

PHOSPHINIMINES AS POTENTIAL  
TECHNETIUM  
ENVIRONMENTAL SENSORS

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Doctor of Philosophy

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by  
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The undersigned, appointed by the Dean of the graduate School, have examined the dissertation entitled

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TECHNETIUM  
ENVIRONMENTAL SENSORS

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“Fear not, for I am with you; be not dismayed, for I am your God. I will strengthen you, yes, I will help you, I will uphold you with My righteous right hand.” Isaiah 41:10

“I can do all things through Christ which strengthens me.” Philippians 4:13

This work would not be possible without the strength, patience, and perseverance the Lord has bestowed. The glory belongs to Him alone.

I would like to further dedicate this dissertation to my mother, Ellen Russell. Without her time, patience, and support it would not have been possible. I would also like to thank the rest of my family – my father Glen Russell, brother Jacob Russell, and sister Laura Russell.

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## LIST OF ABBREVIATIONS

AG-4x4	Dimethyl aminomethyl functional weakly basic anion exchange resin, BioRad
Aliquat-336	Tricaprylmethylammonium chloride
APCI	Atmospheric Pressure Chemical Ionization
bis-MSB	1,4-(bis(2-methylstyryl))benzene
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane
CH <sub>3</sub> CN	Acetonitrile
cpm	Counts per minute
cps	Counts per second
DMSO	Dimethylsulfoxide
ESI	Electrospray ionization
ICP-MS	Inductively coupled plasma mass spectrometry
LSC	Liquid Scintillation Counting
MURR	University of Missouri Research Reactor
PPh <sub>2</sub> anthracenyl	(9-anthracenyl)diphenylphosphane
PPh <sub>2</sub> naphthyl	naphthalen-1-yl-diphenylphosphane
POPOP	1,4-bis(5-phenyloxazol-2-yl)benzene
PPO	2,5-diphenyloxazole
THF	Tetrahydrofuran

# PHOSPHINIMINES AS POTENTIAL TECHNETIUM ENVIRONMENTAL SENSORS

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## ABSTRACT

Phosphinimines,  $R_3P=NSiMe_3$ , undergo hydrolysis to form the phosphiniminium cation,  $R_3P=NH_2^+$ , which forms the ion pair  $[R_3P=NH_2^+][X^-]$  in the presence of an anion. Preliminary studies show that in the presence of  $TcO_4^-$ ,  $Ph_3P=NSiMe_3$  forms  $[Ph_3P=NH_2^+][TcO_4^-]$  and  $[Ph_3P=NH_2^+]$  is selective for  $TcO_4^-$  over other anions. Technetium-99 is present as environmental contamination in the form of  $^{99}TcO_4^-$ , which is extremely mobile. Currently available methods to measure this contamination are time consuming and tedious. A method to preconcentrate and measure  $^{99}Tc$  environmental contamination in a quick and efficient manner is needed. The selectivity of the phosphiniminium cation for  $TcO_4^-$  may make phosphinimines suitable for such preconcentration and possibly for measurement. Several phosphinimines were synthesized and characterized for their stability and selectivity with  $^{99}TcO_4^-$ , including  $Ph_3P=NSiMe_3$ , (9-anthracenyl) $Ph_2P=NSiMe_3$ , (1-naphthyl) $Ph_2P=NSiMe_3$ , and (p-COOMe) $C_6H_4Ph_2P=NSiMe_3$ . (9-anthracenyl) $Ph_2P=NSiMe_3$  and (1-naphthyl) $Ph_2P=NSiMe_3$  include possible reporter groups and (p-COOMe) $C_6H_4Ph_2P=NSiMe_3$  contains a linking moiety for incorporating reporter groups or attaching the phosphinimine to a polymer support. The use of internal and external reporter groups to generate a signal in the presence of  $TcO_4^-$  is also investigated.

## **CHAPTER 1: INTRODCUTION**

### **1.1 Origin of environmental radioactive contamination**

#### **1.1.1 The History and use of radioactivity**

The twentieth century was a time of technological leaps for the fields of nuclear and radiochemistry. The first radioactive emissions were captured by Henri Becquerel in 1896 as he accidentally exposed photographic plates to uranium, which resulted in Becquerel, Marie Curie, and Pierre Curie receiving the 1903 Nobel Prize for the discovery of radioactivity. James Chadwick discovered neutrons in 1932 making possible the discovery of fission in 1938 by Lise Meitner, Otto Hahn, and Fritz Strausmann. By 1939, Germany had begun work on the military use of fission technology. With the threat of a German victory in World War II, the United States and Great Britain began work on the nuclear bomb. The Manhattan Project formally began in 1942 with the first reactor and reprocessing plant built and in operation at the Hanford site in Washington State by 1944, less than two years after Enrico Fermi and his team at the University of Chicago demonstrated that a controlled nuclear chain reaction was possible. The urgent need for success due to World War II and the use of untested technology led to radioactive contamination of the environment that continues today.<sup>1</sup>

Due to the necessity of secrecy for portions of the Manhattan Project and for the protection of citizens, numerous nuclear sites were developed, each with its specific function. Examples include Hanford, Washington (the production of plutonium for nuclear bombs); Savannah River, South Carolina (the production of plutonium for nuclear bombs); Rocky Flats, Colorado (manufacture of plutonium bomb-triggers); and Fernald Feed Materials Production Center, Ohio (uranium processing). A total of 16

major facilities across the United States researched, manufactured, assembled, and tested nuclear materials and bombs.<sup>2</sup> All of these sites have some form of environmental contamination, dependant on their specific function. The site located at Hanford, Washington is one of the most well-known due to the pervasiveness of the contamination.

Ground was broken for the 640 square-mile Hanford site in March of 1943.<sup>1</sup> This site was chosen for its sparse population, location adjacent to a major water source for cooling the nuclear reactors (Columbia River), and for the quality of the soil. By late 1944, billions of gallons of liquids and billions of cubic meters of gases were being emitted from the plants.<sup>1</sup> A total of eight single-pass / open-coolant reactors were built over the life-span of the site. The first reactor, B-reactor, went critical in September 1944. Plutonium was produced and reprocessed in significant quantities by February 1945. The reactors contained mainly  $^{238}\text{U}$ , which when bombarded with neutrons of the correct energy, absorbed a neutron to generate  $^{239}\text{U}$ . This then beta decayed to produce  $^{239}\text{Pu}$ , a fissionable material. The reactor fuel was then reprocessed to isolate the plutonium for manufacturing the nuclear bombs. The byproducts of the process when  $^{235}\text{U}$ ,  $^{238}\text{U}$ , or  $^{239}\text{Pu}$  undergoes fission are called “fission products.” These fission products include a wide variety of radionuclides with a variety of half-lives. The radionuclides produced in larger quantities with sufficiently long half-lives to be of continual concern include  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$ , and  $^{90}\text{Sr}$ .

### **1.1.2 River Pollution**

By 1955 there were eight single-pass / open-coolant reactors operating at Hanford.<sup>1</sup> The coolant in these reactors was water from the Columbia River. River water

was pumped into the reactors to remove excess heat that would otherwise damage the reactor. The hot water was then dumped back into the river after a single pass through the reactor core. Coolant water must be very pure to avoid making the impurities radioactive while it was inside the reactor; the engineers at Hanford thought the Columbia River was a perfect source since it was already sufficiently pure. The reactors were all experimental and the first of their kind; the fuel rods broke and cracked under the high temperature and radiation. This exposed kilograms of uranium and fission products in each fuel rod to river water, dissolving the radioactive and hazardous chemicals in the fuel.<sup>2</sup> By December 1946, an estimated 40,000 Ci had been released in the reactor coolant – a discharge rate of 1,500 Ci/month.<sup>1</sup> This was a decrease from the peak of 900 Ci/day.<sup>1</sup> Radionuclides of immediate concern were <sup>32</sup>P, <sup>76</sup>As, <sup>65</sup>Zn, <sup>51</sup>Cr, and <sup>239</sup>Np; all were beta-emitters that affect the GI tract, bones, reproduction, and blood-formation.<sup>1</sup> These radionuclides were found in shellfish at the mouth of the Columbia River, which is a principal hatchery and fishery for salmon and steelhead trout.<sup>1</sup> The fish downstream of the Hanford site contained 100,000-170,000 times the radioactivity of the fish upstream that had not been exposed to water from the reactors.<sup>1</sup> Most of the radioactivity was contained in the liver, kidneys, and muscle tissue; the radionuclides included <sup>32</sup>P, <sup>76</sup>As, <sup>65</sup>Zn, <sup>51</sup>Cr, and <sup>239</sup>Np. Studies done in 1975 found long-lived radionuclides in river sediments, an estimated 1000 Ci of <sup>65</sup>Zn, 4000 Ci of <sup>60</sup>Co, 2000 Ci of <sup>152</sup>Eu, 3000 Ci of <sup>3</sup>H, 10,000 Ci of <sup>99</sup>Tc, and <1000 Ci of other radionuclides.<sup>1</sup> As aquatic life, algae, insects, and fowl drank the river water and ate plants that have incorporated river water, the radionuclides traveled up the food chain and became more concentrated, up to



hundreds of thousands of times.<sup>1</sup> The eight single-pass reactors were shutdown between 1964 and 1971.<sup>1</sup>

### **1.1.3 Groundwater Pollution**

When selecting the Hanford site, the scientists and engineers believed that the sand and gravel soil was nearly ideal for disposal of radioactive wastes.<sup>1</sup> The soil at Hanford contains sand and gravel, and sits on the Touchet Formation, glacial outwash sands, gravels, and fine volcanic ash that average 100-250 ft. This then sits on the Ringold Formation of silt, clay, and wind-deposited Palouse soils approximately 1,200 ft thick. The deepest layer is a basalt plateau.<sup>1</sup> The groundwater is in a number of confined and unconfined aquifers interspersed with basaltic ridges.<sup>1</sup> Water enters either the Columbia River to the southeast or the Yakima River to the southwest. The groundwater level varies from a few feet below the surface to 300 feet.<sup>1</sup>

Millions of curies of radioactivity were directly released into the Columbia River, air, and soil of the Columbia Basin.<sup>1</sup> Disposal of the low-level ( $<5 \times 10^{-5}$   $\mu\text{Ci/mL}$ ) and intermediate-level ( $5 \times 10^{-5}$  to  $100 \mu\text{Ci/mL}$ ) wastes involved pouring them on the ground in trenches, pools, and cribs.<sup>1</sup> The releases totaled millions of gallons each day.<sup>1</sup> Contrary to what the scientists believed, the radionuclides did not adsorb to the soil. Rather, they passed through the top layer of sand and gravel, through the Touchet Formation, and into the Ringold Formation. The radionuclides are still mobile in this layer, but less so than in the layers above it. The groundwater, however, is either in this layer or above it. Additionally, there are large differences in the types and coarseness of the sand and gravel soil such that the radionuclides migrated differently in different

locations thus complicating matters.<sup>1</sup> Once the soil that contained the radioactive waste dried, the wind carried the soil contaminated with dry radionuclides to the surrounding areas.<sup>1</sup> To prevent the dry soil from being blown away by the wind, “reverse-wells” were used. These were dry shafts for low-level liquid waste; however, this only allowed the waste to get closer to the water table.<sup>1</sup> The radionuclides of particular concern for both inhalation and groundwater contamination included <sup>99</sup>Tc, <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>144</sup>Ce, <sup>129</sup>I, <sup>91</sup>Y, <sup>152</sup>Eu, <sup>154</sup>Eu, <sup>239</sup>Pu, and <sup>238</sup>U.<sup>1</sup> In 1945, wells present on site were contaminated with uranium and it had spread offsite to wells at Benton City by mid 1947.<sup>1</sup> By 1956, <sup>60</sup>Co was found in the groundwater beneath Hanford.<sup>1</sup> The total volume released to the soil is estimated at 120 billion gallons, containing 3.2 million Ci of beta-emitters, 280,000 g of plutonium, and 120,000 kg of uranium.<sup>1</sup>

**Table 1: Radionuclides of concern for inhalation and groundwater contamination<sup>3</sup>**

Radionuclide	Half-life (t <sub>1/2</sub> )	Decay Mode	Energy (MeV)	Potential Hazard
<sup>99</sup> Tc	2.13x10 <sup>5</sup> y	β <sup>-</sup>	0.294	Ingestion
<sup>90</sup> Sr	28.78 y	β <sup>-</sup>	0.546	Mimics Ca
<sup>137</sup> Cs	30.1 y	β <sup>-</sup> γ	0.514 0.662 ( <sup>137m</sup> Ba)	Mimics K
<sup>144</sup> Ce	284.6 d	β <sup>-</sup> γ	0.318 0.1335	Mimics Ca
<sup>129</sup> I	1.7x10 <sup>7</sup> y	β <sup>-</sup>	0.194	Goes to thyroid
<sup>91</sup> Y	58.5 d	β <sup>-</sup> γ	1.544 1.205	Mimics Ca
<sup>152</sup> Eu	13.54 y	EC β <sup>-</sup> γ	0.727 0.699 0.344	Mimics Ca
<sup>154</sup> Eu	8.6 y	β <sup>-</sup> γ	0.58 0.123, 1.274	Mimics Ca
<sup>239</sup> Pu	2.41x10 <sup>4</sup> y	α	5.156	Mimics Ca
<sup>238</sup> U	4.47x10 <sup>9</sup> y	α	4.197	Mimics Ca

#### **1.1.4 Underground tanks**

Due to the urgency to produce sufficient plutonium for the war needs, the Hanford site did not initially reprocess fuel or treat radioactive or hazardous waste. Several tank farms were built from 1943 to 1985. There are a total of 177 cylindrical underground storage tanks ranging in capacity from 55,000 to 1.1 million gallons.<sup>2</sup> The tanks contained 54 million gallons of hazardous and radioactive waste as of 1998.<sup>2</sup> The first tanks built were single-shell; there was a single carbon steel wall and floor covered by a dome and outer shell of concrete.<sup>2</sup> Beginning in 1968, double-shell tanks were constructed; these contained two carbon steel liners and a single steel dome liner with the entire tank encased in reinforced concrete.<sup>2</sup> A total of 149 single-shell tanks and 28 double-shell tanks were constructed at the site<sup>2</sup> out of carbon steel rather than stainless steel, and the pipes were cast-iron<sup>1</sup> due to cost considerations. The waste was made alkaline by the addition of large volumes of sodium hydroxide in an attempt to prevent corrosion of the tanks. This was not successful, and 68 tanks are known or suspected of leaking at least 1 million gallons of waste into the soil and groundwater.<sup>1</sup> The groundwater below the tank farms eventually flows into the Columbia River.<sup>2</sup>

The first leak was suspected in 1956 and confirmed in 1961 from tank 104-U.<sup>2</sup> Cleaning up the tanks is made more difficult by the fact that the contents of the tanks are heterogeneous, and that across tanks the contents are different.<sup>4</sup> The tank contents include a sludge at the bottom comprised of insoluble residues, solid excess salt, and precipitated residues; next is a residual liquid saturated with salt and suspended salt crystals; and on the top is a floating crust of low-density salts.<sup>4</sup> Each tank also contains different radionuclides and different chemicals depending on when the waste was

generated (several different processes were used), what was added to the tank in an attempt to stabilize it, and whether it was mixed with any other tank contents. Cleaning up the tank waste is a process that has been ongoing with no end in sight. Thus waiting to clean up the tanks before tackling the groundwater and soil contamination is not an option. The groundwater and soil contamination continues to increase and to migrate.

Contamination to the environment came first from the known release of radioactive coolant water and radioactive waste to the Columbia River, ground, and air. It now continues to come from the aging and leaking underground tanks.

#### **1.1.5 Evidence of contamination at other nuclear sites<sup>1</sup>**

Each site developed during the Manhattan Project has environmental contamination with radionuclides and/or hazardous chemicals related to its specific function. Not all the sites possess <sup>99</sup>Tc contamination.

- Hanford, WA    ▪ Released millions of gallons of low-level radioactive waste to the ground each day, released radioactive gases into the atmosphere. Underground tank farms were leaking beginning in the 1950s. The river, river sediment, soil, and groundwater surrounding the Hanford site is thoroughly contaminated with radionuclides as well as harmful chemicals.<sup>1</sup>
- Savannah River Site, SC    ▪ By the 1950s there were five weapons-production reactors and two chemical reprocessing plants. The site and the reactors were shutdown by the late 1980s due to safety concerns and violations –

broken and disengaged radiation-monitors, disconnected sprinklers, geological fault under the site. Savannah River Site also contains a tank farm for storage of radioactive wastes.<sup>1</sup>

- Rocky Flats, CO  
▪ Plutonium and toxic chemicals were released to the air and soil during the 35 years of operation. The DOE was forced to buy land adjacent to the site as a buffer zone, and it went from the original 10 square-miles to thousands of acres. In 1988, employees and a DOE inspector inhaled radioactive particles. Inspectors found uncalibrated radiation-monitors, antiquated fire-alarm systems, and toxic wastes leaching into the groundwater. The site is 16 miles from Denver.<sup>1</sup>
- Fernald Feed Materials Production Center, OH  
▪ The 1050 acre uranium-processing complex operated from 1952 until 1986. The site was shut down in December 1984 and it was found that excessive amounts of uranium dust and oxides had been released through ventilation systems. Approximately 230 tons of radioactive material had leaked into the Greater Miami River valley over 30 years; 337 tons of UF<sub>6</sub> could not be located; thousands of kilograms of uranium dust vented to the atmosphere and surface water; 5 million kilograms of radioactive and hazardous substances were released to pits and swamps and then into the groundwater; 200,000 canisters and barrels with mixed and hazardous wastes could not be identified. The State of Ohio was

awarded \$1 million and oversight for the cleanup. The local population was awarded \$78 million for lost property values and health needs.<sup>1</sup>

- Idaho National Engineering Laboratory
- A total of \$456 million was awarded for 5.5 years to cleanup buried waste.<sup>1</sup>
- Oak Ridge Reservation, TN
- There was a discharge of 2.4 million pounds of mercury from the Y-12 Nuclear Weapons Components Plant. The groundwater contains polychlorinated biphenyls (PCBs), heavy metals, and radioactive substances. Toxic and radioactive wastes were allowed to drain into White Oak Creek, which feeds into the Clinch River – traces of plutonium were found 40 miles downstream in 1990.<sup>1</sup>
- Pantex, TX
- The site released dimethylformamide and acetone into the soil and Ogallala aquifer, a major water source for the State of Texas and neighboring states.<sup>1</sup>

## 1.2 Production of technetium

Technetium-99 is produced from the thermal neutron fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  in 6% yield. Technetium-99 emits a 0.292 MeV  $\beta^-$  with a half-life of  $2.15 \times 10^5$  years. Most radionuclides require approximately 10 half-lives before they can be considered to have decayed to background levels. This means that  $^{99}\text{Tc}$  requires approximately 2 million years, before all the  $^{99}\text{Tc}$  that has been produced to date will be considered to have

decayed. This long half-life makes  $^{99}\text{Tc}$  a concern for long-term storage and environmental contamination.

### **1.3 Technetium in the environment**

Under aerobic environmental conditions, technetium is present as  $\text{TcO}_4^-$  and is easily taken up in plants, algae, lichen, and some sea life, such as crustaceans and clams.<sup>5</sup>  $\text{TcO}_4^-$  migrates easily through the environment due to its low negative charge, while radionuclides such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  do not. Soils contain negatively charged species such as zeolites and humic acids to which cations such as  $^{137}\text{Cs}^+$  and  $^{90}\text{Sr}^{2+}$  readily sorb. The anionic  $\text{TcO}_4^-$  is repelled by these species and so migrates quickly and enters the food chain.  $\text{TcO}_4^-$  is not an ingestion hazard to humans since it is readily excreted from the body in urine. Many plants, algae, lichen, and sea life take up and retain  $\text{TcO}_4^-$ , and then metabolize it to a more lipophilic form that does not excrete from the body, similar to that observed with mercury uptake. Between 1956 and 1981,  $^{99}\text{Tc}$  was measured in lichen and then in the reindeer that feed on the lichen.<sup>5</sup> While people do not eat lichen, they do eat reindeer as well as sea life such as lobsters, clams, and certain fish and thus ingest and incorporate the  $^{99}\text{Tc}$ . This could pose a serious health risk and potentially cause cancer. In 1984, trees at Oak Ridge National Laboratory in Oak Ridge, TN tested positive for  $^{99}\text{Tc}$ . Burning this wood would release  $^{99}\text{Tc}$  into the air, and animals that eat wood and nuts would ingest  $^{99}\text{Tc}$ . Technetium-99 does have a geochemical sink in anaerobic soils because it forms  $\text{TcO}_2$ , which is an insoluble colloid.<sup>5</sup> As soon as these soils are exposed to water or oxygen,  $\text{TcO}_2$  forms  $\text{TcO}_4^-$  and it again becomes mobile.

For safety and clean up purposes, there is great interest in monitoring the location and movement of this ion.

#### **1.4 Sensing: Anionic, fluorescent, scintillation**

The process of sensing involves the production of a qualitative or quantitative signal in the presence of a specific analyte.<sup>6</sup> The sensor generates the signal in recognition of or binding by the analyte through characteristic and measurable properties of the analyte.<sup>7</sup> The sensor itself generally has three components: (i) chemical receptor for the analyte, (ii) signal transduction process where the binding event is converted into a physical change, and (iii) a method of measuring the signal.<sup>8</sup> The first and third distinguish different types of sensors: the type of analyte detected (*i.e.*, cation, anion) and the type of signal generated (*i.e.* fluorescence, luminescence).

Anion sensing is the qualitative detection or quantitative determination of a negatively charged species by a device, which translates its presence into a physical signal.<sup>6</sup> Anion sensing is less developed than cation sensing and is generally more difficult.<sup>8</sup> Anion interactions are generally weaker than cation interactions with their respective molecules.<sup>6</sup> Additional differences include: ionic size (anions are usually larger than cations,  $\text{Cl}^-$  0.167 nm,  $\text{K}^+$  0.133 nm about the same as  $\text{F}^-$ ), a number of different geometries (spherical  $\text{Cl}^-$ , linear  $\text{CN}^-$ , tetrahedral  $\text{SO}_4^{2-}$ , trigonal planar  $\text{NO}_3^-$ ), and a narrower pH window with potentially variable ionization (carbonate vs bicarbonate).<sup>8</sup>  $\text{TcO}_4^-$ , the major environmental form of technetium, is a negatively charged, tetrahedral anion.<sup>5</sup> The low charge of  $\text{TcO}_4^-$  that makes it mobile in the environment, also makes it difficult to detect since it does not bind strongly to most



reagents. A pertechnetate sensor would require strong and selective binding (*i.e.*, minimal or no competition from environmental anions such as chloride, nitrate, phosphate, sulfate, and humic acid) and a signal indicating its binding.

Fluorescent sensing involves the emission of light on binding by the analyte,<sup>9</sup> and is popular due to its high sensitivity and selectivity.<sup>10</sup> There are many advantages to using a fluorescent or luminescent molecule for sensing: high sensitivity, high selectivity, short response times ( $< 10^{-9}$  s), sampling not needed, nondestructiveness, and processes can be studied in real time.<sup>11</sup> Modifying functional groups on the fluor can change the fluorescence spectrum observed. Electron-donating substituents cause a shift in the absorption and fluorescence spectrum in addition to increasing the molar absorption coefficient.<sup>10</sup> The spectra of fluors with electron-donating substituents are often broad and structureless in comparison with the parent aromatic hydrocarbon.<sup>10</sup> The ability to modify spectra with substituents can be advantageous when designing a specific fluorescent sensor.

Since  $^{99}\text{Tc}$  is a beta emitter, radiometric sensing via scintillation counting is one method for generating a signal when  $\text{TcO}_4^-$  is bound to the sensor. Each time a  $\beta^-$  particle is emitted, the energy is transferred to a scintillator (or fluor), which then emits light. Scintillation is a term applied to fluorescence emission when it is generated by a radionuclide transferring energy to the fluor. In fluorescence detection, binding of the anion will result in a modification of the original fluorescence signal (*i.e.*, it will fluoresce in the presence of the anion but not in its absence; the wavelength of the fluorescence peak will shift; etc.). In scintillation detection, the presence of a  $\beta^-$  emitting

radionuclide excites the fluor to generate the signal of light, which is then collected and used to count the radionuclide present in the sample.

### **1.5 Current methods of detection for technetium-99**

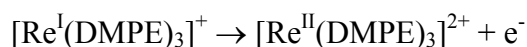
Environmental samples often have small, although possibly toxic, quantities of the element being measured. Samples must often be collected and sent to a laboratory for any necessary separations, sample preparation, and finally analysis. Preconcentration is often a required step, complicating and increasing the time required to analyze each sample. Many conventional methods of detecting species such as heavy metals often require expensive instrumentation such as atomic absorption, inductively coupled plasma, and fluorimetry.<sup>12</sup> Radionuclides can often be detected based on what is emitted from the nucleus, however different instrumentation is required for each type of emission ( $\gamma$  vs.  $\beta^-$ ). Instrumentation is often expensive and usually requires a trained operator. Thus, analyzing environmental samples from a large site or a large number of sites can be time consuming, costly, and labor intensive. There is a need for portable, fast, and low-cost analysis methods for a variety of different environmental contaminants including  $^{99}\text{Tc}$ .

Technetium-99 is very mobile in the environment, is present as  $\text{TcO}_4^-$ , and is present with a wide variety of other anions. Technetium-99 is a pure  $\beta^-$  emitter with a long half-life. For detection,  $^{99}\text{Tc}$  must be separated from other interferences (both radioactive and anionic), preconcentrated, and detected. Current methods for measuring  $^{99}\text{Tc}$  include sequential injection analysis<sup>13-15</sup>, spectroelectrochemical detection<sup>16</sup>, inductively coupled plasma mass spectrometry (ICP-MS)<sup>17, 18</sup>, absorptive stripping voltammetry<sup>19</sup>, and liquid scintillation counting (LSC)<sup>20</sup> following preconcentration.

The technique of sequential injection analysis was applied by Egorov et. al to preconcentrate and measure  $^{99}\text{Tc}$ .<sup>13-15</sup> This method uses an anion-exchange extractant coated onto a polymeric resin to selectively bind  $\text{TcO}_4^-$  in order to preconcentrate it prior to measurement. The  $^{99}\text{TcO}_4^-$  is measured *in situ* by scintillation detection through a primary fluor (usually PPO - 2,5-diphenyloxazole) and a secondary fluor (usually bis-MSB - 1,4-bis(2-methylstyryl)benzene) that were also coated onto the polymeric resin. Using Aliquat-336 (tricaprylmethylammonium chloride),<sup>14</sup> a long-chain quaternary ammonium ion extractant, and solutions of dilute acid (0.01-0.02 M  $\text{HNO}_3$ ), the sensor was able to selectively measure  $^{99}\text{TcO}_4^-$  in the presence of  $^{90}\text{Sr}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$ . The detection efficiency for  $^{99}\text{TcO}_4^-$  ( $\beta^-$  particle) was reported to be  $44-47 \pm 3 \%$  (depending on the calibration method used) with a detection limit of 3 dpm/mL in a 30-minute count time. The sensor developed preconcentrated and measured the amount of  $^{99}\text{TcO}_4^-$  present, however the samples had to be acidic (which most environmental and tank wastes are not, thus requiring pretreatment). There was no analysis of the selectivity for  $\text{TcO}_4^-$  over other common anions such as chloride, nitrate, phosphate, etc., present in both the environment and nuclear wastes in high concentrations, and chemoluminescence problems with the fluor were reported. Using AG-4x4, a dimethylaminomethyl ammonium functional weakly basic anion exchange resin, Egorov et al.<sup>15</sup> were able to sufficiently preconcentrate  $\text{TcO}_4^-$  under slightly acidic or slightly basic conditions. The AG-4x4 resin has a low selectivity for  $\text{TcO}_4^-$  and was not compared to other environmentally relevant anions. The detection efficiency for  $^{99}\text{TcO}_4^-$  ( $\beta^-$  particle) was reported as  $22 \pm 2 \%$  with a detection limit of 6.85 Bq/L in a 10 minute count time. Sequential injection analysis has the benefit of reducing the exposure to workers and

reducing secondary wastes such as gloves, vials, etc. Both Aliquat-336 and AG-4x4 can be regenerated for continued use.

In spectroelectrochemical sensing,<sup>16</sup> the analyte is taken up selectively, electrolyzed selectively, and partitioned into a film where it is then selectively monitored spectroscopically. This process has been shown to work with  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$ ,<sup>16</sup> a non-radioactive analogue to  $[\text{}^{99\text{m}}\text{Tc}^{\text{I}}(\text{DMPE})_3]^+$ , where DMPE = 1,2-bis(dimethylphosphino)ethane. The goal was to develop technetium myocardial perfusion imaging agents.



In order to sense  $[\text{Re}^{\text{II}}(\text{DMPE})_3]^{2+}$ , the complex must partition into the coating, undergo a one-electron electrochemical oxidation, and absorb visible light. This discriminates against most, if not all, possible interferents.

Inductively coupled plasma mass spectrometry (ICP-MS)<sup>17, 18</sup> can measure  $^{99}\text{Tc}$  with high sensitivity from soil and plant samples. This method has the benefit that common environmental anions do not interfere with the measurement. The only interferences of concern would be at mass 99; Tagami et. al<sup>17</sup> found that  $^{98}\text{MoH}$  was not an interferent in their samples. However, due to the low concentration of  $^{99}\text{Tc}$  in the environment, all the samples must undergo significant preconcentration, resulting in additional waste. Following preconcentration, the sample must have < 300 ppm of total element concentration for the operation of the instrument.<sup>17</sup> A major drawback to this method is the high cost of the instrument itself.

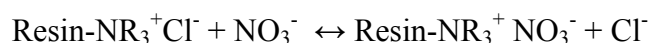
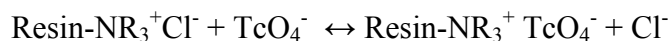
Adsorption stripping voltammetry can be used to measure  $\text{TcO}_4^-$  and  $\text{Tc(IV)}$  with a detection limit of  $5 \times 10^{-11}$  g Tc / mL.<sup>19</sup> This process relies on optimum amounts of

thiocyanate, and the sensitivity was reduced considerably in the presence of larger quantities of anions like chloride and sulfate. This makes it unsuitable for analysis of large quantities of environmental samples.

Liquid scintillation is a radiometric method that can be used as a very accurate measurement of  $^{99}\text{Tc}$ . However, in order to avoid very long count times, the sample must be significantly preconcentrated by some other method. The addition of water and some organic solvents such as chloroform and acetonitrile result in quenching. LSC has been reported using solvent extraction to preconcentrate the  $^{99}\text{Tc}$  activity, with cyclohexanone as the extractant.<sup>20</sup> This method uses 1 M  $\text{H}_2\text{SO}_4$  with 100% cyclohexanone and shows > 98% separation from  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , U, Np, Pu, Am, Ru, I, and rare earth elements. This method has the drawback that the samples must be significantly acidified and large amounts of mixed wastes are generated. The selectivity in the presence of other anions such as chloride, nitrate, etc. was not reported.

Ion-exchange chromatography is a separation method that can be applied to anions or cations. It has been used for the separation of  $\text{TcO}_4^-$  in lab scale separations or as part of methods like sequential injection analysis, discussed above. Resins, often polystyrene or ethylvinylbenzene, are coated with or co-polymerized with ion-exchange groups.<sup>21</sup> For anions, quaternary ammonium groups provide the positive charge required; and for cations, sulfonate, carboxyl, or phosphonate groups provide the negative charge required. A mobile phase containing multiple ions to be separated is introduced to the column; ion-exchange processes occur between the mobile phase and the ion-exchange functional groups bonded to the support material. The ion-exchange resins carry functional groups with a fixed charge and counter ions that are located in the vicinity of

the functional groups to achieve electrical neutrality.<sup>21</sup> A solute ion replaces the counter ion and is temporarily retained by the fixed charge. Separation of multiple ions is determined by the different affinities toward the stationary phase. If a solution of  $\text{TcO}_4^-$  and  $\text{NO}_3^-$  are introduced to a quaternary ammonium resin, two competing equilibria result.<sup>21</sup>



Small and/or highly charged anions have large hydration energies which increases their effective size/charge ratio. This increase in size/charge makes it more difficult for these anions to approach the positively charged ammonium groups as the number of alkyl groups in the chain increases. The larger the alkyl chain, the more selective the anion-exchanger will be for low hydration energy anions like  $\text{TcO}_4^-$  and  $\text{I}^-$ .

