INL/CON-23-71112-Revision-2

2023 American Society for Mass Spectrometry (ASMS) 71st Annual Conference on Mass Spectrometry and Allied Topics

June 2023

Brittany D Hodges, Christopher A Zarzana, JungSoo Kim

INL/CON-23-71112-Revision-2

2023 American Society for Mass Spectrometry (ASMS) 71st Annual Conference on Mass Spectrometry and Allied Topics

Brittany D Hodges, Christopher A Zarzana, JungSoo Kim

June 2023

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Investigation of Transient Species through Metal Clusters of Triphenylphosphine Chalcogenides with Sodium

Brittany D.M. Hodges

Research Scientist, Idaho National Laboratory

JungSoo Kim, Christopher A. Zarzana

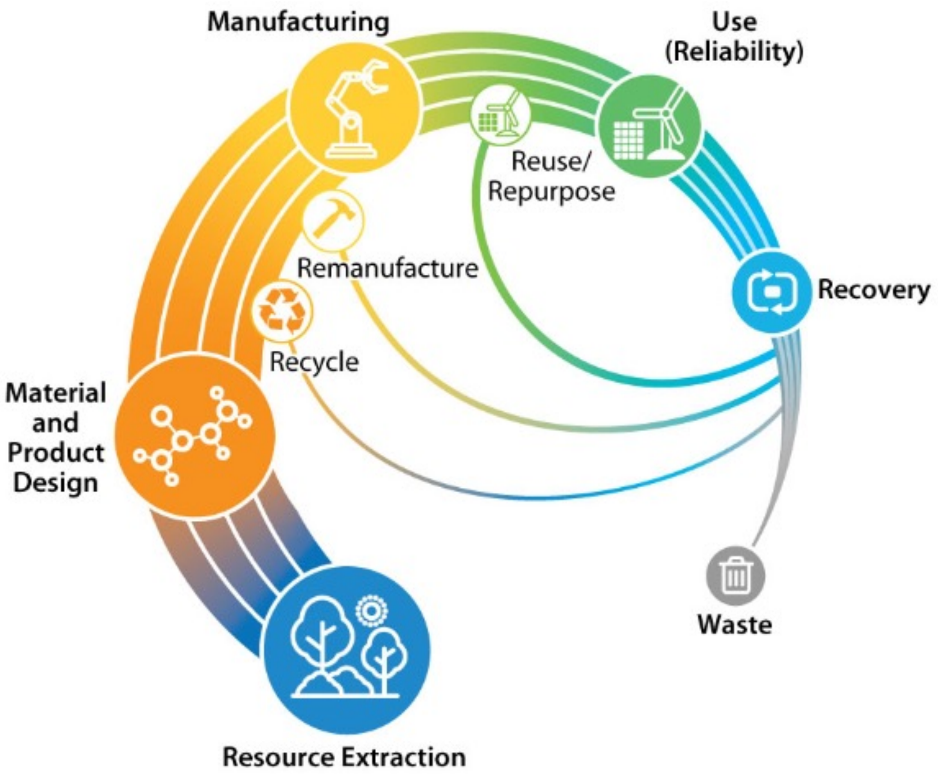
71st Conference on Mass Spectrometry and Allied Topics
American Society For Mass Spectrometry, Houston, TX

June 8, 2023 ThOD PM

The authors declare no competing financial interest.

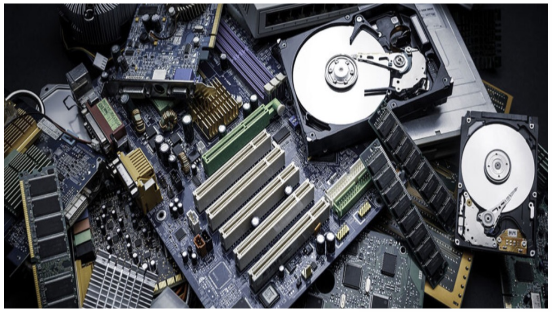
INL/CON-23-71112

Circular Economy for Critical Materials



https://www.nrel.gov/about/circular-economy.html

Understanding Metal-Ligand Interactions: Recycling and Recovery of Critical Materials and Rare Earth Elements



MAGAZINE · RARE EARTH METAL

Recycling Efforts May Undermine China's Rare-Earth Monopoly

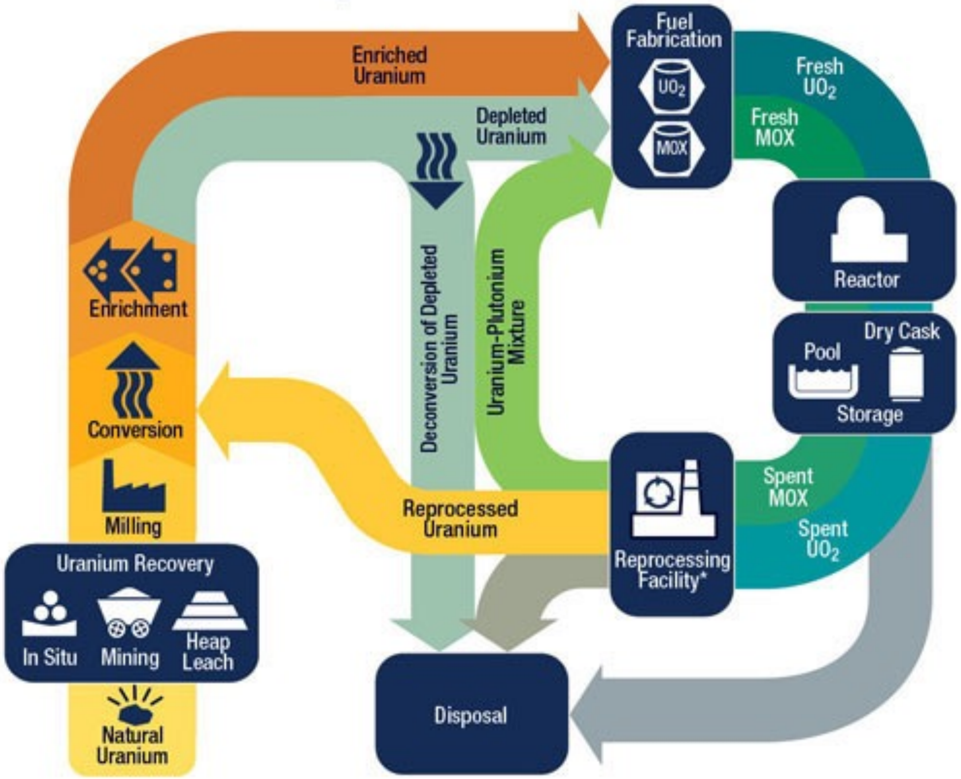
BY EAMON BARRETT
July 27, 2019 at 8:00 AM MDT

Most Popular

https://www.snexplores.org/article/recycling-rare-earth-elements-hard-reuse-greener-technology
https://fortune.com/2019/07/27/rare-earth-metals-recycling-us-china/

