR peak(s) in spectrum depending on its chemical environment.

b.) Highlights selected P-groups and their predicted chemical shifts in ^{31}P NMR spectrum.

Chapter 2

SYNTHESIS AND CHARACTERIZATION OF PN MONOANIONIC LIGANDS AND THEIR REACTIVITY WITH ACTINIDES

ABSTRACT

In this study we present the synthesis and characterization of a new preliminary Th complex containing a previously known ligand (N-(2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide, short NP) provided by our collaborator, Stephan Hohloch at the University of Innsbruck, Austria^[26]. The NP ligand has been extensively studied in its reactivity with Ln(III) metal ranging from lanthanum(III) to lutetium(III) producing numerous heteroleptic complexes containing either one or two NP ligands. Previous reactivity of NP with actinides (An) have been observed in 2018 by Schelter and Mindiola et al. where an extensive library of complexes were observed. Our work focuses on the introduction of a preliminary NP-Th (**1**) complex to ultimately draw comparisons between the two An metals.

Furthermore, in an effort to synthesize new non-Cp ancillary ligands, we report a novel monoanionic anilidophosphine ligands [(TrippPH)-2-(C₆H₄)N(Me₂)], (**3**), short as **PN**; - *bold shows the anionic reactivity site*; T_{ipp} = 2,4,6-ⁱPr₃C₆H₂. The precursor of the PN ligand was also reported [(TrippPCL)-2-(C₆H₄)N(Me₂)], (**2**), along with its As (**4**) analogue; abbreviated as EN-Cl (E=P, As).

Further characterization NMR (¹H, ¹³C, and ³¹P) techniques have been used in determining the purity of the NP-Th complexes and the novel PN ligand and its precursor EN. The reactivity of the PN with any An or Ln metals have yet to be determined.

INTRODUCTION

Over the last decades, the chemistry of actinides has flourished with novel findings and applications across many disciplines^[36]. For a while the difference between actinides (An) and lanthanides (Ln) was considered to be minute, but with recent discoveries the differences between the two series has sparked interest in possible new applications, structures, and catalytic properties unique to that of An^[43]. The most influential and commonly used ligand are the cyclopentadienide ligands ($Cp^n = C_5R_5$) which dominate majority of f-element complexes^[20,21]. Though the Cp ligand remains influential, a new shift towards alternative ligands has been seen for potential catalytic systems, and molecular magnetism^[43].

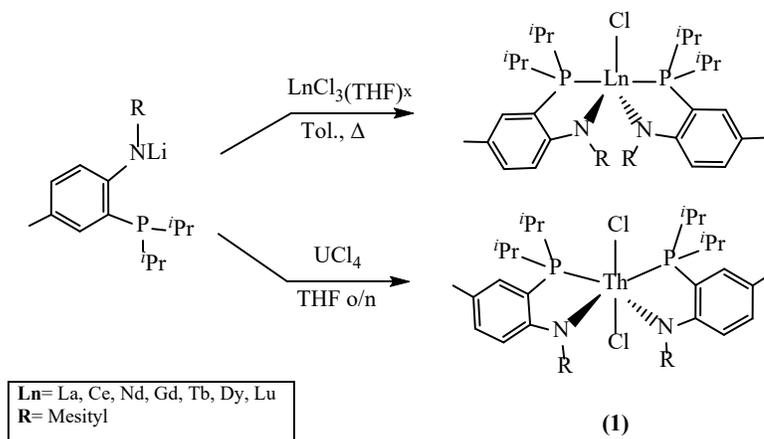
The PN(P) class of ligand is no stranger in organometallic or main group chemistry and has recently been applied to both Ln and An complexes. Izod et al., reported two new ligands monoanionic at the P center, $Ar\{C_6H_4-2-CH_2NMe_2\}P^-$; [Ar = Mes (II), Tripp (III); Mes = 2,4,6-Me₃C₆H₂, Tripp = 2,4,6-ⁱPr₃C₆H₂]^[27]. These complexes were reacted with transition metal and Ln, but no reactivity was tested with An. Hohloch and coworkers reported the reactivity of the NP ligand, (N-(2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide^[26], with seven Ln(III) metals. Numerous NP-U complexes were reported by Schelter and Mindiola et al. opening the possibilities for further reactivity with other An-metals. Here we report the first diagnostic results of the NP-Th(IV) complex. Though a crystal structure was not obtained, NMR (observed ¹H and ³¹P) have provided with preliminary data supporting the synthesis of the NP-Th complex.