Several key problems exist with using anion-exchangers, such as Aliquat-336 and AG-4x4. The anion-exchanger does not preconcentrate the anions present. The sample must be sufficiently preconcentrated before separation. Using large elution volumes or large sample volumes will cause loss of separation as bleeding of bands of anions occurs. Ion-exchange columns also do not have a sensing method; conductivity and UV-Vis detection are the two most common methods of determining when, how much, and which anion has eluted.<sup>21</sup> UV-Vis cannot be used to detect  $\text{TcO}_4^-$  and conductivity measurements when other anions are present in significantly higher concentration makes analysis difficult. Anion-exchange can be used to separate  $\text{TcO}_4^-$  from other anions but

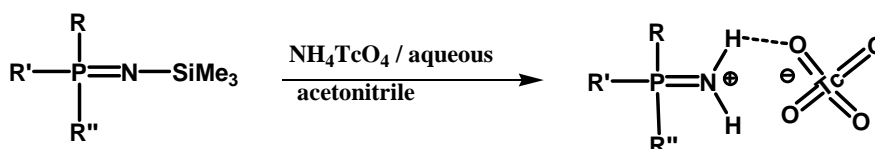
does not provide a solution to the preconcentration and analysis problems seen in other methods to quantify  $\text{TcO}_4^-$ .

## 1.6 Phosphinimines

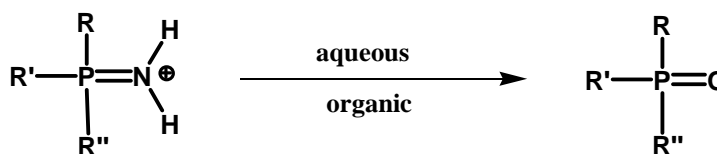
Phosphinimines of the type  $\text{R}_3\text{P}=\text{NSiMe}_3$  (sometimes referred to as azaphosphanes) have been shown to form kinetically inert compounds with early transition metals.<sup>22, 23</sup> Metal halides react with  $\text{R}_3\text{P}=\text{NSiMe}_3$  to eliminate  $\text{Me}_3\text{SiX}$  (where  $\text{X}$  = halide), while metal oxides react through migration of  $\text{Me}_3\text{Si}$  onto the oxygen of the metal center.<sup>23</sup>  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  has been shown to form  $\text{Ph}_3\text{P}=\text{N-ReO}_3$  or  $[\text{Ph}_3\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  depending on the reaction conditions.<sup>23</sup> The corresponding  $\text{Ph}_3\text{P}=\text{N-TcO}_3$  and  $[\text{Ph}_3\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  have also been produced.<sup>22</sup> The neutral  $\text{Ph}_3\text{P}=\text{N-MO}_3$  ( $\text{M} = \text{Re}, \text{Tc}$ ) can be formed on reaction of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  and  $\text{NH}_4\text{MO}_4$  in the absence of water.<sup>22, 23</sup> This neutral compound is of interest for nuclear medicine applications, since  $^{99\text{m}}\text{Tc}$  and  $^{188}\text{Re}$  are used for imaging the body and cancer therapy, respectively. The ion pair  $[\text{Ph}_3\text{P}=\text{NH}_2^+][\text{MO}_4^-]$  can be generated by reaction of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  dissolved in an organic solvent mixed with an aqueous solution of  $\text{NH}_4\text{MO}_4$  or  $\text{NaMO}_4$  (Scheme 1).<sup>22, 23</sup> Formation of the ion pair may allow for selective separation of  $\text{TcO}_4^-$  in the presence of other anions,<sup>22</sup> and preliminary studies on the selectivity of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  for  $\text{TcO}_4^-$  have been reported.<sup>24</sup> The phosphinimine undergoes a hydrolysis reaction in the presence of water to form the phosphiniminium cation, which forms an ion pair in the presence of an anion (Scheme 1). The phosphiniminium cation is not stable on its own, and if not stabilized by an anion will undergo further hydrolysis to form the phosphine oxide (Scheme 2). The  $[\text{Ph}_3\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  ion pair appears to have considerable stability since Eble et. al.<sup>22</sup>

did not observe degradation of the ion pair to free pertechnetate in aqueous solution. The ability to extract  $\text{TcO}_4^-$  in the presence of other anions could make phosphinimines useful for monitoring or cleanup of environmental contamination and/or nuclear waste separations.

**Scheme 1. Hydrolysis of phosphinimine and formation of ion pair**



**Scheme 2. Hydrolysis of phosphiniminium cation to phosphine oxide**



## 1.7 Objective

The overall goal of this project is to develop a sensor using phosphinimines that can preconcentrate and measure  $^{99}\text{Tc}$  environmental contamination in a fast and efficient manner. Cleanup of nuclear waste for reprocessing and/or cleanup of tank waste may also be possible using phosphinimines. The purpose of this portion of the project is to synthesize several phosphinimines and characterize their stability and selectivity with  $^{99}\text{TcO}_4^-$ . The phosphinimine analogs evaluated include  $\text{Ph}_3\text{P}=\text{NSiMe}_3$ , (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$ , (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$ , and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$ . Preliminary studies with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  showed the



phosphiniminium cation to be selective for  $^{99m}\text{TcO}_4^-$  over other anions.<sup>24</sup>

(9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$ , (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$ , and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  are previously unreported phosphinimines.

(9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  and (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  include possible reporter groups and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  contains a linking moiety for attaching reporter groups or attaching the phosphinimine to a polymer support. The phosphiniminium cations of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  and (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  showed selectivity for  $\text{TcO}_4^-$  over other anions and form stable complexes. The use of internal and external reporter groups to generate a signal was investigated with these two phosphinimines. The phosphiniminium cations of (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  show selectivity but the phosphiniminium perrhenate complexes show instability in solution.

## CHAPTER 2: SYNTHESIS OF COMPOUNDS

### 2.1 Introduction

The goal of this project is to use phosphinimines,  $R_3P=N-SiMe_3$ , as extractants to preconcentrate  $TcO_4^-$  (the major form of technetium in the environment)<sup>5</sup> in the presence of other anions for analysis, separation, or cleanup of environmental samples and/or nuclear waste samples. Phosphinimines hydrolyze under acidic and neutral conditions to form the phosphiniminium ion,  $R_3P=NH_2^+$ . This cation then forms an ion pair with anions to stabilize the charge (Scheme 1). To produce a sensor using phosphinimine extractants, the extractant must bind  $TcO_4^-$  selectively and a reporter must generate a measurable signal. The phosphinimines synthesized include  $Ph_3P=NSiMe_3$ , (9-anthracenyl) $Ph_2P=NSiMe_3$ , (1-naphthyl) $Ph_2P=NSiMe_3$ , and (p-COOMe) $C_6H_4Ph_2P=NSiMe_3$ . The synthesis of the new phosphinimines of the type  $R_2R'P=NSiMe_3$ , where  $R = Ph$ ,  $R' = 9\text{-anthracenyl}$ ,  $1\text{-naphthyl}$ , (p-COOMe) $C_6H_4$  along with their characterization are described.

The crystal structures of  $[Ph_3P=NH_2^+][ReO_4^-]$ <sup>23</sup> and  $[Ph_3P=NH_2^+][^{99}TcO_4^-]$ <sup>22</sup> have been reported and are isostructural. Preliminary studies for extraction of the  $[Ph_3P=NH_2^+][TcO_4^-]$  ion pair have been reported and show the phosphinimine to be selective for  $^{99m}TcO_4^-$  over other anions.<sup>24</sup> While the phosphiniminium cation of  $Ph_3P=NSiMe_3$  (**1**) shows selectivity for  $TcO_4^-$ , this phosphinimine does not contain a reporter group; an external reporter would be necessary.

(9-anthracenyl) $Ph_2P=NSiMe_3$  (**2**) was synthesized to incorporate the anthracene moiety for use as a fluorescent or scintillation reporter. Anthracene is a fluorescent molecule that is also a known scintillator.<sup>25</sup>

(1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) was synthesized to incorporate the naphthyl moiety. Naphthyl also fluoresces and is a known alpha scintillator.<sup>25</sup> This molecule was also synthesized for comparison with Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) and (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**).

(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) was synthesized as a precursor molecule. The COOMe is present as a protecting group for COOH. The protecting group can be removed chemically and then reacted further to attach another group to this site. Possible attachment options include a polymer support or a reporting group. Reporting groups could include fluorescent molecules like fluorescein or groups that change color, oxidation state, etc.

The attempted synthesis of (anthracen-9-ylmethyl)diphenylphosphine (**10**) was performed to produce a phosphinimine that would allow further investigation of the fluorescent and scintillation properties of the phosphinyl anthracene moiety.

The selectivity and extraction behavior of the phosphinimines for TcO<sub>4</sub><sup>-</sup> is reported in Chapter 3: Radiochemistry. The fluorescence and scintillation properties of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) as a possible method of signal generation in the presence of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> is reported in Chapter 4: Fluorescence / Scintillation Sensor Design. The extraction of TcO<sub>4</sub><sup>-</sup> using Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) or (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) in the presence of external scintillators as a method of signal generation is reported in Chapter 4: Fluorescence / Scintillation Sensor Design.

## 2.2 Experimental

**General Considerations.** *Caution!*  $^{99}\text{Tc}$  emits a 0.292 MeV  $\beta^-$  with a half-life of  $2.15 \times 10^5$  years. Although common laboratory glassware provides adequate shielding for  $^{99}\text{Tc}$ , standard radiation safety procedures must be used at all times.

**Materials.**  $^{99}\text{Tc}$  was obtained from Oak Ridge National Laboratory as ammonium pertechnetate. Ammonium perrhenate was purchased from Strem. Azidotrimethylsilane was purchased from either Aldrich or Acros. (9-anthracenyl)diphenylphosphane<sup>26</sup> ( $\text{PPh}_2\text{anthracenyl}$ ), naphthalen-1-yl-diphenylphosphane<sup>27</sup> ( $\text{PPh}_2\text{naphthyl}$ ), and methyl 4-(diphenylphosphino)benzoate<sup>28</sup> ( $\text{PPh}_2\text{C}_6\text{H}_4(\text{p-COOMe})$ ) were prepared according to literature procedures. Silica gel was obtained from J. T. Baker, heated to 110 °C overnight in an oven and used without further purification. Only doubly distilled water was used.

Unless noted, all common laboratory chemicals were of reagent grade or better. Solvents used for nonaqueous syntheses were purchased as anhydrous Sure Seal solvents from Aldrich. Solvents included tetrahydrofuran (THF), toluene and dimethylsulfoxide (DMSO).  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{99}\text{Tc}$ - NMR spectra were recorded on a Bruker 250 or 500 MHz instrument at 25°C in deuterated solvents purchased from Cambridge Isotope Laboratories.  $^1\text{H}$  chemical shifts are reported in ppm relative to the  $^1\text{H}$  impurity in that solvent and  $^{31}\text{P}$  chemical shifts are reported in ppm relative to an external 85%  $\text{H}_3\text{PO}_4$  standard.  $^{99}\text{Tc}$  chemical shifts were reported relative to  $\text{NH}_4^{99}\text{TcO}_4$  set to zero in water;  $\text{NH}_4^{99}\text{TcO}_4$  in acetonitrile was observed at 13.61 ppm. ESI and APCI mass spectra were recorded on a Finnigan TSQ7000 in acetonitrile. Elemental analysis of  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) was performed by Quantitative Technologies

Inc. (QTI, Whitehouse, NJ). Elemental analysis of  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  (**4**) was performed by Atlantic Microlab, Inc. (Norcross, GA). Thin layer chromatography (TLC) on  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  (**4**) was performed on a BioScan System 200 Imaging Scanner. The reactions to synthesize  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**),  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**),  $(1\text{-naphthyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**),  $(p\text{-COOMe})\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) and  $((9\text{-anthracenyl})\text{-CH}_2)\text{Ph}_2\text{P}$  (**10**) were carried out on a Schlenk-line under  $\text{N}_2$  using general airfree techniques.

**$\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1).**  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  was prepared according to a modification of the literature procedure.<sup>23, 29</sup> Triphenylphosphine (Acros) was heated to 125 °C under  $\text{N}_2$  with three to six equivalents  $\text{N}_3\text{SiMe}_3$  (Acros or Aldrich) in a dry and  $\text{N}_2$  filled round-bottom flask for 5 hours using standard airfree Schlenk-line techniques. The excess azide was removed by vacuum distillation and the remaining solid was crystallized from acetonitrile at -20°C to yield pure  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  which was then stored in a desiccator.

**$(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (2).** Azidotrimethylsilane (11.1 mL, 80.8 mmol) was added to  $\text{PPh}_2\text{anthracenyl}$  (9.8 g, 27.0 mmol) dissolved in 200 mL of toluene in a dry and  $\text{N}_2$  filled round-bottom flask. The solution was refluxed under  $\text{N}_2$  at 110°C for 8 days yielding (**2**). An additional 5 mL of azidotrimethylsilane was added each day. The excess azide was removed by vacuum distillation to yield pure (**2**) which was then stored in a desiccator. Yield: 10.2 g (83.9%) isolated.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C):  $\delta$  ppm 6.84-8.46 (m, 20H, Ar), 0.26 (s, 9H,  $\text{SiMe}_3$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 25°C):  $\delta$  ppm -6.86. MS APCI ( $m/z$ ) 450.23, calc'd 449.17  $\text{C}_{29}\text{H}_{28}\text{NPSi}$ .

**$[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (3). Method 1.**  $\text{NH}_4\text{ReO}_4$  (0.240 g, 0.896 mmol) dissolved in the minimum volume water (4 mL) was added dropwise to a solution

of **(2)** (0.400 g, 0.890 mmol) dissolved in the minimum volume of acetonitrile (35 mL), under N<sub>2</sub>, while stirring for 5-10 minutes. The reaction mixture was stirred for 2-4 hours. The solvent was removed and the solid was washed with toluene to remove unreacted **(2)** and phosphine oxide. X-ray quality crystals were obtained from acetonitrile/water (89/11 % ratio) at -20°C and then melting the ice leaving the crystals. Crystals for all other analyses were obtained from the slow evaporation of acetonitrile. Yield 0.45 g (80%) isolated. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 25°C): δ ppm 7.28-9.16 (m, 20H, Ar), 2.20 (s, 2H, NH<sub>2</sub>). <sup>31</sup>P NMR (CD<sub>3</sub>CN, 25°C): δ ppm 34.55. Anal. for C<sub>26</sub>H<sub>21</sub>NO<sub>4</sub>Re Found (Calcd): C, 50.05 (49.68)%; H, 3.05 (3.37)%; N, 2.41 (2.23)%. MS +ESI (*m/z*) 378.12, calc'd 378.14 (C<sub>26</sub>H<sub>21</sub>NP<sup>+</sup>); -ESI (*m/z*) 248.89, calc'd 248.93 (<sup>185</sup>ReO<sub>4</sub><sup>-</sup>), 250.88, calc'd 250.94 (<sup>187</sup>ReO<sub>4</sub><sup>-</sup>).

**Method 2 – Optimization of yield for (3).** NH<sub>4</sub>ReO<sub>4</sub> (0.1230 g, 0.4590 mmol) dissolved in 5 mL of 0.15 M HCl was added dropwise to a solution of **(2)** (0.2000 g, 0.4453 mmol) dissolved in 30 mL of acetonitrile in a round-bottom flask, under N<sub>2</sub>, while stirring for 5-10 minutes. The reaction mixture was stirred for 1 hour. The solvent was removed by vacuum. The product was not isolated since this was an optimization of the previous procedure. The yield was quantitative by <sup>31</sup>P NMR. <sup>31</sup>P NMR (CD<sub>3</sub>CN, 25°C): δ ppm 33.55. MS +ESI (*m/z*) 378.02, calc'd 378.14 (C<sub>26</sub>H<sub>21</sub>NP<sup>+</sup>); -ESI (*m/z*) 248.77, calc'd 248.93 (<sup>185</sup>ReO<sub>4</sub><sup>-</sup>), 250.77, calc'd 250.94 (<sup>187</sup>ReO<sub>4</sub><sup>-</sup>).

**[(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (4).** NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> (0.030 g, 0.166 mmol) dissolved in 0.83 mL of water was added dropwise to a solution of **(2)** (0.0740 g, 0.165 mmol) dissolved in 10-15 mL of acetonitrile, while stirring under air. The reaction was stirred for approximately 1 hour. X-ray quality crystals were obtained from slow

evaporation of acetonitrile. The yield was determined using aluminum backed silica gel developed in saline and counted on the BioScan 200 Imaging instrument. The product remained at the origin ( $R_f = 0$ ) while the  $^{99}\text{TcO}_4^-$  traveled with the solvent front ( $R_f = 1$ ). Yield: 48.2 (%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm 7.36-9.14 (m, 20H, Ar), 2.13 (s, 2H,  $\text{NH}_2$ ).  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm 34.68.  $^{99}\text{Tc}$  NMR ( $\text{CD}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm 14.66. Anal. for  $\text{C}_{26}\text{H}_{21}\text{NO}_4\text{Tc}$  Found (Calcd): C, 57.55 (57.69)%; H, 4.07 (3.91)%; N, 2.78 (2.59)%.

**[(9-anthracenyl) $\text{Ph}_2\text{P}=\text{NH}_2^+$ ][benzoate] (5).** Sodium benzoate (0.06 g, 0.49 mmol) dissolved in 5 mL of water ( $\text{pH} = 6$ ) was added dropwise to a solution of (2) (0.20 g, 0.45 mmol) dissolved in 30 mL of acetonitrile in a round-bottom flask, under  $\text{N}_2$  while stirring. The reaction was stirred for 3.5 hours. Solvent was removed, the solid was washed with toluene to remove any phosphine oxide, and the final product was taken up in acetonitrile. X-ray quality crystals were grown from  $\text{CH}_2\text{Cl}_2$  but were found to be anthraquinone.  $^{31}\text{P}$  NMR of reaction ( $\text{CH}_3\text{CN}$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm 28.39. MS +ESI ( $m/z$ ) 377.94, calc'd 378.14 ( $\text{C}_{26}\text{H}_{21}\text{NP}^+$ ).  $^{31}\text{P}$  NMR of mother liquor ( $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm 31.47, 23.59, many signals between 16.31 - 41.98.

**(1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (6).** Azidotrimethylsilane (8 mL, 18.0 mmol) was added to  $\text{PPh}_2\text{naphthyl}$  (5.63 g, 58.2 mmol) dissolved in 60 mL of toluene in a dry and  $\text{N}_2$  filled round-bottom flask. The solution was refluxed under  $\text{N}_2$  at  $110^\circ\text{C}$  for 2 days yielding (6). An additional 2 mL of azidotrimethylsilane was added on the second day. The excess azide was removed by vacuum distillation to yield pure (6) which was then stored in a dessicator. Yield: 4.50 g (62.4%) isolated.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ):  $\delta$  ppm

7.34-8.45 (m, 17H, Ar), -0.092 (s, 9H, SiMe<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ ppm 0.025. MS APCI (*m/z*) 400.01, calc'd 399.16 C<sub>25</sub>H<sub>21</sub>NPSi.

**[(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (7).** NH<sub>4</sub>ReO<sub>4</sub> (0.3961 g, 1.48 mmol) dissolved in 9 mL of water was added dropwise to a solution of (6) (0.59 g, 1.48 mmol) dissolved in 15 mL of dichloromethane in a round-bottom flask, under N<sub>2</sub>, while stirring. The reaction mixture was stirred for 30 minutes. The solvent was removed and the solid was washed with toluene to remove unreacted (6) and phosphine oxide. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ ppm 7.18-7.84 (m, 17H, Ar), 2.34 (s, 2H, NH<sub>2</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C): δ ppm 37.47. MS +ESI (*m/z*) 327.95, calc'd 328.12 (C<sub>22</sub>H<sub>19</sub>NP<sup>+</sup>); -ESI (*m/z*) 248.77, calc'd 248.93 (<sup>185</sup>ReO<sub>4</sub><sup>-</sup>), 250.75, calc'd 250.94 (<sup>187</sup>ReO<sub>4</sub><sup>-</sup>).

**(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (8).** Azidotrimethylsilane (2 mL, 14.6 mmol) was added to PPh<sub>2</sub>C<sub>6</sub>H<sub>5</sub>(p-COOMe) (0.23 g, 0.718 mmol) in a dry and N<sub>2</sub> filled round-bottom flask. The solution was refluxed under N<sub>2</sub> at 110°C overnight yielding (8). The excess azide was removed by vacuum distillation to yield pure (8) which was then stored in a dessicator. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 25°C): δ ppm 7.53-8.12 (m, 26H, Ar), -0.064 (s, 9H, SiMe<sub>3</sub>), 3.95 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>3</sub>CN, 25°C): δ ppm 0.22. MS APCI (*m/z*) 408.04, calc'd 407.15 C<sub>23</sub>H<sub>26</sub>NO<sub>2</sub>PSi.

**[(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (9).** NH<sub>4</sub>ReO<sub>4</sub> (0.0940 g, 0.3504 mmol) dissolved in 4 mL of water was added dropwise to a solution of (8) (0.1510 g, 0.3705 mmol) dissolved in 4 mL of dichloromethane in a round-bottom flask, under N<sub>2</sub>, while stirring. The reaction was stirred vigorously for 30 minutes. The reaction was centrifuged for 10 minutes. The dichloromethane was removed by vacuum distillation



yielding (**9**). MS +ESI ( $m/z$ ) 335.93, calc'd 336.11 ( $C_{20}H_{19}NO_2P^+$ ); -ESI ( $m/z$ ) 248.76, calc'd 248.93 ( $^{185}ReO_4^-$ ), 250.74, calc'd 250.94 ( $^{187}ReO_4^-$ ).

**Attempted synthesis of ((9-anthracenyl)-CH<sub>2</sub>)Ph<sub>2</sub>P (**10**). Method 1.** Lithium diphenylphosphide (0.5 M in THF, 5 mL, 2.5 mmol) was cooled to -70°C under N<sub>2</sub> in a dry ice/ethanol bath. 9-(chloromethyl)anthracene (0.56 g, 2.47mmol) in 10 mL of anhydrous THF was added dropwise while stirring. The reaction was stirred at -70°C for 1 hour, allowed to warm to room temperature over 1 hour, and finally heated to 80°C overnight. Heat was then removed and as the reaction cooled a precipitate formed. Reaction at 30 minutes:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm -9.41, -15.49, -39.99. Reaction at 1 hour: no change. Reaction at room temperature:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm -9.24, -15.44. Reaction after heating 2 hours:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm -9.43, -15.42, -51.61. Reaction after heating overnight:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm 36.11, -9.41, -15.49. Solution above precipitate:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm 34.58, 33.32, 32.83, 32.50, 32.35, 31.81, 29.96, 28.77, 27.18, -10.94, -16.99. Precipitate:  $^{31}P$  NMR (THF, 25°C):  $\delta$  ppm 31.75, -11.88, -17.09.

**Method 2.** Lithium diphenylphosphide (0.5 M in THF, 5 mL, 2.5 mmol) was cooled to -70°C under N<sub>2</sub> in a dry ice/ethanol bath. 9-(chloromethyl)anthracene (0.56 g, 2.47 mmol) in 5 mL of anhydrous THF was added dropwise while stirring. The reaction was stirred at -70°C for 30 minutes and then refluxed for 21 hours. The color of the reaction was blood red for 9 hours after beginning of reflux. At 9 hours the solution became brown red with a brown flocculent precipitate and after 21 hours the solution was a yellow brown with a brown flocculent precipitate.  $^{31}P$  NMR (CH<sub>3</sub>CN, 25°C):  $\delta$  ppm

35.68, -9.37, -15.34, -51.43 (reaction mixture). MS +ESI ( $m/z$ ) no peaks of possible product, oxide, or starting materials.

**Method 3.** n-BuLi (1.4 mL of 1.6 M in hexanes, 2.24 mmol) was cooled to  $-70^{\circ}\text{C}$  under  $\text{N}_2$  in a dry ice/ethanol bath and diluted with 5 mL of anhydrous THF. 9-(chloromethyl)anthracene (0.5005 g, 2.21 mmol) in 10 mL of anhydrous THF was added dropwise while stirring. The reaction was allowed to stir for 30 minutes. Chlorodiphenylphosphide (0.4 mL, 2.23 mmol) in 6 mL of anhydrous THF was added dropwise while stirring. The reaction was allowed to stir for 1 hour and then the  $^{31}\text{P}$  NMR spectrum was acquired.  $^{31}\text{P}$  NMR ( $\text{CH}_3\text{CN}$ ,  $25^{\circ}\text{C}$ ):  $\delta$  ppm 112.39, 83.06, 8 peaks between 42.17-13.63, -21.98, -22.82.

**Method 4.** Diphenylphosphine (0.45 mL, 2.59 mmol) was added, under  $\text{N}_2$ , to 10 mL of stirring anhydrous DMSO. Potassium hydroxide (0.163 g, 2.9 mmol) in 1.43 mL of water was added dropwise while stirring. The color changed from clear colorless to a clear orange. After 15 minutes of stirring, 9-(chloromethyl)anthracene (0.5607 g, 2.47 mmol) in 10 mL of DMSO was added dropwise. The color changed to bright yellow. The reaction was heated to  $135^{\circ}\text{C}$  over 1 hr and heated at  $135^{\circ}\text{C}$  for an additional hour. The oil bath was removed and 50 mL of distilled water was added to the reaction. A precipitate immediately formed. This was stirred in an ice bath for 1 hour. An additional 20 mL of distilled water was added and the reaction was stirred for 1 hour. The solution was filtered and a yellow solid collected. After heating:  $^{31}\text{P}$  NMR (DMSO,  $25^{\circ}\text{C}$ ):  $\delta$  ppm 28.78, 24.86, 20.72, -8.29, -39.68. Final solid:  $^{31}\text{P}$  NMR (DMSO,  $25^{\circ}\text{C}$ ):  $\delta$  ppm 28.03 24.87. MS +ESI ( $m/z$ ) 415.01, calc'd 463.19  $\text{C}_{30}\text{H}_{30}\text{NPSi}$ , calc'd 415.12  $\text{C}_{27}\text{H}_{21}\text{NaOP}$ .

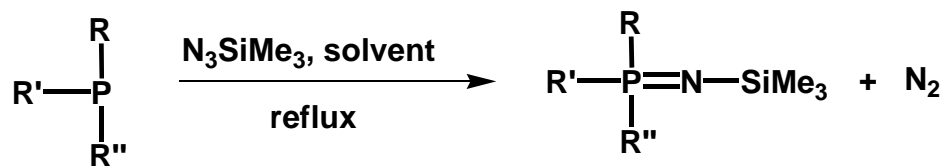
**X-ray Structure Determinations and Refinements for (3) and (4).** Intensity data were obtained at  $-100^{\circ}\text{C}$  on a Bruker SMART CCD Area Detector system using the  $\omega$  scan technique with Mo  $K\alpha$  radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multi-scan method. The structure was solved by direct methods with full-matrix least-squares refinement, using the SHELX package.<sup>30, 31</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the refinement using a riding model, with fixed isotropic  $U$ . The final difference map contained no features of chemical significance. Selected bond distances and bond angles of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**) are given in Table 4. Space group, lattice parameters and other relevant information for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**) along with the data are given in Appendix 1.

## 2.3 Results and Discussion

Phosphinimines, R<sub>3</sub>P=N-SiMe<sub>3</sub>, were synthesized as potential extractants for preconcentrating TcO<sub>4</sub><sup>-</sup> in the presence of other anions for analysis, separation, or cleanup. (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) contains the anthracene moiety, which is a known scintillator,<sup>25</sup> while (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) incorporates the naphthyl moiety, which has been reported as an alpha scintillator.<sup>25</sup> (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) contains a protected linker arm to potentially append reporter groups or attach the phosphinimine to a polymer.

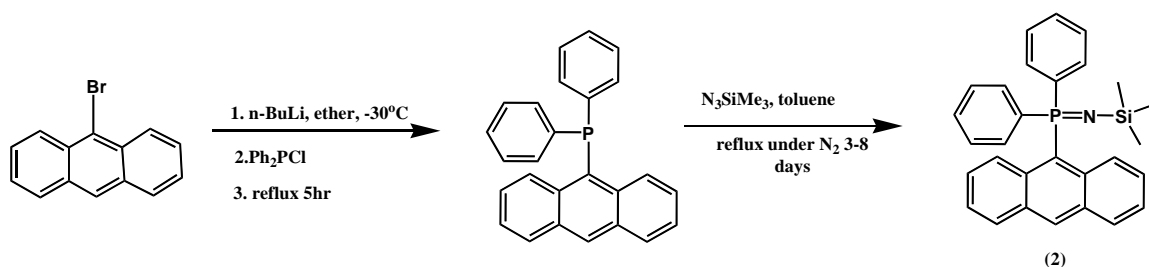
**Synthesis.** To produce (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) or (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**), PPh<sub>2</sub>anthracenyl or PPh<sub>2</sub>naphthyl were refluxed in toluene with N<sub>3</sub>SiMe<sub>3</sub> (Schemes 3, 4, 5 and Table 2). To produce (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**), PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(p-COOMe) and N<sub>3</sub>SiMe<sub>3</sub> were refluxed under N<sub>2</sub> (Scheme 6). The reactions were monitored by <sup>31</sup>P NMR to determine the completion time as the starting material peak decreased and then disappeared and the product peak appeared. (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) is a dark red-brown solid, (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) is a light tan or off white solid, and (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) is a dark brown oil.

**Scheme 3: General synthesis of phosphinimines**

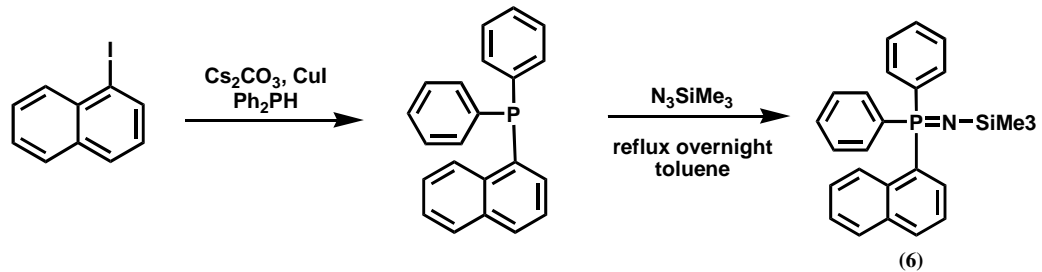


R, R', R'' = alkyl, aryl

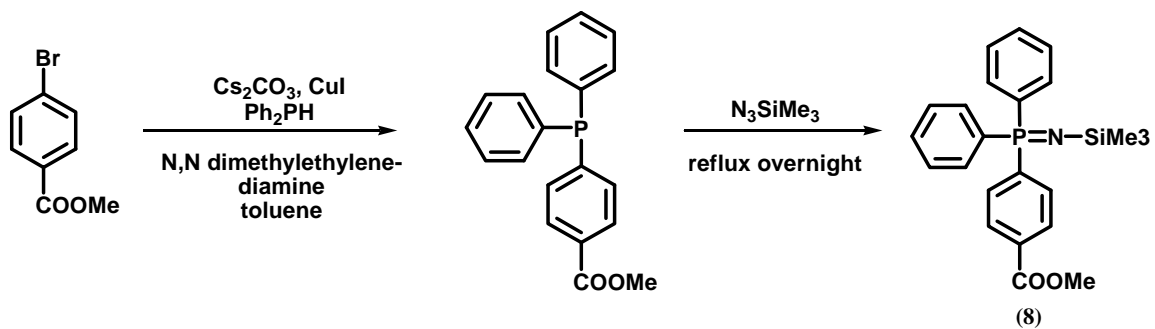
**Scheme 4. Synthesis of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**)**



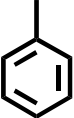
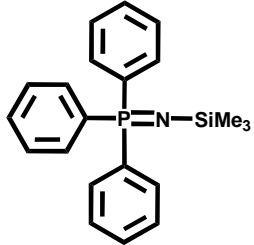
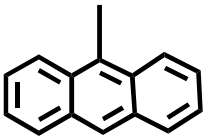
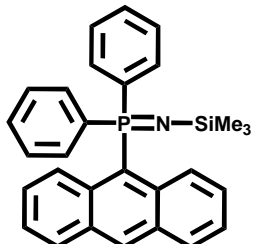
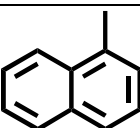
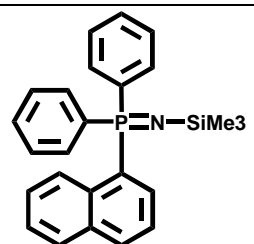
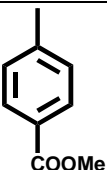
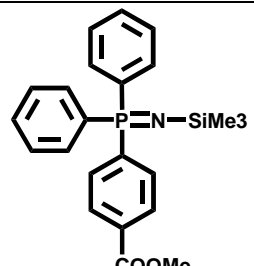
**Scheme 5. Synthesis of (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (6)**



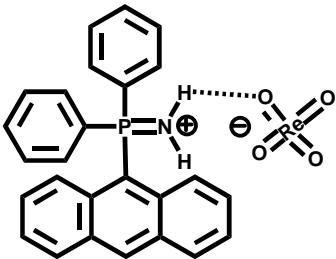
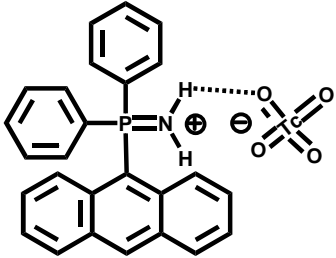
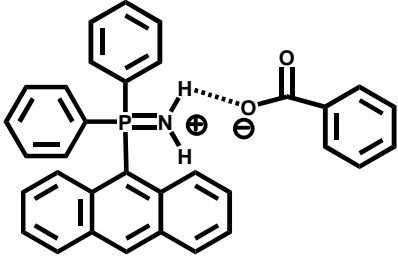
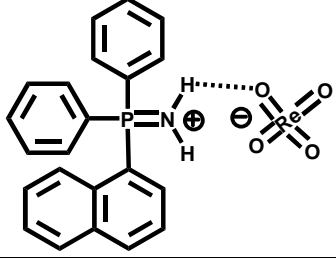
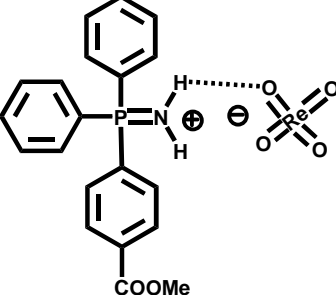
**Scheme 6. Synthesis of (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (8)**



**Table 2: Phosphinimines synthesized**

Compound	R, R'	R''	Solvent	Product	Color / Form
1	Phenyl		None		Colorless / Solid
2	Phenyl		Toluene		Red-brown / Solid
6	Phenyl		Toluene		Tan or off-white / Solid
8	Phenyl		None		Dark brown / Oil

**Table 3: Phosphiniminium permetalates synthesized**

Compound	Phosphinimine	Anion	Product	Color of Crystal
3	2	$\text{ReO}_4^-$		Yellow
4	2	$\text{TcO}_4^-$		Yellow-brown
5	2	Sodium benzoate		N/A
7	6	$\text{ReO}_4^-$		N/A
9	8	$\text{ReO}_4^-$		N/A

Reaction of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) with NH<sub>4</sub>ReO<sub>4</sub> and NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> yielded [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**), respectively (Scheme 1, Table 3). Crystals for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) were grown by slow evaporation from acetonitrile. Unreacted NH<sub>4</sub>TcO<sub>4</sub> co-crystallized as colorless crystals. While (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) is mildly moisture sensitive (*i.e.*, hydrolyzes to the phosphine oxide upon exposure to water over time) and should be stored in a desiccator, [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) do not degrade as solids or in solution.