Understanding Metal-Ligand Interactions: Nuclear Fuel Cycle

The Nuclear Fuel Cycle



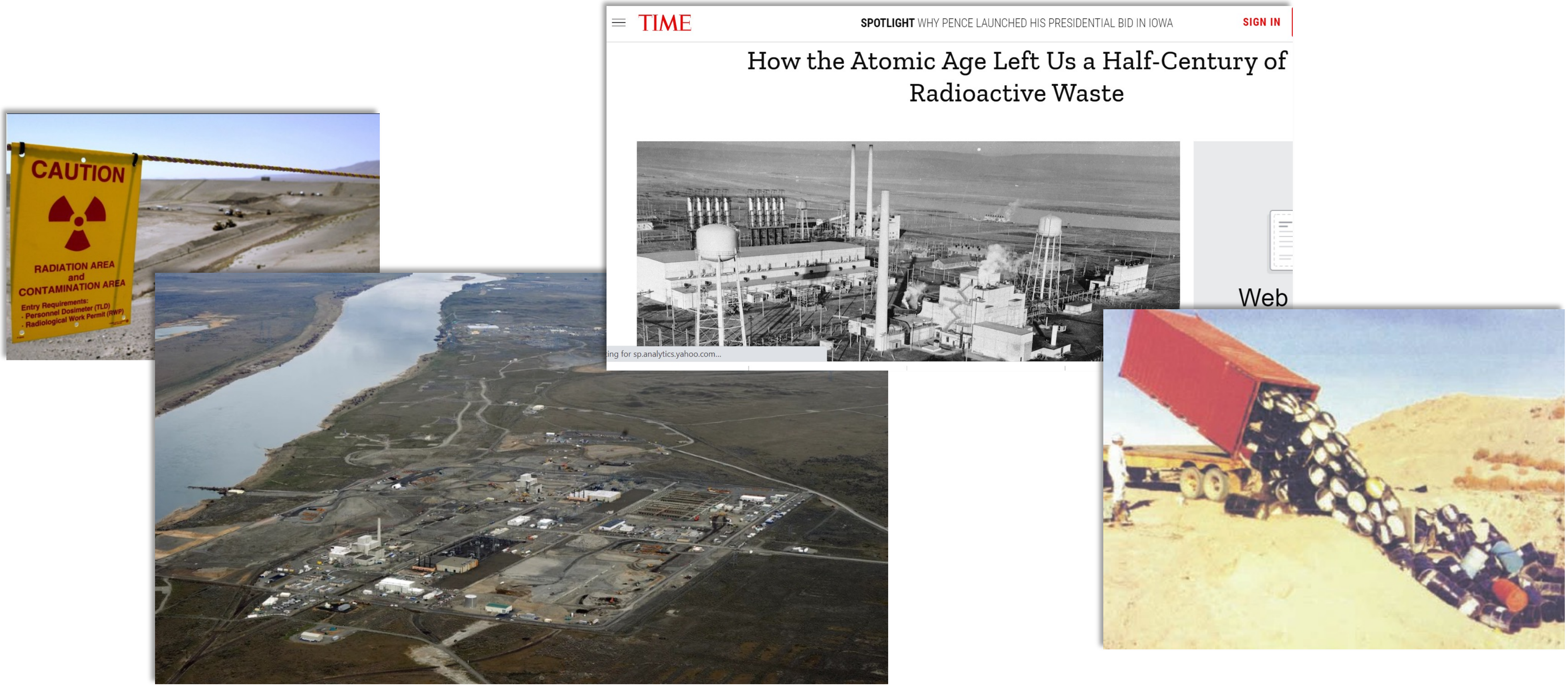
* Reprocessing of spent nuclear fuel, including mixed-oxide (MOX) fuel, is not practiced in the United States.
Note: The NRC has no regulatory role in mining uranium.

As of January 2019

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

https://www.nrc.gov/materials/fuel-cycle-fac/stages-fuel-cycle.html

Understanding Metal-Ligand Interactions: Environmental Management of Waste



TIME

SPOTLIGHT WHY PENCE LAUNCHED HIS PRESIDENTIAL BID IN IOWA

SIGN IN

How the Atomic Age Left Us a Half-Century of Radioactive Waste

Web

ing for sp.analytics.yahoo.com...

https://www.pbs.org/newshour/science/nuclear-waste-tunnel-collapses-hanford-site-washington-state

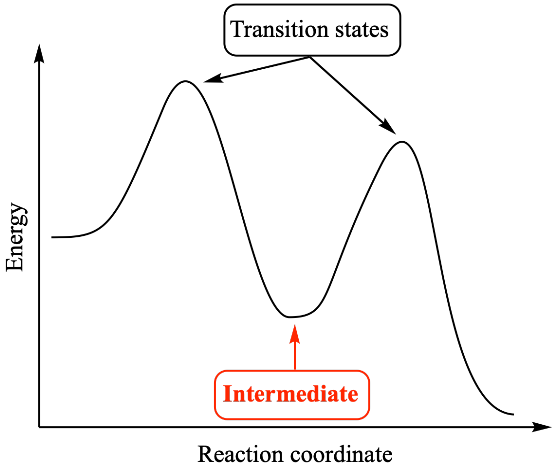
https://www.pbs.org/newshour/science/nuclear-waste-tunnel-collapses-hanford-site-washington-state

https://time.com/3672177/hanford-radioactive-waste-history/

https://www.researchgate.net/figure/Aerial-view-of-the-Radioactive-Waste-Management-Complex-The-yellow-area-shows-the_fig2_250129611

Why should we care about any of this?

- Transport of metal ions across boundary of aqueous to organic phases (and vice versa) is a critical step in nuclear fuel reprocessing and critical material recovery
- Initial metal coordination environment may be significantly different from the final one
  - metal transitions through a series of transient species as it passes from one phase to another.
- ***Thus, we need to understand the role of metal ligand interactions and the roles of transition states and intermediates***



Triphenyl Phosphine Ligands Have Been of Interest For Metal Interactions

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Dalton Trans.*, 2019, **48**, 50

Received 18th July 2018,
Accepted 25th September 2018

A sulphur and uranium fiesta! Synthesis, structure, and characterization of neutral terminal uranium(VI) monosulphide, uranium(VI) η^2-disulphide, and uranium(IV) phosphine sulphide complexes†

Justin K. Pagano, David S. J. Arney, Brian L. Scott, David E. Morris, Jaqueline L. Kiplinger* and Carol J. Burns*

nloaded by INL Research Library on 6/7/2023 9:24:54 PM.

J. Am. Chem. Soc. **1995,** *117,* 6597–6598 6597

Lanthanide and Actinide Contractions: Relativistic and Shell Structure Effects

Michael Seth,[†] Michael Dolg,[‡] Peter Fulde,[‡] and Peter Schwerdtfeger*,[†]

Department of Chemistry, University of Acklan
Private Bag 92019, Auckland, New Zealan
Max-Planck-Institut für Physik komplexer System
Dresden, Aussenstelle Stuttgar
Heisenbergstrasse 1, 70569 Stuttgart, German

Received November 29, 199

In the last decade superheavy element chemistry and physic has become an active and exciting field. Recent progress i the study of elements beyond $Z = 103$ shows that these element reveal some interesting and often unexpected chemistry. uperheavy nuclei beyond $Z = 109$ may be muc eviously predicted,[2−4] opening the way for atom nistry.[1] While the chemistry of element 104 ha in some detail,[1,5] the chemistry of the element harge greater than 105 is virtually unknown an al estimates of physical and chemical propertie blished from relativistic Xα calculations by Frick nts with nuclear charge greater than 111 have no n identified so far (elements 110 and 111 hav ed just recently by the Darmstadt group of th

tions on the elements 104−118 do indeed suggest the existence of such a contraction.[6]

To separate the relativistic effects from the f-shell contribution to the actinide contraction, we applied the method as formulated by Bagus et al.[10] and Pyykkö[11] performing numerical atomic Hartree−Fock (HF)[12] and Dirac−Fock (DF)[13] calculations with

---

Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Dalton Trans.*, 2022, **51**, 7118

Theoretical unraveling of the separation of trivalent Am and Eu ions by phosphine oxide ligands with different central heterocyclic moieties†

Pin-Wen Huang

The treatment of nuclear spent fuels, especially the separation of minor actinides, is an imperative task for the healthy development of the nuclear industry. Up to now, it still remains a worldwide challenge to separate trivalent An^{3+} from Ln^{3+} because of their similar chemical properties. Therefore, investigating the mechanism behind the selective extraction of An^{3+} by theoretical methods is necessary. In this work, three phosphine oxide ligands with the same side structures but different bridging frameworks, Ph_2PyPO,

L Research Library on 6/7/2023 9:27:55 PM.

