Experiment 13: Transformations of a common ligand, triphenyl phosphine

Objective.

Main group compounds are typically less well studied in the United States relative to Europe and Canada. This experiment will introduce you to some main group compounds, including reactivity, bonding, and spectroscopic characterization. This experiment is adapted from an experiment created by Bradley M. Wile, Ohio Northern University, and posted on VIPEr on 6/9/19.

Background.

Triphenylphosphine, Ph_3P is a very common ligand in inorganic chemistry. It is a white crystalline solid, and slowly reacts with dioxygen to form impure triphenylphosphine oxide. Some of the oxygen atoms end up in between the P-C bonds, which is why it is impure.

The chalcogens, the main group VI elements, are reactive and form many interesting compounds. The elemental forms of the chalcogens vary substantially going down the periodic table, from the non-metallic O_2 to the metallic tellurium. Part of your writeup will be to determine the common elemental forms of these elements (structures and basic information). Similarly, the halogens vary from gaseous fluorine to solid iodine, but the reactivity of the halides as a group is generally quite similar.

This experiment is an exploratory, research-like experiment, and you will work with a partner on it. First you will observe the reaction of PPh_3 (or another similar phosphine) with elements, and then you will select characterization methods to evaluate in order to determine the structure of the product. That product then reacts with I_2 to form a new product, which you also must identify. Part of your job in this experiment is to verify the bonding, structure, and reactivity of these compounds using the experimental and computational resources we have available in the department. As this is a research based experiment, no references are provided, and you are discouraged from looking for references about your proposed compound until after you have decided on its structure. The goal here is to select characterization methods, and interpret the results, not to get the *correct* answer. Your final writeup for this experiment will be a complete analysis of all 6 of the reactions studied, including literature research.

Note: phosphine complexes of S and Se are used as insecticides and are closely related to nerve gasses. Handle all complexes prepared in this experiment with care.

Group work

In this experiment, each pair of students will use the same phosphine to carry out all of the reactions. Divide up the work. synthesize products of triphenylphosphine. You will then examine the reaction chemistry of your synthesized compounds (those with S and Se only) with elemental iodine, I_2. Characterization of these compounds will require purification by recrystallization and, possibly, repeated synthesis. The final writeup will incorporate information from all five reactions, so you will share data with your partner.

Possible Discussion Questions

1) What are the standard state structures for the chalcogens? Do any of the elements have allotropes? Which chalcogens have NMR active nuclei?
2) What are the standard state structures for the halogens? Do any of the elements have allotropes? Do any of them have NMR active nuclei?
3) What is the MO diagram for I_2?
4) What is the MO diagram for I_3^-?
5) Propose a structure (based on Lewis/VSEPR) for the products of the reaction of triphenylphosphine with Br_2, S, or Se, and the subsequent reaction with I_2.
6) Carry out a Gaussian calculation to optimize the geometry of your proposed structure (you may wish to model triphenylphosphine as PMe_3 or PH_3 to simplify the calculations).
7) How is the calculated structure similar or different from your initial proposal?
8) What MOs are most important for bonding in the compounds you made?

Synthesis 13.1 reaction of triphenylphosphine with either Br_2, S, Se or Te.

Bromine

Dissolve your chosen phosphine (2 mmol) in dichloromethane[†] (10 mL) in a round bottom flask. Add bromine (0.2 mL, about 5-10 drops until the reaction has color from excess bromine; *Br_2 is volatile and toxic, work in the hood*). Stir the reaction and slowly add saturated sodium carbonate solution (10 mL) using a pipette. After addition, stir until any color change stops; a biphasic solution should result. Separate the layers using a separatory funnel, wash the aqueous layer with dichloromethane, and dry the organic layer over magnesium sulfate. Filter and remove the solvent by rotary evaporation. The product can be recrystallized from acetone or toluene.

Sulfur (procedure 1)

In a 50 mL round bottom flask equipped with a magnetic stir bar, combine your chosen phosphine (2 mmol), molecular sulfur (71 mg, 2.2 mmol), and 10 mL of toluene. Place a water-cooled condenser (clamp 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. If no precipitate is immediately visible, chill your flask in ice or leave it (labeled) in the freezer until next week. Vacuum filter the solution (use a small Hirsch funnel) to recover the white to off-white precipitate. If any remaining sulfur is observed, recrystallize your solid from hot acetone, hot-filtering to remove it. Collect your product by vacuum filtration after cooling to room temperature or in an ice bath. The product can be recrystallized from toluene or acetone (reagent grade).

[†] The department is phasing out the use of DCM due to its hazardous nature. Work with the instructor to select a different solvent for this reaction.

Selenium
Follow the procedure for Sulfur above, but use elemental selenium. The compound can be recrystallized from boiling acetone or ethanol (200 proof).

Tellurium
The synthesis of the corresponding compound with Te requires the use of KTeCN or the tetraphenylarsonium salt of TeCN; the *byproduct* of this reaction is KCN or $(Ph_4As)CN$. As cyanide salts are highly toxic, we will not synthesize this complex in this course. The synthesis is quite complicated, low-yielding, and requires extensive purification.

Synthesis 13.2 the iodine reaction
Prepare the corresponding product by combining your product from synthesis 13.1 (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. Label your sample! During the next laboratory period, collect your product by vacuum filtration, wash the crystals with 5 mL of hexanes. Even if a product does not precipitate, some characterization methods can still be employed!

Characterization methods to evaluate, discuss, or consider
Melting point
IR
NMR (^{1}H, ^{13}C, ^{31}P, other nuclei?)
UV-Vis of d-d transitions (ε, Δ_o)
Gaussian calculations to compare observed and calculated IR stretches
Gaussian calculations to visualize orbitals
Polarimetry
Mass spectrometry
Single crystal X-ray diffraction

Waste disposal. Halogenated organic solvents and other organic solvents should be placed in the appropriate container. Solid waste may be placed in the trash.

References

1. These will be provided by the instructor as needed/requested