Reaction of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) with sodium benzoate yielded [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][benzoate] (**5**). Over a week in CH<sub>2</sub>Cl<sub>2</sub>, X-ray quality crystals were grown of anthraquinone. The crystals showed no <sup>31</sup>P NMR signal while the mother liquor showed a variety of products from the rearrangement.

Reaction of (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) with NH<sub>4</sub>ReO<sub>4</sub> yielded [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) (Scheme 1, Table 3). Crystals of [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) were not grown since (**7**) degrades in solution. Solutions of [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) in solvents such as acetonitrile, dichloromethane, or the reaction mixture of dichloromethane/water led to decomposition after 1-3 hours.

Reaction of (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) with NH<sub>4</sub>ReO<sub>4</sub> yielded [(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**9**) (Scheme 1, Table 3). The yield for (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) was not determined since the product is a thick oil that hydrolyzed quickly in air. [(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**9**) is not stable in



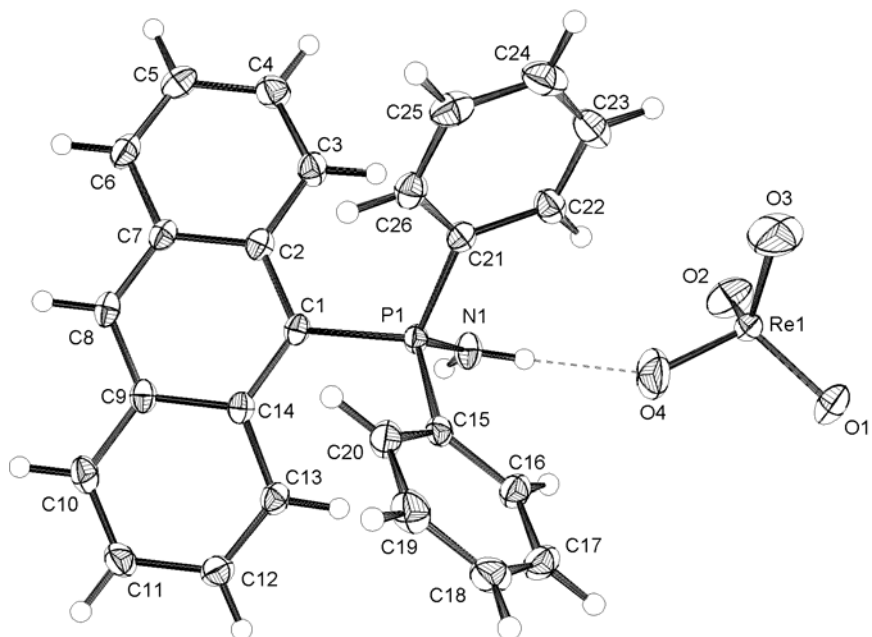
solution, decomposing in minutes, so no crystals were grown or NMR spectrum recorded. The product was identified by mass spectrometry.

**NMR Characterization.** The NMR spectrum for (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) was taken in benzene, while [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**) were run in acetonitrile. From the NMR spectra, it is seen that [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**) have almost the same effect on both the <sup>1</sup>H and <sup>31</sup>P nuclei, however this chemical environment is significantly different from (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**). The <sup>31</sup>P peak shifted from -6.86 ppm for (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) to 34.55 ppm for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and 34.68 ppm for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**). The same effect is observed in the <sup>1</sup>H NMR spectra for the aromatic resonances, which shift from 6.84-8.46 for (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) to 7.38-9.17 for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and 7.36-9.14 for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**). The formation of the ion pair does not significantly change the <sup>99</sup>Tc NMR chemical shift for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) since the technetium coordination sphere has not significantly changed; 14.66 ppm for [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) and 13.61 ppm for NH<sub>4</sub><sup>+</sup><sup>99</sup>TcO<sub>4</sub><sup>-</sup> in acetonitrile. The same trends are observed in the <sup>1</sup>H and <sup>31</sup>P NMR spectra for (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) and [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**).

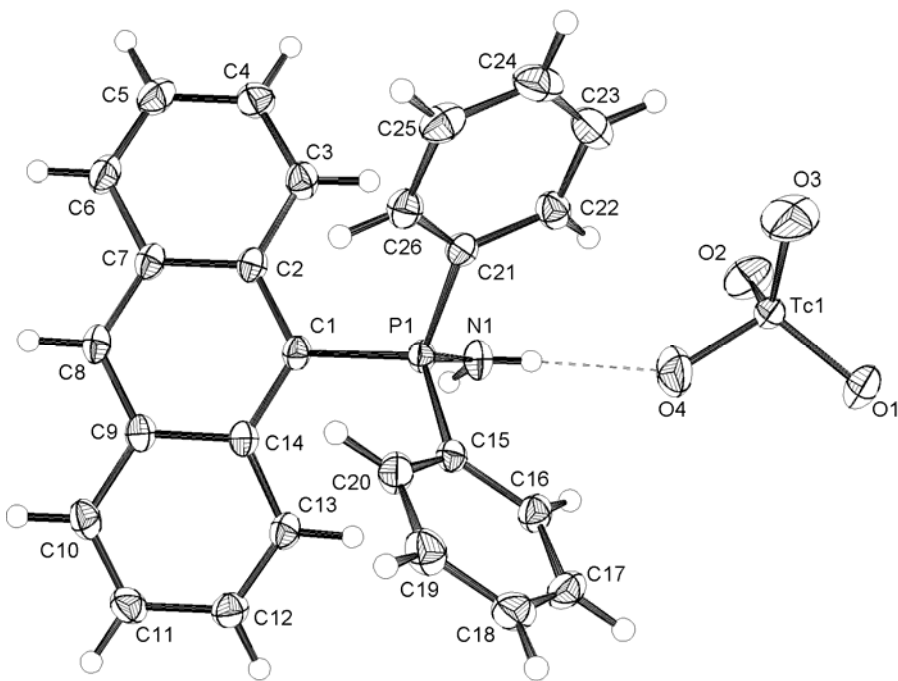
**X-ray Crystallography.** Yellow crystals of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and yellow-brown crystals of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) were obtained

as described and were stable to air and water during the analysis and for months afterward. Details of the X-ray structure experiments are given in Appendix 1 and the bond lengths and angles of interest are listed in Table 4. Figures 1 and 2 show the ORTEP<sup>30, 31</sup> diagrams of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**), respectively. The two structures are isostructural and show a strong hydrogen bond between an iminium proton and an oxygen on MO<sub>4</sub><sup>-</sup> in each unit cell. The extended lattice shows that [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**) form dimers, with each MO<sub>4</sub><sup>-</sup> bound to two phosphiniminium ligands and each phosphiniminium hydrogen bonded to two MO<sub>4</sub><sup>-</sup> moieties. The structure is symmetrical, with each unit cell containing only one half of each dimer. The hydrogen bond distances between the iminium proton and the M-O oxygen for perrhenate (1.95 Å) was slightly shorter than for pertechnetate (2.06 Å). The M-O bond distances observed for both the perrhenate (1.703-1.728(2) Å) and pertechnetate (1.6907-1.7126(16) Å) are typical for these species.<sup>32</sup> The structures for [Ph<sub>3</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>]<sup>22</sup> and [Ph<sub>3</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>]<sup>23</sup> were previously reported and also showed a strong hydrogen bond between the iminium protons and an oxygen on two different MO<sub>4</sub><sup>-</sup> moieties. Both were reported as dimers with two oxygen groups on each MO<sub>4</sub><sup>-</sup> bound to two iminium protons, one each on two different phosphiniminium cations. [Ph<sub>3</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] was shown to have oxygen-nitrogen bond distances of 2.871 and 2.951 Å, M-O distances of 1.690-1.727(7) Å, and the hydrogen bond distances were not reported.<sup>23</sup> [Ph<sub>3</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] was shown to have oxygen-nitrogen bond distances of 2.855 and 2.973 Å, M-O distances of 1.690-1.708(4) Å, and hydrogen bond distances of 1.89(6) and 2.23(6) Å.<sup>22</sup>

**Figure 1. ORTEP representation of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (3), with 50% thermal ellipsoids**



**Figure 2. ORTEP representation of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (4), with 50 % thermal ellipsoids**



**Table 4. Selected Bond Distances (Å) and Bond Angles (deg) of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>ReO<sub>4</sub><sup>-</sup>] (3) and of [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (4)**

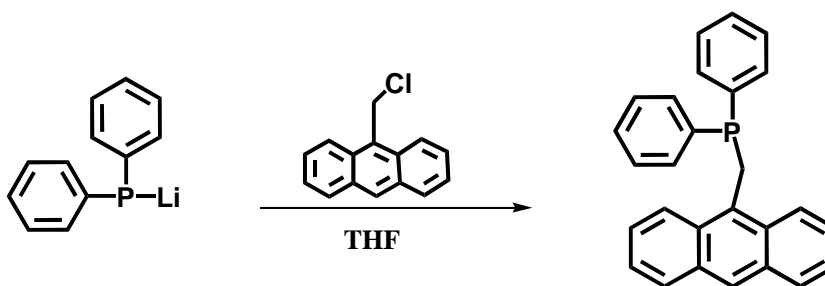
	<b>2</b>	<b>3</b>
	<b>(M = Re)</b>	<b>(M = Tc)</b>
M1-O1	1.724(2)	1.7091(15)
M1-O2	1.716(2)	1.7041(16)
M1-O3	1.703(3)	1.6907(18)
M1-O4	1.728(2)	1.7126(16)
N1-H2N*	0.71(4)	0.80(3)
N1-H1N*	0.85(4)	0.76(3)
O4-H1N*	1.95	2.06
P1-N1	1.616(2)	1.6207(17)
P1-C1	1.788(2)	1.7890(17)
P1-C15	1.808(2)	1.8053(18)
P1-C21	1.803(2)	1.8037(19)
O1-M1-O4	108.05(11)	107.80(8)
O2-M1-O1	109.34(11)	109.15(8)
O2-M1-O4	109.43(13)	109.59(9)
O3-M1-O1	112.04(13)	112.25(9)
O3-M1-O2	109.16(15)	109.29(11)
O3-M1-O4	108.78(16)	108.73(12)
N1-P1-C1	108.35(13)	108.32(9)
N1-P1-C15	113.91(12)	114.16(9)
N1-P1-C21	108.46(13)	108.51(9)
C1-P1-C21	112.09(12)	111.96(8)
H2N-N1-H1N*	114(4)	119(3)

\* Denotes hydrogen atoms located on the nitrogen

**Attempted Synthesis of ((9-anthracenyl)-CH<sub>2</sub>) Ph<sub>2</sub>P (10).** This phosphine was of interest as a comparator to (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) since it would allow further investigation of the fluorescence and scintillation properties of the anthracene moiety. All reactions were followed by <sup>31</sup>P NMR. The <sup>31</sup>P NMR chemical shift for Ph<sub>2</sub>PLi is δ ppm -15.890 and for Ph<sub>2</sub>PCl is 84.24.

Method 1 is shown in Scheme 7. A solution of Ph<sub>2</sub>PLi was cooled during the addition of 9-chloromethylantracene. The major <sup>31</sup>P NMR peak after the addition and stirring was the Ph<sub>2</sub>PLi starting material. Heating overnight did not produce the desired product as the major product, if at all. Starting material, a variety of oxides, and unidentified materials were generated.

**Scheme 7. Attempted Synthesis of ((9-anthracenyl)-CH<sub>2</sub>) Ph<sub>2</sub>P (10) by Method 1 and 2**

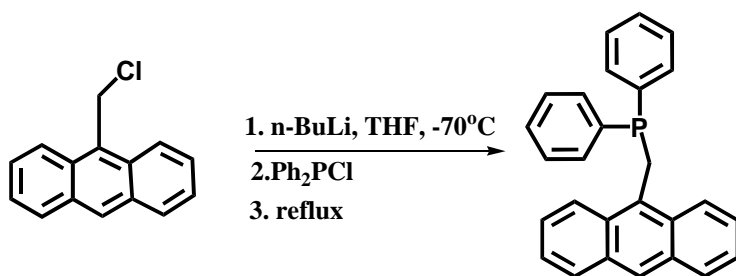


Method 2 was a modification of Method 1, except the reaction was cooled at -70°C for 30 minutes and then heated to reflux for 21 hours. The reaction was heated to a higher temperature in an attempt to induce the reaction to proceed without producing as many side products as Method 1. The major species at the end of reaction was the starting material of Ph<sub>2</sub>PLi as determined by the -15.493 ppm peak in the <sup>31</sup>P NMR. This

method was abandoned after determining by mass spectrometry that none of the peaks in the NMR spectrum belonged to the product.

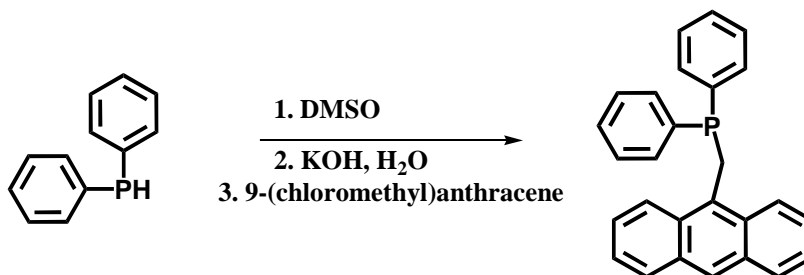
Method 3 was an attempt to lithiate the methyl on the anthracene group instead of using a lithiated phosphine as shown in Scheme 8. This method produced a large number of products as determined by  $^{31}\text{P}$  NMR spectroscopy and was abandoned.

**Scheme 8. Attempted Synthesis of ((9-anthracenyl)-CH<sub>2</sub>) Ph<sub>2</sub>P (10) by Method 3**



Method 4 was a modification of a literature procedure to produce tripodal  $\text{CH}_3\text{CC}(\text{CH}_2\text{PPh}_2)_3$ <sup>33</sup> (Scheme 9). The product solution contained several products. The solid product contained mainly the sodiated oxide as determined by mass spectrometry.

**Scheme 9. Attempted Synthesis of ((9-anthracenyl)-CH<sub>2</sub>) Ph<sub>2</sub>P (10) by Method 4**



## 2.4 Conclusion

Three previously unreported phosphinimines, ((9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub>) (**2**), (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**), and (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**), were synthesized from the respective phosphines and are moisture sensitive. (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) reacts with NH<sub>4</sub>ReO<sub>4</sub> and NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> to produce [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**), respectively.

[(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**) and [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (**4**) are stable to moisture and oxygen both as solids and in solution. The crystal structures of both are reported and they are isostructural. (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) was reacted with sodium benzoate to produce [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][benzoate] (**5**). [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][benzoate] (**5**) was not stable and reacted further to form anthraquinone crystals and a variety of products containing phosphorous.

(1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) and (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) were reacted with NH<sub>4</sub>ReO<sub>4</sub> to produce [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) and [(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**9**), respectively. [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) and [(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**9**) were not stable in solution. The instability of [(1-naphthyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**7**) reduces the usefulness of (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**6**) as an extractant and eliminates the use of the naphthyl group as a reporter moiety. In addition to the instability of

[(p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**9**), (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) also hydrolyzes quickly in air, eliminating it as a useful extractant. Attempted synthesis of ((9-anthracenyl)-CH<sub>2</sub>)Ph<sub>2</sub>P (**10**) by four different methods did not produce ((9-anthracenyl)-CH<sub>2</sub>)Ph<sub>2</sub>P (**10**). While the synthesis of ((9-anthracenyl)-CH<sub>2</sub>)Ph<sub>2</sub>P (**10**) is

probably not impossible, it is not straight forward by common methods to produce derivatized phosphines.



## CHAPTER 3: RADIOCHEMISTRY

### 3.1 Introduction

Phosphinimines hydrolyze to form the phosphiniminium cation,  $R_3P=NH_2^+$ , which can form an ion pair with an anion to stabilize the charge (Scheme 1).  $[Ph_3P=NH_2^+][ReO_4^-]$ <sup>23</sup> and  $[Ph_3P=NH_2^+][TcO_4^-]$ <sup>22</sup> are known and the crystal structures have been reported. Preliminary studies on the selectivity of  $Ph_3P=NSiMe_3$  for  $TcO_4^-$  through the formation of  $[Ph_3P=NH_2^+][TcO_4^-]$  have been reported.<sup>24</sup> This study suggested that the selectivity of the phosphiniminium cation of  $Ph_3P=NSiMe_3$  (**1**) for  $TcO_4^-$  in the presence of other anions was excellent and further investigations were warranted. In studies performed here, the selectivity of phosphiniminium cations of  $Ph_3P=NSiMe_3$  (**1**), (9-anthracenyl) $Ph_2P=NSiMe_3$  (**2**), (1-naphthyl) $Ph_2P=NSiMe_3$  (**6**), and (p-COOMe) $C_6H_4Ph_2P=NSiMe_3$  (**8**) for  $TcO_4^-$  was challenged with a variety of anions including  $Cl^-$ ,  $NO_3^-$ ,  $I^-$ , acetate, and benzoate. In addition to selectivity studies, studies were undertaken to investigate the optimal conditions for the formation of the  $[R_3P=NH_2^+][TcO_4^-]$  ion pair including solvent and solid phase extraction studies, column capacity through concentration and volume changes, and competition with macroscopic quantities of  $^{99}TcO_4^-$ .

### 3.2 Experimental

**General Considerations.** *Caution!  $^{99}Tc$  emits a 0.292 MeV  $\beta^-$  with a half-life of  $2.15 \times 10^5$  years,  $^{99m}Tc$  emits a 140 keV  $\gamma$ -ray with a half-life of 6.0 h, and  $^{186}Re$  emits a 137 keV  $\gamma$ -ray and a 1.07 MeV  $\beta^-$  with a half-life of 90 h. Although common laboratory glassware provides adequate shielding for  $^{99}Tc$ , standard radiation safety procedures*

*must be used at all times.  $^{99m}\text{Tc}$  and  $^{186}\text{Re}$  should be handled only in a controlled environment by qualified personnel trained in radiation safety.*

**Materials.**  $^{99m}\text{Tc}$  was eluted with normal saline as sodium pertechnetate from a  $^{99}\text{Mo}/^{99m}\text{Tc}$  generator (Bristol Myers Squibb or Mallinckrodt Medical, Inc.).  $^{186}\text{Re}$  was produced at the University of Missouri Research Reactor (MURR) from a 96.4% enriched  $^{185}\text{Re}$  target.  $^{99}\text{Tc}$  was obtained from Oak Ridge National Laboratory as ammonium pertechnetate and used as a macroscopic carrier in experiments where noted. Ammonium perhenate was purchased from Strem and used as a macroscopic carrier in experiments where noted. Dichloromethane, chloroform, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, sodium fumarate, lactic acid, benzoic acid, acetic acid, sodium iodide, sodium chloride, sodium fumarate, and sodium hydroxide were all used as purchased. Hydriodic acid was used as purchased, in the absence of stabilizers. Silica gel was obtained from J. T. Baker, heated to 110 °C overnight in an oven and used without further purification. Only doubly distilled water was used. Unless noted, all common laboratory chemicals were of reagent grade or better.

All samples containing both  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  were counted with a HPGe semiconductor detector with Canberra electronics and Maestro multichannel analysis software (EG&G Ortec, Inc.). Energy calibrations were based on a  $^{57}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$  mixed source. Samples containing  $^{99m}\text{TcO}_4^-$  were counted on a NaI(Tl) well detector with Canberra electronics and a SCA with a Counter/Timer setup. Liquid scintillation analysis was used to verify any concentrations for  $^{99}\text{TcO}_4^-$ . Liquid scintillation counting (LSC) was performed on a Tracor Analytic Delta 300 Liquid Scintillation System. Thin layer chromatography (TLC) to verify  $^{99}\text{Tc}$  was present as  $^{99}\text{TcO}_4^-$  was performed on a

BioScan System 200 Imaging Scanner. Paper TLC (purchased from Whatman, 1 Chr chromatography paper) was performed for each sample in saline and in diethyl ether.  $\text{TcO}_2$  is a colloid and stays at the origin ( $R_f = 0$ ) regardless of solvent.  $\text{TcO}_4^-$  moves with the solvent front in saline ( $R_f = 1$ ) and remains at the origin in ether ( $R_f = 0$ ).

**General Solvent Extraction Competition Procedure.** The aqueous phase consisted of the desired anion (0.15 M) containing approximately 1  $\mu\text{Ci}$  of  $^{99\text{m}}\text{TcO}_4^-$  and 5  $\mu\text{Ci}$  of  $^{186}\text{ReO}_4^-$ . The organic phase consisted of 5 mg/mL of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$ . The organic phase (5 mL) and the aqueous phase (1 mL) were mixed by vortexing in a test tube for 2 minutes and then separated by centrifugation for 10 minutes. Aliquots (75-220  $\mu\text{L}$ ) of each phase were taken and counted. The solution acidity (1 mM, 0.1 M, 0.15 M, 0.2 M, 0.5 M, 1 M, 2 M), phosphinimine concentration (0.34 mg/mL, 1 mg/mL, 3 mg/mL, 4 mg/mL, 5 mg/mL, 10 mg/mL), vortex time (30 s, 1 min, 2 min), centrifugation time (5 min, 10 min), and aqueous/organic phase volumes (100  $\mu\text{L}$  / 5 mL, 500  $\mu\text{L}$  / 5 mL, 1 mL / 5 mL, 2.5 mL / 5 mL, 5 mL / 5 mL) were all optimized (data contained in Appendix 2). Solutions were prepared fresh daily. All data points were performed in triplicate.

**General Solid Phase Extraction Competition Procedure.** Silica was pre-dried overnight at 110  $^\circ\text{C}$  in an oven. Phosphinimine ( $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**), or (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**)) (0.5 g) was then sorbed onto 5 g of dried silica gel from a chloroform or dichloromethane slurry. This was allowed to slowly dry over 3 or more days in a desiccator (to prevent hydrolysis). Columns were prepared from plastic disposable columns (Fisher) containing small plastic frits, which were each filled with 0.5

g of the coated silica. One mL of the aqueous phase of the desired anion and containing approximately 1  $\mu\text{Ci}$   $^{99\text{m}}\text{TcO}_4^-$  and 3  $\mu\text{Ci}$   $^{186}\text{ReO}_4^-$  was added to the top of the dry column. This was allowed to elute through the column and the effluent was collected until no more aqueous phase eluted. This was then washed with four 1 mL aliquots of the desired aqueous phase without radioactivity, with each fraction collected separately. All 5 column fractions and the column were then counted. The first fraction did not contain a full 1 mL as much of this went to wetting the column. All data points were performed in triplicate.

**General Solid Extraction 1:1 Competition Procedure.** The general solid phase extraction competition procedure was followed using  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) with the addition of 1 mM  $^{99}\text{TcO}_4^-$  or 10 mM  $\text{ReO}_4^-$  carrier added to the first mL of aqueous phase containing the desired anion with approximately 1  $\mu\text{Ci}$  of  $^{99\text{m}}\text{TcO}_4^-$  and 3  $\mu\text{Ci}$  of  $^{186}\text{ReO}_4^-$ . The permetallate ( $^{99}\text{TcO}_4^-$  or  $^{185/187}\text{ReO}_4^-$ ) was added as the ammonium salt. The concentration of  $\text{NH}_4\text{TcO}_4$  was verified by liquid scintillation analysis. The ionic strength was kept constant by varying the concentration of NaCl. When no other anions were present, 0.15 M NaCl was used. Sodium acetate or sodium iodide, 10 mM, was then added to 0.14 M NaCl to make up the aqueous phase. All experiments were performed in triplicate.

**General Concentration Column Capacity Procedure.** The general solid phase extraction competition procedure using  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) was followed with  $^{99}\text{TcO}_4^-$  carrier added to the first mL of aqueous phase containing 0.15 M NaCl with approximately 1  $\mu\text{Ci}$  of  $^{99\text{m}}\text{TcO}_4^-$  and 3  $\mu\text{Ci}$  of  $^{186}\text{ReO}_4^-$ . Pertechnetate was added as  $\text{NH}_4^{99}\text{TcO}_4$  in 0.11 mM, 0.52 mM, 1 mM, and 5.2 mM concentrations as noted. The

concentration was verified by liquid scintillation analysis. All experiments were performed in triplicate.

**General Volume Column Capacity Procedure.** Columns of phosphinimine coated silica were prepared using  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) as in the general solid phase extraction competition procedure. The aqueous phase of 0.15 M NaCl, 1.3 mM  $\text{NH}_4^{99}\text{TcO}_4$ , and approximately 1  $\mu\text{Ci}$  of  $^{99\text{m}}\text{TcO}_4^-$  was added to the top of the dry column in 1 mL aliquots. Each aliquot was allowed to elute and the eluent and column were counted. This was repeated until the eluent fraction began to show counts above background, which occurred at 6 mL total volume. Then each column was washed with 1 mL of 0.15 M NaCl.

### 3.3 Results and Discussion

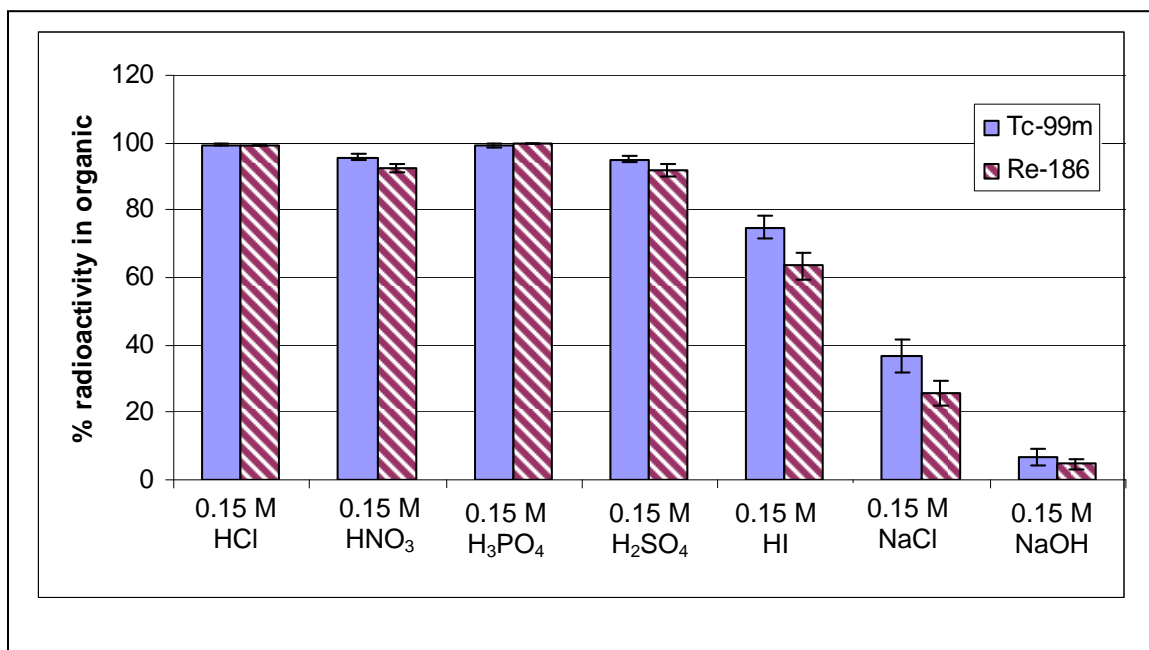
The goal of this project is to use phosphinimines,  $R_3P=N-SiMe_3$ , as extractants to preconcentrate  $TcO_4^-$  in the presence of other anions for analysis or cleanup of environmental samples or cleanup of nuclear waste samples. The selectivity of the phosphiniminium cation of  $Ph_3P=NSiMe_3$  (**1**) for  $TcO_4^-$  and  $ReO_4^-$  was investigated by challenge with a variety of anions in large excess, with anions that were equimolar, under different pH conditions, and under both solvent extraction and solid phase extraction conditions. The selectivity the phosphiniminium cation of (9-anthracenyl) $Ph_2P=NSiMe_3$  (**2**), (1-naphthyl) $Ph_2P=NSiMe_3$  (**6**), and (p-COOMe) $Ph_3P=NSiMe_3$  (**8**) for  $TcO_4^-$  and  $ReO_4^-$  was investigated by challenge with a variety of anions in large excess.  $HReO_4$  and  $HTcO_4$  are both strong acids in aqueous solution with  $pK_a < 0$ .<sup>34</sup> In solution both are dissociated to form  $ReO_4^-$  and  $TcO_4^-$ .

**Solvent Extraction.**  $Ph_3P=NSiMe_3$  (**1**) was dissolved in chloroform and contacted with an aqueous solution containing  $^{99m}TcO_4^-$ ,  $^{186}ReO_4^-$ , and 0.15 M of either HCl,  $HNO_3$ ,  $H_3PO_4$ ,  $H_2SO_4$ , HI, NaCl, or NaOH.  $TcO_4^-$  and  $ReO_4^-$  are not soluble in chloroform so that any radioactivity extracted into the organic phase is the result of ion pair formation. The results are shown in Figure 3 and Table 5. Greater than 95% of the  $^{99m}TcO_4^-$  and > 92% of the  $^{186}ReO_4^-$  radioactivity was extracted into the organic phase under acidic conditions in the presence of  $Cl^-$ ,  $NO_3^-$ ,  $H_3PO_4/H_2PO_4^-$ , and  $HSO_4^-/SO_4^{2-}$ . Under neutral conditions using NaCl, the percent of the ion pair formed was significantly lower due to partial secondary hydrolysis to the phosphine oxide (Scheme 2). Under basic conditions (pH  $\approx$  12.5) < 7% of the radioactivity was extracted for either  $^{99m}TcO_4^-$  or  $^{186}ReO_4^-$  due to secondary hydrolysis to the phosphine oxide. Under acidic conditions

the positively charged  $\text{Ph}_3\text{P}=\text{NH}_2^+$  is stabilized, whereas under neutral and basic conditions the secondary hydrolysis to the phosphine oxide is promoted.  $\text{Ph}_3\text{P}=\text{O}$  is not charged and cannot form the ion pair, thereby reducing the amount of anion that can be extracted.