A novel ligand, **PN**: [(TrippPH)-2-(C₆H₄)N(Me₂)], was synthesized along with its arsenic precursor, **AsN-Cl**: [(TrippAsCl)-2-(C₆H₄)N(Me₂)]. These new ligands were synthesized to create a catalogue of ligand- transition metals, Ln, and An in the hopes to show trends and coordination differences between each series.

RESULTS AND DISCUSSION

Synthesis of NP-Th(IV) Complex

A previously reported NP ligand from Hohloch and co-workers showed an extensive array of complexes using Ln(III) metals^[26]. Our group collaborated in utilizing the NP ligand in hopes that it would provide insight into its coordination with An metals. **Scheme 2-1** shows the general reaction of both the Ln route and the Th. The lithiated NP reacted with the ThCl₄(DME)₂ at room temperature in the glovebox to yielded the yellow product **(1)**.

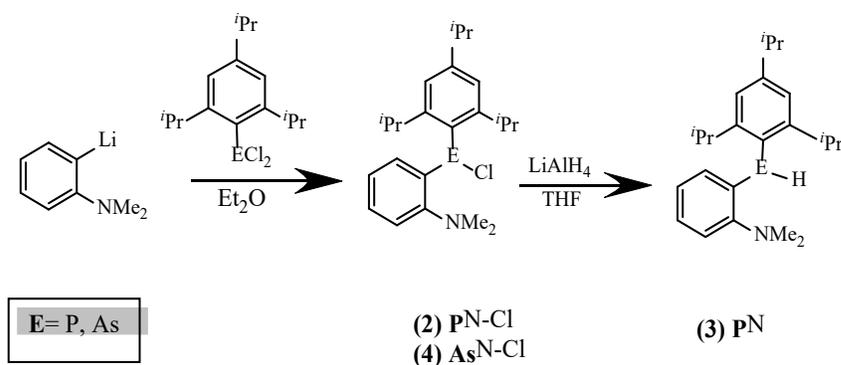


Scheme 2-1 Shows the previous NP-Ln(III) complexes in comparison to the new NP- Th(IV) complex.

A crystal structure of NP-Th has yet to be determined given the notorious lack in solubility observed of Th complexes. On the contrary, Th is diamagnetic and therefore ¹H, ¹³C, and ³¹P NMR spectrum data was obtained.

Synthesis of EN Ligand

The main goal in obtaining the **PN** ligand is to eventually use them as alternatives to the **Cp** ligands and therefore obtaining a bulky backbone was essential. The Tripp substituent (Tripp = 2,4,6-ⁱPr₃C₆H₂) was used to fulfill this, in which the ligand retained enough bulky character to enable controlled reactivity on the anionic phosphorous. It's because of this that the isolation of **(2)** and **(4)** were successfully achieved, preventing any other side reactions to occur. The same concept applies to the **AsN-Cl** analogue which behaved similarly to that of **PN-Cl**. **Scheme 2-2** shows the full reaction to achieve **(2)-(4)**.



Scheme 2-2 Shows the overall reaction scheme of the EN-Cl precures and PN ligand

Carefully controlling the stoichiometry and conditions when reacting TrippECl₂ with 1.1 equivalent of Li-(2,NMe₂-C₆H₄) at -78°C resulted in the yellow and white product, **(3)** 44% yield and **(5)** 30% yield, respectively, following with the LiAlH₄ reduction resulting in the secondary phosphine product **(4)** at 32% yield.

The PH coupling constant, ($J_{P-H} = 200$ Hz), in the ¹H NMR along with the ³¹P{H} singlet peak shifting from 67.8 ppm to -91.11 ppm is as expected for **(3)** and **(4)**. The ¹H spectrum for **(5)** showed some impurities but all of the diagnostic peaks were determined. At this time the **AsN** ligand has not been isolated without any major impurity.