COMMUNICATIONS CHEMISTRY

Corrected: Publisher Correction

ARTICLE

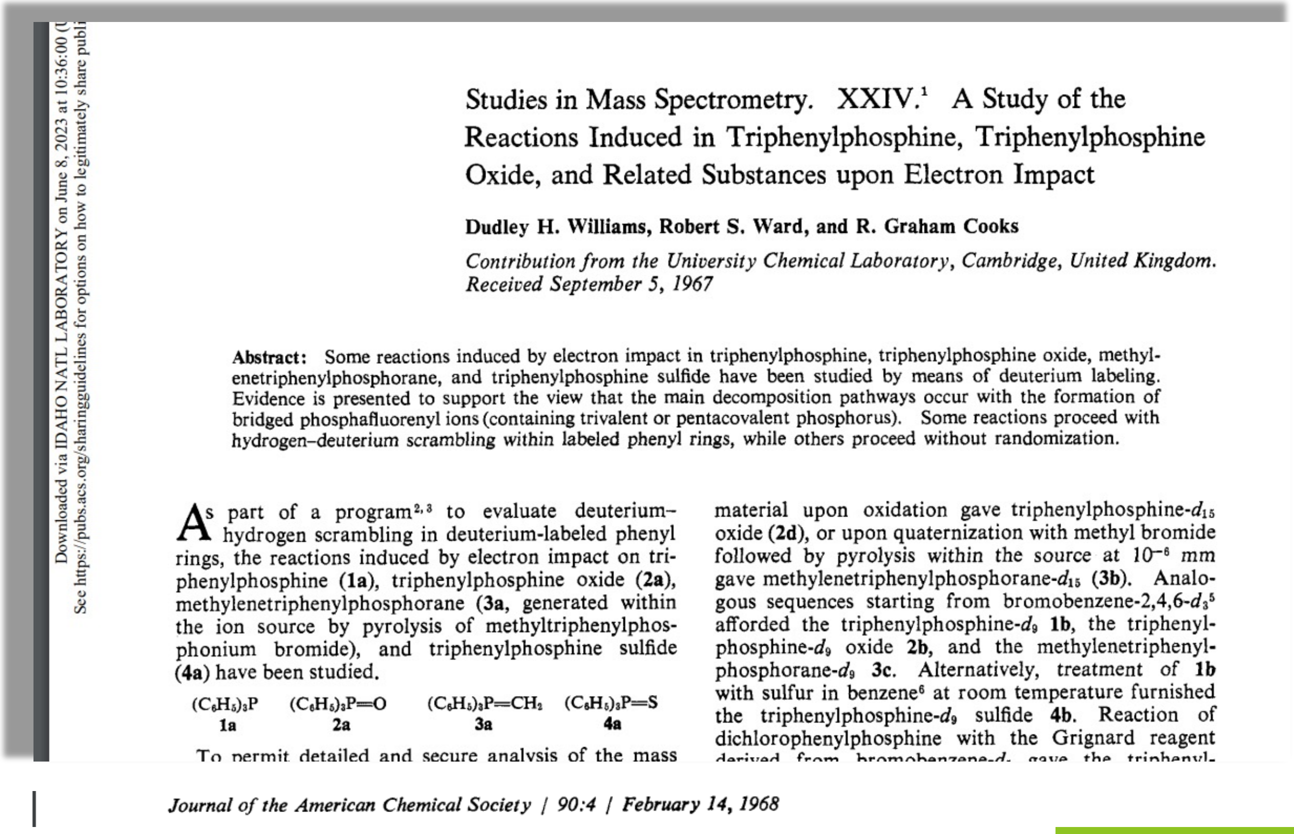
https://doi.org/10.1038/s42004-019-0249-6 OPEN

Conversion of triphenylphosphine oxide to organophosphorus via selective cleavage of C-P, O-P, and C-H bonds with sodium

Jian-Qiu Zhang[1,2], Jingjing Ye[1,2], Tianzeng Huang[1,2], Hiroyuki Shinohara[3], Hiroyoshi Fujino[3] & Li-Biao Han[1,2*]

For over half a century, thousands of tons of triphenylphosphine oxide $Ph_3P(O)$ have been produced every year from the chemical industries as a useless chemical waste. Here we disclose efficient transformations of $Ph_3P(O)$ with cheap resource-abundant metallic sodium finely dispersed in paraffin oil. $Ph_3P(O)$ can be easily and selectively transformed to three reactive organophosphorus intermediates—sodium diphenylphosphinite, sodium 5H-benzo[b]phosphindol-5-olate and sodium benzo[b]phosphindol-5-ide—that efficiently give the corresponding functional organophosphorus compounds in good yields. These functional organophosphorus compounds are difficult to prepare but highly industrially useful compounds. This may allow $Ph_3P(O)$ to be used as a precious starting material for highly valuable

Triphenyl Phosphine Ligands- Graham Cooks in 1968!



Studies in Mass Spectrometry. XXIV.[1] A Study of the Reactions Induced in Triphenylphosphine, Triphenylphosphine Oxide, and Related Substances upon Electron Impact

Dudley H. Williams, Robert S. Ward, and R. Graham Cooks

Contribution from the University Chemical Laboratory, Cambridge, United Kingdom.
Received September 5, 1967

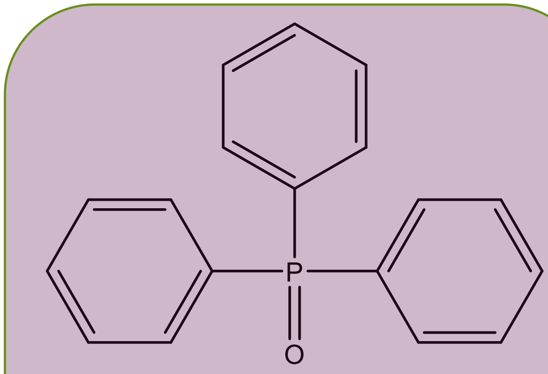
Abstract: Some reactions induced by electron impact in triphenylphosphine, triphenylphosphine oxide, methylenetriphenylphosphorane, and triphenylphosphine sulfide have been studied by means of deuterium labeling. Evidence is presented to support the view that the main decomposition pathways occur with the formation of bridged phosphafluorenyl ions (containing trivalent or pentacovalent phosphorus). Some reactions proceed with hydrogen–deuterium scrambling within labeled phenyl rings, while others proceed without randomization.

As part of a program[2,3] to evaluate deuterium–hydrogen scrambling in deuterium-labeled phenyl rings, the reactions induced by electron impact on triphenylphosphine (**1a**), triphenylphosphine oxide (**2a**), methylenetriphenylphosphorane (**3a**, generated within the ion source by pyrolysis of methyltriphenylphosphonium bromide), and triphenylphosphine sulfide (**4a**) have been studied.