Iodide was used as a positive control because it does compete with  $^{99\text{m}}\text{TcO}_4^-$  to some extent. Injection of  $\text{Na}^{99\text{m}}\text{TcO}_4^-$  intravenously results in  $^{99\text{m}}\text{TcO}_4^-$  uptake in the thyroid, salivary glands, gastric mucosa, and the choroid plexus of the brain.<sup>35</sup> These are the same organs that take up  $^{131}\text{I}^-$ .  $^{99\text{m}}\text{TcO}_4^-$  can be used to image the thyroid for its structure<sup>36, 37</sup> and to test thyroid function.<sup>37, 38</sup> Iodide and  $\text{TcO}_4^-$  behave similarly in the body due to a similarity in size and charge.<sup>35, 37, 39</sup> However, while they are taken up similarly in the body based on electrostatics, the pertechnetate is not metabolized in the same way and the thyroid does not incorporate it to produce iodine containing hormones.<sup>40</sup> Figure 3 also shows that  $^{99\text{m}}\text{TcO}_4^-$  is retained better than  $^{186}\text{ReO}_4^-$  which will be discussed later. The phosphinimine is not stable in solution and hydrolyzes to the phosphine oxide overnight in chloroform when exposed to air.

**Figure 3. Solvent Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  in the Organic Phase for (1)**



**Table 5. Solvent Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  in the Organic Phase for (1)**

Competing Anion	$^{99m}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.15 M HCl	99.4 ± 0.1	99.30 ± 0.06
0.15 M HNO <sub>3</sub>	95.6 ± 0.9	92 ± 1
0.15 M H <sub>3</sub> PO <sub>4</sub>	99.1 ± 0.5	99.72 ± 0.07
0.15 M H <sub>2</sub> SO <sub>4</sub>	95.0 ± 0.9	92 ± 2
0.15 M HI	75 ± 3	63 ± 4
0.15 M NaCl	37 ± 5	26 ± 4
0.15 M NaOH	7 ± 3	5 ± 2

**Solid Phase Extraction Competition Studies.** Columns were prepared from phosphinimine coated silica. An aqueous solution containing  $^{99m}\text{TcO}_4^-$ ,  $^{186}\text{ReO}_4^-$ , and 0.15 M of either HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HI, NaCl, NaI, NaOH, sodium fumarate,

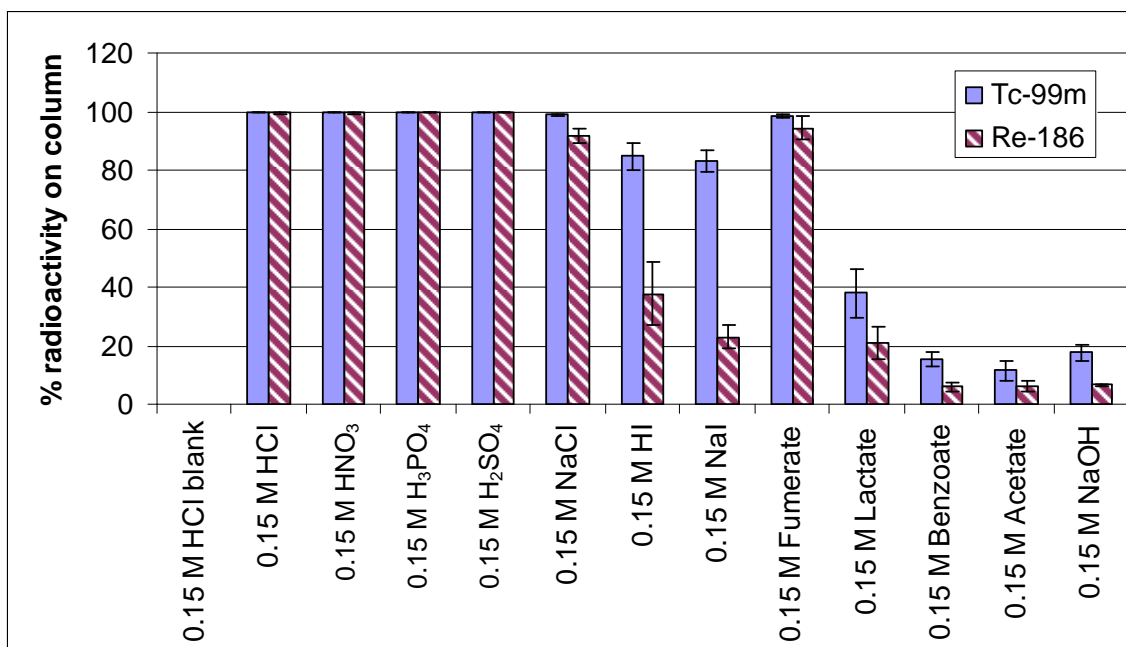


sodium benzoate, sodium lactate, or sodium acetate was added to the column and allowed to elute. The column was then washed with the same solution without  $^{99m}\text{TcO}_4^-$  or  $^{186}\text{ReO}_4^-$ . There was no difference in results for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) if the column was prewashed with the desired anion. A solution of  $^{99m}\text{TcO}_4^-$  in 0.15 M HCl was added to a column of pure silica, and no  $\text{TcO}_4^-$  adhered to the silica indicating that the phosphinimine was responsible for  $\text{TcO}_4^-$  binding. The activity extracted onto the column is present as the ion pair.

The phosphininium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) extracted 99% of the radioactivity onto the column under acidic conditions and in competition with HCl,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and NaCl. Under neutral conditions this was also seen for sodium fumerate with  $^{99m}\text{TcO}_4^-$ . HI, NaI, sodium acetate, sodium lactate, and sodium benzoate competed with both  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$ , and sodium fumerate competed with  $^{186}\text{ReO}_4^-$ . This is seen in Figure 4 from the large reduction in the amount of activity bound to the column. NaOH also prevents binding of  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$  due to secondary hydrolysis of the phosphinimine to the phosphine oxide. Figure 4 shows that  $^{99m}\text{TcO}_4^-$  is retained better than  $^{186}\text{ReO}_4^-$ , which will be discussed later. When sorbed onto the silica, the phosphinimine is stable for weeks or longer. Coating onto the silica stabilizes the phosphinimine to some degree, as suggested from the overall improvement in extraction ability over the solvent extraction method. During solvent extraction, dissolved phosphinimine comes into contact with water, which can result in hydrolysis to the phosphininium cation and further hydrolysis to the phosphine oxide. During solid phase extraction, the phosphinimine is not dissolved and is not soluble in water. This

insolubility limits the exposure of the phosphinimine or phosphiminium cation to water and further hydrolysis.

**Figure 4. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1)**



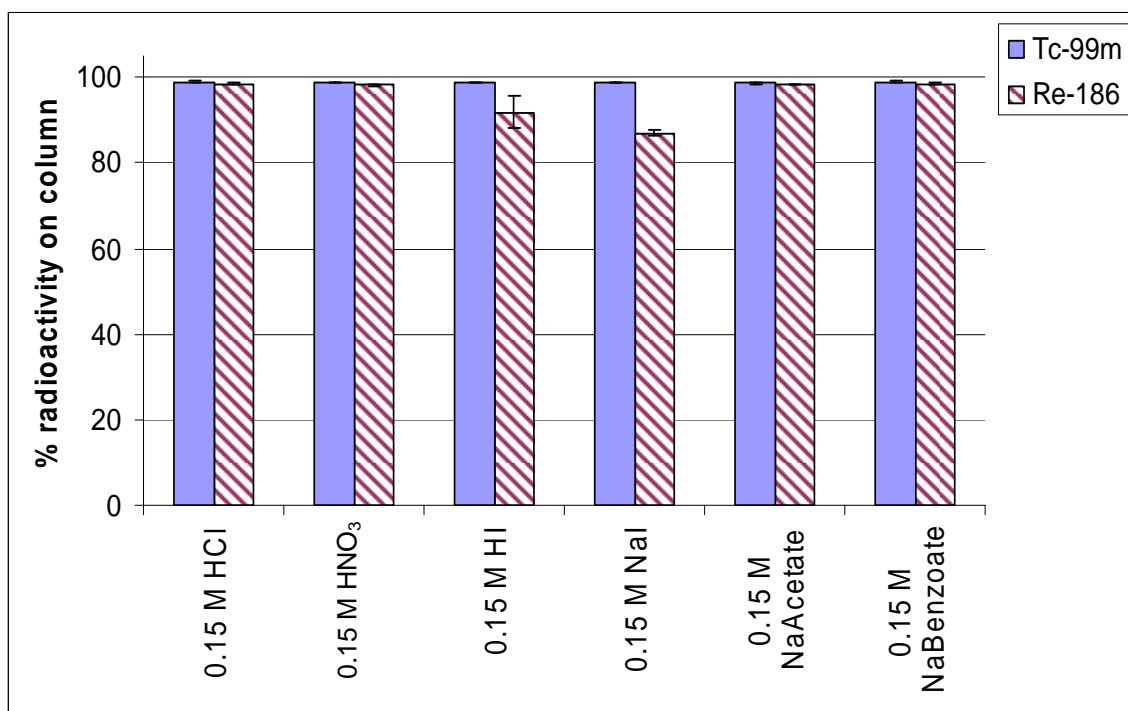
**Table 6. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**)**

Competing Anion	$^{99m}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.15 M HCl blank	0.26	0.26
0.15 M HCl	$99.7 \pm 0.2$	$99.6 \pm 0.3$
0.15 M $\text{HNO}_3$	$99.7 \pm 0.2$	$99.4 \pm 0.1$
0.15 M $\text{H}_3\text{PO}_4$	$99.6 \pm 0.1$	$99.6 \pm 0.04$
0.15 M $\text{H}_2\text{SO}_4$	$99.6 \pm 0.1$	$99.6 \pm 0.1$
0.15 M NaCl	$99.0 \pm 0.3$	$92 \pm 2$
0.15 M HI	$85 \pm 5$	$38 \pm 11$
0.15 M NaI	$83 \pm 4$	$23 \pm 4$
0.15 M Fumerate	$98.4 \pm 0.4$	$94 \pm 4$
0.15 M Lactate	$38 \pm 8$	$21 \pm 5$
0.15 M Benzoate	$15 \pm 2$	$6 \pm 1$
0.15 M Acetate	$11 \pm 3$	$6 \pm 2$
0.15 M NaOH	$18 \pm 3$	$6.5 \pm 0.4$
1mM $\text{ReO}_4^-$	$0.5 \pm 0.1$	$0.30 \pm 0.07$

Using the phosphiniminium cation of (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) or (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**), under acidic and neutral conditions and in competition with HCl,  $\text{HNO}_3$ , HI, NaCl, NaI, sodium acetate, and sodium benzoate, >98% of the  $^{99m}\text{TcO}_4^-$  was bound to the column. Under acidic and neutral conditions and in competition with HCl,  $\text{HNO}_3$ , NaCl, sodium acetate, and sodium benzoate >98% of the  $^{186}\text{ReO}_4^-$  was bound to the column. HI and NaI competed somewhat with  $^{186}\text{ReO}_4^-$ , showing a small reduction in activity bound to the column as seen in Figures 5 and 6. This is in direct contrast to the phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) where HI, NaI, acetate, benzoate, and lactate (Figure 4) all competed significantly, with only 10-85% of  $^{99m}\text{TcO}_4^-$

extracted, depending on the challenging anion. Figures 5 and 6 also show that  $^{99m}\text{TcO}_4^-$  is retained better than  $^{186}\text{ReO}_4^-$ , which will be discussed below.

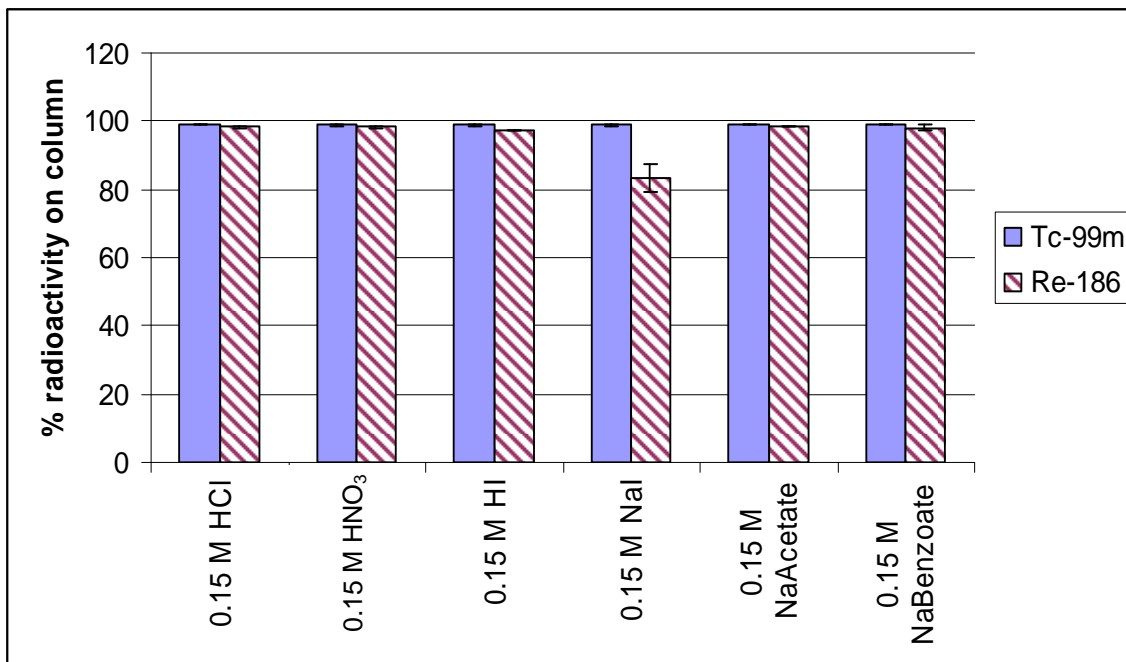
**Figure 5. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (2)**



**Table 7. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (2)**

Competing Anion	$^{99m}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.15 M HCl	$98.99 \pm 0.07$	$98.5 \pm 0.1$
0.15 M HNO <sub>3</sub>	$98.91 \pm 0.03$	$98.2 \pm 0.2$
0.15 M HI	$98.8 \pm 0.1$	$92 \pm 4$
0.15 M NaI	$98.73 \pm 0.06$	$87.0 \pm 0.6$
0.15 M Na Acetate	$98.6 \pm 0.2$	$98.3 \pm 0.2$
0.15 M Na Benzoate	$98.95 \pm 0.09$	$98.4 \pm 0.2$

**Figure 6. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (6)**

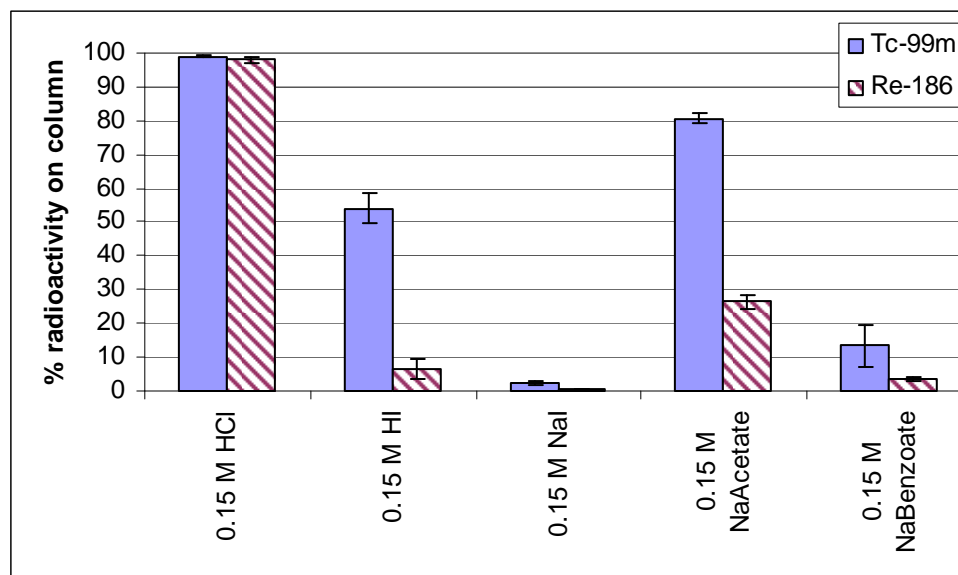


**Table 8. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (6)**

Competing Anion	$^{99m}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.15 M HCl	$98.9 \pm 0.1$	$98.3 \pm 0.2$
0.15 M HNO <sub>3</sub>	$98.9 \pm 0.2$	$98.4 \pm 0.3$
0.15 M HI	$98.8 \pm 0.2$	$97.4 \pm 0.2$
0.15 M NaI	$98.8 \pm 0.1$	$83 \pm 4$
0.15 M Na Acetate	$98.85 \pm 0.08$	$98.5 \pm 0.1$
0.15 M Na Benzoate	$99.20 \pm 0.09$	$98.1 \pm 0.8$

Using the phosphiniminium cation of (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**), under acidic conditions with HCl, >98% of the  $^{99m}\text{TcO}_4^-$  or  $^{186}\text{ReO}_4^-$  was bound to the column. HI, NaI, sodium acetate, and sodium benzoate showed varying degrees of competition with both  $^{99m}\text{TcO}_4^-$  or  $^{186}\text{ReO}_4^-$ , as seen in Figure 7 and Table 9.

**Figure 7. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (8)**



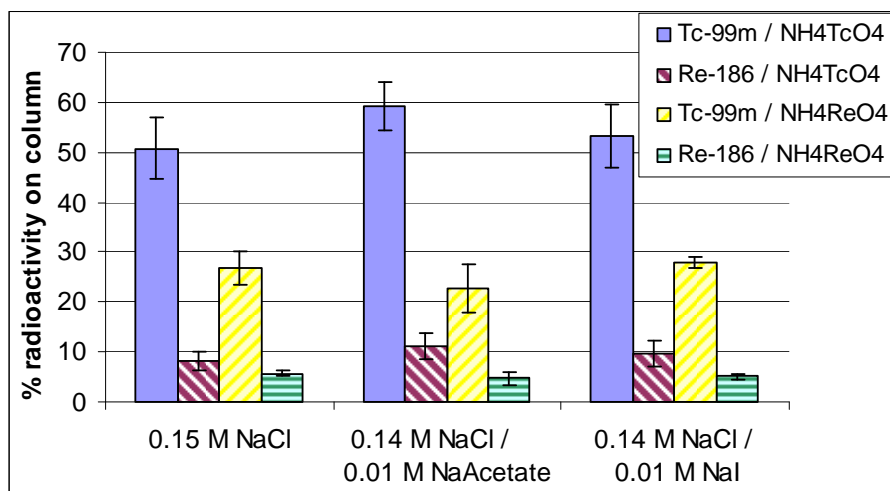
**Table 9. Solid Phase Extraction – Percentage of  $^{99m}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column for (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (8)**

Competing Anion	$^{99m}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.15 M HCl	99.0 ± 0.2	98.0 ± 0.8
0.15 M HI	54 ± 4	6 ± 3
0.15 M NaI	2.4 ± 0.5	0.46 ± 0.06
0.15 M Na Acetate	81 ± 1	26 ± 2
0.15 M Na Benzoate	13 ± 6	3.4 ± 0.6

**Solid Phase Extraction 1:1 Competition Studies.** Columns were prepared from phosphinimine coated silica. An aqueous solution containing  $^{99m}\text{TcO}_4^-$ ,  $^{186}\text{ReO}_4^-$ , and 1 mM  $\text{NH}_4^{99}\text{TcO}_4$  or 10 mM  $\text{NH}_4\text{ReO}_4$  and the competing anion was added to the column and allowed to elute. The competing anion was either none (just NaCl), 10 mM sodium acetate, or 10 mM NaI. The column was washed with the same solution without any carrier,  $^{99m}\text{TcO}_4^-$  or  $^{186}\text{ReO}_4^-$ . In the previous studies (solvent extraction and solid phase

extraction), the tracer concentration was approximately  $10^{-12}$  M whereas the competing anions were all present at 0.15 M. In order to see if the competition effect was real or due to the large excess of competitor, the most effective organic competitor (acetate) and the most effective inorganic competitor (iodide) were added in equimolar concentration to either the  $^{99}\text{TcO}_4^-$  or  $\text{ReO}_4^-$  carrier. NaCl was also tested as a comparison since NaCl did not affect the  $\text{TcO}_4^-$  or  $\text{ReO}_4^-$  and was used to keep the ionic strengths constant with the acetate and iodide binding studies. As seen in Figure 8, within error, the acetate and iodide do not compete with  $\text{TcO}_4^-$  or  $\text{ReO}_4^-$ . The phosphiniminium cation is specific for  $\text{TcO}_4^-$  or  $\text{ReO}_4^-$  over acetate and iodide. The results are shown in Figure 8 and Table 10.

**Figure 8. 1:1 Competition experiment using  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with 1 mM  $\text{NH}_4^{99}\text{TcO}_4$  or 10 mM  $\text{NH}_4\text{ReO}_4$**



All data points contain 1 mM  $\text{NH}_4^{99}\text{TcO}_4$  or 10 mM  $\text{NH}_4\text{ReO}_4$ . Ionic strength was kept constant in all samples at 0.16 M.

**Table 10. 1:1 Competition experiment using Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) with 1 mM NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> or 10 mM NH<sub>4</sub>ReO<sub>4</sub> – Percentage of <sup>99m</sup>TcO<sub>4</sub><sup>-</sup> and <sup>186</sup>ReO<sub>4</sub><sup>-</sup> Remaining on Column**

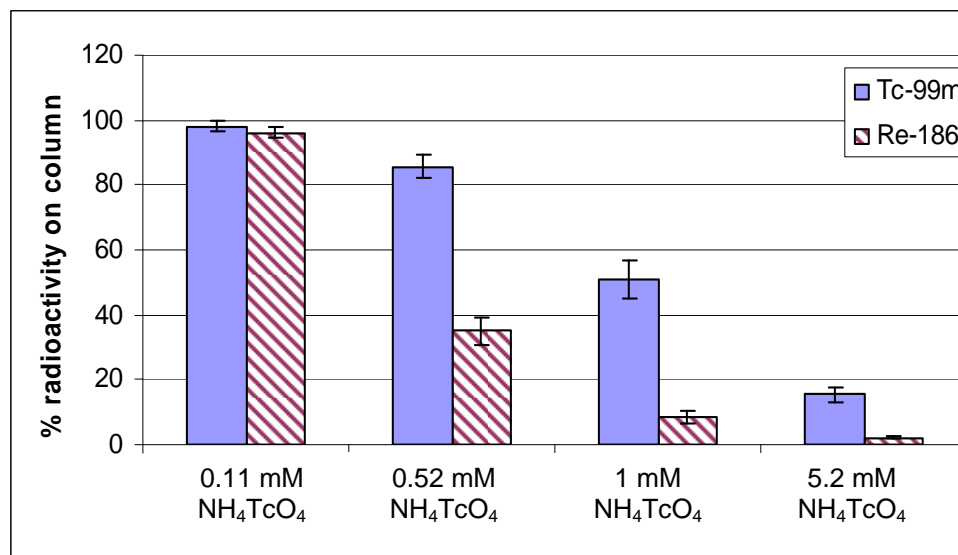
Competing Anion	[carrier]	<sup>99m</sup> TcO <sub>4</sub> <sup>-</sup>	<sup>186</sup> ReO <sub>4</sub> <sup>-</sup>
0.15 M NaCl	0 M	99.0 ± 0.3	92 ± 2
0.15 M NaCl	1 mM NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub>	51 ± 6	8 ± 2
0.14 M NaCl / 10 mM acetate	1 mM NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub>	59 ± 5	11 ± 2
0.14 M NaCl / 10 mM NaI	1 mM NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub>	53 ± 6	10 ± 3
0.15 M NaCl	10 mM NH <sub>4</sub> ReO <sub>4</sub>	27 ± 3	5.7 ± 0.6
0.14 M NaCl / 10 mM acetate	10 mM NH <sub>4</sub> ReO <sub>4</sub>	23 ± 5	5 ± 1
0.14 M NaCl / 10 mM NaI	10 mM NH <sub>4</sub> ReO <sub>4</sub>	28 ± 1	5.1 ± 0.5

**Column Capacity.** The column capacity was tested under two different sets of conditions: (1) the concentration of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> was increased keeping the volume constant at 1 mL, and (2) the concentration of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> in 1 mL remained constant and successive 1 mL aliquots of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> solution were added to the column. The concentration determination showed that approximately 0.1 mM <sup>99</sup>TcO<sub>4</sub><sup>-</sup> could be added to the column before breakthrough occurred. As the concentration of <sup>99</sup>TcO<sub>4</sub><sup>-</sup>, increased breakthrough became more severe. The volume determination showed that approximately 5 to 6 mL of 0.1 mM <sup>99</sup>TcO<sub>4</sub><sup>-</sup> could be added to the column before breakthrough occurred. Each column contained a theoretical maximum of 0.1 mmol Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) (0.5 g / column, 10% loading phosphinimine) if the coating was complete (no coating of glassware) and no phosphinimine degraded to the phosphine oxide. In case (1), 1 mL of 0.1 mM TcO<sub>4</sub><sup>-</sup> has 1x10<sup>-4</sup> mmol of TcO<sub>4</sub><sup>-</sup> while 6 mL of 0.1 mM TcO<sub>4</sub><sup>-</sup> has 6x10<sup>-4</sup> mmol of TcO<sub>4</sub><sup>-</sup> (case (2)). The phosphinimine is present in large excess in both cases. Using a larger volume of dilute <sup>99</sup>TcO<sub>4</sub><sup>-</sup> allowed more <sup>99</sup>TcO<sub>4</sub><sup>-</sup> to be taken up on the column. This would be a



situation similar to an environmental water sample where the  $^{99}\text{TcO}_4^-$  concentration is very small. A small volume of increasing concentrations of  $^{99}\text{TcO}_4^-$  resulted in increasing breakthrough. This situation would be similar to a nuclear waste sample where the  $^{99}\text{TcO}_4^-$  concentration could be quite high. The breakthrough problem could then be solved by increasing the column size or the amount of phosphinimine on the column. The difference in elution profiles for dilute and concentrated samples is not unexpected. Ion-exchange resins often show similar elution profiles. The ion is in equilibrium between the mobile and stationary phases. Dilute samples have access to many exchange sites and travel slowly down the column increasing the separation capability of the column. Concentrated samples quickly fill and block exchange sites so the ions travel quickly and reduce separation.<sup>41</sup> While the phosphinimine coated silica is not an ion-exchange resin, the phosphinimine is forming ion pairs that associate and dissociate at a certain rate in a very similar process to ion-exchange. The results for the concentration determination are shown in Figure 9 and Table 11. The results for the volume determination are shown in Figures 10 and 11.

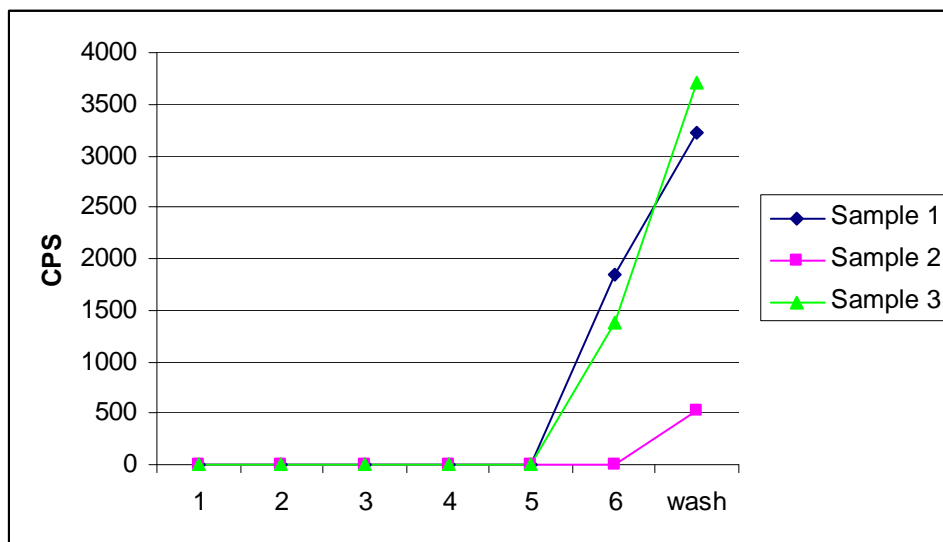
**Figure 9. Concentrated column capacity experiment for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $\text{NH}_4\text{TcO}_4$**



**Table 11. Concentrated column capacity experiment for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $\text{NH}_4\text{TcO}_4$  – Percentage of  $^{99\text{m}}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$  Remaining on Column**

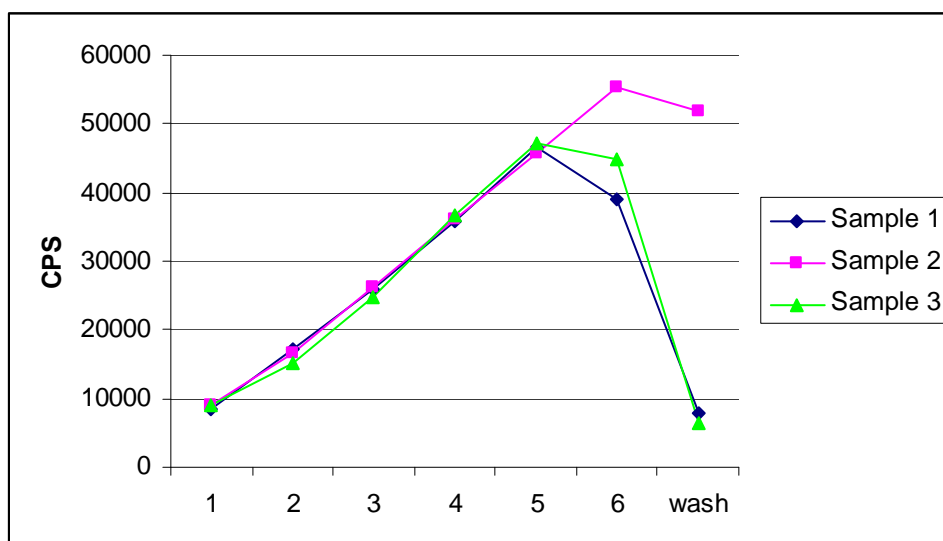
[carrier]	$^{99\text{m}}\text{TcO}_4^-$	$^{186}\text{ReO}_4^-$
0.1 mM $\text{NH}_4\text{TcO}_4$	$98 \pm 2$	$96 \pm 2$
0.52 mM $\text{NH}_4\text{TcO}_4$	$86 \pm 4$	$35 \pm 4$
1 mM $\text{NH}_4\text{TcO}_4$	$51 \pm 6$	$8 \pm 2$
5.2 mM $\text{NH}_4\text{TcO}_4$	$15 \pm 2$	$2.3 \pm 0.4$

**Figure 10. Dilute column capacity experiment for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with 0.13 mM  $\text{NH}_4\text{TcO}_4$  – CPS in Fractions**



\*Note: All samples in triplicate shown. No standard deviation calculated.

**Figure 11. Dilute column capacity experiment for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with 0.13 mM  $\text{NH}_4\text{TcO}_4$  – CPS on Column**

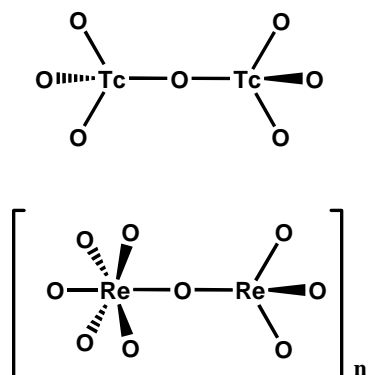


\*Note: All samples in triplicate shown. No standard deviation calculated.

**TcO<sub>4</sub><sup>-</sup> vs. ReO<sub>4</sub><sup>-</sup>.** In each data set tested, the phosphinimine demonstrated a preference for TcO<sub>4</sub><sup>-</sup> over ReO<sub>4</sub><sup>-</sup>. Both anions have the same charge and almost the same size. The ionic radii are 0.37 Å and 0.38 Å for Tc(VII) and Re(VII), respectively.<sup>32</sup> The M=O distance is 1.69 Å for both TcO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup>.<sup>22, 23</sup> ReO<sub>4</sub><sup>-</sup> is often used as a surrogate for TcO<sub>4</sub><sup>-</sup> since it is not radioactive and often assumed to have the same chemistry due to the similarity in size and charge.<sup>42</sup> If the formation of the ion pair is an electrostatic interaction and if it is the size to charge ratio that makes it specific for TcO<sub>4</sub><sup>-</sup>, then it should have an equal specificity for ReO<sub>4</sub><sup>-</sup>. The bowl shaped cyclotrimeratrylene (CTV) molecules have also been reported to be more selective for TcO<sub>4</sub><sup>-</sup> than ReO<sub>4</sub><sup>-</sup>.<sup>43, 44</sup> For the same size and charge, both TcO<sub>4</sub><sup>-</sup> and ReO<sub>4</sub><sup>-</sup> should fit into the bowl in the same manner, but this was not found experimentally. TcO<sub>4</sub><sup>-</sup> was always extracted into nitromethane inside the CTV better than ReO<sub>4</sub><sup>-</sup>, 84% vs. 71%, respectively. In the literature there are occasional reports where Tc and Re are not identical.<sup>42</sup> An example of this is Tc<sub>2</sub>O<sub>7</sub><sup>45</sup> and Re<sub>2</sub>O<sub>7</sub>(OH<sub>2</sub>)<sub>2</sub>.<sup>46</sup> In the crystal structure of Tc<sub>2</sub>O<sub>7</sub> all the Tc atoms are tetrahedral TcO<sub>4</sub><sup>-</sup> with one oxo group bridging the two Tc centers. Re<sub>2</sub>O<sub>7</sub>(OH<sub>2</sub>)<sub>2</sub> is an extended lattice of alternating [ReO<sub>4</sub>] and octahedral [ReO<sub>6</sub>H<sub>2</sub>] bound through bridging oxo groups (Scheme 10), with the coordination sphere expanded to include two water molecules. In this instance only 50% of all the Re is tetrahedral. Neither of the extraction results with the phosphinimine or CTV can be explained by ReO<sub>4</sub><sup>-</sup> having a tetrahedral shape alone. Both sets of results can be explained by some fraction of the Re present having an octahedral coordination sphere. An octahedral coordination sphere would distort the size to charge ratio and result in the preference for TcO<sub>4</sub><sup>-</sup>. Since not every Re would be octahedral and it is in a transient equilibrium, only a slight preference is observed for

$\text{TcO}_4^-$ . The tetrahedral shape is shown in the crystal structures since the most stable form crystallizes. This structure is not always representative of solution behavior.