EXPERIMENTAL

General Considerations. All syntheses were performed under an atmosphere of dry nitrogen either on a Schlenk-line or in a glovebox. All reagent-grade gasses were used as received and all solvents were dried over columns of activated alumina and molecular sieves in a solvent purification system by MBRAUN, USA. The compounds NP-Li and the $\text{ThCl}_4(\text{DME})_2$ were prepared according to literature procedures. All NMR spectra were recorded on either a 300 or 500 MHz Bruker NMR spectrometer, with spectra being referenced to residual solvent.

Synthesis of NP-Th, (1).

In the glovebox, a vibrant yellow solution was prepared with the provided lithiated NP ligand (150mg, 0.216 mmol) and thf (2 mL), which was then added dropwise to a stirring solution of $\text{ThCl}_4(\text{DME})_2$ (120 mg, 0.217 mmol) and THF (2mL). The $\text{ThCl}_4(\text{DME})_2$ is a white solid and upon the addition of the yellow ligand the color changed to a vibrant yellow which remained the same for the final product. The reaction was allowed to react for 18 hours before drying to a solid under vacuum. The product was rinsed with pentane and filtered through Celite[®] resulting in the removal of LiCl leaving a clear yellow solution. Any residual solvents were removed under reduced pressure resulting in a yellow viscous oil as the final product.

^1H NMR (500 MHz, C_6D_6 , 25 °C): δ = 6.95 (d, 2H, $\text{H}_{m\text{-aryl}}$), 6.83 (s, 4H, $\text{H}_{m\text{-Mes}}$), 6.64 (s, 2H, $\text{H}_{o\text{-aryl}}$), 6.62 (d, 2H, $\text{H}_{o\text{-aryl}}$), 2.42 (s, 12H, Aryl $p\text{-Me}_3$), 2.16 (d, 12H, Mes-Me_3), 2.04 (m, 4H, $\text{H-}^i\text{Pr}_2$), 1.19 (dd, 6H, $^i\text{Pr}_2$), 1.03 (dd, 6H, $^i\text{Pr}_2$).

^{31}P (C_6D_6 , 25 °C): δ 32.76 (s, PN^- , 2P).

Synthesis of 1-P(H)Tripp-2-(Me₂)N(C₆H₄), (PN).

The PN ligand was synthesized in two steps:

Step 1: Synthesis of 1-P(Cl)Tripp-2-(Me₂)N(C₆H₄), PN-Cl, (2).

A 100 mL Schlenk-flask containing a yellow ether solution (10 mL) of TrippPCl₂ (175 mg, 1.28 mmol) was cycled onto a high-vacuum Schlenk-line and cooled to -78°C by submersion in an acetone and dry ice bath. A syringe was charged with a white solution of Li-aniline (330 mg, 0.844mmol) and ether (20 mL) and added dropwise to the stirring TrippPCl₂ solution. The mixture changed color to an opaque white, then allowed to warm up to room temperature and left to stir for 16 hours. When completed, the pale-yellow solution was dried under vacuum and washed with pentane before filtering. The filtrate was then dried under vacuum resulting in a yellow viscous oil, (44% yield). Purity was determined by ¹H and ³¹P NMR spectroscopy.

¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 7.07 (m, 6H, H_{aryl}), 4.22 (m, 2H, H_{tripp o-ⁱpr}), 2.72 (m, 1H, H_{tripp p-ⁱpr}), 1.94 (s, 6H, NMe₂), 1.16 (d, 6H, Tripp p-ⁱPr, J_H = 2.1 Hz), 0.94 (d, 12H, Tripp o-ⁱPr, J_H = 6 Hz).

³¹P NMR (C₆D₆, 25 °C): δ 32.76 (s, PN, 2P).

Step 2: : Synthesis of 1-P(H)Tripp-2-(Me₂)N(C₆H₄), PN, (3)

A 100 mL Schlenk-flask containing a solution of (2) and thf (15 mL) was cooled to -78°C. Separately, a syringe was charged with 1.5 mol LiAlH₄ and thf (15 mL) added dropwise to the cold stirring PN-Cl solution. The solution was slowly brought to room temperature and allowed to stir for 16 hours. The flask was then brought to 0 °C before adding 1-2 mL of degassed water then warming the reaction back to room temperature and left to stir for 15 min before drying under vacuum. To the solid, pentane was added

then filtered, drying the filtrate to a solid resulting in the pale-yellow product (32% yield). The ligand was characterized by NMR spectroscopy.

