MANUAL: ATOMIC INTERCALATION FOR 2D LAYERED MATERIALS

Kristie J. Koski
Department of Chemistry, University of California, Davis, 1 Shields Ave., Davis CA 95616, USA
e-mail: koski@ucdavis.edu

PERIODIC TABLE OF INTERCALANTS:

Fig 1: This document details how to perform intercalation of the following elements:

References:

M. Wang, D. Williams, G. Lahti, S. Teshima, D. Dominguez-Aguilar, K. J. Koski, Chemical intercalation of heavy metal, semimetal, and semiconductor atoms into 2D layered chalcogenides. *2D Materials,* **5**, 045005 (2018)

K.J. Koski, J.J. Cha, B.W. Reed, C.D. Wessells, D. Kong, and Y.Cui, High density chemical intercalation of zero-valent copper into Bi_2Se_3 nanoribbons, *J. Am. Chem. Soc.*,**134**, 7584 (2012).

K.J. Koski, C.D. Wessells, B.W. Reed, J.J. Cha, D. Kong, and Y.Cui, Chemical intercalation of zero-valent metals into 2D layered Bi_2Se_3 Nanoribbons. *J. Am. Chem. Soc.* **134**, 13773 (2012).

E.W. Ong, M.J. McKelvy, G. Ouvrard, and W.S. Glaunsinger, Mercury intercalates of titanium disulfide: novel intercalation compounds. *Chem. Mater.* **4**, *14-17* (1992)

Glassware:
Liebig Condenser (CG-1218-A-20)
Three-neck Round Bottom Flask (CG-1524-A-02)
Stopper (CG-3022-06)
Glass thermometer adapter [email: roccoware.glassworks@gmail.com and ask for 14/20 THERMOWELL (50ML) and/or 14/20 THERMOWELL (25ML) – both work Cost: ~$19/piece Contact name: Tony. Also, it's possible to use a thermometer with 14/20 Ace-glass thermometer adapter (8300-07). Do not use a metal thermocouple placed into the solvent. It'll cause deposition of the metal onto the thermocouple not intercalation.]

Chemicals: Ag, Au, Bi, Co, Cr, Cu, Fe, Ge, In, Mn, Mo, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Sn, and W

Ag – silver nitrate; 5,5,7,12,12,14-hexamethyl-1,4,8,11- tetraazocyclotetradecane, acetone (Expensive $$$)
Au – Gold(I) chloride, acetone
Bi – Bismuth chloride, Stannous chloride, acetone
Co – Dicobalt octacarbonyl, acetone
Cr – Bis(benzene) chromium(0), acetone
Cu – Tetrakis Acetonitrile Copper hexafluorophosphate, acetone
Fe – Iron pentacarbonyl, acetone
Ge – Germanium bromide, octadecene
In – Indium(I) chloride, acetone
Mn – Manganese carbonyl, acetone
Mo – Molybdenum carbonyl, acetone
Ni – Tetrakis(triphenylphosphine) nickel(0), bis(1,5-cyclooctadiene) nickel(0), acetone
Os – Osmium (III) chloride hydrate, Stannous chloride, acetone
Pb – Lead (II) chloride, Stannous chloride, acetone
Pd – Palladium (II) chloride, Stannous chloride, acetone
Pt – Tetrakis (triphenylphosphine) platinum(0)), acetone (Expensive $$$)
Rh – Rhodium (III) chloride hydrate, Stannous chloride, acetone
Ru – Ruthenium (III) chloride hydrate, Stannous chloride, acetone
Sb – Antimony (III) chloride, Stannous chloride, acetone
Sn – Tartaric Acid ($C_4H_6O_6$); Stannous chloride, acetone
W – Tungsten hexacarbonyl, octadecene

BASIC SYNTHESIS SETUP:

Reflux glassware setup:

Fig 2: This is a schematic diagram of the reflux setup to perform zero-valent metal intercalations using a water bath as a heat source. Although advisable never to go quite to reflux (boiling), the reflux column acts to prevent solution loss.
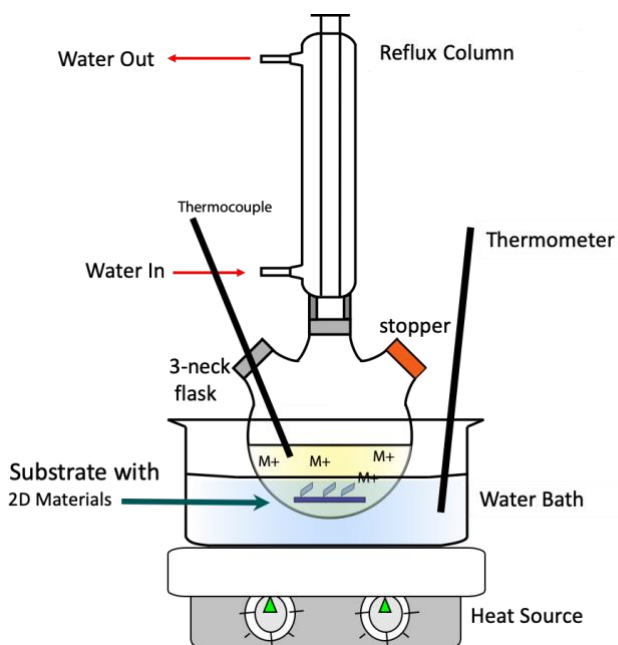
Fig 3: This is a photo of the actual setup currently in use in the Koski lab attached to a Schlenk line and using a heating controller and heating mantle + thermocouple for control of temperature.
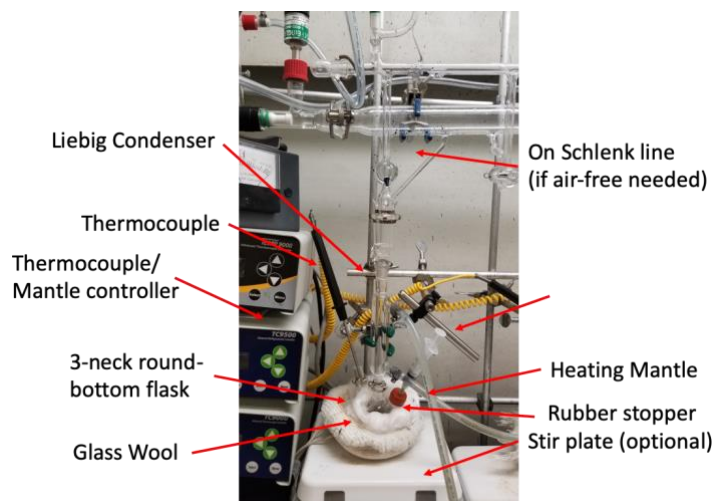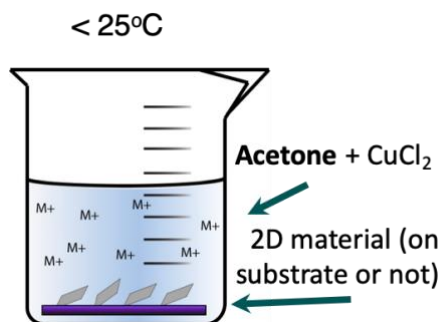

Fig 4: This type of simple setup can be used for deintercalation if no heating is needed (most deintercalations). Fig 2 can also be used for deintercalation.

DEGASSING OCTADECENE (Ge, W):

- **Freeze-Pump-Thaw:** On a Schlenck line, place octadecene in a heavy-walled (critical) single-neck round bottom flask or a sealed Schlenk flask. Freeze it by immersing in liquid nitrogen. Once frozen, open the flask to high vaccum and pump for about 5 minutes. Keep the octadecene in liquid N_2. Place solvent back under N_2 and let thaw. Repeat 3 times. Remove solution using a needle and syringe into a N_2 filled septa vial.

- **Purging:** So, this is what I do for octadecene…. This is really hard on a vacuum pump. Place octadecene in a round bottom flask. Heat to $110^{\circ}C$ and place under vacuum for about 30 minutes. Refill with N_2. Keeping under N_2 atmosphere, bubble N_2 or Ar into the flask using a long needle. Bubble for about an hour or two.

Store degassed octadecene in a glovebox.

DEINTERCALATION OF ATOMS FROM A LAYERED OXIDE

If intercalation is performed into a layered oxide, there are two easy ways to zero-valent metals can be deintercalated through oxidative deintercalation using hydrogen peroxide or iodine (or bromine) in acetonitrile. Success and speed of deintercalation depends upon the oxidation potential of the intercalated metal. For example, H_2O_2 is a stronger oxidative reagent and can deintercalate Sn, Cu, and Co more effectively than iodine. Similarly, Co- is easier to deintercalate than Sn using either hydrogen peroxide or iodine simply because Sn has a weaker propensity to be oxidized (lookup oxidation potentials).