**Scheme 10.  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7(\text{OH}_2)_2$**



Note: two of the oxygens around the octahedral Re are water groups.

### 3.4 Conclusions

Under solvent extraction conditions, the phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) is selective for  $\text{TcO}_4^-$  over other inorganic anions that are common in the environment and over  $\text{ReO}_4^-$ . The iodide ion competes well due to its size and charge, but is not an environmentally common ion. Basic and neutral conditions promote a secondary hydrolysis so that solvent extraction experiments must be done under acidic conditions. Solvent extraction is not desirable since it must be done under acidic conditions, the phosphinimine is not stable in solution, and would generate mixed waste if  $^{99}\text{TcO}_4^-$  was used. Under solid phase extraction conditions, the phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) shows an even better selectivity for  $\text{TcO}_4^-$  than under the solvent extraction conditions. The solid phase extraction experiments also show that the

pH window has been expanded to include neutral conditions. Basic conditions still promote a secondary hydrolysis reaction. The solid phase extraction experiments with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) also showed that a variety of organic anions compete well with  $\text{TcO}_4^-$ , which would be a serious drawback for many environmental samples. Phosphinimines (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) and (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) overcome this drawback and show that for  $\text{TcO}_4^-$ , none of the anions tested were able to compete and the phosphiniminium cations are selective for  $\text{TcO}_4^-$ . The phosphiniminium cation of (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) has selectivity problems similar or more severe than  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), and would not make a suitable extractant in its present form. The 1:1 competition experiments with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) showed that for organic and inorganic anions that do compete with  $\text{TcO}_4^-$  when in large excess, they do not compete with  $\text{TcO}_4^-$  when in equal concentrations. The column capacity studies show that the phosphimine columns are able to hold significantly larger amounts of  $\text{TcO}_4^-$  when it is added in a dilute solution versus a concentrated solution. Based on high selectivities of the phosphiniminium cations of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), and (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) for  $\text{TcO}_4^-$  even in the presence of many other anions, phosphinimines may be useful for the removal of  $\text{TcO}_4^-$  from both environmental samples and nuclear waste samples.

## CHAPTER 4: FLUORESCENCE / SCINTILLATION SENSOR DESIGN

### 4.1 Introduction

Sensors produce a qualitative or quantitative signal that can be measured in recognition of or binding by a specific analyte.<sup>6, 7</sup> Different types of sensors can be distinguished by the type of analyte detected (i.e., cation, anion) and the type of signal generated (i.e., fluorescence, luminescence).<sup>8</sup> In Chapter 3: Radiochemistry, the ability of several phosphinimines to extract  $\text{TcO}_4^-$  in the presence of other anions was demonstrated. Phosphinimines are capable of forming anion sensors based on this selectivity. However, a functioning sensor requires a signal to be generated in the presence of the correct anion.

Fluorescence and scintillation sensing involve the emission of light by a fluor. In fluorescence, once the anion of choice is bound to the phosphinimine the fluorescent signal would be generated, quenched, or shifted in wavelength. The result would be a difference between the original fluorescent signal without the anion and the signal with the anion bound.

Scintillation is fluorescent emission by a fluor that has been excited by an energy transfer from a radionuclide. All the energy from each nuclear emission, in this case  $\beta^-$  emission, is transferred to the fluor, which then emits light, or scintillates. Technetium-99 is a  $\beta^-$  emitting radionuclide and scintillation can be a method of signal generation when  $^{99}\text{TcO}_4^-$  is in the presence of a fluor. Since  $\text{TcO}_4^-$  should be the only  $\beta^-$  emitting anion present, the influence of other anions on the fluor itself is unimportant as long as the sensor is selective for  $\text{TcO}_4^-$ .

Phosphinimines,  $R_3P=N-SiMe_3$ , hydrolyze in the presence of water to the phosphiminium cation,  $R_3P=NH_2^+$ , that can be used as extractants for the separation and preconcentration of  $TcO_4^-$  in the presence of other anions. The fluorescence and scintillation properties of (9-anthracenyl) $Ph_2P=NSiMe_3$  (**2**) were investigated as a possible method of signal generation in the presence of  $^{99}TcO_4^-$ . In addition to a reporter group attached to the phosphinine,  $Ph_3P=NSiMe_3$  (**1**) or (9-anthracenyl) $Ph_2P=NSiMe_3$  (**2**) were each investigated in the presence of an external scintillator.

## 4.2 Experimental

**General Considerations.** *Caution!  $^{99}Tc$  emits a 0.292 MeV  $\beta^-$  with a half-life of  $2.15 \times 10^5$  years and  $^{99m}Tc$  emits a 140 keV  $\gamma$ -ray with a half-life of 6.0 h. Although common laboratory glassware provides adequate shielding for  $^{99}Tc$ , standard radiation safety procedures must be used at all times.  $^{99m}Tc$  should be handled only in a controlled environment by qualified personnel trained in radiation safety.*

**Materials.** Technetium-99m was eluted with normal saline as sodium pertechnetate from a  $^{99}Mo/^{99m}Tc$  generator (Bristol Myers Squibb or Mallinckrodt Medical, Inc.). Technetium-99 was obtained from Oak Ridge National Laboratory as ammonium pertechnetate and used as a macroscopic carrier in experiments where noted. HPLC grade dichloromethane and toluene, and sodium chloride were purchased from Fisher Scientific. Scintillation grade anthracene was purchased from Fluka. Scintillation grade 2,5-diphenyloxazole (PPO), bis-MSB, and 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) were purchased from Acros. Silica gel was obtained from J. T. Baker, heated to 110 °C overnight in an oven and used without further purification. Only doubly



distilled water was used. Unless noted, all common laboratory chemicals were of reagent grade or better.

Absorbance and fluorescence emission measurements were recorded on an HP 8453 Diode-Array UV/VIS spectrometer (Santa Clara, CA) and Varian Cary Eclipse Fluorometer (Palo Alto, CA), respectively. All spectra were collected in 1 cm<sup>2</sup> Suprasil quartz cuvettes at room temperature. Liquid scintillation counting (LSC) was performed on a PerkinElmer Tri-Carb 2900 TR Liquid Scintillation Analyzer. Samples containing <sup>99m</sup>TcO<sub>4</sub><sup>-</sup> were counted in a NaI(Tl) well detector with Canberra electronics and a SCA with a Counter/Timer setup.

**UV/Vis Absorbance and Fluorescence Measurements.** A 15 W Xenon arc lamp excitation source (pulsed at 80 Hz) was used for the fluorescence measurements. Samples were excited at 341 nm, and the emission was collected from 355–700 nm in 2 nm increments, using excitation and emission slit widths of 5 nm, a scan rate of 120 nm/min, and an averaging time of 0.5 seconds. All emission spectra were blank and absorbance corrected.

**Sample preparation.** Stock solutions (~10<sup>-3</sup> M) of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**), [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (**3**), [(9-anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][<sup>99</sup>TcO<sub>4</sub><sup>-</sup>] (**4**), anthracene, anthracene + NH<sub>4</sub>ReO<sub>4</sub>, anthracene + NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub>, and NH<sub>4</sub><sup>99</sup>TcO<sub>4</sub> were prepared in acetonitrile (ACN), while PPh<sub>2</sub>(anthr) was prepared in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) because it is not soluble in ACN. Samples (~10<sup>-5</sup> M) were prepared by quantitatively transferring known aliquots of the stock solutions into volumetric flasks and diluting to volume with toluene or liquid scintillation (LSC) cocktail (Ecosafe cocktail). All toluene samples were analyzed by UV-Vis absorbance and fluorescence

spectroscopy and liquid scintillation counting. Ecosafe cocktail samples were analyzed by liquid scintillation counting only. All samples were prepared the day of analysis, and for liquid scintillation counting purposes, samples were allowed to sit in the dark for 30 minutes prior to analysis.

**General Solid Phase Extraction Competition Procedure.** Silica gel was pre-dried overnight at 110 °C in an oven. Phosphinimine ( $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**)) (0.5 g) was then sorbed onto 5 g of dried silica gel from a dichloromethane slurry. This slurry was allowed to slowly dry over 3 or more days in a desiccator (to minimize absorption of water). Columns were prepared from plastic disposable columns (Fisher) containing small plastic frits and were each filled with 0.5 g of the coated silica. One mL of 0.15 M NaCl containing approximately 0.1 mM  $^{99}\text{TcO}_4^-$  and 1  $\mu\text{Ci}$   $^{99\text{m}}\text{TcO}_4^-$  was then added to the top of the dry column, and allowed to elute through the column. The effluent was collected until no more aqueous phase eluted. Then 1 mL of the particular aqueous phase containing the competitor anion but without radioactivity was added to the top of the column, and this was collected until no more aqueous phase eluted. This was repeated 3 additional times. All 5 column fractions and the column were then counted. The first fraction did not contain a full 1 mL, as most of this went to wetting the column. All data points were performed in triplicate.

**General Solid Phase Extraction Scintillation Procedure.** The general solid phase extraction procedure was followed. When coating the phosphinimine onto silica gel from a dichloromethane slurry, the primary scintillator (PPO) and the secondary scintillator (bis-MSB or POPOP) were added to the slurry in addition to the phosphinimine. The following weight percents compared to the silica were followed:

10% phosphinimine, 10% primary scintillator, 3% secondary scintillator. The weight percents were optimized and this data is presented in Appendix 3. Columns were prepared and run according to the same method as the general solid phase extraction procedure.

#### 4.3 Results and Discussion

No group in the molecule  $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$  (**1**) is capable of generating or altering a signal in the presence of  $\text{TcO}_4^-$ , thus requiring external groups such as PPO or anthracene to produce a scintillation signal. (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) incorporates the anthracene molecule, which is a known scintillator,<sup>25</sup> directly into the phosphinimine moiety. The fluorescence and scintillation properties of (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) are reported. While (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) incorporates the alpha scintillating naphthyl moiety,<sup>25</sup> the fluorescence and scintillation properties of (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) are not reported due to the instability of  $[(1\text{-naphthyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**7**), which degrades in solution on the order of minutes to hours.

For the fluorescence and scintillation studies of (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) and its derivatives, samples ( $10^{-5}$  M) were prepared by diluting stock solutions ( $10^{-3}$  M) in toluene. These samples were analyzed by UV-Vis absorption and fluorescence spectroscopy and liquid scintillation counting (LSC). By LSC, samples ( $10^{-5}$  M) were counted in toluene alone and also in LSC cocktail, with a total sample volume of 10 mL. Toluene was selected since less polar solvents do not disrupt charge transfer in samples.<sup>47</sup>

Anthracene and  $\text{PPh}_2(9\text{-anthracenyl})$  both show three distinct peaks in their spectra. The spectra of  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**),  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**), and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  (**4**) do not show these structural features. Rather, the features include a small peak representing the anthracene moiety and an intense broad band typically seen in charge transfer situations, see Figure 12. The phosphinimine functional group may donate electrons into the anthracene system through a conjugated network, resulting in a broad and often structureless spectrum when compared to the original fluorophore.<sup>10</sup>

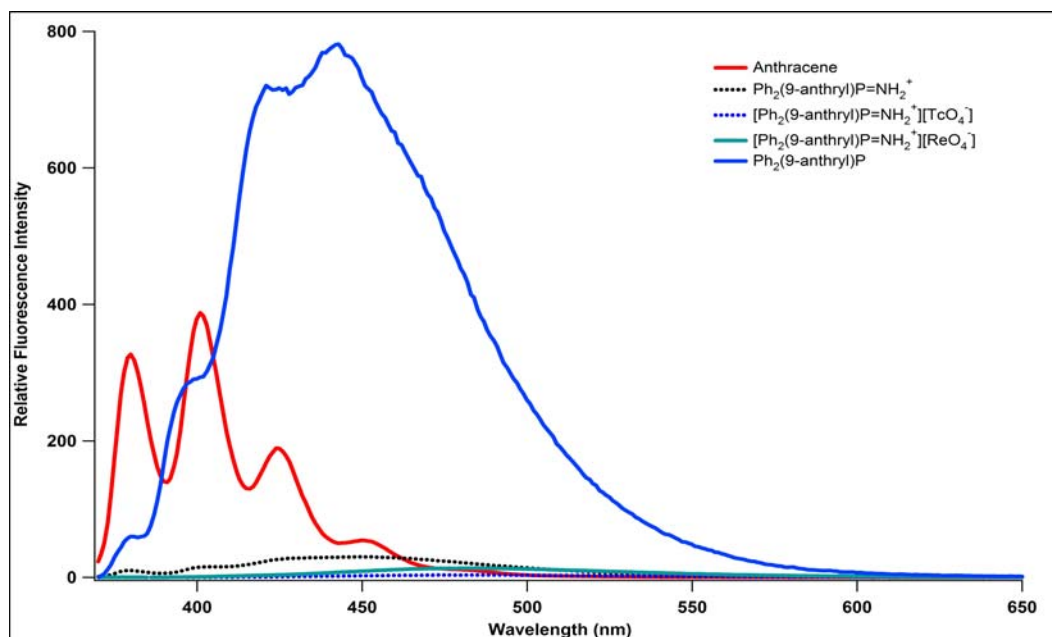
If the band is indeed due to charge transfer, two mechanisms are possible. First,  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) is fully conjugated, and charge transfer may occur through the bonds present in the phosphinimine. Second, as seen in other systems, photoexcited anthracene may form intramolecular excited complexes, exciplexes, with tertiary amines.<sup>47, 48</sup> This exciplex would be the result of direct interaction of the anthracene moiety with the imine nitrogen through space.<sup>48</sup>

The intensity of this broad band is attenuated for  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) compared to  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**), and both show a significant intensity reduction compared to  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**). Due to the lanthanide contraction, Re and Tc have almost identical sizes and thus  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$  also have identical sizes. The ionic radii are 0.37 Å and 0.38 Å for Tc(VII) and Re(VII), respectively.<sup>32</sup> The volt-equivalents for  $\text{ReO}_4^-$  (2.588)<sup>34</sup> and  $\text{TcO}_4^-$  (3.300)<sup>34</sup> show that they are very similar in their oxidation-reduction potential and in their electron-withdrawing character. This similarity is seen in the small difference between the fluorescence intensity of

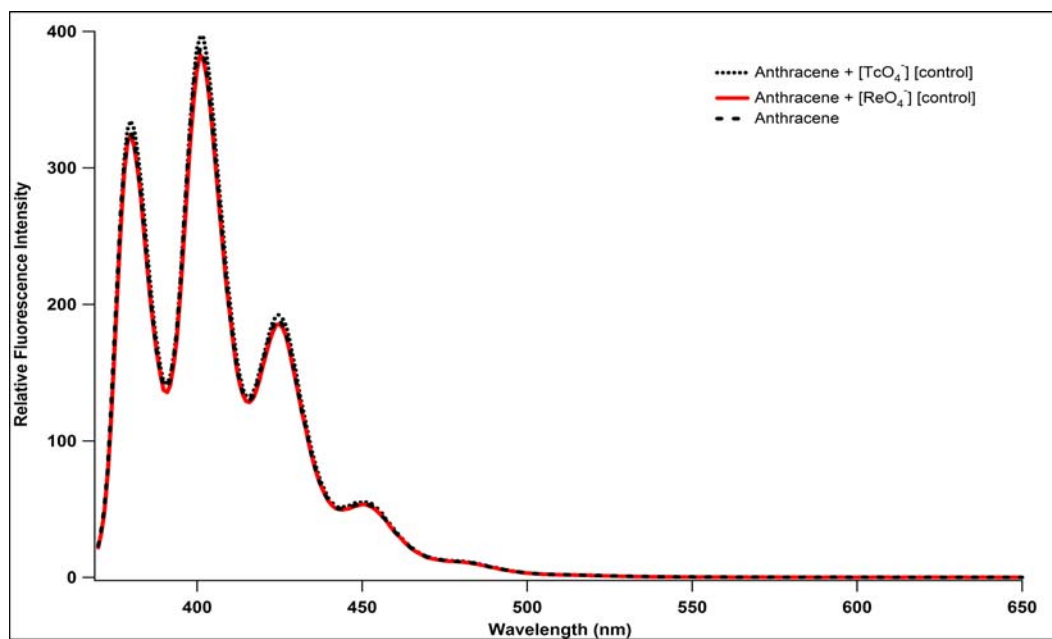
$[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) when compared to the significant quenching that  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) show over  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**).

The fluorescence peak shift does not change for  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**),  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**), or  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**). The only noticeable difference in the spectra is the reduction in the fluorescent signal with the electron-withdrawing substituents. Using this intensity attenuation or quenching of fluorescence as a sensing process can be done but is difficult. The number of attenuated fluors in the presence of  $^{99}\text{TcO}_4^-$  will be small compared to the number of unattenuated fluors since the concentration of  $^{99}\text{TcO}_4^-$  will be low in environmental samples. Quenching can also be caused by other factors in addition to the presence of the target analyte,<sup>11</sup> such as chemical degradation. The attenuation or quenching of the fluorescent intensity makes  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) a poor candidate for a  $^{99}\text{TcO}_4^-$  sensor. The fluorescence data is shown in Figures 12 and 13.

**Figure 12: Fluorescence Spectra for Anthracene,  $\text{PPh}_2(\text{anthracenyl})$ ,  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (2),  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (3), and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  (4)**



**Figure 13. Anthracene, anthracene with  $\text{NH}_4\text{TcO}_4$ , and anthracene with  $\text{NH}_4\text{ReO}_4$**



The samples measured for fluorescence were also measured for activity by LSC in both toluene and LSC cocktail. The counting data is shown in Table 12. As expected, the samples that contain no  $^{99}\text{Tc}$  (radioactivity) do not generate any counts above background. These samples (A-G) include a blank containing no solute (A), only anthracene (B),  $\text{PPh}_2(9\text{-anthracenyl})$  (C),  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) (D),  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) with HCl to ensure hydrolysis to  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+$  (E),  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) (F), and anthracene +  $\text{NH}_4\text{ReO}_4$  (G). Sample (H) contains  $10^{-5}$  M anthracene and  $\text{NH}_4^{99}\text{TcO}_4$ , and sample (J) contains  $10^{-5}$  M  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**). Although the total anthracene and  $^{99}\text{TcO}_4^-$  concentrations are equal in both (H) and (J),  $10^{-5}$  M anthracene and  $\text{NH}_4^{99}\text{TcO}_4$  (H) and  $10^{-5}$  M  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) (J), the count rate increased in sample (J) where the ion pair was present. This is due to the proximity of the anthracene to  $^{99}\text{TcO}_4^-$  in sample (J), whereas in sample (H) both anthracene and  $^{99}\text{TcO}_4^-$  would be distributed evenly in solution. Sample (I) contains  $10^{-3}$  M anthracene and  $10^{-5}$  M  $\text{NH}_4^{99}\text{TcO}_4$ . The count rate increased in sample (I) compared to both samples (H) and (J) due to an increase in fluor concentration, which increases the likelihood of a beta particle interaction with the fluor. Sample (K) contains  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) plus  $\text{NH}_4^{99}\text{TcO}_4$ . The count rate is lower in  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) plus  $\text{NH}_4^{99}\text{TcO}_4$  (K) than in  $10^{-5}$  M anthracene and  $\text{NH}_4^{99}\text{TcO}_4$  (H) and  $10^{-5}$  M  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) (J) since the anthracene is in close proximity to the nonradioactive  $\text{NH}_4\text{ReO}_4$ . Counts are still seen since  $\text{NH}_4^{99}\text{TcO}_4$  is present in solution with the anthracene moiety. Sample (L) contains  $\text{NH}_4^{99}\text{TcO}_4$  alone. The count rate for this sample (in LSC cocktail only) is significantly

higher than in sample (J) (in toluene), which contains  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**),  $116300 \pm 117$  versus  $7900 \pm 126$ . The same amount of  $\text{NH}_4^{99}\text{TcO}_4$  is present in both samples but the count rate where anthracene is the only scintillator is significantly lower. In addition, the count rate for  $10^{-5}$  M  $\text{NH}_4^{99}\text{TcO}_4$  (in LSC cocktail only) is higher than for  $10^{-5}$  M  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) (in LSC cocktail). Both samples contain the same amount of  $^{99}\text{TcO}_4^-$  and their count rates should be comparable or possibly higher in sample (J) (in LSC cocktail) with the additional anthracene fluor. As seen in the solid scintillation studies below,  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) may cause quenching, which would prevent light emission and lower the count rate. The trends observed with the toluene samples are also seen with the LSC cocktail samples, only with higher count rate observed as a result of the large amount of fluor present in LSC cocktail.



**Table 12. Fluorescence samples prepared in toluene and LSC cocktail measured for activity**

	Sample	cpm in Toluene	cpm in LSC cocktail
A	Blank	41 ± 5	130 ± 12
B	Anthracene	47 ± 4	140 ± 10
C	Ph <sub>2</sub> (9anthracenyl)P	35 ± 5	100 ± 10
D	Ph <sub>2</sub> (9anthracenyl)P=NSiMe <sub>3</sub> ( <b>2</b> )	47 ± 6	110 ± 9
E	[Ph <sub>2</sub> (9anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][Cl <sup>-</sup> ] control	49 ± 3	240 ± 20
F	[Ph <sub>2</sub> (9anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][ReO <sub>4</sub> <sup>-</sup> ] ( <b>3</b> )	47 ± 4	120 ± 9
G	Anthracene + NH <sub>4</sub> ReO <sub>4</sub>	50 ± 3	96 ± 8
H	Anthracene (10 <sup>-5</sup> M) + NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub> (10 <sup>-5</sup> M)	2450 ± 29	28000 ± 125
I	Anthracene (10 <sup>-3</sup> M) + NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub> (10 <sup>-5</sup> M)	14200 ± 619	N/A
J	[(9-anthracenyl)Ph <sub>2</sub> P=NH <sub>2</sub> <sup>+</sup> ][ <sup>99</sup> TcO <sub>4</sub> <sup>-</sup> ] ( <b>4</b> )	7900 ± 126	85000 ± 297
K	[Ph <sub>2</sub> (9anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][ReO <sub>4</sub> <sup>-</sup> ] ( <b>3</b> ) + NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub>	1900 ± 49	N/A
L	NH <sub>4</sub> <sup>99</sup> TcO <sub>4</sub>	N/A	116300 ± 117

\*Note: All sample contain 10<sup>-5</sup> M unless otherwise noted. N/A = Not Applicable

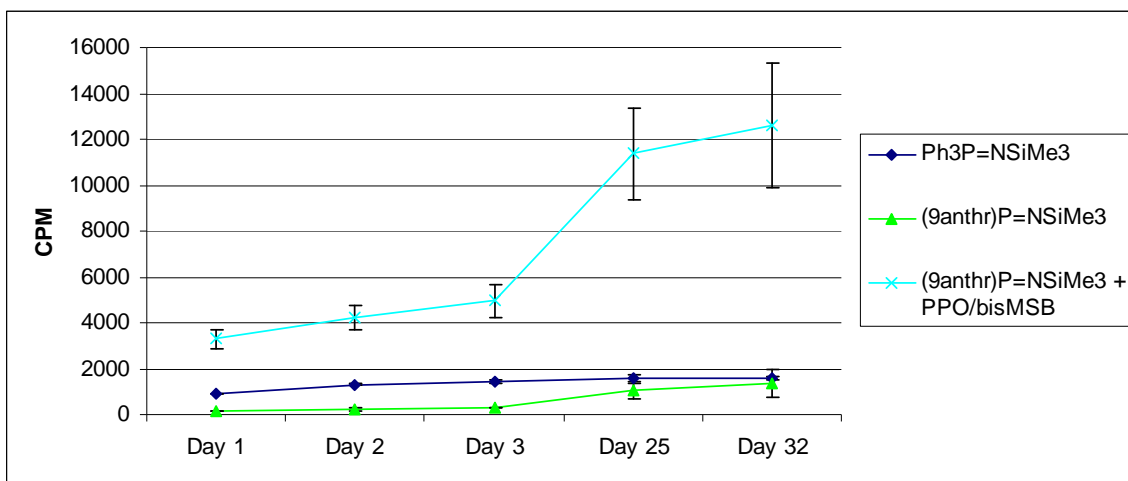
In addition to using a reporter unit attached to the phosphinimines (as with (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**)), external reporters can also be used. The method reported here is similar to that of Egorov et. al at Pacific Northwest National Laboratory.<sup>14</sup> Columns were prepared with either Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) or (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub>

(**2**) alone and with either  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) in the presence of external scintillators (PPO and bis-MSB). It is necessary to use bis-MSB or POPOP as wavelength shifters for PPO since PPO does not emit light in the most sensitive wavelength region (i.e., 363 nm vs.  $\sim 450$  nm)<sup>25</sup> for the photomultiplier tubes. The secondary fluors bis-MSB and POPOP absorb light emitted by PPO in the presence of radioactivity and reemit it in the sensitive wavelength region. Solubility problems were encountered with POPOP (crystallized out of solution without coating the silica) and so it was not used in the preparation of the columns. Anthracene emits light in the sensitive wavelength region and does not require a secondary fluor. It could potentially be used to replace both PPO and bis-MSB.

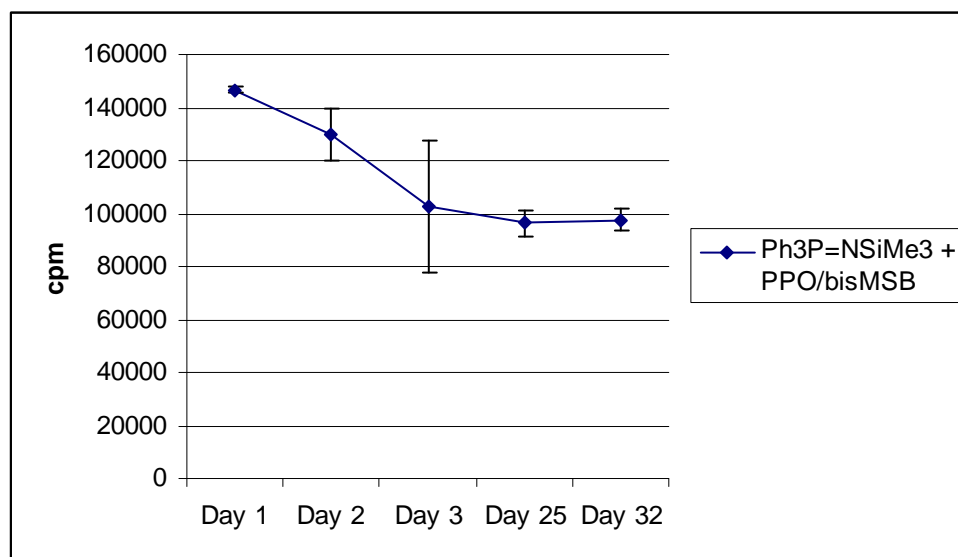
Solutions containing  $^{99}\text{TcO}_4^-$  in 0.15 M NaCl were run through the columns to generate the phosphiminium permethylate. The presence of  $^{99\text{m}}\text{TcO}_4^-$  allowed detection using a NaI(Tl) detector to ensure the column was run properly and the data matched the extraction behavior observed in Chapter 3: Radiochemistry. The data for  $^{99\text{m}}\text{TcO}_4^-$  tracer is present in Appendix 3. The columns were placed in 20 mL LSC vials and then placed in the LSC instrument, where the scintillation properties of each column were measured over time. The scintillation data is shown in Figures 14 and 15. Silica coated with only  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) showed a count rate of  $900 \pm 10$  cpm while silica coated with (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) showed a count rate of  $200 \pm 31$  cpm. The samples using (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), however, showed an increase in scintillation over time to approximately the same count rate as samples using  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**). This suggests that (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) is quenching the count rate and this quenching goes away over the course of approximately 1 month. Samples using

$\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) with PPO/bis-MSB showed a large count rate of  $150,000 \pm 1319$  cpm, which then decreased over the course of 1 month. If the initial large count rate was not the result of scintillation caused by  $^{99}\text{TcO}_4^-$  it could have been the result of chemoluminescence resulting in scintillation that was not the result of  $\beta^-$  particle emission.<sup>25</sup> The decrease of the signal over time could be the result of reduction of the chemoluminescence or photobleaching of the fluor. Samples containing (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) with PPO/bis-MSB showed a count rate of  $3000 \pm 409$  cpm, which increased over the course of 1 month. This was still significantly lower than the samples containing  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) with PPO/bis-MSB, and could be due to (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) quenching the scintillation. This result is similar to the increase in the count rate with (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) alone. These results were not anticipated. Since (**2**) contains a known scintillator (anthracene) and was already observed to scintillate in toluene in the presence of  $^{99}\text{TcO}_4^-$ , it was expected that samples containing (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) would result in increased scintillation compared to  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and that samples containing (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) with PPO/bis-MSB would show increased scintillation compared to samples containing  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and PPO/bis-MSB.

**Figure 14: Counts per minute (cpm) for solid phase extraction samples**



**Figure 15: Counts per minute (cpm) for solid phase extraction samples**



Note difference in scale for Figure 14 and Figure 15.

#### 4.4 Conclusion

The fluorescence properties of (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) show an intense broad band typically seen in charge transfer that is not present in anthracene or the corresponding phosphine. The intensity of this broad band is attenuated for

$[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**) because of the electron-withdrawing nature of  $\text{MO}_4^-$ . The phosphiniminium cation of  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) scintillates in the presence of the beta emitting  $^{99}\text{TcO}_4^-$  to produce a signal as demonstrated by the  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][^{99}\text{TcO}_4^-]$  (**4**). Based on this result, silica was coated with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) alone or in the presence of PPO/bis-MSB. The results showed that  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) alone or with PPO/bis-MSB had a very low scintillation count rate that increased over the course of one month.  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) alone produced a very low scintillation count rate, which remained constant over time since no scintillator was present.  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) with PPO/bis-MSB produced a large count rate initially that decreased over the course of one month. The solid scintillator columns did not produce a steady signal over time so that  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) alone, and  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) with PPO/bis-MSB cannot be used to generate a scintillation sensor. This could be resolved by two different methods. First, the phosphinimine could be altered to prevent the chemoluminescence or quenching problems observed. The altered phosphinimine may also have superior selectivity for  $^{99}\text{TcO}_4^-$ . Altering the phosphinimine could include attaching different fluors in the place of anthracene or changing substituent groups so that the signal generated with external scintillators would be constant over time. Second, the external scintillator could be changed. Other scintillators, such as anthracene, are known and could be used to replace PPO or bis-MSB.

## CHAPTER 5: FUTURE GOALS

To complete the radiochemical characterization data set for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), several additional studies should be performed. The results for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) show that it is stable and the phosphiniminium cation extracts  $\text{TcO}_4^-$  under acidic and neutral conditions but undergoes hydrolysis in strong base. While many environmental samples have the potential to be basic, they will not usually be strongly basic. A pH study of the stability of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) from pH 7-12 using phosphate buffer solutions would show at what pH significant hydrolysis of the phosphinimine to the phosphine oxide begins. Expanding the pH window eliminates sample pretreatment, which would decrease waste generation and expense. After establishing the pH window for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), it would be valuable to investigate the pH window for  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**). Since the phosphiniminium cation of  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) already shows much better selectivity for  $\text{TcO}_4^-$  over other anions, it would be useful to determine whether it is stable over a wider pH window.