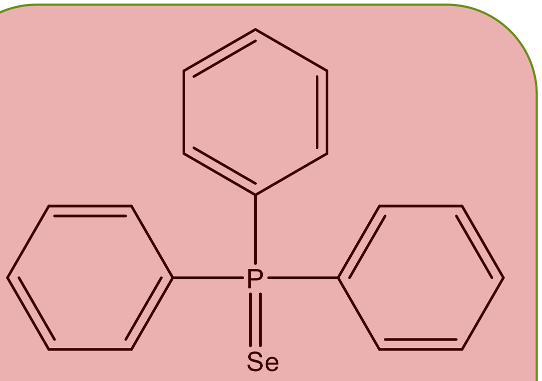
$(C_6H_5)_3P$ **1a** $(C_6H_5)_3P{=}O$ **2a** $(C_6H_5)_3P{=}CH_2$ **3a** $(C_6H_5)_3P{=}S$ **4a**

To permit detailed and secure analysis of the mass material upon oxidation gave triphenylphosphine-d_{15} oxide (**2d**), or upon quaternization with methyl bromide followed by pyrolysis within the source at 10^{-6} mm gave methylenetriphenylphosphorane-d_{15} (**3b**). Analogous sequences starting from bromobenzene-2,4,6-d_3[5] afforded the triphenylphosphine-d_9 **1b**, the triphenylphosphine-d_9 oxide **2b**, and the methylenetriphenylphosphorane-d_9 **3c**. Alternatively, treatment of **1b** with sulfur in benzene[6] at room temperature furnished the triphenylphosphine-d_9 sulfide **4b**. Reaction of dichlorophenylphosphine with the Grignard reagent derived from bromobenzene-*d* gave the triphenyl-

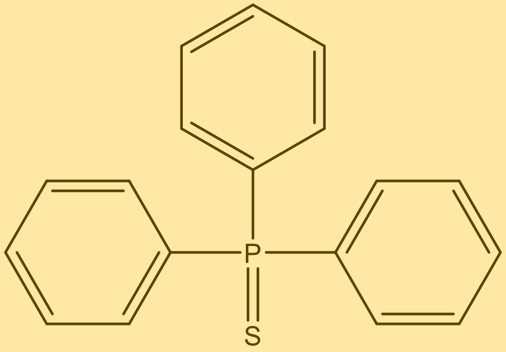
Triphenylphosphine Ligands with Oxygen, Selenide, and Sulfur



Triphenylphosphine Oxide
(TPPO)



Triphenylphosphine Selenide
(TPPSe)



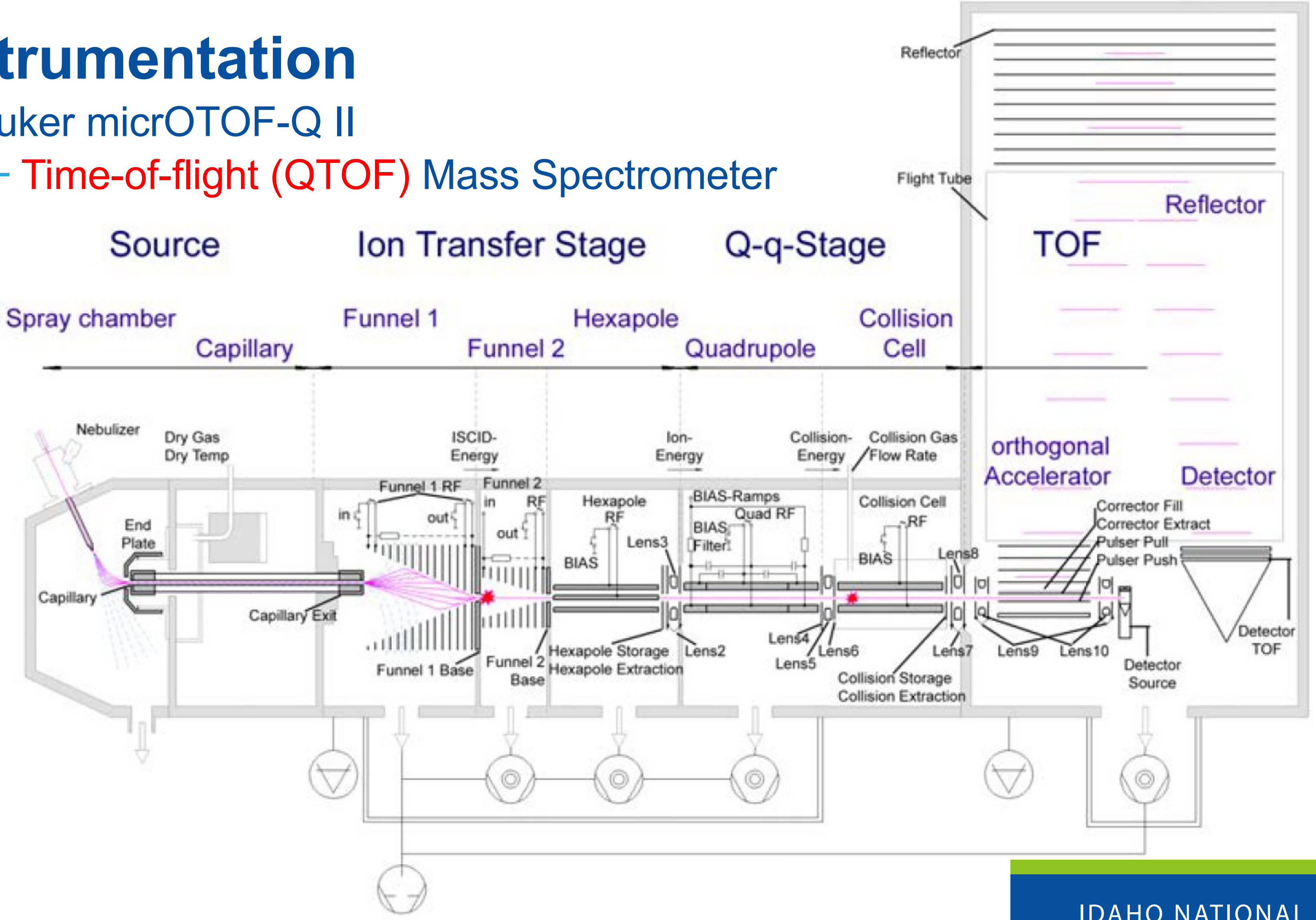
Triphenylphosphine Sulfide
(TPPS)

Methods

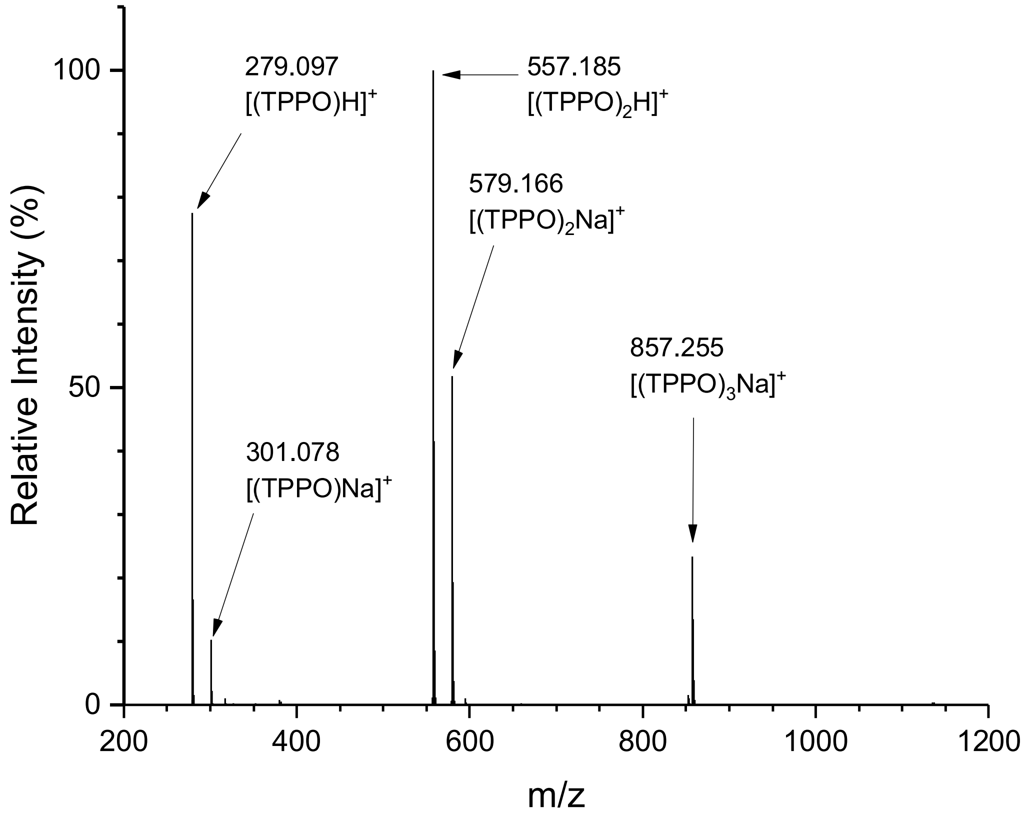
- Metal cluster ions of sodiated ligands were formed via electrospray on the commercial Bruker ESI ion source
- Homodimers or heterodimers of ligands were formed with sodium
  - Concentrations for optimal cluster formation were experimentally derived, and ranged from 10-100µM
- Sodium dimers formed via electrospray ionization were isolated and fragmented via collisionally induced dissociation (CID)
- All experiments shown here were performed on Bruker microTOF-QII (Q-TOF)

