**Triphenylphosphine: Transformations of a Common Ligand**

*Adapted from* “Synthesis of Triphenylphosphine Oxide and Triphenylphosphine Sulfide” *in* Inorganic Experiments, 3rd Edn. *by Iain A. Smellie.*1

**Objective**

This experiment will introduce several procedures and techniques common to the synthetic inorganic laboratory. You will prepare a complex using multiple synthetic steps, and evaluate your products using IR, NMR, UV-Vis, and GC-MS. You will also practice electron counting, and searching the literature for structures similar to your target complex. At the conclusion of this experiment, you will be required to prepare the first full lab report for the course. Peer review and small group discussion of this lab report will provide useful suggestions for your final report.

**Before You Come to Lab...**

Read and understand the experimental procedure. Decide on a plan for your time in the laboratory, and prepare a flowchart or other summary of your proposed activities for each day (no more than one page!), and submit this to your instructor no later than 8:00 AM on the day of lab. Identify any reagents or solvents required using a reaction table like that you would prepare for an organic chemistry experiment, and identify any questions you have about the procedure. Don’t forget that this is a two week experiment, so a plan should be made before each meeting.

In addition, please include a qualitative (i.e. “back-of-the-envelope”) MO diagram for the homonuclear diatomic I2 molecule in your pre-lab planning for the first full week of lab. You may wish to refer to your general chemistry notes/text when doing this.

Your first full lab period will involve the isolation and characterization of Ph3PS and the preparation of Ph3PSI2, and the second full lab period will focus on the isolation and characterization of the final product. We will begin the pre-lab exercises in week 2 of the semester (see your course schedule, above).

**Safety, Hazards & Waste**

All procedures should be conducted in a fumehood, and gloves should be worn when handling all reagents. Always wash your hands thoroughly before leaving the laboratory. A lab coat should be worn at all times when handling these compounds. All organic reagents and solvents are flammable, and may be hazardous in some cases (avoid inhalation). In addition, metals salts and organic reagents are irritants, and some are cancer-suspect agents. Iodine should be handled with care and disposed in the halogenated waste, along will all dichloromethane solutions. All other organic waste should be disposed of in the non-halogenated waste container.

**Procedure**

Each student will prepare their own samples for this experiment, following the protocol described below. As with all synthetic experiments, your yield and purity will comprise a portion of your grade for this activity, so careful manipulations are advised.

**Day 1, Preparation of Ph3PS**: Following the safety lecture, you will prepare Ph3PS and allow your product to sit for the week. In a 50 mL round bottom flask equipped with a magnetic stir bar, combine triphenylphosphine (525 mg, 2 mmol), molecular sulfur (71 mg, 2.2 mmol), and 10 mL of 95% ethanol. Place a water-cooled condenser (wire your condenser hoses in place!) on the round bottom flask, initiate stirring, and bring your solution to reflux. After 45 minutes of heating, allow your flask to cool to room temperature. Before leaving for the day, ensure that your flask is cool and the water flow is turned off.

**Day 2, Isolation and purification of Ph3PS, preparation of Ph3PSI2**: Vacuum filter the solution from last week to recover the white to off-white precipitate. If any insoluble S8 is observed, recrystallize your solid from acetone, hot-filtering to remove any insoluble yellow S8. Filter to isolate your product, and record your yield of Ph3PS.

Prepare Ph3PSI2 by combining triphenylphosphine sulfide (74 mg, 0.25 mmol), molecular iodine (64 mg, 0.25 mmol), and 5 mL dichloromethane in a new 20 mL scintillation vial fitted with a magnetic stir bar. Cap the vial, initiate stirring, and allow components to stir for the remainder of the laboratory period. Before leaving for the week, reduce the volume of your solution to approximately half of the original volume using the rotovap or a nitrogen stream. Replace the cap, and allow your reaction to stand until next laboratory period.

Using WebMO, calculate the frontier MOs for I2 and Ph3PS using the STO-3G functional. If you need assistance logging into WebMO or setting up these calculations, see your instructor or your TA.