Two additional anions should also be investigated with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and possibly with  $(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), bicarbonate and uranyl nitrate.  $\text{TcO}_4^-$  is known to react and form complexes with carbonates<sup>49, 50</sup> and they could interfere with  $\text{TcO}_4^-$  extraction. Due to pH,  $\text{HCO}_3^-$  would be the most readily available carbonate species in the environment and the competition of this species with  $\text{TcO}_4^-$  should be investigated. Nuclear waste streams come from reprocessing of nuclear fuel and usually begin by dissolving the fuel in nitric acid.<sup>51</sup> Depending on the specific process used, the solution undergoes a series of chemical treatments. Once uranium, in the form of uranyl nitrate, is purified,  $\text{TcO}_4^-$  is a major contaminate and handling problem. If

phosphinimines are selective for  $\text{TcO}_4^-$  over uranyl nitrate they could be used as extractants to purify nuclear waste or in reprocessing technology.

The phosphininium cations of phosphinimines  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) have been shown to be selective for  $\text{TcO}_4^-$  under laboratory conditions. Natural waters with a known quantity of  $\text{TcO}_4^-$  added should be tested to determine if the phosphinimines are selective under actual environmental conditions. Waters from a variety of sources around the country that are or are known to be similar to waters that are potentially contaminated should be tested.

Silica was used as a solid support in these studies due to its ready availability and low cost. Several problems exist with using silica, including instability at high and low pH, inconsistencies between manufacturers, batch numbers, and lot numbers, and severe optical quenching when using a scintillator. Other supports should be investigated that alleviate these problems. Scintillating organic fibers and beads were considered but dissolve in organic solvents, eliminating the ability to coat the phosphinimine on the surface. Porous microbeads and similar supports from companies like Eichrom may provide suitable supports for further studies.

Of the phosphinimines reported here,  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) are mildly moisture sensitive but the phosphininium cations form stable complexes with pertechnetate and perrhenate. (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) is mildly moisture sensitive but the phosphininium cation does not form a stable complex with perrhenate and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) is extremely moisture sensitive and the phosphininium cation does not form stable ion pairs with perrhenate. This instability is shown in the degradation of the ion pair in

solution over the course of minutes to hours. Additional phosphinimine derivatives should be synthesized to test for their stability, stability of the ion pairs, and their extraction abilities. These derivatives could include additional functionalization of (p-COOMe)C<sub>6</sub>H<sub>4</sub>Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**8**) to add a polymer or reporter group, possibly increasing the stability of this phosphinimine. Derivatives could also include other types of reporter groups, multiple phosphinimine groups in a linear chain or attached to a tripodal ligand, alkyl phosphinimines to compare to the aryl phosphinimines reported here.

In addition to synthesizing other phosphinimines, a method to generate a signal is still required in order to generate a sensor. The internal anthracene reporter on (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) did not function as a suitable scintillator. Using PPO/bis-MSB as external reporters in the presence of Ph<sub>3</sub>P=NSiMe<sub>3</sub> (**1**) or (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (**2**) did not generate a reliable signal. Synthesizing phosphinimines with other internal reporters such as fluorescein or utilizing other external reporters such as anthracene are possible methods to produce a reliable signal.

Once a method of producing a reliable signal is developed, a functioning sensor should be assembled or generated. It would require a sensor material that could be introduced and removed (possibly in a column format), a measurement chamber, photomultiplier tube(s), a method of processing the signal, etc. The efficiency and sensitivity would need to be measured to compare to current methods.



## CHAPTER 6: CONCLUSION

Four phosphinimines were synthesized, fully characterized, and tested radiometrically for the ability to extract  $\text{TcO}_4^-$  in the presence of a variety of other anions. Both  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) are mildly moisture sensitive but the phosphiniminium cations form stable complexes with  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$ . The crystal structures of  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{ReO}_4^-]$  (**3**) and  $[(9\text{-anthracenyl})\text{Ph}_2\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$  (**4**) are reported and they are isostructural. (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) are more moisture sensitive than  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), but the greatest difference is the instability of the complexes of the phosphiniminium cations with  $\text{ReO}_4^-$ . This instability makes both (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) poor choices for use in a sensor.

All four phosphinimines were tested in the presence of a variety of inorganic and organic anions. The phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) is more selective for  $\text{TcO}_4^-$  than  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ ,  $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ , and fumarate. Iodide, acetate, benzoate, and lactate all compete significantly with  $\text{TcO}_4^-$  when they are in large excess. Iodide and acetate in equimolar concentration do not compete with  $\text{TcO}_4^-$ , and it is reasonable to assume that benzoate and lactate behave similarly. The phosphiniminium cations of (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) and (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) showed significantly less competition of other anions with  $\text{TcO}_4^-$  than the phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**). However, they are more expensive and time consuming to produce, and the phosphiniminium perrhenate complexes with (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**) are not stable. The phosphiniminium cation of (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) is

selective for  $\text{TcO}_4^-$  in the presence of some anions but the sensitivity of the phosphinimine to moisture makes it difficult to handle.

The fluorescent and scintillation properties of (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) were investigated. The anthracene moiety does fluoresce, but the emission is significantly altered in the presence of the imine group, going from a sharp, four peak emission to a broad charge transfer band. The presence of  $\text{ReO}_4^-$  or  $\text{TcO}_4^-$  affect the emission even more significantly, reducing the intensity of emission drastically. [(9-anthracenyl) $\text{Ph}_2\text{P}=\text{NH}_2^+$ ][ $\text{TcO}_4^-$ ] (**4**) also scintillates in toluene in the presence of  $^{99}\text{TcO}_4^-$  but shows a quenching effect of the scintillation in LSC cocktail. This quenching effect is also present in the solid phase extraction scintillation experiments. (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) alone shows less scintillation in the presence of  $^{99}\text{TcO}_4^-$  than  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) when coated onto a solid support. (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) in the presence of PPO/bis-MSB shows significantly less scintillation in the presence of  $^{99}\text{TcO}_4^-$  than  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) in the presence of PPO/bis-MSB when coated onto a solid support. The most significant problem with the solid extraction scintillation experiments for either  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) or (**2**), either alone or in the presence of PPO/bis-MSB, is the lack of a reproducible signal over time. The count rate for all the samples changed over the course of a month.

The phosphiniminium cation of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**), (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**), (1-naphthyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**6**), and (p-COOMe) $\text{C}_6\text{H}_4\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**8**) are selective for  $\text{TcO}_4^-$  in the presence of other anions to varying degrees. The high stability and selectivity in the presence of  $^{99}\text{TcO}_4^-$  makes the phosphiniminium cations of  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (**1**) and (9-anthracenyl) $\text{Ph}_2\text{P}=\text{NSiMe}_3$  (**2**) promising extractants for either

use in a scintillation sensor or for pertechnetate separation. This separation method is an improvement over other methods like anion-exchange chromatography in both the selectivity for  $\text{TcO}_4^-$  and in the ability to sample large volumes. Large volumes of contaminated water can be run through phosphinimine columns resulting in both preconcentration of  $\text{TcO}_4^-$  and remediation of the water. To date, preconcentration involves tedious and time consuming chemistry by a trained technician. The phosphinimines provide an easy to implement preconcentration method that could be both time and cost effective. A variety of analysis methods could then be implemented if the amount of  $\text{TcO}_4^-$  needs to be determined. Having a method that is fast and easy to implement has the benefits of reduced worker exposure to hazardous chemicals and radioactivity in addition to the reduction of chemical waste and secondary wastes like gloves, vials, etc. With further development, the column material or phosphinimine extractant could be equipped with reporter groups to determine the amount of  $\text{TcO}_4^-$  without further analysis. If other suitable derivatives could be synthesized, a library of extractants could be formed showing which phosphinimine to use in which extraction situation or water sample.

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# APPENDIX 1: CRYSTAL DATA AND STRUCTURE REFINEMENT FOR

[(9anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (3) and [(9anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (4)

**X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters of (3) and (4)**

	<b>3</b>	<b>4</b>
Formula	C <sub>26</sub> H <sub>21</sub> NO <sub>4</sub> Pre	C <sub>26</sub> H <sub>21</sub> NO <sub>4</sub> PTc
Fw	628.61	540.41
cryst syst	Monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1/n</sub>	<i>P</i> 2 <sub>1/n</sub>
<i>a</i> (Å)	11.3047(5)	11.2876(3)
<i>b</i> (Å)	16.3983(8)	16.3619(4)
<i>c</i> (Å)	12.2469(6)	12.2203(3)
α (deg)	90	90
β (deg)	92.3440(10)	92.16
γ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	2268.40(19)	2255.32(10)
<i>Z</i>	4	4
ρ <sub>calcd</sub> (g/cm <sup>3</sup> )	1.841	1.592
<i>T</i> , K	173(2)	173(2)
μ, mm <sup>-1</sup>	5.461	0.743
λ source (Å)	0.71073	0.71073
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.0193	0.0266
<i>R</i> <sub>w</sub> ( <i>F</i> ) <sup>a</sup>	0.0489	0.0736
GOF	1.025	1.064

$$^a R = (\sum | |F_o| | - |F_c| | / \sum |F_o| | ). R_w = [\sum \varpi (|F_o|^2 - |F_c|^2)^2 / \sum \varpi (|F_o|^2)^2]^{1/2}.$$



## Crystal data and structure refinement for [(9anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][ReO<sub>4</sub><sup>-</sup>] (3)

Table 1. Crystal data and structure refinement for laanthre.

Identification code	
d:\xtals\jurisson\leah\laanthre\laanthre	
Empirical formula	C <sub>26</sub> H <sub>21</sub> N O <sub>4</sub> P Re
Formula weight	628.61
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	?, ?
Unit cell dimensions	a = 11.3047(5) Å alpha = 90 deg. b = 16.3983(8) Å beta = 92.3440(10) deg. c = 12.2469(6) Å gamma = 90 deg.
Volume	2268.40(19) Å <sup>3</sup>
Z, Calculated density	4, 1.841 Mg/m <sup>3</sup>
Absorption coefficient	5.461 mm <sup>-1</sup>
F(000)	1224
Crystal size	0.50 x 0.30 x 0.15 mm
Theta range for data collection	2.08 to 27.11 deg.
Limiting indices	-14<=h<=12, -21<=k<=20, - 15<=l<=15
Reflections collected / unique	15994 / 5001 [R(int) = 0.0220]
Completeness to theta = 27.11	99.5 %
Max. and min. transmission	0.4947 and 0.1710
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5001 / 0 / 306

Goodness-of-fit on $F^2$	1.025
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0193, wR2 = 0.0489
R indices (all data)	R1 = 0.0217, wR2 = 0.0500
Largest diff. peak and hole	0.873 and -0.695 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthre.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Re(1)	10357(1)	6014(1)	1805(1)	22(1)
P(1)	7426(1)	3418(1)	1298(1)	17(1)
O(1)	11882(2)	6011(1)	1909(2)	36(1)
N(1)	7931(2)	4156(1)	578(2)	24(1)
C(1)	6217(2)	2955(2)	541(2)	18(1)
O(2)	9888(2)	6737(2)	871(2)	45(1)
C(2)	5052(2)	3265(2)	629(2)	19(1)
O(3)	9748(3)	6212(2)	3026(2)	68(1)
C(3)	4796(2)	4061(2)	1040(2)	24(1)
O(4)	9894(2)	5062(2)	1361(2)	53(1)
C(4)	3655(2)	4338(2)	1069(2)	28(1)
C(5)	2688(3)	3846(2)	697(3)	30(1)
C(6)	2893(2)	3088(2)	287(2)	27(1)
C(7)	4072(2)	2783(2)	224(2)	20(1)
C(8)	4287(2)	2028(2)	-253(2)	21(1)
C(9)	5428(2)	1768(2)	-472(2)	20(1)
C(10)	5620(3)	1047(2)	-1093(2)	25(1)
C(11)	6714(3)	852(2)	-1424(2)	28(1)

C(12)	7693(2)	1370(2)	-1141(2)	25(1)
C(13)	7561(2)	2034(2)	-489(2)	21(1)
C(14)	6422(2)	2257(2)	-109(2)	18(1)
C(15)	8533(2)	2673(2)	1717(2)	19(1)
C(16)	9724(2)	2859(2)	1630(2)	24(1)
C(17)	10579(2)	2315(2)	2040(2)	28(1)
C(18)	10247(3)	1602(2)	2532(2)	31(1)
C(19)	9057(3)	1419(2)	2630(2)	32(1)
C(20)	8197(2)	1949(2)	2220(2)	26(1)
C(21)	6981(2)	3826(2)	2585(2)	20(1)
C(22)	7481(2)	4560(2)	2961(2)	25(1)
C(23)	7224(3)	4848(2)	3987(2)	33(1)
C(24)	6472(3)	4414(2)	4641(2)	34(1)
C(25)	5976(3)	3684(2)	4265(2)	30(1)
C(26)	6231(2)	3385(2)	3241(2)	24(1)

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Table 3. Bond lengths [Å] and angles [deg] for laanthre.

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Re(1)-O(3)	1.703(3)
Re(1)-O(2)	1.716(2)
Re(1)-O(1)	1.724(2)
Re(1)-O(4)	1.728(2)
P(1)-N(1)	1.616(2)
P(1)-C(1)	1.788(2)
P(1)-C(21)	1.803(3)
P(1)-C(15)	1.808(2)
C(1)-C(14)	1.419(3)
C(1)-C(2)	1.420(3)
C(2)-C(3)	1.433(4)
C(2)-C(7)	1.433(3)
C(3)-C(4)	1.369(4)
C(4)-C(5)	1.419(4)
C(5)-C(6)	1.363(4)
C(6)-C(7)	1.429(4)
C(7)-C(8)	1.395(4)
C(8)-C(9)	1.394(4)
C(9)-C(10)	1.428(4)
C(9)-C(14)	1.436(3)
C(10)-C(11)	1.355(4)
C(11)-C(12)	1.426(4)
C(12)-C(13)	1.362(4)
C(13)-C(14)	1.433(3)
C(15)-C(16)	1.389(3)

C(15)-C(20)	1.398(4)
C(16)-C(17)	1.394(4)
C(17)-C(18)	1.374(4)
C(18)-C(19)	1.388(4)
C(19)-C(20)	1.382(4)
C(21)-C(26)	1.393(4)
C(21)-C(22)	1.399(4)
C(22)-C(23)	1.385(4)
C(23)-C(24)	1.389(5)
C(24)-C(25)	1.392(5)
C(25)-C(26)	1.387(4)
O(3)-Re(1)-O(2)	109.16(15)
O(3)-Re(1)-O(1)	112.04(13)
O(2)-Re(1)-O(1)	109.34(11)
O(3)-Re(1)-O(4)	108.78(16)
O(2)-Re(1)-O(4)	109.43(13)
O(1)-Re(1)-O(4)	108.05(11)
N(1)-P(1)-C(1)	108.35(13)
N(1)-P(1)-C(21)	108.46(13)
C(1)-P(1)-C(21)	112.09(12)
N(1)-P(1)-C(15)	113.91(12)
C(1)-P(1)-C(15)	111.46(11)
C(21)-P(1)-C(15)	102.52(11)
C(14)-C(1)-C(2)	120.3(2)
C(14)-C(1)-P(1)	119.63(18)
C(2)-C(1)-P(1)	120.01(18)
C(1)-C(2)-C(3)	123.7(2)
C(1)-C(2)-C(7)	118.8(2)

C(3)-C(2)-C(7)	117.4(2)
C(4)-C(3)-C(2)	121.0(2)
C(3)-C(4)-C(5)	121.1(3)
C(6)-C(5)-C(4)	119.7(3)
C(5)-C(6)-C(7)	120.9(3)
C(8)-C(7)-C(6)	120.9(2)
C(8)-C(7)-C(2)	119.3(2)
C(6)-C(7)-C(2)	119.8(2)
C(9)-C(8)-C(7)	122.0(2)
C(8)-C(9)-C(10)	121.1(2)
C(8)-C(9)-C(14)	119.3(2)
C(10)-C(9)-C(14)	119.5(2)
C(11)-C(10)-C(9)	121.0(2)
C(10)-C(11)-C(12)	119.7(2)
C(13)-C(12)-C(11)	121.0(3)
C(12)-C(13)-C(14)	121.0(2)
C(1)-C(14)-C(13)	123.9(2)
C(1)-C(14)-C(9)	118.7(2)
C(13)-C(14)-C(9)	117.4(2)
C(16)-C(15)-C(20)	120.1(2)
C(16)-C(15)-P(1)	119.5(2)
C(20)-C(15)-P(1)	120.12(19)
C(15)-C(16)-C(17)	119.4(3)
C(18)-C(17)-C(16)	120.3(3)
C(17)-C(18)-C(19)	120.3(3)
C(20)-C(19)-C(18)	120.1(3)
C(19)-C(20)-C(15)	119.6(3)
C(26)-C(21)-C(22)	120.2(2)
C(26)-C(21)-P(1)	120.7(2)

C(22)-C(21)-P(1)	118.9(2)
C(23)-C(22)-C(21)	119.7(3)
C(22)-C(23)-C(24)	120.3(3)
C(23)-C(24)-C(25)	119.9(3)
C(26)-C(25)-C(24)	120.4(3)
C(25)-C(26)-C(21)	119.5(3)

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Symmetry transformations used to generate equivalent atoms:



Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthre.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$$

	U11	U22	U33	U23	U13	U12
Re(1)	18(1)	25(1)	23(1)	-2(1)	1(1)	-1(1)
P(1)	15(1)	16(1)	18(1)	-1(1)	-3(1)	-1(1)
O(1)	20(1)	39(1)	49(1)	6(1)	-3(1)	-4(1)
N(1)	25(1)	24(1)	21(1)	3(1)	-2(1)	-7(1)
C(1)	16(1)	19(1)	18(1)	2(1)	-3(1)	-2(1)
O(2)	38(1)	44(1)	53(1)	16(1)	-1(1)	11(1)
C(2)	19(1)	22(1)	18(1)	3(1)	-2(1)	0(1)
O(3)	52(2)	121(3)	32(1)	-15(2)	10(1)	11(2)
C(3)	22(1)	21(1)	27(1)	0(1)	-6(1)	1(1)
O(4)	43(1)	35(1)	81(2)	-9(1)	-10(1)	-14(1)
C(4)	27(1)	26(1)	31(1)	-2(1)	-3(1)	5(1)
C(5)	18(1)	35(2)	36(2)	1(1)	-1(1)	5(1)
C(6)	17(1)	35(2)	29(1)	0(1)	-1(1)	-4(1)
C(7)	16(1)	25(1)	20(1)	1(1)	-1(1)	-2(1)
C(8)	19(1)	25(1)	20(1)	1(1)	-4(1)	-6(1)
C(9)	21(1)	22(1)	16(1)	1(1)	-3(1)	-4(1)
C(10)	27(1)	25(1)	24(1)	-5(1)	-6(1)	-4(1)

C(11)	30(2)	25(1)	27(1)	-8(1)	-5(1)	2(1)
C(12)	21(1)	30(1)	24(1)	-3(1)	0(1)	3(1)
C(13)	19(1)	24(1)	19(1)	0(1)	-3(1)	0(1)
C(14)	18(1)	19(1)	16(1)	3(1)	-3(1)	-1(1)
C(15)	19(1)	19(1)	18(1)	-3(1)	-4(1)	0(1)
C(16)	19(1)	29(1)	23(1)	-1(1)	-2(1)	0(1)
C(17)	19(1)	40(2)	25(1)	-3(1)	-3(1)	4(1)
C(18)	31(2)	30(2)	31(2)	-5(1)	-9(1)	12(1)
C(19)	37(2)	20(1)	38(2)	2(1)	-7(1)	3(1)
C(20)	22(1)	22(1)	33(1)	-1(1)	-4(1)	-2(1)
C(21)	17(1)	20(1)	21(1)	0(1)	-5(1)	4(1)
C(22)	27(1)	21(1)	26(1)	-2(1)	-4(1)	1(1)
C(23)	41(2)	28(1)	29(1)	-8(1)	-5(1)	4(1)
C(24)	39(2)	41(2)	24(1)	-7(1)	-1(1)	13(1)
C(25)	24(1)	40(2)	26(1)	5(1)	3(1)	7(1)
C(26)	21(1)	26(1)	26(1)	2(1)	-3(1)	0(1)

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Table 5. Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthre.

	x	y	z	U(eq)
H(3)	5428	4402	1297	28
H(4)	3508	4869	1344	33
H(5)	1901	4044	732	36
H(6)	2244	2759	41	32
H(8)	3637	1680	-435	26
H(10)	4971	699	-1279	30
H(11)	6828	373	-1842	33
H(12)	8449	1249	-1411	30
H(13)	8233	2355	-284	25
H(16)	9954	3353	1293	28
H(17)	11395	2437	1979	34
H(18)	10834	1233	2807	37
H(19)	8833	929	2980	38
H(20)	7383	1821	2280	31
H(22)	7994	4859	2513	29
H(23)	7564	5346	4245	40
H(24)	6296	4614	5344	41
H(25)	5458	3388	4712	36
H(26)	5898	2885	2990	29
H(2N)	7830(30)	4140(20)	0(30)	27(10)
H(1N)	8540(30)	4440(20)	790(30)	43(10)

Table 6. Torsion angles [deg] for laanthre.

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N(1)-P(1)-C(1)-C(14)	95.1(2)
C(21)-P(1)-C(1)-C(14)	-145.28(19)
C(15)-P(1)-C(1)-C(14)	-31.0(2)
N(1)-P(1)-C(1)-C(2)	-87.5(2)
C(21)-P(1)-C(1)-C(2)	32.1(2)
C(15)-P(1)-C(1)-C(2)	146.41(19)
C(14)-C(1)-C(2)-C(3)	-164.5(2)
P(1)-C(1)-C(2)-C(3)	18.1(3)
C(14)-C(1)-C(2)-C(7)	11.5(3)
P(1)-C(1)-C(2)-C(7)	-165.88(18)
C(1)-C(2)-C(3)-C(4)	177.7(2)
C(7)-C(2)-C(3)-C(4)	1.6(4)
C(2)-C(3)-C(4)-C(5)	0.2(4)
C(3)-C(4)-C(5)-C(6)	-0.9(4)
C(4)-C(5)-C(6)-C(7)	-0.3(4)
C(5)-C(6)-C(7)-C(8)	-176.2(3)
C(5)-C(6)-C(7)-C(2)	2.1(4)
C(1)-C(2)-C(7)-C(8)	-0.7(3)
C(3)-C(2)-C(7)-C(8)	175.6(2)
C(1)-C(2)-C(7)-C(6)	-179.0(2)
C(3)-C(2)-C(7)-C(6)	-2.7(4)
C(6)-C(7)-C(8)-C(9)	170.4(2)
C(2)-C(7)-C(8)-C(9)	-8.0(4)
C(7)-C(8)-C(9)-C(10)	-171.3(2)
C(7)-C(8)-C(9)-C(14)	5.7(4)

C(8)-C(9)-C(10)-C(11)	171.5(3)
C(14)-C(9)-C(10)-C(11)	-5.5(4)
C(9)-C(10)-C(11)-C(12)	0.5(4)
C(10)-C(11)-C(12)-C(13)	3.8(4)
C(11)-C(12)-C(13)-C(14)	-3.0(4)
C(2)-C(1)-C(14)-C(13)	162.1(2)
P(1)-C(1)-C(14)-C(13)	-20.5(3)
C(2)-C(1)-C(14)-C(9)	-13.8(3)
P(1)-C(1)-C(14)-C(9)	163.63(18)
C(12)-C(13)-C(14)-C(1)	-177.9(2)
C(12)-C(13)-C(14)-C(9)	-2.0(4)
C(8)-C(9)-C(14)-C(1)	5.3(3)
C(10)-C(9)-C(14)-C(1)	-177.7(2)
C(8)-C(9)-C(14)-C(13)	-170.9(2)
C(10)-C(9)-C(14)-C(13)	6.1(3)
N(1)-P(1)-C(15)-C(16)	14.4(2)
C(1)-P(1)-C(15)-C(16)	137.3(2)
C(21)-P(1)-C(15)-C(16)	-102.6(2)
N(1)-P(1)-C(15)-C(20)	-171.6(2)
C(1)-P(1)-C(15)-C(20)	-48.7(2)
C(21)-P(1)-C(15)-C(20)	71.4(2)
C(20)-C(15)-C(16)-C(17)	0.5(4)
P(1)-C(15)-C(16)-C(17)	174.5(2)
C(15)-C(16)-C(17)-C(18)	-0.4(4)
C(16)-C(17)-C(18)-C(19)	-0.3(4)
C(17)-C(18)-C(19)-C(20)	0.8(4)
C(18)-C(19)-C(20)-C(15)	-0.7(4)
C(16)-C(15)-C(20)-C(19)	0.0(4)
P(1)-C(15)-C(20)-C(19)	-173.9(2)

N(1)-P(1)-C(21)-C(26)	162.6(2)
C(1)-P(1)-C(21)-C(26)	43.0(2)
C(15)-P(1)-C(21)-C(26)	-76.7(2)
N(1)-P(1)-C(21)-C(22)	-22.9(2)
C(1)-P(1)-C(21)-C(22)	-142.4(2)
C(15)-P(1)-C(21)-C(22)	97.9(2)
C(26)-C(21)-C(22)-C(23)	-0.2(4)
P(1)-C(21)-C(22)-C(23)	-174.8(2)
C(21)-C(22)-C(23)-C(24)	-0.2(4)
C(22)-C(23)-C(24)-C(25)	0.1(4)
C(23)-C(24)-C(25)-C(26)	0.3(4)
C(24)-C(25)-C(26)-C(21)	-0.6(4)
C(22)-C(21)-C(26)-C(25)	0.6(4)
P(1)-C(21)-C(26)-C(25)	175.1(2)

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Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for laanthre.

Hydrogen bonds with  $H \cdots A < r(A) + 3.200$  Angstroms and  $\angle DHA > 110$  deg.

D-H	d(D-H)	d(H...A)	$\angle DHA$	d(D...A)	A
N1-H2N	0.710	2.388	163.02	3.074	O1 [ -x+2, -y+1, -z ]
N1-H1N	0.855	1.953	176.24	2.806	O4

# Crystal data and structure refinement for [(9anthracenyl)Ph<sub>2</sub>P=NH<sub>2</sub><sup>+</sup>][TcO<sub>4</sub><sup>-</sup>] (4)

Table 1. Crystal data and structure refinement for laanthtc.

Identification code	laanthtc
Empirical formula	C <sub>26</sub> H <sub>21</sub> N O <sub>4</sub> P Tc
Formula weight	540.41
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2 <sub>1</sub> /n
Unit cell dimensions deg. 92.16 deg. deg.	a = 11.2876(3) Å    alpha = 90 b = 16.3619(4) Å    beta = c = 12.2203(3) Å    gamma = 90
Volume	2255.32(10) Å <sup>3</sup>
Z, Calculated density	4, 1.592 Mg/m <sup>3</sup>
Absorption coefficient	0.743 mm <sup>-1</sup>
F(000)	1096
Crystal size	0.55 x 0.50 x 0.50 mm
Theta range for data collection	2.08 to 27.12 deg.
Limiting indices 15<=l<=15	-13<=h<=14, -20<=k<=20, -
Reflections collected / unique	15944 / 4979 [R(int) = 0.0179]
Completeness to theta = 27.12	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.71 and 0.58
Refinement method F <sup>2</sup>	Full-matrix least-squares on
Data / restraints / parameters	4979 / 0 / 306
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0266, wR <sub>2</sub> = 0.0736

R indices (all data)	$R1 = 0.0292, wR2 = 0.0754$
Largest diff. peak and hole	1.026 and -0.425 e.Å <sup>-3</sup>



Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthtc.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Tc(1)	10349(1)	6015(1)	1817(1)	24(1)
P(1)	7443(1)	3417(1)	1288(1)	19(1)
O(1)	11863(1)	6031(1)	1920(2)	39(1)
N(1)	7950(2)	4159(1)	562(2)	26(1)
C(1)	6233(2)	2953(1)	534(1)	20(1)
O(2)	9872(2)	6730(1)	887(2)	47(1)
C(2)	5070(2)	3267(1)	621(1)	21(1)
O(3)	9728(2)	6201(2)	3030(2)	67(1)
C(3)	4809(2)	4063(1)	1028(2)	26(1)
O(4)	9923(2)	5063(1)	1373(2)	51(1)
C(4)	3669(2)	4343(1)	1058(2)	30(1)
C(5)	2700(2)	3851(1)	685(2)	32(1)
C(6)	2905(2)	3092(1)	284(2)	29(1)
C(7)	4086(2)	2779(1)	220(1)	23(1)
C(8)	4299(2)	2020(1)	-256(1)	24(1)
C(9)	5442(2)	1761(1)	-477(1)	22(1)
C(10)	5636(2)	1038(1)	-1099(2)	27(1)
C(11)	6733(2)	842(1)	-1435(2)	30(1)
C(12)	7710(2)	1361(1)	-1156(2)	28(1)
C(13)	7577(2)	2028(1)	-506(1)	24(1)
C(14)	6442(2)	2251(1)	-118(1)	21(1)
C(15)	8547(2)	2672(1)	1712(1)	21(1)
C(16)	9747(2)	2859(1)	1620(2)	25(1)
C(17)	10597(2)	2313(1)	2032(2)	30(1)
C(18)	10265(2)	1600(1)	2530(2)	34(1)
C(19)	9072(2)	1414(1)	2627(2)	34(1)
C(20)	8209(2)	1947(1)	2214(2)	29(1)
C(21)	6994(2)	3827(1)	2579(1)	22(1)
C(22)	7496(2)	4562(1)	2952(2)	26(1)
C(23)	7233(2)	4850(1)	3985(2)	35(1)
C(24)	6478(2)	4416(1)	4636(2)	36(1)
C(25)	5982(2)	3686(1)	4265(2)	31(1)
C(26)	6239(2)	3386(1)	3235(2)	26(1)

Table 3. Bond lengths [Å] and angles [deg] for laanthtc.