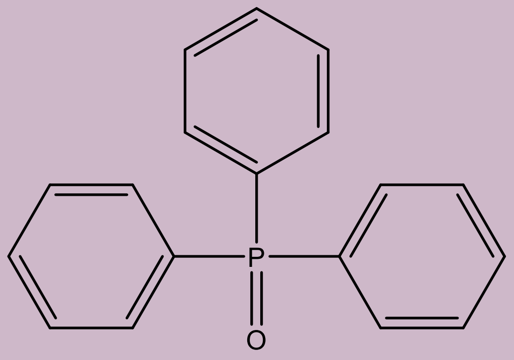
Instrumentation

- Bruker micrOTOF-Q II
  - Time-of-flight (QTOF) Mass Spectrometer



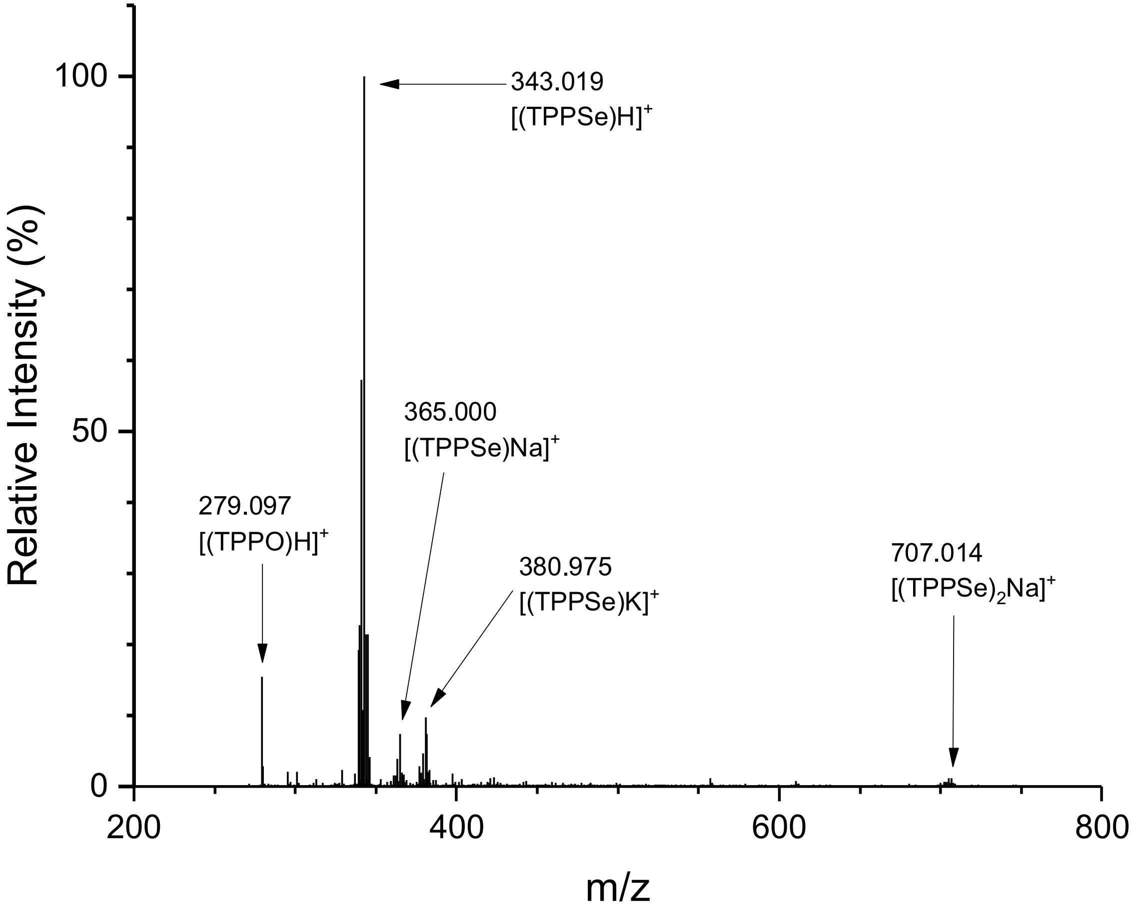
MS1 of SodiumTriphenylphosphine Oxide (TPPO)

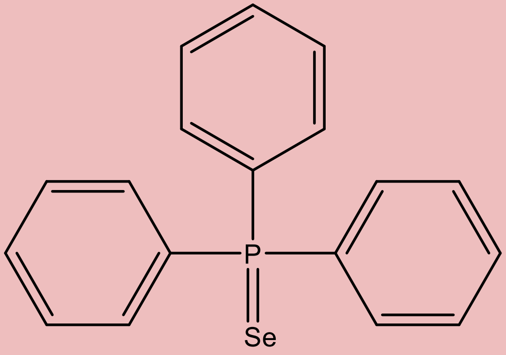




Triphenylphosphine Oxide
(TPPO)

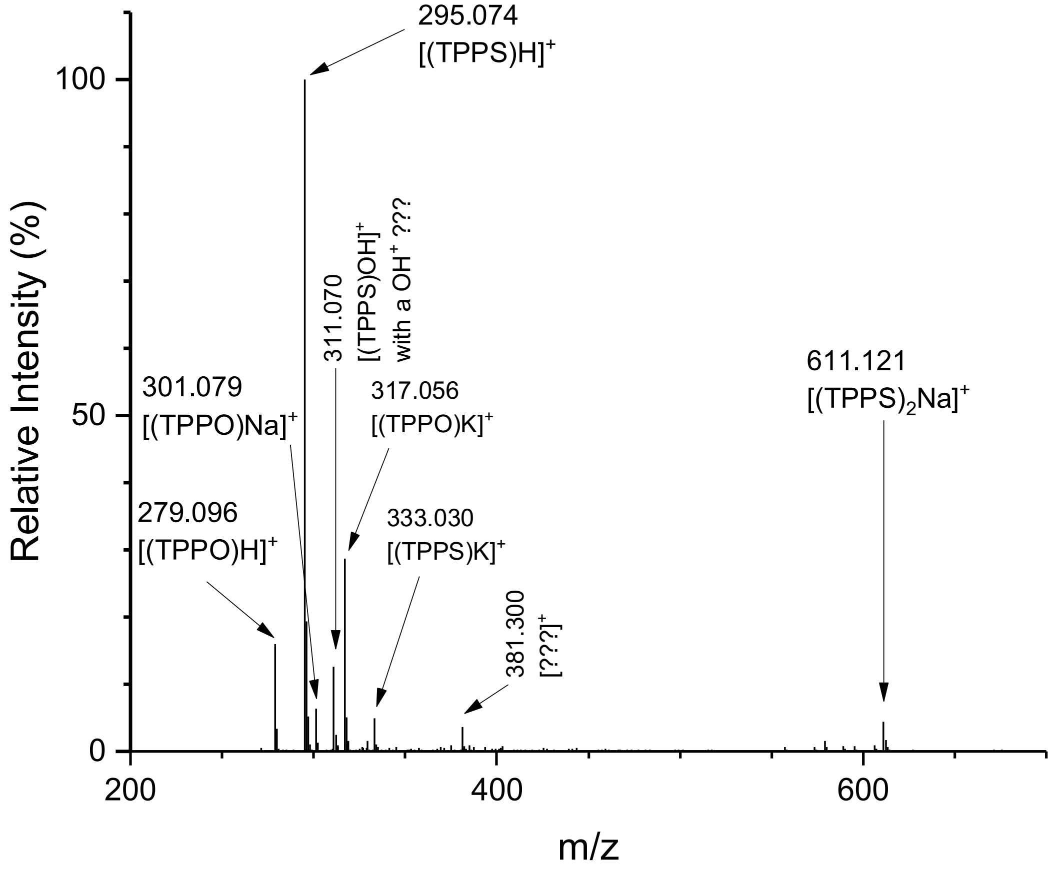
MS1 of SodiumTriphenylphosphine Selenide (TPPSe)