^1H NMR (C_6D_6 , 25 °C): δ = 7.16 (s, 1H, H_{aryl}), 7.03 (t, 1H, H_{aryl}), 6.93 (d, 1H, H_{aryl}), 6.67 (t, 1H, H_{aryl}), 5.37 and 6.12 (s, 1H, PH, $J_{\text{P-H}} = 200$ Hz), 3.88 (q, 2H, $\text{H}_{\text{Tripp } o\text{-ipr}}$), 2.77 (m, 1H, $\text{H}_{\text{Tripp } p\text{-ipr}}$), 2.61 (s, 6H, NMe_2), 1.19 (m, 18H, 6Me).

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): δ -91.12 (s, **PN**, 1P).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 500 MHz): δ = 155.10 (m, 2C, C-P), 154.78 (m, 2C, $\text{C}_{\text{aryl}}\text{-}^i\text{pr}$), 150.48 (s, 1C, $\text{C}_{\text{aryl}}\text{-N}$), 133.20 (m, 1C, $p\text{-C}_{\text{Tripp}}$), 132.5 (m, 1CH, $o\text{-C}_{\text{aryl}}$), 123.82 (s, 1CH, $m\text{-C}_{\text{aryl}}$), 121.56 (m, 1CH, $p\text{-C}_{\text{aryl}}$), 119.15 (s, 1CH, $o\text{-C}_{\text{aryl}}$), 44.59 (m, 2CH₃, NMe_2), 34.46 (s, 1CH, C $p\text{-ipr}$), 32.83 (m, 2CH, $m\text{-C}_{\text{Tripp}}$), 29.68 (s, 2CH, C $o\text{-ipr}$), 24.10 (m, 4CH₃, C $o\text{-ipr}$), 23.77 (s, CH₃, 2C $p\text{-ipr}$).

Synthesis of 1-As(Cl)Tripp-2-(Me₂)N(C₆H₄), (AsN-Cl).

Step 1: Synthesis of 1-As(Cl)Tripp-2-(Me₂)N(C₆H₄), AsN-Cl, (4).

The same steps as **(2)** were taken to synthesize AsN-Cl. In this reaction 60 mg of TrippAsCl₂ (0.171 mmol) was used along with 24mg of Li-analine (0.062 mmol). The color of the solution upon the Li-analine addition was pale off-white, eventually resulting in a white solid product (30% yield). Purity was determined by ^1H and NMR spectroscopy.

^1H (C_6D_6 , 25 °C): δ = 8.27 (m, 1H, H_{aryl}), 7.12 (d, 1H, H_{aryl} , $J_{\text{H}} = 12.2$), 7.05 (br. s, 2H, $m\text{-H}_{\text{Tripp}}$), 6.67 (m, 2H, H_{aryl}), 4.05 (sept., 2H, $\text{H}_{\text{Tripp } o\text{-ipr}}$), 2.72 (sept., 1H, $\text{H}_{\text{Tripp } p\text{-ipr}}$), 1.92 (s, 6H, NMe_2), 1.36 (d, 6H, $p\text{-}^i\text{Pr}$, $J_{\text{H}} = 11$ Hz), 1.17 (d, 6H, $p\text{-}^i\text{Pr}$, $J_{\text{H}} = 8.5$ Hz), 0.933 (d, 12H, $o\text{-}^i\text{Pr}$, $J_{\text{H}} = 11$ Hz).

FUTURE WORK

For the NP-An reactivity, the next natural step would be to obtain a clean and reproducible NP-Th structure and explore reactivity with transuranic metals. Additionally, extending the list to NP-An(III) complexes and compare them to the already existing NP-Ln(III).

As for the PN ligand, similar experiments to the NP can be done with both Ln(III) and An(III/IV). The same can be done with the AsN once a pure product has been obtained. Further substituting include changing the Tripp group with a Mes group, similar to the Izod reported ligands. These changes should provide an array of bulkiness to the PN ligand and its coordination to various Ln and An metals.

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