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Tc(1)-O(3)	1.6907(18)
Tc(1)-O(2)	1.7041(16)
Tc(1)-O(1)	1.7091(15)
Tc(1)-O(4)	1.7126(16)
P(1)-N(1)	1.6207(17)
P(1)-C(1)	1.7890(17)
P(1)-C(21)	1.8037(19)
P(1)-C(15)	1.8053(18)
N(1)-H(2N)	0.80(3)
N(1)-H(1N)	0.76(3)
C(1)-C(2)	1.417(2)
C(1)-C(14)	1.422(2)
C(2)-C(3)	1.430(3)
C(2)-C(7)	1.438(2)
C(3)-C(4)	1.367(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.419(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.359(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.432(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.396(3)
C(8)-C(9)	1.394(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.427(3)
C(9)-C(14)	1.440(2)
C(10)-C(11)	1.357(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.423(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.362(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.429(2)
C(13)-H(13)	0.9500
C(15)-C(20)	1.395(3)
C(15)-C(16)	1.398(2)
C(16)-C(17)	1.392(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.374(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.389(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.389(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(26)	1.393(3)
C(21)-C(22)	1.399(3)
C(22)-C(23)	1.390(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(3)
C(23)-H(23)	0.9500

C(24)-C(25)	1.388(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.391(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
O(3)-Tc(1)-O(2)	109.29(11)
O(3)-Tc(1)-O(1)	112.25(9)
O(2)-Tc(1)-O(1)	109.15(8)
O(3)-Tc(1)-O(4)	108.73(12)
O(2)-Tc(1)-O(4)	109.59(9)
O(1)-Tc(1)-O(4)	107.80(8)
N(1)-P(1)-C(1)	108.32(9)
N(1)-P(1)-C(21)	108.51(9)
C(1)-P(1)-C(21)	111.96(8)
N(1)-P(1)-C(15)	114.16(9)
C(1)-P(1)-C(15)	111.45(8)
C(21)-P(1)-C(15)	102.37(8)
P(1)-N(1)-H(2N)	114.2(19)
P(1)-N(1)-H(1N)	121.0(19)
H(2N)-N(1)-H(1N)	119(3)
C(2)-C(1)-C(14)	120.58(15)
C(2)-C(1)-P(1)	119.92(13)
C(14)-C(1)-P(1)	119.46(13)
C(1)-C(2)-C(3)	124.08(16)
C(1)-C(2)-C(7)	118.61(16)
C(3)-C(2)-C(7)	117.22(16)
C(4)-C(3)-C(2)	121.37(18)
C(4)-C(3)-H(3)	119.3
C(2)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	121.11(19)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(6)-C(5)-C(4)	119.66(19)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(5)-C(6)-C(7)	121.15(18)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	121.03(16)
C(8)-C(7)-C(2)	119.48(16)
C(6)-C(7)-C(2)	119.45(17)
C(9)-C(8)-C(7)	121.79(16)
C(9)-C(8)-H(8)	119.1
C(7)-C(8)-H(8)	119.1
C(8)-C(9)-C(10)	121.15(17)
C(8)-C(9)-C(14)	119.48(17)
C(10)-C(9)-C(14)	119.30(17)
C(11)-C(10)-C(9)	121.15(18)
C(11)-C(10)-H(10)	119.4
C(9)-C(10)-H(10)	119.4
C(10)-C(11)-C(12)	119.58(18)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(13)-C(12)-C(11)	121.09(18)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5

C(12)-C(13)-C(14)	121.17(17)
C(12)-C(13)-H(13)	119.4
C(14)-C(13)-H(13)	119.4
C(1)-C(14)-C(13)	124.13(16)
C(1)-C(14)-C(9)	118.39(16)
C(13)-C(14)-C(9)	117.34(16)
C(20)-C(15)-C(16)	120.22(17)
C(20)-C(15)-P(1)	120.24(14)
C(16)-C(15)-P(1)	119.29(14)
C(17)-C(16)-C(15)	119.19(18)
C(17)-C(16)-H(16)	120.4
C(15)-C(16)-H(16)	120.4
C(18)-C(17)-C(16)	120.60(19)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(17)-C(18)-C(19)	120.34(18)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
C(20)-C(19)-C(18)	120.04(19)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(15)	119.61(18)
C(19)-C(20)-H(20)	120.2
C(15)-C(20)-H(20)	120.2
C(26)-C(21)-C(22)	120.38(17)
C(26)-C(21)-P(1)	120.63(14)
C(22)-C(21)-P(1)	118.77(15)
C(23)-C(22)-C(21)	119.40(19)
C(23)-C(22)-H(22)	120.3
C(21)-C(22)-H(22)	120.3
C(24)-C(23)-C(22)	120.31(19)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	120.25(19)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	120.22(19)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	119.44(19)
C(25)-C(26)-H(26)	120.3
C(21)-C(26)-H(26)	120.3

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthtc.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [ h^2 a^{*2} U11 + \dots + 2 h k a^* b^* U12 ]$$

	U11	U22	U33	U23	U13	U12
Tc(1)	20(1)	27(1)	25(1)	-2(1)	1(1)	-1(1)
P(1)	17(1)	19(1)	20(1)	-1(1)	-3(1)	-2(1)
O(1)	23(1)	41(1)	51(1)	5(1)	-4(1)	-3(1)
N(1)	26(1)	25(1)	25(1)	2(1)	-3(1)	-7(1)
C(1)	18(1)	21(1)	21(1)	1(1)	-4(1)	-1(1)
O(2)	41(1)	45(1)	54(1)	14(1)	-2(1)	12(1)
C(2)	20(1)	24(1)	20(1)	2(1)	-3(1)	-1(1)
O(3)	54(1)	117(2)	32(1)	-15(1)	11(1)	11(1)
C(3)	25(1)	24(1)	28(1)	1(1)	-6(1)	1(1)
O(4)	42(1)	35(1)	75(1)	-8(1)	-8(1)	-12(1)
C(4)	28(1)	27(1)	34(1)	-1(1)	-3(1)	6(1)
C(5)	20(1)	38(1)	38(1)	1(1)	-1(1)	5(1)
C(6)	18(1)	36(1)	31(1)	-1(1)	-2(1)	-3(1)
C(7)	19(1)	29(1)	21(1)	2(1)	-2(1)	-3(1)
C(8)	21(1)	28(1)	23(1)	0(1)	-4(1)	-6(1)
C(9)	23(1)	24(1)	18(1)	1(1)	-4(1)	-2(1)
C(10)	29(1)	26(1)	26(1)	-4(1)	-6(1)	-4(1)
C(11)	33(1)	29(1)	28(1)	-8(1)	-6(1)	3(1)
C(12)	25(1)	33(1)	25(1)	-3(1)	-1(1)	3(1)
C(13)	21(1)	28(1)	23(1)	0(1)	-3(1)	-2(1)
C(14)	22(1)	22(1)	17(1)	2(1)	-2(1)	-2(1)
C(15)	20(1)	22(1)	21(1)	-4(1)	-4(1)	2(1)
C(16)	23(1)	30(1)	23(1)	-2(1)	-2(1)	-1(1)
C(17)	20(1)	42(1)	28(1)	-3(1)	-3(1)	6(1)
C(18)	34(1)	33(1)	35(1)	-6(1)	-11(1)	12(1)
C(19)	38(1)	23(1)	40(1)	2(1)	-8(1)	1(1)
C(20)	25(1)	24(1)	36(1)	1(1)	-5(1)	-2(1)
C(21)	19(1)	23(1)	22(1)	-1(1)	-4(1)	3(1)
C(22)	28(1)	22(1)	28(1)	-1(1)	-3(1)	1(1)
C(23)	43(1)	29(1)	32(1)	-7(1)	-5(1)	4(1)
C(24)	41(1)	43(1)	25(1)	-7(1)	0(1)	13(1)
C(25)	25(1)	42(1)	27(1)	5(1)	2(1)	5(1)
C(26)	24(1)	28(1)	27(1)	1(1)	-2(1)	0(1)

Table 5. Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for laanthtc.

	x	y	z	U(eq)
H(3)	5440	4405	1284	31
H(4)	3523	4875	1333	36
H(5)	1913	4052	715	39
H(6)	2254	2762	41	34
H(8)	3647	1671	-434	29
H(10)	4987	688	-1281	33
H(11)	6848	361	-1852	36
H(12)	8468	1241	-1429	33
H(13)	8250	2352	-306	29
H(16)	9980	3353	1281	30
H(17)	11415	2434	1969	37
H(18)	10853	1232	2809	41
H(19)	8848	922	2976	41
H(20)	7393	1819	2274	34
H(22)	8011	4861	2504	32
H(23)	7574	5348	4246	42
H(24)	6298	4619	5339	44
H(25)	5466	3389	4716	38
H(26)	5903	2885	2982	32
H(2N)	7840(20)	4103(15)	-80(20)	38(7)
H(1N)	8470(20)	4422(16)	780(20)	33(7)

Table 6. Torsion angles [deg] for laanthtc.

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N(1)-P(1)-C(1)-C(2)	-87.18(16)
C(21)-P(1)-C(1)-C(2)	32.43(17)
C(15)-P(1)-C(1)-C(2)	146.42(14)
N(1)-P(1)-C(1)-C(14)	95.13(15)
C(21)-P(1)-C(1)-C(14)	-145.26(14)
C(15)-P(1)-C(1)-C(14)	-31.27(16)
C(14)-C(1)-C(2)-C(3)	-164.39(17)
P(1)-C(1)-C(2)-C(3)	17.9(2)
C(14)-C(1)-C(2)-C(7)	12.0(2)
P(1)-C(1)-C(2)-C(7)	-165.69(13)
C(1)-C(2)-C(3)-C(4)	177.76(18)
C(7)-C(2)-C(3)-C(4)	1.4(3)
C(2)-C(3)-C(4)-C(5)	0.0(3)
C(3)-C(4)-C(5)-C(6)	-0.5(3)
C(4)-C(5)-C(6)-C(7)	-0.6(3)
C(5)-C(6)-C(7)-C(8)	-175.89(19)
C(5)-C(6)-C(7)-C(2)	2.0(3)
C(1)-C(2)-C(7)-C(8)	-1.0(2)
C(3)-C(2)-C(7)-C(8)	175.60(16)
C(1)-C(2)-C(7)-C(6)	-178.95(17)
C(3)-C(2)-C(7)-C(6)	-2.3(3)
C(6)-C(7)-C(8)-C(9)	170.01(17)
C(2)-C(7)-C(8)-C(9)	-7.9(3)
C(7)-C(8)-C(9)-C(10)	-171.21(17)
C(7)-C(8)-C(9)-C(14)	5.8(3)
C(8)-C(9)-C(10)-C(11)	171.43(19)
C(14)-C(9)-C(10)-C(11)	-5.6(3)
C(9)-C(10)-C(11)-C(12)	0.4(3)
C(10)-C(11)-C(12)-C(13)	3.8(3)
C(11)-C(12)-C(13)-C(14)	-2.7(3)
C(2)-C(1)-C(14)-C(13)	161.44(17)
P(1)-C(1)-C(14)-C(13)	-20.9(2)
C(2)-C(1)-C(14)-C(9)	-14.0(2)
P(1)-C(1)-C(14)-C(9)	163.66(13)
C(12)-C(13)-C(14)-C(1)	-177.89(17)
C(12)-C(13)-C(14)-C(9)	-2.4(3)
C(8)-C(9)-C(14)-C(1)	5.1(2)
C(10)-C(9)-C(14)-C(1)	-177.81(16)
C(8)-C(9)-C(14)-C(13)	-170.63(16)
C(10)-C(9)-C(14)-C(13)	6.4(2)
N(1)-P(1)-C(15)-C(20)	-171.46(15)
C(1)-P(1)-C(15)-C(20)	-48.33(17)
C(21)-P(1)-C(15)-C(20)	71.50(16)
N(1)-P(1)-C(15)-C(16)	14.23(17)
C(1)-P(1)-C(15)-C(16)	137.35(14)
C(21)-P(1)-C(15)-C(16)	-102.81(15)
C(20)-C(15)-C(16)-C(17)	0.3(3)
P(1)-C(15)-C(16)-C(17)	174.59(14)
C(15)-C(16)-C(17)-C(18)	-0.4(3)
C(16)-C(17)-C(18)-C(19)	0.1(3)
C(17)-C(18)-C(19)-C(20)	0.4(3)
C(18)-C(19)-C(20)-C(15)	-0.5(3)

C(16)-C(15)-C(20)-C(19)	0.2(3)
P(1)-C(15)-C(20)-C(19)	-174.04(15)
N(1)-P(1)-C(21)-C(26)	162.31(15)
C(1)-P(1)-C(21)-C(26)	42.81(17)
C(15)-P(1)-C(21)-C(26)	-76.67(16)
N(1)-P(1)-C(21)-C(22)	-23.09(17)
C(1)-P(1)-C(21)-C(22)	-142.58(14)
C(15)-P(1)-C(21)-C(22)	97.93(15)
C(26)-C(21)-C(22)-C(23)	-0.1(3)
P(1)-C(21)-C(22)-C(23)	-174.70(15)
C(21)-C(22)-C(23)-C(24)	-0.3(3)
C(22)-C(23)-C(24)-C(25)	0.5(3)
C(23)-C(24)-C(25)-C(26)	-0.2(3)
C(24)-C(25)-C(26)-C(21)	-0.2(3)
C(22)-C(21)-C(26)-C(25)	0.4(3)
P(1)-C(21)-C(26)-C(25)	174.88(14)

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Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for laanthtc.

Hydrogen bonds with  $H \cdots A < r(A) + 3.200$  Angstroms and  $\angle DHA > 110$  deg.

D-H	d(D-H)	d(H...A)	$\angle DHA$	d(D...A)	A
N1-H2N	0.800	2.291	162.65	3.064	O1 [ -x+2, -y+1, -z ]
N1-H1N	0.764	2.058	176.32	2.821	O4



## **APPENDIX 2: RADIOCHEMICAL COUNTING DATA**

## SECTION 1: OPTIMIZATION OF SOLVENT EXTRACTION

**Table 1: Solvent Extraction Optimization Data for Vortex Time with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

	organic cpm	aqueous cpm	% in organic phase	organic phase	phosphinimine	aqueous phase	vortex time
1	170	5699	2.90	toluene	0.34 mg/mL	1 mM NaCl	30 s
2	155	6377	2.37	toluene	0.34 mg/mL	1 mM NaCl	1 min
3	191	5928	3.12	toluene	0.34 mg/mL	1 mM NaCl	2 min
4	1297	3974	24.61	$\text{CHCl}_3$	0.34 mg/mL	1 mM NaCl	30 s
5	3085	7132	30.19	$\text{CHCl}_3$	0.34 mg/mL	1 mM NaCl	1 min
6	2899	5946	32.78	$\text{CHCl}_3$	0.34 mg/mL	1 mM NaCl	2 min

**Table 2: Solvent Extraction Optimization Data for Phosphinimine Concentration with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

	organic counts	phase minutes	cpm	aqueous counts	phase minutes	cpm	% in organic phase	organic phase	phosphinimine	aqueous phase	vortex Time
1	15406	2	7703.0	19658	1	19658	28.15	toluene	0.34 mg/mL	1 mM HCl	30s
2	11129	4	2782.3	25403	2	12701.5	17.97	toluene	0.34 mg/mL	1 mM HCl	2 min
3	13914	1	13914	17287	2	8643.5	61.68	$\text{CHCl}_3$	0.34 mg/mL	1 mM HCl	30 s
4	17794	1	17794	14828	2	7414.0	70.59	$\text{CHCl}_3$	0.34 mg/mL	1 mM HCl	2 min
5	224	1	224	29140	1	29140	0.76	toluene	1 mg/mL	1 mM NaCl	2 min
6	16851	4	4212.75	23684	1	23684	15.10	toluene	1 mg/mL	1 mM HCl	2 min
7	8462	1	8462	9064	1	9064	48.28	$\text{CHCl}_3$	1 mg/mL	1 mM NaCl	2 min
8	15100	1	15100	12756	1	12756	54.21	$\text{CHCl}_3$	1 mg/mL	1 mM HCl	2 min
9	564	1	564	25465	1	25465	2.17	toluene	5 mg/mL	1 mM NaCl	2 min
10	2173	1	2173	13704	1	13704	13.69	toluene	5 mg/mL	1 mM HCl	2 min
11	129671	1	129671	19812	1	19812	86.75	$\text{CHCl}_3$	5 mg/mL	1 mM NaCl	2 min
12	8880	1	8880	6521	1	6521	57.66	$\text{CHCl}_3$	5 mg/mL	1 mM HCl	2 min
13	517	1	517	18679	1	18679	2.69	toluene	10 mg/mL	1 mM NaCl	2 min
14	2360	1	2360	28522	1	28522	7.64	toluene	10 mg/mL	1 mM HCl	2 min
15	13640	1	13640	17924	1	17924	43.21	$\text{CHCl}_3$	10 mg/mL	1 mM NaCl	2 min
16	13924	1	13924	31487	1	31487	30.66	$\text{CHCl}_3$	10 mg/mL	1 mM HCl	2 min

**Table 3: Solvent Extraction Optimization Data for Aqueous Volume with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

	organic cpm	Aqueous Cpm	% in organic phase	organic phase	phosphinimine mg/mL	organic mL used	aqueous phase	aqueous mL used	$\mu\text{L}$ counted
1	26356	51330	33.93	$\text{CHCl}_3$	10	1	0.15 M NaCl	1	250
2	9149	14473	38.73	$\text{CHCl}_3$	10	5	0.15 M NaCl	2.5	250
3	13816	11076	55.50	$\text{CHCl}_3$	10	5	0.15 M NaCl	1	250
4	12783	17794	41.81	$\text{CHCl}_3$	10	5	0.15 M NaCl	0.5	250
5	3317	4536	42.24	$\text{CHCl}_3$	10	5	0.15 M NaCl	0.1	50
6	555	88261	0.62	toluene	10	1	0.15 M NaCl	1	250
7	482	36751	1.29	toluene	10	5	0.15 M NaCl	2.5	250
8	1275	77781	1.61	toluene	10	5	0.15 M NaCl	1	250

**Table 4: Second Solvent Extraction Optimization Data for Concentration after Optimization of Aqueous Volume with  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

	organic cpm	Aqueous Cpm	% in organic phase	Organic Phase	phosphinimines mg/mL	organic mL used	aqueous phase	aqueous mL used	$\mu\text{L}$ counted
1	38350	1907	95.26	$\text{CHCl}_3$	10	1	0.15 M HCl	1	225
2	8980	189	97.94	$\text{CHCl}_3$	10	5	0.15 M HCl	2.5	225
3	13055	174	98.68	$\text{CHCl}_3$	10	5	0.15 M HCl	1	225
4	13209	260	98.07	$\text{CHCl}_3$	10	5	0.15 M HCl	0.5	225
5	4455	363	92.47	$\text{CHCl}_3$	10	5	0.15 M HCl	0.1	75
6	5870	18685	23.91	$\text{CHCl}_3$	0.34	5	0.15 M NaCl	1	225
7	7921	16582	32.33	$\text{CHCl}_3$	1	5	0.15 M NaCl	1	225
8	8140	8954	47.62	$\text{CHCl}_3$	5	5	0.15 M NaCl	1	225
9	6913	7491	47.99	$\text{CHCl}_3$	10	5	0.15 M NaCl	1	225
10	3794	1852	67.20	$\text{CHCl}_3$	0.34	5	0.15 M HCl	1	225
11	7573	3353	69.31	$\text{CHCl}_3$	1	5	0.15 M HCl	1	225
12	8475	185	97.86	$\text{CHCl}_3$	5	5	0.15 M HCl	1	225
13	9600	166	98.30	$\text{CHCl}_3$	10	5	0.15 M HCl	1	225

## SECTION 2: SOLVENT EXTRACTION EXPERIMENTS

**Table 5: Solvent Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample	organic counts	phase minutes	cpm	aqueous counts	phase minutes	cpm	% in organic phase	standard deviation	average % in organic	phosphorim ine mg/mL	organic mL used	organic phase	aqueous mL used	aqueous phase	Aqueous μL counted
1B	14861	2	7430.5	599	2	299.5	96.125	0.819	95.817	3	5	$\text{CHCl}_3$	1	0.15 M HCl	500
1C	17104	2	8552	632	2	316	96.437			3	5	$\text{CHCl}_3$	1	0.15 M HCl	375
1D	11251	2	5625.5	606	2	303	94.889			3	5	$\text{CHCl}_3$	1	0.15 M HCl	225
2B	20443	2	10221.5	483	2	241.5	97.692	0.938	98.536	4	5	$\text{CHCl}_3$	1	0.15 M HCl	500
2C	27122	2	13561	449	2	224.5	98.371			4	5	$\text{CHCl}_3$	1	0.15 M HCl	375
2D	12224	2	61121	558	2	279	99.546			4	5	$\text{CHCl}_3$	1	0.15 M HCl	225
3A	10762	2	5381	472	2	236	95.798			5	5	$\text{CHCl}_3$	1	0.15 M HCl	225
3B	13869	2	6934.5	422	2	211	97.047	1.092	96.757	5	5	$\text{CHCl}_3$	1	0.15 M HCl	500
3C	25453	2	12726.5	473	2	236.5	98.176			5	5	$\text{CHCl}_3$	1	0.15 M HCl	375
3D	11349	2	5674.5	472	2	236	96.007			5	5	$\text{CHCl}_3$	1	0.15 M HCl	225
4A	13366	2	6683	607	2	303.5	95.656	0.602	96.167	5	5	$\text{CHCl}_3$	1	0.2 M HCl	225
4B	17513	2	8756.5	608	2	304	96.645			5	5	$\text{CHCl}_3$	1	0.2 M HCl	500
4C	10975	1	10975	371	1	371	96.730			5	5	$\text{CHCl}_3$	1	0.2 M HCl	375
4D	11662	2	5831	532	2	266	95.637			5	5	$\text{CHCl}_3$	1	0.2 M HCl	225
5A	13067	2	6533.5	1428	2	714	90.148	5.864	90.190	5	5	$\text{CHCl}_3$	1	0.4697 M HCl	225
5B	15654	2	7827	2477	2	1238.5	86.338			5	5	$\text{CHCl}_3$	1	0.4697 M HCl	500
5C	11296	1	11296	770	1	770	93.618			5	5	$\text{CHCl}_3$	1	0.4697 M HCl	375
5D	11050	2	5525	2267	2	1133.5	82.977			5	5	$\text{CHCl}_3$	1	0.4697 M HCl	225
5E	11152	2	5576	243	2	121.5	97.867			5	5	$\text{CHCl}_3$	1	0.4697 M HCl	225
6B	17003	2	8501.5	2283	2	1141.5	88.162	2.343	87.200	5	5	$\text{CHCl}_3$	1	1 M HCl	500
6C	10805	1	10805	1348	1	1348	88.908			5	5	$\text{CHCl}_3$	1	1 M HCl	375
6D	9922	2	4961	1816	2	908	84.529			5	5	$\text{CHCl}_3$	1	1 M HCl	225
7A	10144	2	5072	4260	2	2130	70.425	4.066	75.293	5	5	$\text{CHCl}_3$	1	2 M HCl	225

**Continuation of Table 5: Solvent Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample	organic counts	phase minutes	cpm	aqueous counts	phase minutes	cpm	% in organic phase	standard deviation	average % in organic	Phosphorimine mg/mL	organic mL used	organic phase	aqueous mL used	aqueous phase	Aqueous μL counted
7B	15265	2	7632.5	6430	2	3215	70.362			5	5	$\text{CHCl}_3$	1	2 M HCl	500
7C	9118	1	9118	2829	1	2829	76.320			5	5	$\text{CHCl}_3$	1	2 M HCl	375
7D	10387	2	5193.5	3294	2	1647	75.923			5	5	$\text{CHCl}_3$	1	2 M HCl	225
7E	10051	2	5025.5	2637	2	1318. 5	79.217			5	5	$\text{CHCl}_3$	1	2 M HCl	225
7F	9900	2	4950	2551	2	1275. 5	79.512			5	5	$\text{CHCl}_3$	1	2 M HCl	225
8B	15436	2	7718	3711	2	1855. 5	80.618	0.966	80.291	5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph2	500
8D	11185	2	5592.5	2615	2	1307. 5	81.051			5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph2	225
8E	9236	2	4618	2425	2	1212. 5	79.204			5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph2	225
9B	17296	0.17	103776	28541	0.17	17124 6	37.734	2.569	38.904	5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph4	500
9C	9369	1	9369	13018	1	13018	41.850			5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph4	375
9D	8161	2	4080.5	13819	2	6909. 5	37.129			5	5	$\text{CHCl}_3$	1	0.15 M NaCl ph4	225
1A	9327	2	4663.5	183	1	183	96.224			5	5	$\text{CHCl}_3$	1	0.15 M HCl	150
1B	13663	2	6831.5	174	1	174	97.516			5	5	$\text{CHCl}_3$	1	0.15 M HCl	150
1C	12072	2	6036	174	1	174	97.198	0.673	96.979	5	5	$\text{CHCl}_3$	1	0.15 M HCl	150
2A	13305	2	6652.5	456	1	456	93.585			5	5	$\text{CHCl}_3$	1	0.15 M HNO3	150
2B	12392	2	6196	459	1	459	93.103			5	5	$\text{CHCl}_3$	1	0.15 M HNO3	150
2C	12871	2	6435.5	473	1	473	93.153	0.265	93.280	5	5	$\text{CHCl}_3$	1	0.15 M HNO3	150
4A	13810	2	6905	170	1	170	97.597			5	5	$\text{CHCl}_3$	1	0.15 M H3PO4	150
4B	13470	2	6735	155	1	155	97.750			5	5	$\text{CHCl}_3$	1	0.15 M H3PO4	150
4C	13059	2	6529.5	176	1	176	97.375	0.189	97.574	5	5	$\text{CHCl}_3$	1	0.15 M H3PO4	150
5A	422	2	211	35849	1	35849	0.585			5	5	$\text{CHCl}_3$	1	0.15 M NaOH	150
5B	439	2	219.5	32411	1	32411	0.673			5	5	$\text{CHCl}_3$	1	0.15 M NaOH	150
5C	459	2	229.5	34691	1	34691	0.657	0.047	0.638	5	5	$\text{CHCl}_3$	1	0.15 M NaOH	150

Continuation of Table 5: Solvent Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$

sample	organic counts	phase minutes	cpm	aqueous counts	phase minutes	cpm	% in organic phase	standard deviation	average % in organic	Phosphorimine mg/mL	organic mL used	organic phase	aqueous mL used	aqueous phase	Aqueous μL counted
1A	14010	1	14010	578	1	578	96.038			5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	150
1B	17136	1	17136	415	1	415	97.635			5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	150
1C	17286	1	17286	466	1	466	97.375	0.857	97.016	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	150
2A	13471	1	13471	10290	1	10290	56.694			5	5	$\text{CHCl}_3$	1	0.15 M HI (w/l2)	150
2B	13741	1	13741	11170	1	11170	55.160			5	5	$\text{CHCl}_3$	1	0.15 M HI (w/l2)	150
2C	14387	1	14387	9372	1	9372	60.554	2.779	57.469	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/l2)	150

**Table 6: Solvent Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$  and  $^{186}\text{ReO}_4^-$**

sample	Tc-99m		Re-186							phosphinimine mg/mL	Organic mL used	organic phase	aqueous mL used	aqueous phase	$\mu\text{L}$ counted
	time (sec)	organic counts	aqueous counts	% in org phase	std deviation	average % in organic	organic counts	aqueous counts	% in org phase						
1A	120	15046	104	99.314			17593	124	99.300	5	5	$\text{CHCl}_3$	1	0.15 M HCl	225
1B	120	14794	91	99.389			17073	132	99.233	5	5	$\text{CHCl}_3$	1	0.15 M HCl	225
1C	120	14707	69	99.533	0.112	99.412	16915	110	99.354	5	5	$\text{CHCl}_3$	1	0.15 M HCl	225
2A	120	8496	474	94.716			25891	2285	91.890	5	5	$\text{CHCl}_3$	1	0.15 M $\text{HNO}_3$	225
2B	120	8696	419	95.403			26114	2337	91.786	5	5	$\text{CHCl}_3$	1	0.15 M $\text{HNO}_3$	225
2C	120	9934	356	96.540	0.921	95.553	30864	2067	93.723	5	5	$\text{CHCl}_3$	1	0.15 M $\text{HNO}_3$	225
3A	120	6744	56	99.176			20544	55	99.733	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_3\text{PO}_4$	225
3B	120	7619	109	98.590			24233	85	99.650	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_3\text{PO}_4$	225
3C	120	9389	43	99.544	0.481	99.103	28681	61	99.788	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_3\text{PO}_4$	225
4A	120	9782	538	94.787			25181	2452	91.127	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	225
4B	120	11136	474	95.917			27465	1845	93.705	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	225
4C	120	10201	631	94.175	0.884	94.960	22435	2347	90.529	5	5	$\text{CHCl}_3$	1	0.15 M $\text{H}_2\text{SO}_4$	225
5A	120	1552	37628	3.961			1527	51412	2.884	5	5	$\text{CHCl}_3$	1	0.15 M NaOH	225
5B	120	2351	29412	7.402			2530	45659	5.250	5	5	$\text{CHCl}_3$	1	0.15 M NaOH	225
5C	120	2771	28172	8.955	2.556	6.773	2825	45544	5.841	5	5	$\text{CHCl}_3$	1	0.15 M NaOH	225
6A	120	8865	3165	73.691						5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
6B	120	10886	2758	79.786						5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
6C	120	7845	2480	75.981	3.079	76.486				5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
7A	120	8682	3191	73.124			28377	17815	61.433	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
7B	120	9270	3486	72.672			26760	17424	60.565	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
7C	120	9144	2474	78.705	3.361	74.834	25617	11915	68.254	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/out $\text{I}_2$ )	225
8A	120	10154	8594	54.160			17492	24748	41.411	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/ $\text{I}_2$ )	225
8B	120	9922	9078	52.221			17006	26082	39.468	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/ $\text{I}_2$ )	225
8C	120	10903	8168	57.171	2.494	54.517	18254	22754	44.513	5	5	$\text{CHCl}_3$	1	0.15 M HI (w/ $\text{I}_2$ )	225





**Table 9: Solid Phase Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Column	% on column	average	standard deviation	Aqueous Phase	g Loaded on Silica	Batch
32	38	46	41	45	44	51673	99.58756529	99.7	0.2	0.15 M HCl	0.4906	3
33	42	60	52	39	52	49179	99.50428941			0.15 M HCl	0.4971	3
2	17	17	18	16	0	62243	99.89086999			0.15 M HCl	0.5011	1
12	43	40	23	37	57	98532	99.79743143	99.6	0.1	0.15 M $\text{HNO}_3$	0.4998	2
27	30	43	55	39	41	50925	99.59321769			0.15 M $\text{HNO}_3$	0.5031	3
28	59	43	43	47	46	52840	99.5516033			0.15 M $\text{HNO}_3$	0.502	3
16	41	41	49	46	53	61234	99.62579721	99.57	0.06	0.15 M $\text{H}_3\text{PO}_4$	0.5011	2
18	47	48	42	47	28	50636	99.58307111			0.15 M $\text{H}_3\text{PO}_4$	0.5026	2
19	46	32	50	33	40	40455	99.50560803			0.15 M $\text{H}_3\text{PO}_4$	0.501	2
17	40	32	49	37	35	72687	99.73518112	99.6	0.1	0.15 M $\text{H}_2\text{SO}_4$	0.501	2
20	46	32	50	33	40	40455	99.50560803			0.15 M $\text{H}_2\text{SO}_4$	0.5009	2
21	46	38	50	39	46	61442	99.64483223			0.15 M $\text{H}_2\text{SO}_4$	0.5031	2
47	22	52	196	722	1395	21926	90.18220705	85	5	0.15 M HI	0.5033	5
48	18	110	447	1130	1994	17458	82.51642482			0.15 M HI	0.5015	5
49	15	43	290	1094	1815	14750	81.91258955			0.15 M HI	0.5002	5
41	18	51	98	126	128	35028	98.81237835	99.0	0.3	0.15 M NaCl	0.5004	5
42	19	43	74	81	135	32529	98.92947295			0.15 M NaCl	0.5008	5
43	24	30	43	77	63	38228	99.38385545			0.15 M NaCl	0.5008	5
44	64	17477	20617	2969	474	291	0.694643369	0.5	0.1	1 mM $\text{ReO}_4$	0.5011	5
45	50	16368	17876	3200	1019	287	0.739690722			1 mM $\text{ReO}_4$	0.5021	5
46	45	16995	19573	2500	437	152	0.382852249			1 mM $\text{ReO}_4$	0.5024	5
39	45	30537	61452	12940	1848	472	0.439912763			1 mM $\text{ReO}_4$	0.504	4
40	50	25884	64266	8884	1556	528	0.521904159			1 mM $\text{ReO}_4$	0.5039	4
41	39	26213	59953	6387	1383	415	0.439665219			1 mM $\text{ReO}_4$	0.5016	4
93	40	94	422	944	1882	12503	78.70947435	83	4	0.15 M NaI	0.5037	8
94	39	65	244	705	1594	14724	84.76195959			0.15 M NaI	0.502	8
95	29	76	326	812	1228	14477	85.42010857			0.15 M NaI	0.5028	8

sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Column	% on column	average	standard deviation	Aqueous Phase	g Loaded on Silica	Batch
90	33	39	48	76	139	16767	98.04116478	98.5	0.4	0.15 M sodium fumarate	0.5039	8
91	44	37	40	38	36	17208	98.87950353			0.15 M sodium fumarate	0.5001	8
92	47	32	49	43	61	16687	98.62876057			0.15 M sodium fumarate	0.5007	8
68	26	38	182	6000	14878	12014	36.25445108	38	8	0.15 M lactate	0.5015	7
69	47	59	428	10128	11945	10050	30.77441284			0.15 M lactate	0.5012	7
70	38	43	90	4062	12392	14822	47.13327185			0.15 M lactate	0.5036	7
61	35	56	679	12066	7403	4121	16.91707718	15	2	0.15 M benzoate	0.5003	7
72	60	48	2577	11924	5480	2825	12.32870734			0.15 M benzoate	0.5012	7
73	41	41	2393	12577	7019	4225	16.06708245			0.15 M benzoate	0.5004	7
56	52	176	2606	42937	53083	12583	11.29158179	11	3	0.15 M Acetate	0.5001	6
57	35	35	285	29415	55779	14708	14.67029734			0.15 M Acetate	0.5017	6
58	44	97	3492	44429	41476	7996	8.198166793			0.15 M Acetate	0.5026	6
50	41	413	3393	19247	67529	23557	20.6314591	18	3	0.15 M NaOH	0.5023	6
51	54	891	5993	36878	68959	23761	17.40273627			0.15 M NaOH	0.501	6
52	34	228	3007	34744	64861	17675	14.66208762			0.15 M NaOH	0.5021	6