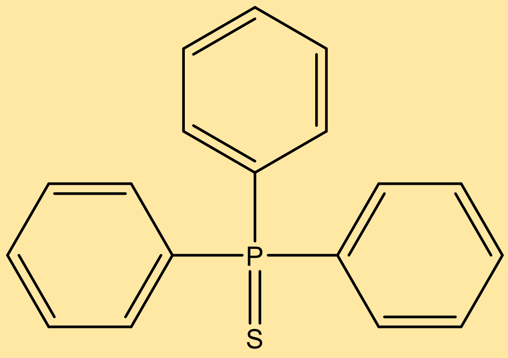




Triphenylphosphine Selenide
(TPPSe)

MS1 of SodiumTriphenylphosphine Sulfide (TPPS)

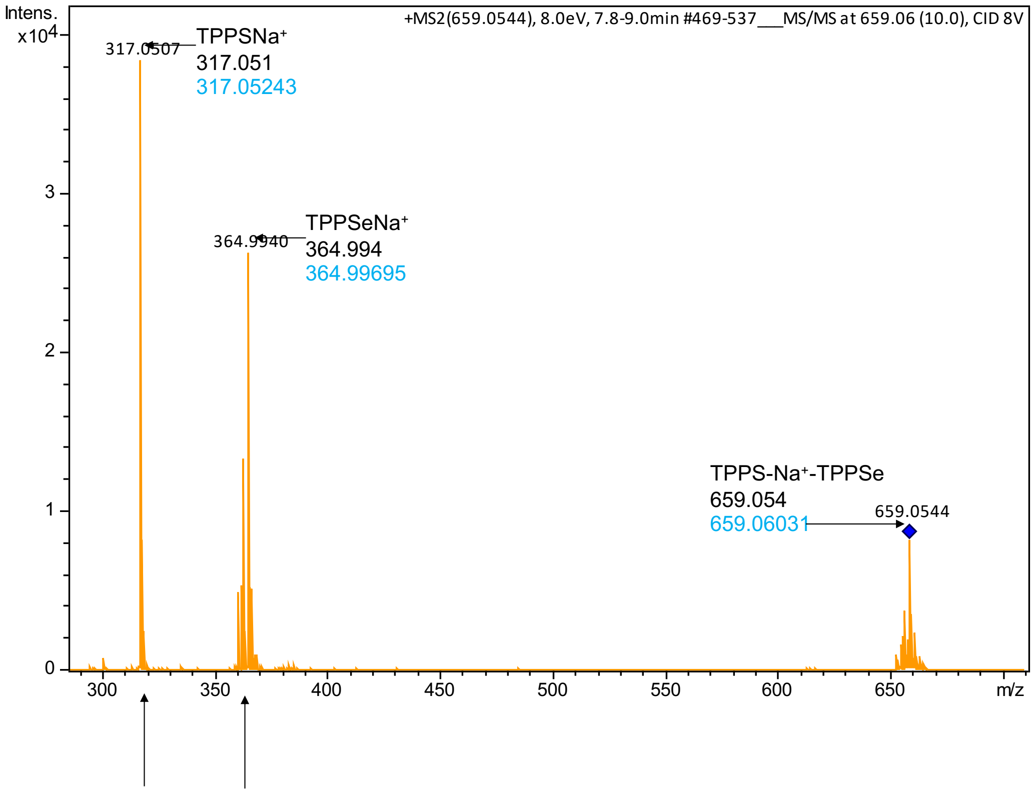




Triphenylphosphine Sulfide
(TPPS)

CID of Mixed Ligand Cluster [(TPPS)(TPPSe)Na]$^+$

QTOF



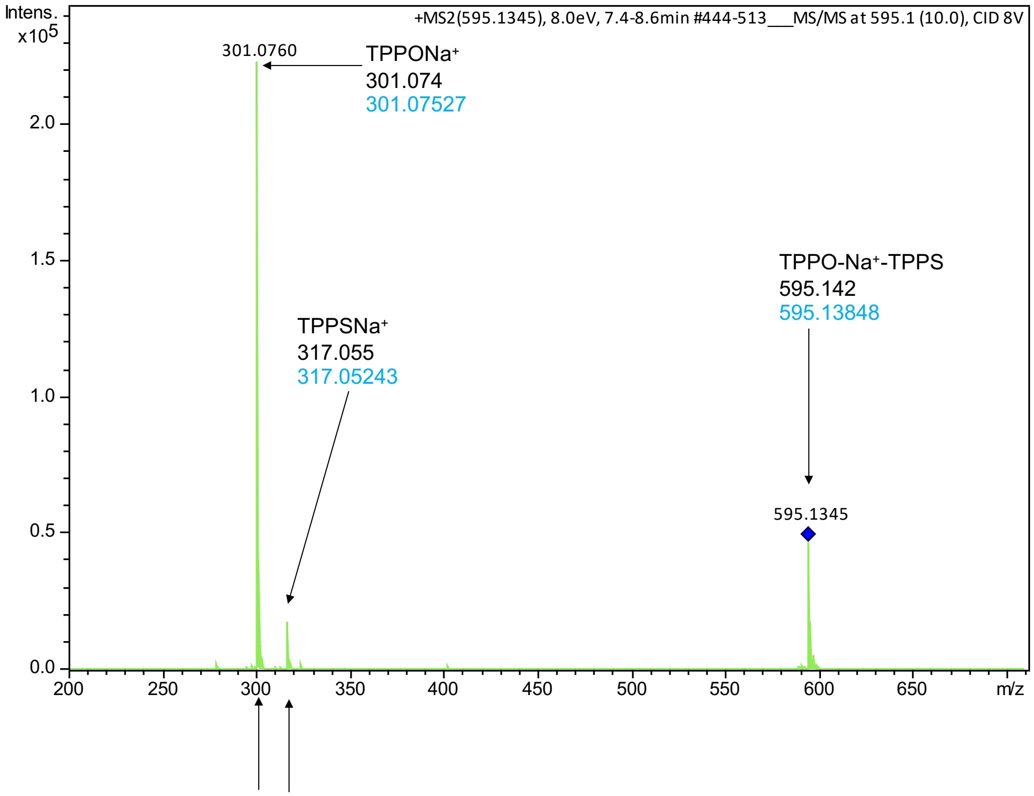
Branching ratio:

43 : 57

MS/MS at 659.06 (10.0 Width)
CID 8V

10 uM TPPS + 10 uM TPPSe
CID

CID of Mixed Ligand Cluster [(TPPS)(TPPO)Na]$^+$



TPPONa$^+$
301.074
301.07527

TPPSNa$^+$
317.055
317.05243

TPPO-Na$^+$-TPPS
595.142
595.13848

Branching ratio:
91 : 9

QTOF
10 uM TPPO + 100 uM TPPS

MS/MS at 595.1 (10.0 Width)
CID 8V

10 uM TPPO + 100 uM TPPS
CID

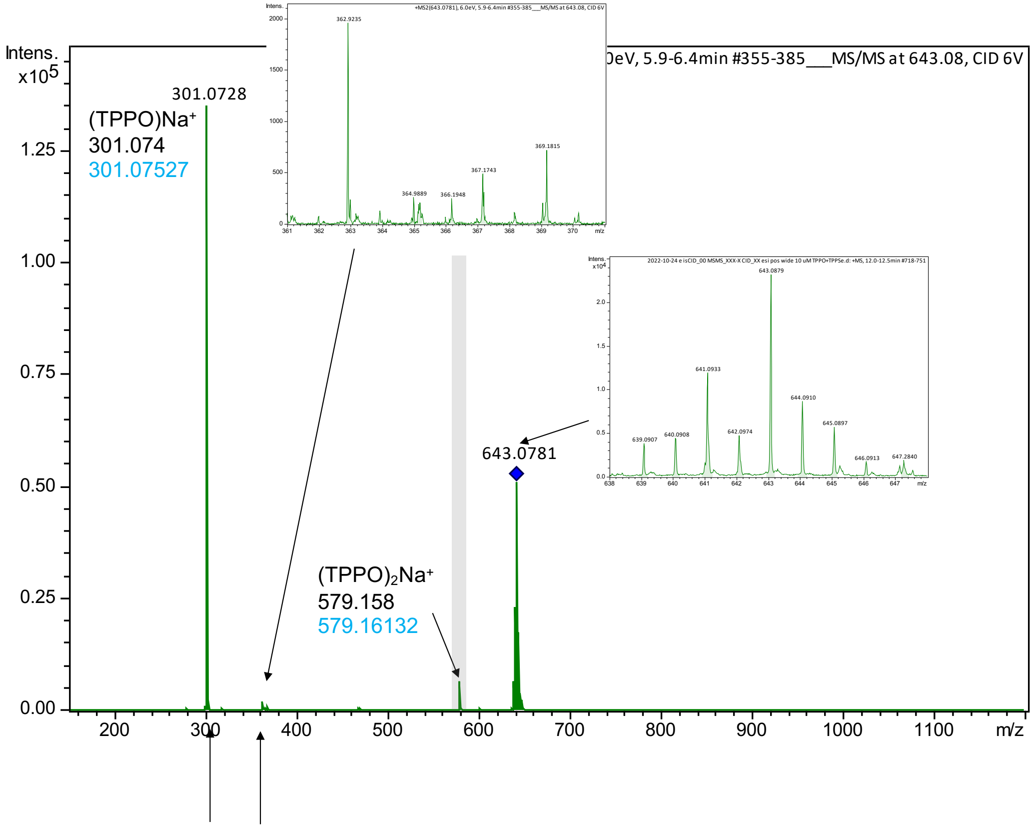
CID of Mixed Ligand Cluster [(TPPSe)(TPPO)Na]$^+$

QTOF

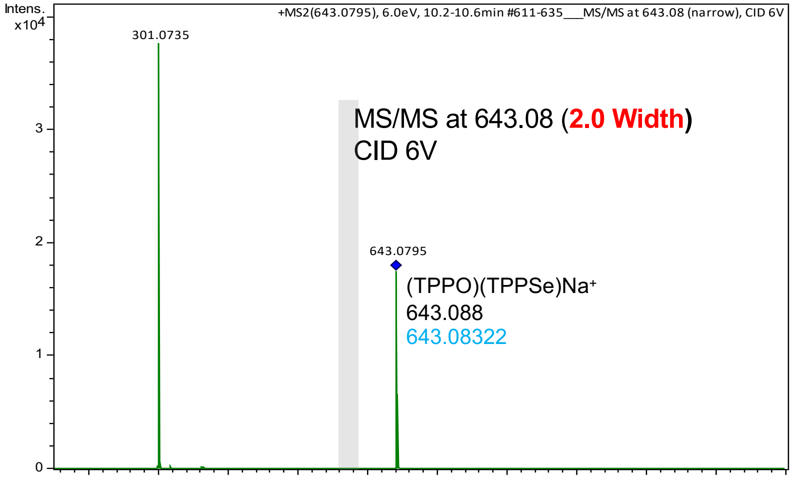
10 uM TPPO + 100 uM TPPSe

MS/MS at 643.08 (**10.0 Width**)
CID 6V

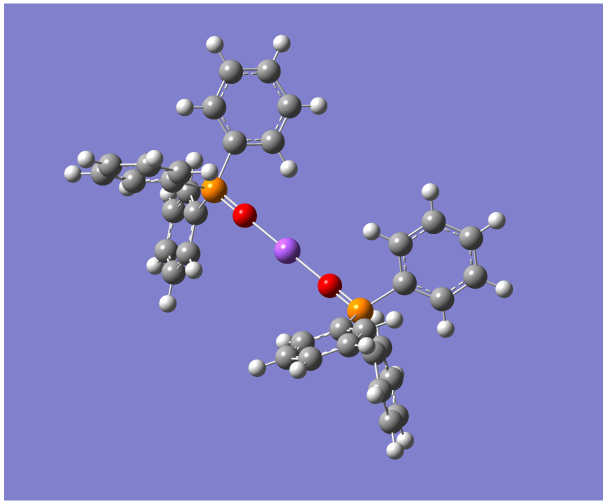
10 uM TPPO + 100 uM TPPSe
CID



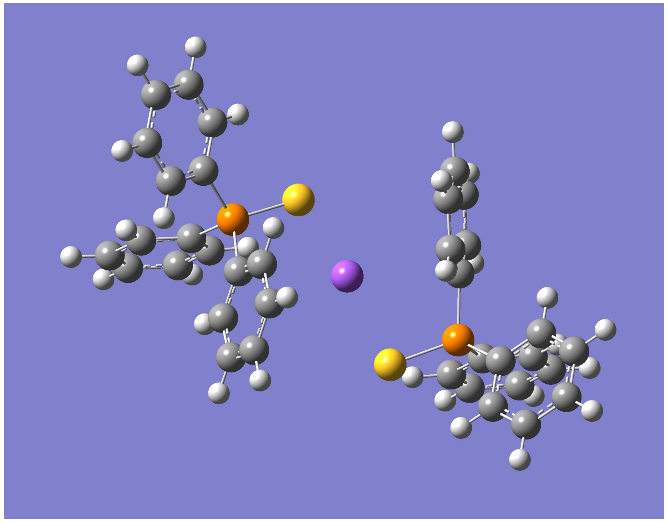
Branching ratio:
100 : 0



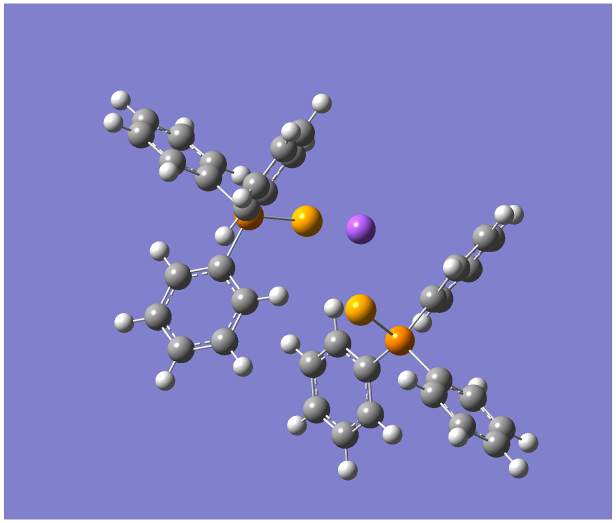
Density Functional Theory Calculations: Homodimers