If you have time, you may perform any of the characterization described below on Ph3P or Ph3PS. You should negotiate use of required instruments with your labmates so that you are not in one another’s way.

**Day 3, Isolation of Ph3PSI2 and characterization of products**: Filter your reaction mixture to isolate the dark brown/red product, wash the crystals with 5 mL of hexanes, and record your yield of Ph3PSI2. Fully characterize your products using the following techniques/experiments. All students should record 1H and 31P spectra. All other characterization may be pooled as a group (such that each group only needs on GC-MS, FT-IR spectrum etc.).

NMR: You should obtain 1H and 31P spectra for Ph3P, Ph3PS, and Ph3PSI2 in CDCl3 solution. Your instructor will provide assistance with acquiring 31P NMR spectra. Use the P31CPD experiment, and manually set NS=256 (256 scans of the sample, instead of the standard 16).

IR: You should obtain FT-IR spectra for all products using the KBr pellet method. See your instructor or a TA for a demonstration of how to prepare your sample using this method.

GC-MS: Prepare a dilute sample of your recrystallized Ph3PS in dichloromethane solution. Run these samples on the GC-MS using Ph3PS.mth, and use the resulting chromatogram to assess the identity and purity of your product. Your TA or instructor will assist you with setting up this experiment.

UV-Vis: Using the Spec 200 spectrometers, obtain UV-Vis spectra of both I2 and your Ph3PSI2 in dichloromethane solution between 200 to 800 nm. Recall that Beer’s Law is valid between absorbances of ~0.1 to 1.2, for each λmax. Save and export each spectrum as a .csv file, and prepare a plot for your report with both spectra on the same set of axes. Your TA will assist you with the acquisition of these spectra.

**For Your Report**

You will be submitting a preliminary draft of your report for this experiment for consideration in the “peer review” activity described below. To facilitate this process, your “draft” report should be double spaced, with plenty of room left for margin notes.

Your report for this experiment should include all spectral data (inserted electronically as an appendix or a figure in the text), yields for both products, and balanced chemical equations for the reactions that take place. Additionally, please provide answers to the following questions:

1. Describe the orbitals involved in the following interactions:
   1. Ph3PS donates two electrons to I2 (dative bonding)
   2. I2 donates two electrons to Ph3PS (dative bonding)
   3. Ph3PS and I2 form a covalent bond

Using the orbital diagram you prepared before coming to lab, and the MOs generated using WebMO, how would these orbitals be oriented? What does this tell you about the likelihood of each of the scenarios described above (a-c)? Draw a Lewis representation of Ph3PSI2 (including lone pairs and formal charges where necessary), and indicate which description you believe to be most likely.

1. Draw Lewis structures for the reaction that occurs between Ph3P and S8, and assign oxidation numbers for phosphorus and sulfur atoms in all species. What kind of reaction takes place when triphenylphosphine reacts with molecular sulfur?
2. How do the 31P chemical shifts for Ph3P, Ph3PS, and Ph3PSI2 compare? What does this suggest about how chemical shift in the 31P NMR experiment correlate to oxidation state of the phosphorus? How useful are 1H NMR spectra, relative to 31P spectra for this experiment?
3. How do the IR spectra for Ph3P, Ph3PS, and Ph3PSI2 compare? What stretching frequencies appear/disappear/shift? What conclusions about the structure of each product are supported by your spectra? Consult the chemical literature for IR stretches for P-S and I2. Can you see these stretching frequencies in your spectra? Comment on the usefulness of IR for this experiment.
4. Using SciFinder, find an example of a metal complex with a phosphine sulfide ligand (sulfur bound to a metal). Provide a CAS number, citation, and the correct electron count for the complex. (*Bonus points if you provide a complex not cited by another student*).

Your final report should include all data, and any changes made as a result of the peer review process.

**References**

1. Smellie, I.A.“Synthesis of Triphenylphosphine Oxide and Triphenylphosphine Sulfide.” *Inorganic Experiments, 3rd Ed.* Woolins, J.D., Ed. Wiley-VCH: Weinheim, 2010; pp. 81-85.