**Continuation of Table 9: Solid Extraction Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{186}\text{ReO}_4^-$**

sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Column	% on column	average	standard deviation	Aqueous Phase	g Loaded on Silica	Batch
32	36	51	38	42	34	35240	99.43286025	99.6	0.3	0.15 M HCl	0.4906	3
33	45	53	38	53	42	36365	99.36878347			0.15 M HCl	0.4971	3
2	25	22	16	30	0	72031	99.8710554			0.15 M HCl	0.5011	1
12	38	24	53	83	334	78434	99.32629233	99.41	0.08	0.15 M $\text{HNO}_3$	0.4998	2
27	44	45	36	47	45	39956	99.45983621			0.15 M $\text{HNO}_3$	0.5031	3
28	35	69	42	33	49	41404	99.45234435			0.15 M $\text{HNO}_3$	0.502	3
16	48	40	48	44	34	55968	99.61909508	99.62	0.04	0.15 M $\text{H}_3\text{PO}_4$	0.5011	2
18	40	24	33	43	48	54563	99.65662728			0.15 M $\text{H}_3\text{PO}_4$	0.5026	2
19	44	45	51	28	26	45939	99.57947673			0.15 M $\text{H}_3\text{PO}_4$	0.501	2
17	46	42	27	43	45	63247	99.68006304	99.61	0.09	0.15 M $\text{H}_2\text{SO}_4$	0.501	2
20	47	45	51	50	38	45929	99.49956672			0.15 M $\text{H}_2\text{SO}_4$	0.5009	2
21	44	41	32	35	31	50182	99.63665244			0.15 M $\text{H}_2\text{SO}_4$	0.5031	2
47	11	767	4622	9961	1404	16757	49.98806754	37	11	0.15 M HI	0.5033	5
48	13	1484	5766	10434	13140	13929	31.11513202			0.15 M HI	0.5015	5
49	20	588	4336	10585	12572	12950	31.54612555			0.15 M HI	0.5002	5
41	39	299	773	1017	1064	27537	89.61241824	92	2	0.15 M NaCl	0.5004	5
42	40	239	509	752	1102	26453	90.91940196			0.15 M NaCl	0.5008	5
43	27	135	393	675	660	30801	94.21859227			0.15 M NaCl	0.5008	5
44	417	38101	12688	741	128	158	0.302490763	0.30	0.07	1 mM $\text{ReO}_4$	0.5011	5
45	368	37896	12629	1269	1030	218	0.408163265			1 mM $\text{ReO}_4$	0.5021	5
46	373	38327	10364	663	114	106	0.212224958			1 mM $\text{ReO}_4$	0.5024	5
39	116	69762	54120	3921	793	331	0.256503646			1 mM $\text{ReO}_4$	0.504	4
40	46	72477	48859	3171	788	431	0.342683586			1 mM $\text{ReO}_4$	0.5039	4
41	68	74233	43531	2243	753	310	0.255906487			1 mM $\text{ReO}_4$	0.5016	4
93	44	762	3026	5077	5432	3332	18.85361851	23	4	0.15 M NaI	0.5037	8
94	42	587	2873	5678	6132	4937	24.38145094			0.15 M NaI	0.502	8
95	43	662	3029	5806	5201	5160	25.92834531			0.15 M NaI	0.5028	8

sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Column	% on column	average	standard deviation	Aqueous Phase	g Loaded on Silica	Batch
90	34	65	190	429	812	13358	89.72326706	94	4	0.15 M sodium fumarate	0.5039	8
91	47	45	50	74	174	14753	97.4245526			0.15 M sodium fumarate	0.5001	8
92	42	42	58	166	314	14429	95.86738423			0.15 M sodium fumarate	0.5007	8
68	32	51	968	12162	11252	5898	19.42495801	21	5	0.15 M lactate	0.5015	7
69	46	57	2383	15542	8136	5203	16.58749641			0.15 M lactate	0.5012	7
70	39	53	476	9688	12508	8325	26.77796005			0.15 M lactate	0.5036	7
61	45	64	5136	16112	3956	1965	7.203607303	6	1	0.15 M benzoate	0.5003	7
72	36	211	10673	12283	2691	1201	4.432552131			0.15 M benzoate	0.5012	7
73	55	164	9995	15240	3974	2022	6.429252782			0.15 M benzoate	0.5004	7
56	71	1236	13795	40120	17832	4659	5.995135949	6	2	0.15 M Acetate	0.5001	6
57	49	111	4296	41136	20102	6008	8.379124711			0.15 M Acetate	0.5017	6
58	46	671	19795	38335	14393	3146	4.118555756			0.15 M Acetate	0.5026	6
50	43	4050	22116	38542	21353	5664	6.17208613	6.5	0.4	0.15 M NaOH	0.5023	6
51	104	6545	29260	38210	12616	5907	6.376157682			0.15 M NaOH	0.501	6
52	52	2866	21895	36878	15443	5763	6.952000676			0.15 M NaOH	0.5021	6

**Table 10: Solid Phase Extraction Data for (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (2) with <sup>99m</sup>TcO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	g loaded on silica	time counted	Batch
78	45	35	52	48	46	20886	98.93	98.99	0.07	0.15 M HCl	0.5021	120 s	1A
79	46	45	42	33	42	21966	99.06			0.15 M HCl	0.5	120 s	1A
80	43	39	45	42	36	19772	98.97			0.15 M HCl	0.5001	120 s	1A
81	42	44	42	34	33	18394	98.95	98.91	0.03	0.15 M HNO <sub>3</sub>	0.5013	120 s	1A
82	45	44	38	45	35	18376	98.89			0.15 M HNO <sub>3</sub>	0.5017	120 s	1A
83	32	44	37	51	41	18485	98.90			0.15 M HNO <sub>3</sub>	0.5028	120 s	1A
84	37	35	39	53	69	17118	98.66	98.77	0.11	0.15 M HI	0.5018	120 s	1A
85	40	36	48	41	39	16826	98.80			0.15 M HI	0.5011	120 s	1A
86	38	41	38	37	45	17304	98.86			0.15 M HI	0.502	120 s	1A
87	40	43	37	29	44	15766	98.79	98.64	0.20	0.15 M Sodium Acetate	0.5027	120 s	1A
88	51	31	44	34	36	15206	98.73			0.15 M Sodium Acetate	0.5006	120 s	1A
89	31	45	40	47	45	12904	98.41			0.15 M Sodium Acetate	0.5014	120 s	1A
108	30	38	42	35	36	16642	98.92	98.95	0.09	0.15 M Sodium Benzoate	0.5018	120 s	2A
109	45	38	50	31	36	20725	99.04			0.15 M Sodium Benzoate	0.5038	120 s	2A
110	38	39	39	54	38	18314	98.88			0.15 M Sodium Benzoate	0.501	120 s	2A
111	48	48	37	42	53	18838	98.80	98.73	0.06	0.15 M NaI	0.5013	120 s	2A
112	46	57	41	50	61	19336	98.70			0.15 M NaI	0.504	120 s	2A
113	32	37	40	54	54	16397	98.69			0.15 M NaI	0.5024	120 s	2A

**Continuation of Table 10: Solid Phase Extraction Data for (9-anthracenyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (2) with <sup>186</sup>ReO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	G loaded on silica	time counted	batch
78	36	52	40	50	43	13962	98.44	98.49	0.14	0.15 M HCl	0.5021	120 s	1A
79	37	40	39	37	41	14161	98.65			0.15 M HCl	0.5	120 s	1A
80	44	35	57	42	47	13670	98.38			0.15 M HCl	0.5001	120 s	1A
81	46	48	42	47	34	11169	98.09	98.19	0.15	0.15 M HNO <sub>3</sub>	0.5013	120 s	1A
82	39	40	38	39	41	11878	98.37			0.15 M HNO <sub>3</sub>	0.5017	120 s	1A
83	50	51	44	47	39	12022	98.11			0.15 M HNO <sub>3</sub>	0.5028	120 s	1A
84	44	41	101	378	913	11931	88.98	91.82	3.75	0.15 M HI	0.5018	120 s	1A
85	54	35	53	105	292	13192	96.07			0.15 M HI	0.5011	120 s	1A
86	46	47	93	321	863	12881	90.39			0.15 M HI	0.502	120 s	1A
87	44	40	51	36	48	13160	98.36	98.29	0.15	0.15 M Sodium Acetate	0.5027	120 s	1A
88	40	41	45	54	36	13294	98.40			0.15 M Sodium Acetate	0.5006	120 s	1A
89	48	41	33	56	37	11210	98.12			0.15 M Sodium Acetate	0.5014	120 s	1A
108	44	31	37	38	37	11069	98.34	98.43	0.17	0.15 M Sodium Benzoate	0.5018	120 s	2A
109	33	42	42	49	39	14654	98.62			0.15 M Sodium Benzoate	0.5038	120 s	2A
110	43	48	55	35	49	13462	98.32			0.15 M Sodium Benzoate	0.501	120 s	2A
111	39	44	126	503	1049	12578	87.72	86.98	0.64	0.15 M NaI	0.5013	120 s	2A
112	48	46	145	520	1214	12821	86.66			0.15 M NaI	0.504	120 s	2A
113	38	43	126	505	1071	11482	86.56			0.15 M NaI	0.5024	120 s	2A

**Table 11: Solid Phase Extraction Data for (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (6) with <sup>99m</sup>TcO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	g loaded on silica	time counted	Batch
96	45	51	44	38	45	19808	98.88672558	98.93136802	0.117533279	0.15 M HCl	0.501	120 s	1N
97	36	49	41	37	43	17594	98.84			0.15 M HCl	0.5021	120 s	1N
98	44	38	50	41	40	22560	99.06			0.15 M HCl	0.5023	120 s	1N
99	44	44	35	42	42	18191	98.87	98.87	0.20	0.15 M HNO <sub>3</sub>	0.5018	120 s	1N
100	44	39	48	52	46	17018	98.67			0.15 M HNO <sub>3</sub>	0.5014	120 s	1N
101	37	39	36	53	43	22169	99.07			0.15 M HNO <sub>3</sub>	0.5016	120 s	1N
102	44	38	41	40	47	20420	98.98	98.82	0.16	0.15 M HI	0.5007	120 s	1N
103	49	48	42	49	40	19370	98.84			0.15 M HI	0.5029	120 s	1N
104	49	47	40	46	58	17606	98.66			0.15 M HI	0.5005	120 s	1N
105	46	47	45	30	36	17475	98.85	98.85	0.08	0.15 M Sodium Acetate	0.5018	120 s	1N
106	42	41	39	33	48	18920	98.94			0.15 M Sodium Acetate	0.5015	120 s	1N
107	36	38	47	37	46	16396	98.77			0.15 M Sodium Acetate	0.503	120 s	1N
162	17	17	17	13	46	13658	99.20	99.20	0.09	0.15 M Sodium Benzoate	0.5012	60 s	2N
163	22	22	22	22	23	12307	99.11			0.15 M Sodium Benzoate	0.5001	60 s	2N
164	16	16	16	16	25	12322	99.28			0.15 M Sodium Benzoate	0.5018	60 s	2N
165	33	33	26	36	36	13372	98.79	98.81	0.11	0.15 M NaI	0.5001	60 s	2N
166	21	22	16	28	35	11305	98.93			0.15 M NaI	0.5029	60 s	2N
167	13	19	26	36	64	12135	98.71			0.15 M NaI	0.5021	60 s	2N



**Continuation of Table 11: Solid Phase Extraction Data for (1-naphthyl)Ph<sub>2</sub>P=NSiMe<sub>3</sub> (6) with <sup>186</sup>ReO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	g loaded on silica	time counted	Batch
96	42	42	47	44	33	12359	98.34	98.33	0.20	0.15 M HCl	0.501	120 s	1N
97	50	38	42	44	41	11271	98.13			0.15 M HCl	0.5021	120 s	1N
98	41	42	46	42	54	15084	98.53			0.15 M HCl	0.5023	120 s	1N
99	51	57	36	31	41	12333	98.28	98.38	0.27	0.15 M HNO <sub>3</sub>	0.5018	120 s	1N
100	38	54	37	46	45	11793	98.17			0.15 M HNO <sub>3</sub>	0.5014	120 s	1N
101	34	43	43	50	40	15798	98.69			0.15 M HNO <sub>3</sub>	0.5016	120 s	1N
102	37	31	48	57	174	13888	97.56	97.35	0.21	0.15 M HI	0.5007	120 s	1N
103	42	45	55	74	171	14318	97.37			0.15 M HI	0.5029	120 s	1N
104	50	49	42	85	162	13146	97.13			0.15 M HI	0.5005	120 s	1N
105	39	45	50	46	47	13731	98.37	98.50	0.14	0.15 M Sodium Acetate	0.5018	120 s	1N
106	49	44	45	47	51	15174	98.47			0.15 M Sodium Acetate	0.5015	120 s	1N
107	38	46	42	33	28	13633	98.65			0.15 M Sodium Acetate	0.503	120 s	1N
162	26	26	26	32	128	8087	97.14	98.08	0.82	0.15 M Sodium Benzoate	0.5012	60 s	2N
163	18	18	18	18	26	7268	98.67			0.15 M Sodium Benzoate	0.5001	60 s	2N
164	22	22	22	22	27	7186	98.42			0.15 M Sodium Benzoate	0.5018	60 s	2N
165	60	60	132	366	806	7204	83.50	83.21	3.98	0.15 M NaI	0.5001	60 s	2N
166	21	25	65	276	533	6179	87.04			0.15 M NaI	0.5029	60 s	2N
167	31	49	220	557	960	6875	79.10			0.15 M NaI	0.5021	60 s	2N

**Table 12: Solid Phase Extraction Data for (p-COOMe)Ph<sub>3</sub>P=NSiMe<sub>3</sub> (8) with <sup>99m</sup>TcO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	g loaded on silica
135	19	39	19	39	39	15693	99.02	98.95	0.17	0.15 M HCl	0.5004
136	24	24	24	24	24	12830	99.07			0.15 M HCl	0.5018
137	37	37	37	37	37	14780	98.76			0.15 M HCl	0.5008
150	18	164	1021	3682	7214	17021	58.45	53.97	4.37	0.15 M HI	0.5035
151	25	126	952	3369	7151	11495	49.72			0.15 M HI	0.502
152	20	596	3021	7254	27	12684	53.74			0.15 M HI	0.504
141	20	68	313	878	1834	12271	79.76	80.63	1.44	0.15 M Sodium Acetate	0.5009
142	24	40	237	704	1486	11578	82.29			0.15 M Sodium Acetate	0.5023
143	15	52	230	838	1752	11428	79.83			0.15 M Sodium Acetate	0.5031
144	20	1999	10376	16744	14975	11382	20.51	13.33	6.35	0.15 M Sodium Benzoate	0.5028
145	70	3896	13924	18755	12179	4499.666667	8.44			0.15 M Sodium Benzoate	0.5027
146	42	3024	11292	17027	13633	5593.5	11.05			0.15 M Sodium Benzoate	0.5002
147	25	5438	18091	15662	6205	1406	3.00	2.42	0.51	0.15 M NaI	0.5042
148	436	11698	20087	10768	3766	1034	2.16			0.15 M NaI	0.5026
149	28	6052	19892	17465	5662	1048	2.09			0.15 M NaI	0.5021

Batch 1C, counted for 60 s

**Continuation of Table 12: Solid Phase Extraction Data for (p-COOMe)Ph<sub>3</sub>P=NSiMe<sub>3</sub> (8) with <sup>186</sup>ReO<sub>4</sub><sup>-</sup>**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	g loaded on silica
135	19	17	19	17	17	5997	98.54	97.99	0.77	0.15 M HCl	0.5004
136	29	29	29	29	29	4867	97.11			0.15 M HCl	0.5018
137	20	20	20	20	20	5883	98.33			0.15 M HCl	0.5008
150	28	1048	5004	8611	5899	2058	9.09	6.41	2.79	0.15 M HI	0.5035
151	21	928	5225	8208	5578	1419	6.64			0.15 M HI	0.502
152	27	2643	8726	9260	10155	1124	3.52			0.15 M HI	0.504
141	15	242	994	1906	2166	1911	26.42	26.38	1.92	0.15 M Sodium Acetate	0.5009
142	14	143	942	2021	1983	2012	28.28			0.15 M Sodium Acetate	0.5023
143	16	229	1012	2082	2037	1738	24.43			0.15 M Sodium Acetate	0.5031
144	37	4477	10147	5808	1958	732	3.16	3.39	0.59	0.15 M Sodium Benzoate	0.5028
145	181	6790	10166	3862	768	919	4.05			0.15 M Sodium Benzoate	0.5027
146	77	5863	10271	4515	996	659	2.94			0.15 M Sodium Benzoate	0.5002
147	48	7931	9851	2423	379	111	0.54	0.46	0.06	0.15 M NaI	0.5042
148	748	11015	7785	1639	289	94	0.44			0.15 M NaI	0.5026
149	42	9431	10876	2644	401	99	0.42			0.15 M NaI	0.5021

Batch 1C, counted for 60 s

**Table 13: Solid Phase Extraction 1:1 Competition Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	Standard deviation	aqueous phase	competition phase
244	22	18	287	2894	3296	5136	44.07	51	6	0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
245	14	14	738	2686	3077	7154	52.28			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
246	17	14	638	3170	3163	8920	56.02			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
227	16	257	882	959	1027	5701	64.48	59	5	0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
228	16	435	936	902	893	3929	55.25			0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
229	24	343	863	1001	972	4392	57.83			0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
230	31	183	954	2062	2221	6557	54.61	53	6	0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
231	18	577	2018	1871	1669	5279	46.18			0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
232	29	308	1327	1780	1959	7761	58.96			0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
233	387	4429	1719	758	429	3364	30.34	27	3	0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
234	343	4764	1536	712	349	2827	26.84			0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
235	328	3970	1645	756	491	2215	23.55			0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
236	199	3982	1689	808	515	1533	17.57	23	5	0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
237	300	3588	1624	650	490	2023	23.32			0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
238	311	3713	1344	743	437	2420	26.98			0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
239	150	3309	1534	897	565	2536	28.21	28	1	0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$
240	21	2489	1710	762	589	2291	29.14			0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$
243	27	2566	1671	695	560	2031	26.90			0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$

Batch 18, counted for 60 s, each column contained 0.50 g coated silica

**Continuation of Table 13: Solid Phase Extraction 1:1 Competition Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{186}\text{ReO}_4^-$**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	Standard deviation	aqueous phase	competition phase
244	18	15	1939	6309	1609	655	6.21	8	2	0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
245	18	38	2542	5253	1589	847	8.23			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
246	20	21	3292	4682	1926	1117	10.10			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
227	23	1386	3657	1746	1290	1320	14.01	11	2	0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
228	26	1793	3561	1612	1067	825	9.29			0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
229	20	1990	3314	1810	1333	971	10.29			0.14 M NaCl / 10 mM acetate	1.2 mM $\text{NH}_4\text{TcO}_4$
230	35	1167	3214	2528	1278	807	8.94	10	3	0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
231	41	2305	3844	1511	1069	729	7.67			0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
232	35	1960	3122	1940	1238	1197	12.61			0.14 M NaCl / 10 mM NaI	1.2 mM $\text{NH}_4\text{TcO}_4$
233	1037	5820	1442	463	220	607	6.33	6	1	0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
234	996	6293	1269	417	195	549	5.65			0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
235	907	5300	1489	587	304	465	5.14			0.15 M NaCl	10 mM $\text{NH}_4\text{ReO}_4$
236	821	5976	1647	572	312	326	3.38	5	1	0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
237	832	5565	1535	534	274	449	4.89			0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
238	856	5758	1318	519	277	553	5.96			0.14 M NaCl / 10 mM acetate	10 mM $\text{NH}_4\text{ReO}_4$
239	592	5678	1563	658	307	529	5.67	5	0	0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$
240	63	5472	2106	687	395	448	4.88			0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$
243	34	5529	2084	670	424	437	4.76			0.14 M NaCl / 10 mM NaI	10 mM $\text{NH}_4\text{ReO}_4$

Batch 18, counted for 60 s, each column contained 0.50 g coated silica

**Table 14: Solid Phase Extraction Column Capacity for Concentrated Samples Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	column	% on column	average	standard deviation	aqueous phase	competition phase
257	23	23	23	23	16	11696	99.09	99.2	0.3	0.15 M NaCl	0.11 mM $\text{NH}_4\text{TcO}_4$
258	29	29	29	29	28	12259	98.84			0.15 M NaCl	0.11 mM $\text{NH}_4\text{TcO}_4$
247	26	20	21	17	22	13768	99.24			0.15 M NaCl	0.13 mM $\text{NH}_4\text{TcO}_4$
248	11	11	11	11	23	16545	99.60			0.15 M NaCl	0.13 mM $\text{NH}_4\text{TcO}_4$
253	22	22	23	279	2061	10974	82.01	85.6	3.6	0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
254	13	13	33	109	1020	9740	89.13			0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
255	18	18	14	54	1981	12500	85.70			0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
244	22	18	287	2894	3296	5136	44.07	50.8	6.1	0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
245	14	14	738	2686	3077	7154	52.28			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
246	17	14	638	3170	3163	8920	56.02			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
250	14	2545	5329	2616	1437	1737	12.70	15.4	2.5	0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$
251	39	2638	4999	2326	1157	2131	16.03			0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$
252	19	2465	5185	1551	1315	2235	17.50			0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$

Batch 18, counted for 60 s, each column contained 0.50 g coated silica

**Continuation of Table 14: Solid Phase Extraction Column Capacity by Concentration Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{186}\text{ReO}_4^-$**

sample	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	Column	% on column	average	standard deviation	aqueous phase	competition phase
257	35	35	35	35	85	8383	97.39	96.2	1.7	0.15 M NaCl	0.11 mM $\text{NH}_4\text{TcO}_4$
258	89	89	89	89	226	8697	93.73			0.15 M NaCl	0.11 mM $\text{NH}_4\text{TcO}_4$
247	24	25	28	45	77	5671	96.61			0.15 M NaCl	0.13 mM $\text{NH}_4\text{TcO}_4$
248	43	43	43	43	57	7166	96.90			0.15 M NaCl	0.13 mM $\text{NH}_4\text{TcO}_4$
253	17	26	129	1623	5824	3255	29.93	35.0	4.4	0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
254	26	26	95	840	4662	3361	37.30			0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
255	26	26	26	607	6345	4247	37.66			0.15 M NaCl	0.52 mM $\text{NH}_4\text{TcO}_4$
244	18	15	1939	6309	1609	655	6.21	8.2	1.9	0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
245	18	38	2542	5253	1589	847	8.23			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
246	20	21	3292	4682	1926	1117	10.10			0.15 M NaCl	1.2 mM $\text{NH}_4\text{TcO}_4$
250	25	6178	4628	847	409	222	1.80	2.3	0.4	0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$
251	22	6583	4140	728	321	295	2.44			0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$
252	18	6381	4135	574	451	305	2.57			0.15 M NaCl	5.2 mM $\text{NH}_4\text{TcO}_4$

Batch 18, counted for 60 s, each column contained 0.50 g coated silica

**Table 15: Solid Phase Extraction Column Capacity by Volume Data for  $\text{Ph}_3\text{P}=\text{NSiMe}_3$  (1) with  $^{99\text{m}}\text{TcO}_4^-$**

sample 201 - 201ms -														
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Batch Ph4, counted for 60 s, each column contained 0.50 g coated silica, eluted with 0.15 M NaCl, Each fraction contained 0.13 mM  $^{99}\text{TcO}_4^-$  except for wash which contained only NaCl

### APPENDIX 3: RAW DATA FOR FLUORESCENCE AND SCINTILLATION STUDIES

**Table 1: Fluorescence Sample CPM using LSC with Toluene instead of Cocktail**

	cpm 1	cpm 2	cpm 3	average cpm	stdev
blank toluene	37	47	40	41	5
Anthracene	44	51	46	47	4
Ph <sub>2</sub> (9-anthracenyl)P	36	39	29	35	5
Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup>	53	45	42	47	6
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][Cl <sup>-</sup> ] (w/ acid)	45	51	51	49	3
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][ReO <sub>4</sub> <sup>-</sup> ]	45	45	52	47	4
anthracene + ReO <sub>4</sub> <sup>-</sup>	48	49	54	50	3
anthracene (10 <sup>-5</sup> M) + TcO <sub>4</sub> <sup>-</sup> (10 <sup>-5</sup> M)	2464	2419	2474	2452	29
anthracene (10 <sup>-3</sup> M) + TcO <sub>4</sub> <sup>-</sup> (10 <sup>-5</sup> M)	14810	14174	13572	14185	619
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][TcO <sub>4</sub> <sup>-</sup> ]	8010	7895	7757	7887	127
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][ReO <sub>4</sub> <sup>-</sup> ] + TcO <sub>4</sub> <sup>-</sup>	1889	1946	1849	1895	49

**Table 2: Fluorescence Sample CPM using LSC with Cocktail**

	cpm 1	cpm 2	cpm 3	average cpm	stdev
blank LSC	113	129	136	126	12
Anthracene	134	135	151	140	10
Ph <sub>2</sub> (9-anthracenyl)P	86	101	105	97	10
Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup>	117	100	109	109	9
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][Cl <sup>-</sup> ] (w/ acid)	220	258	228	235	20
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][ReO <sub>4</sub> <sup>-</sup> ]	128	115	111	118	9
anthracene + ReO <sub>4</sub> <sup>-</sup>	88	103	96	96	8
anthracene (10 <sup>-5</sup> M) + TcO <sub>4</sub> <sup>-</sup> (10 <sup>-5</sup> M)	27992	28188	27956	28045	125
[Ph <sub>2</sub> (9-anthracenyl)P=NH <sub>2</sub> <sup>+</sup> ][TcO <sub>4</sub> <sup>-</sup> ]	85315	84723	85052	85030	297
10 <sup>-5</sup> M TcO <sub>4</sub> <sup>-</sup>	116430	116257	116207	116298	117



**Table 3: Optimization of Solid Extraction Scintillation Experiment for  $^{99m}\text{TcO}_4^-$**

sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Column	% on column	average	standard deviation	Batch	mass (g)				
											silica	Ph3P=N SiMe3	PPO	bis-MSB	POPO P
260	51	34	33	54	55	28408	99.20	98.9	0.6	Ph1	5.007	0.5006	0	0	0
261	46	49	51	51	326	28236	98.18			Ph1					
262	32	51	44	40	50	28111	99.23			Ph1					
263	33	237	247	521	832	18776	90.94	90	1	S1	5	0.5018	0.5008	0.1013	0
264	39	73	240	579	976	16782	89.79			S1					
265	41	120	510	990	1399	22792	88.16			S1					
266	42	44	45	59	82	25020	98.92	98.9	0.2	S2	5.019	0.5002	0.5011	0	0.1000
267	43	38	36	41	58	23487	99.088			S2					
268	40	37	44	88	112	23382	98.645			S2					
278	52	56	60	79	53	53963	99.447	99.2	0.2	S3	5.0043	0.5034	0.5005	0.0985	0
279	41	55	122	139	92	53453	99.167			S3					
280	34	48	91	163	103	53447	99.185			S3					
281	47	57	264	723	1314	51941	95.574	95	1	S4	3.00	0.3012	0.6010	0.0984	0
282	44	155	654	1121	1592	50368	93.388			S4					
283	53	66	240	592	1250	51522	95.903			S4					
284	47	43	55	55	57	49419	99.482	99.48	0.08	S5	3.00	0.3006	0.1509	0.0983	0
285	38	48	37	39	46	48034	99.56			S5					
286	40	34	51	56	108	48932	99.412			S5					
287	44	68	192	504	1121	49400	96.241	97	1	S6	3.00	0.301	0.5025	0	0.1028
288	49	60	228	677	1230	50168	95.718			S6					
289	28	46	89	259	699	51597	97.873			S6					
290	38	45	42	144	437	68794	98.984	98.3	0.7	S8	3.00	0.30	0.30	0.05	0.00
291	41	81	205	507	860	68263	97.578			S8					
292	41	51	105	277	625	68634	98.423			S8					

Each column 0.50 g coated silica, counted on NaI well detector for 10 s, 0.15 M NaCl

Continuation of Table 3: Optimization of Solid Extraction Scintillation Experiment for LSC

sample	cpm on column	average	standard deviation	[TcO4-]	batch	silica	mass (g)				
							Ph3P=NSiMe3	PPO	bis-MSB	POPOP	
260	2427	2500	93	0.13 mM	Ph1	5.007	0.5006	0	0	0	
261	2474			0.13 mM	Ph1						
262	2606			0.13 mM	Ph1						
263	207177	199000	10787	0.13 mM	S1	5	0.5018	0.5008	0.1013	0	
264	203216			0.13 mM	S1						
265	186831			0.13 mM	S1						
266	213161	215000	2745	0.13 mM	S2	5.019	0.5002	0.5011	0	0.1000	
267	218179			0.13 mM	S2						
268	213740			0.13 mM	S2						
278	304128	307800	3867	0.13 mM	S3	5.0043	0.5034	0.5005	0.0985	0	
279	311839			0.13 mM	S3						
280	307459			0.13 mM	S3						
281	293545	293200	3367	0.14 mM	S4	3.00	0.3012	0.6010	0.0984	0	
282	289663			0.14 mM	S4						
283	296370			0.14 mM	S4						
284	238111	236200	3559	0.14 mM	S5	3.00	0.3006	0.1509	0.0983	0	
285	238394			0.14 mM	S5						
286	232093			0.14 mM	S5						
287	268716	268800	1586	0.14 mM	S6	3.00	0.301	0.5025	0	0.1028	
288	267183			0.14 mM	S6						
289	270354			0.14 mM	S6						
290	254545	250000	4001	0.14 mM	S8	3.00	0.30	0.30	0.05	0.00	
291	246619			0.14 mM	S8						
292	249623			0.14 mM	S8						

Each column 0.50 g coated silica, 0.15 M NaCl

**Table 4: Raw data for Solid Extraction Scintillation Experiment for  $^{99m}\text{TcO}_4^-$**

sample	Column	% on column	average	standard deviation	Batch	mass (g)			PPO	bis-MSB
						silica	Ph3P=NSiMe3			
341	12463	100	12400	70	Ph7	10.0065	1.0029		0	0
342	12329	100			Ph7					
343	12448	100			Ph7					
344	11089	100	11500	400	S12	3.0042	3.002		0.3044	0.0914
345	11869	100			S12					
346	11667	100			S12		Ph2(9anthr)P=NSiMe <sub>3</sub>			
347	9615	100	9000	600	AN2	9.0029	0.9		0	0
348	8555	100			AN2					
349	9497	100			AN2		Ph2(9anthr)P=NSiMe <sub>3</sub>			
350	8505	100	8600	100	AS2	3	0.3016		0.302	0.0896
351	8655	100			AS2					
352	8687	100			AS2					

All fractions at or below background radiation levels, each column 0.50 g coated silica, counted on NaI well detector for 12 s, 0.15 M NaCl

**Continuation of Table 4: Raw data for Solid Extraction Scintillation Experiment for LSC**

sample	cpm on Column	average	standard deviation	[TcO4-]	Batch	silica	Ph <sub>3</sub> P=NSiMe <sub>3</sub>	PPO	bis-MSB
341	891	890	10	0.095 mM	Ph7	10.0065	1.0029	0	0
342	891			0.095 mM	Ph7				
343	874			0.095 mM	Ph7				
344	145179	146600	1320	0.095 mM	S12	3.0042	3.002	0.3044	0.0914
345	147008			0.095 mM	S12				
346	147741			0.095 mM	S12		Ph <sub>2</sub> (9anthr)P=NSiMe <sub>3</sub>		
347	177	150	31	0.095 mM	AN2	9.0029	0.9	0	0
348	118			0.095 mM	AN2				
349	164			0.095 mM	AN2		Ph <sub>2</sub> (9anthr)P=NSiMe <sub>3</sub>		
350	3541	3300	409	0.095 mM	AS2	3	0.3016	0.302	0.0896
351	3547			0.095 mM	AS2				
352	2835			0.095 mM	AS2				

Each column 0.50 g coated silica, 0.15 M NaCl

**Table 5: Solid Extraction Scintillation Experiment Over Time for LSC**

sample	Day 1			Day 2			Day 3		
	CPM	Average	Stdev	CPM	Average	Stdev	CPM	Average	Stdev
341	891	900	10	1270	1300	45	1339	1400	83
342	891			1349			1505		
343	874			1273			1410		
344	145179	150000	1319	118777	130000	9505	87423	100000	24748
345	147008			135653			131353		
346	147741			134793			89638		
347	177	200	31	281	200	47	308	300	27
348	118			187			278		
349	164			234			331		
350	3541	3000	409	4387	4000	505	5471	5000	720
351	3547			4612			5284		
352	2835			3647			4141		

**Continuation of Table 5: Solid Extraction Scintillation Experiment Over Time**

sample	Day 25			Day 32			
	CPM	Average	Stdev	CPM	Average	Stdev	
341	1452	1600	133	1486	1600	89	Ph <sub>3</sub> P=NSiMe <sub>3</sub>
342	1596			1596			
343	1718			1663			
344	100672	100000	4797	99289	98000	3924	Ph <sub>3</sub> P=NSiMe <sub>3</sub> PPO and Bis-MSB
345	91167			93212			
346	97045			100551			
347	1351	1000	309	1986	1000	596	(9anthr)Ph <sub>2</sub> P=NSiMe <sub>3</sub>
348	980			1190			
349	738			819			
350	13706	10000	2006	15689	13000	2716	(9anthr)Ph <sub>2</sub> P=NSiMe <sub>3</sub> PPO and BisMSB
351	10265			10703			
352	10200			11331			

## VITA

Leah Marie Arrigo, daughter of Glen and Ellen Russell, was born April 5, 1979 and grew up in Texas. She earned her Bachelors of Science in Chemistry from Texas A&M University – College Station in May 2001. In August 2001, Leah began the Ph.D. program in Chemistry at the University of Missouri – Columbia. She joined Dr. Paul Duval's research group in January of 2002, working on airfree inorganic synthesis of uranyl compounds. In September 2005, Leah transferred to Dr. Silvia Jurisson's group, working on the use of phosphinimines as extractants for technetium environmental contamination. She received her Ph.D. degree in May 2007. Leah has accepted a permanent position in the Analytical Division at Savannah River National Laboratory in South Carolina.