[(TPPO)$_2$Na]$^+$ Homodimer



[(TPPS)$_2$ Na]$^+$ Homodimer



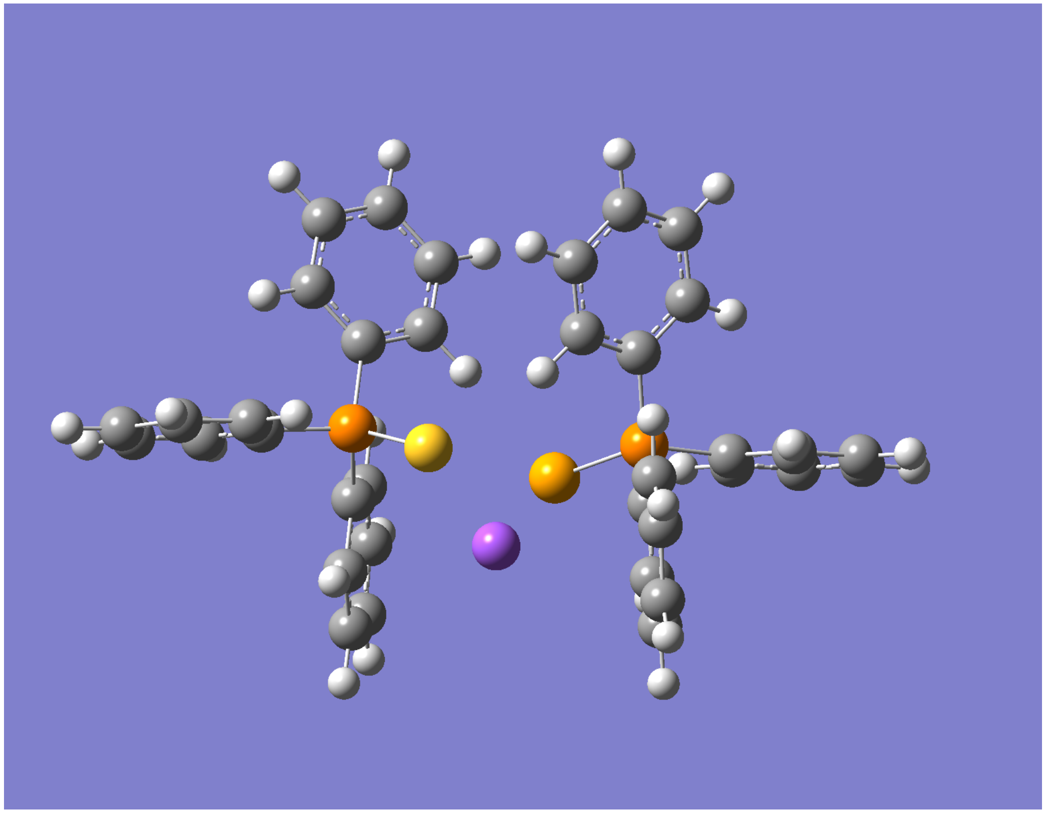
[(TPPSe)$_2$Na]+ Homodimer

- Calculations were performed using Gaussian and viewed in GaussView 6.0.16 (https://gaussian.com/)
- Density Functional Theory Calculations were optimized with B3LYP with Basis Set 6-31+G(d,p) and RwB97XD calculation method

GaussView, Version 6, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

Gaussian 16, Revision C.01, M. J. Frisch, et al, Gaussian, Inc., Wallingford CT, 2016.

Density Functional Theory Calculations - Mixed Heterodimers of $[(\text{TPPS})(\text{TPPSe})\text{Na}]^+$



Conclusions

- Dimers of triphenylphosphine chalcogenides (TPPX where X=oxygen, sulfur, or selenium) and sodium were generated via electrospray and investigated via collisionally induced dissociation.
- CID of the heterodimer complexes $[(TPPO)(TPPS)Na]^+$ and $[(TPPO)(TPPSe)Na]^+$ demonstrated the oxide portion of the dimer was more likely to remain intact
- DFT calculations are ongoing for heterodimers of Oxygen:Sulfur and Oxygen:Selenide

Future Directions

- Metal-triphenylphosphine clusters are being studied to better understand the intrinsic bonding and reactivity of the metal cluster species, and to better understand the transition states between
  - Various additional metals
  - Other ligands (diglycolamides, perchlorates)
  - Mass spectrometry
  - IRMPD

Acknowledgements


Christopher A. Zarzana


Brittany D.M. Hodges


JungSoo Kim

Collaborative Computing Center
Idaho National Laboratory

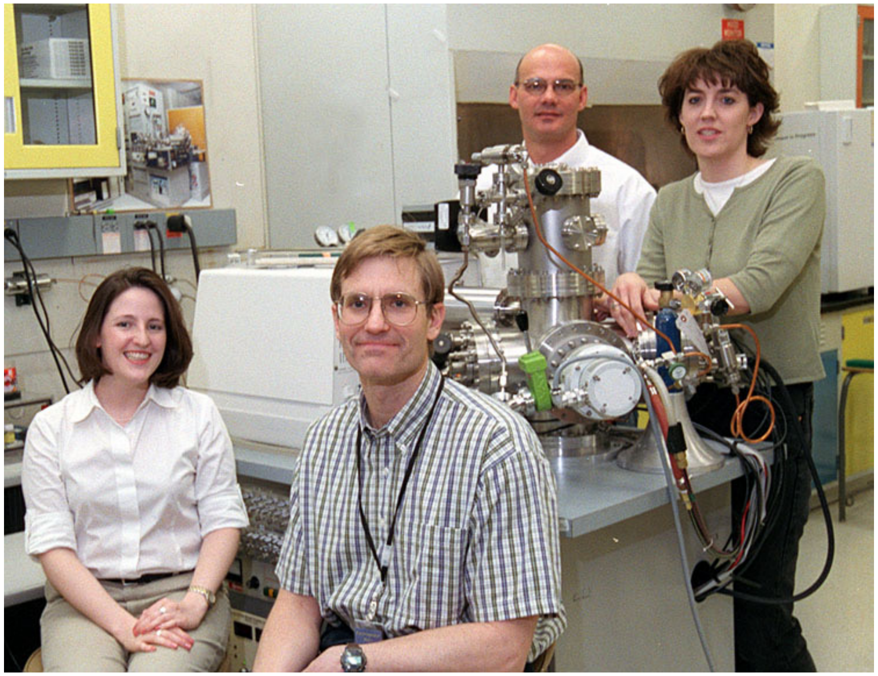
Funding: This work was supported by the U.S. Department of Energy through the INL Laboratory Directed Research & Development (**LDRD**) Program under DOE Idaho Operations Office Contract 22A1059-125.

Calculations: High Performance Computing (**HPC**) was performed using the Idaho National Laboratory computing resources which are supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.
https://hpc.inl.gov/SitePages/Home.aspx

Congratulations on Retirement:
Gary Groenewold and Garold Gresham

Gary Groenewold

Garold "Gary" Gresham



Idaho National Laboratory
Part of the Secondary Ion Mass Spectrometry Group
(SIMS Group)
Circa 2001

INL

Idaho National Laboratory

Instrumentation

- Bruker amaZon speed ETD
  - Quadrupole Ion Trap Mass Spectrometer