For chemical deintercalation using hydrogen peroxide, place the intercalated **oxide** layered material into a beaker. Add in 1mL 30% H_2O_2 solution to 5 mL de-ionized water. Stir (or let sit) at room temperature for 1-2 hours. Rinse the deintercalated oxide with acetone, ethanol, and water and dry. For chemical deintercalation using iodine, use the setup shown in Fig 2. Place the intercalated oxide in 5 ml of acetonitrile dissolved with 0.1 g I_2 (or Br_2) in a round-bottom flask at 60°C for 3 days.

Au.

$$3Au^+(aq) \rightarrow Au^{3+}(aq) + 2Au(0)$$
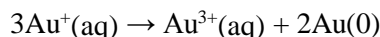
Gold can be intercalated by the disproportionation reduction oxidation of a Au^{+1} salt (see Cu below). Salts that work are gold chloride (Au(I)Cl), Chloro(tricyclohexylphosphine)gold(I), chlorotristriphenyl phosphine gold(I), Chloro(triethylphosphine) gold(I), [1,3-Bis(2,6-diisopropylphenyl) imidazol-2-ylidene] [bis(trifluoromethanesulfonyl) imide]gold(I).

Just use whatever is cheapest so Au(I) – Gold(I) chloride is probably the cheapest choice.

This requires prepare of the glassware before intercalation. Prepare the glassware to achieve a pH of ~7 by letting sit overnight in water (not distilled) or in a base bath. Test the pH of the water; pH should be about 7. After 24 hours, dry the glassware in a drying oven (or overnight on a rack) for an additional 24 hours. These steps are somewhat critical for gold. Without it, the pH may be too acidic forcing more Au^{2+} to form over Au(0) or too basic forming Au^{3+}. This can be seen in the Pourbaix diagram below. The ideal region is the blue box. There is a lot of room for error for achieving the correct pH for gold intercalation. Beware, though, this diagram is for gold in an aqueous solution but it serves as a fairly accurate guide for intercalation in acetone.
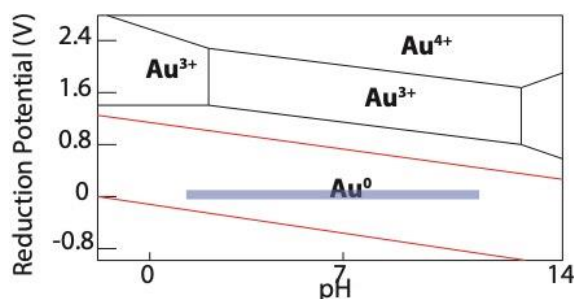
Fig 5. Pourbaix Diagram of gold in water. Blue is the ideal pH region for gold intercalation

Setup the reflux setup shown in Fig 2. There is no need to use an air-free setup unless the chosen Au(I) salt is not air-stable. Heat a solution of 0.01 g gold(I) chloride in 5 mL acetone in the round-bottom flask to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Keep heating just below reflux for 4 hours. After 4 hours, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone will help remove any other salt impurities that may end up on the substrate.

Au +1	acetone	time	~ intercalated in Bi_2Se_3
0.01 g	5 mL	4 hrs	20 atm % $\pm$ 5%

Ag.

$$2Ag^+ + L \rightarrow AgL^{2+} + Ag(0) \qquad L = \text{tetroazocyclic amine}$$
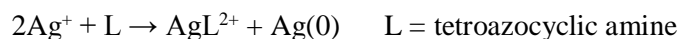
Silver disproportionates in the presence of a tetraazocyclic amine (L above). The tetraazocyclic amine will complex the silver 2+ that is formed, which keeps it locked away from the layered material.

There is no need to prepare the glassware. Setup the reflux aparatus as shown in Fig 2. There is no need to use an air-free setup. Heat a solution of 0.01 g silver nitrate ($AgNO_3$) and 0.1g 5,5,7,12,12,14-hexamethyl-1,4,8,11- tetraazocyclotetradecane in 5 mL acetone in the round-bottom flask to just below reflux (48^oC). Once heated, drop in the 2D material, free or suspended on a substrate, into the round bottom flask. Keep heating just below reflux for 4 hours. After 4 hours, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone will help remove any other salt impurities that may end up on the substrate.

$AgNO_3$	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazocyclotetradecane	acetone	time	~ intercalated in Bi_2Se_3
0.01 g	0.1 g	5 mL	4 hrs	50-60 atm % $\pm$ 5%

Bi.

$$2BiCl_3 + 3SnCl_2 \rightarrow \textbf{2Bi(0)} + 3SnCl_4$$
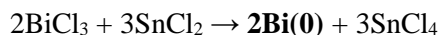
Stannous Chloride (Sn(II) Cl_2) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide. Bismuth, with an oxidation state of 2+ or 3+ can be reduced all the way to Bi(0).

Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375
  $Bi^{3+} + 2e^- \rightarrow Bi$ 0.308
  Total: 0.4455

There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.01 – 0.02 g of $SnCl_2$ in 5 mL.

Heat a solution of 0.016 g bismuth(III) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48^oC). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. **Dropwise**, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional $30 – 45$ mins with heating. Afterwards, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45^oC) will help remove any other salt impurities that may end up on the substrate.

Bi(III)Cl$_3$	SnCl$_2$	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.016 g	0.1 g	5 mL	4 hrs	50-60 atm % $\pm$ 5%

Cr.

$$C_{12}H_{12}Cr + \Delta \rightarrow \textbf{Cr(0)}$$
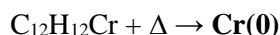
Chromium is intercalated by decomposition of chromium(0) coordination compounds. Because these compounds are so sensitive to air, it is necessary to use a Schlenk line or alternative air-free setup. If a Schlenk line isn't available, setup the reaction as according to Figure 2 and at the top of the reflux column, add the adapter shown in Fig 6, below. Nitrogen or argon gas should feed through one end of the glassware tube with the other left open or sent to a bubbler (put the tube in mineral oil and make sure bubbles come out at a fairly slow rate). Before beginning, place the 2D material in the round-bottom flask, run nitrogen into the column and flask for ~ 30 mins. Alternatively, if on a Schlenk line, place the 2D materials or substrate in the round bottom flask, evacuate, and flush with N$_2$ or argon gas.

Prepare two stock solutions in a glovebox. **Stock solution 1** should have 5mL of acetone in a septa vial. **Stock solution 2** should contain 5~10 mM of bis(benzene) chromium(0). For this stock solution, add about 0.01 g of bis(benzene) chromium(0) to 5mL of anhydrous acetone in a septa capped vial. Inject in 5mL of air-free acetone (kept in a glovebox and completely free from air) to the flask and heat to reflux. The air free acetone can be placed in a septa capped vial and injected with syringe that has been flushed with nitrogen three times from the primary flask to prevent any air getting in. Dropwise, inject the second solution to the flask over the course of 2~3 hours. After injection, wait an additional thirty minutes under reflux. Finally, remove substrates or 2D materials from the solution and rinse with acetone in air.

Fig 6: Adapter to bring in nitrogen (Chemglass AF-0509-B) .

C$_{12}$H$_{12}$Cr	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.01 g	Total = 10 mL	3.5 hrs	6 atm % $\pm$ 2%

Co.

$$Co_2(CO)_8 + \Delta \rightarrow 8CO + \textbf{Co(0)}$$
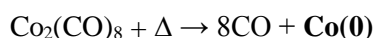
Cobalt is intercalated by decomposition of dicobalt octacarbonyl in solution under inert atmosphere. Again, either use a Schlenk line or use the procedure and setup explained for Cr above.

Setup the reaction as according to Fig 3. Place the 2D material in the round-bottom flask, evacuate and flushed with N2 gas. In a glovebox, create two stock solutions. **Stock solution 1** should be 5 mL of anhydrous acetone. **Stock solution 2** should be created from 0.01-0.03g of dicobalt octacarbonyl dissolved in 3-5mL of air free acetone, respectively. Inject the first stock solution of anhydrous acetone into the round-bottom flask and heat to just below reflux (~45-48C). Dropwise, inject in the cobalt solution 2 over the course of 1.5 hours. After all solution has been injected, allow the mixture to sit just below reflux for 1 more hour. Remove substrates or material from the solution and rinsed with hot acetone and hot ethanol, exposing to air at this point is okay.

Ideally, and if the reaction is done to perfection, the solution will resemble a beautiful purple gel. This gel will keep the excess cobalt long enough to remove the substrate. After removal, the gel will crash out a black cobalt precipitate. If things didn't go quite ideally, there may be some black cobalt metal nanoparticles generated during reaction. These will precipitate out on the flask but may end up on the surface of the 2D material or substrate. These particles are removed by rinsing with ethanol and acetone (25 °C) and/or via sonication of the crystals.

$Co_2(CO)_8$	acetone	time	~ intercalated in Bi_2Se_3
0.01 g	Total = 8 mL	2.5 hours	20-30 atm % $\pm$ 5%

Cu.

$$2Cu^+ \leftrightarrow Cu(0) + Cu^{2+}$$

Copper can be intercalated by disproportionation reduction oxidation of a Cu^{+1} salt. Salts that work are copper(I) iodide (CuI) or tetrakisacetonitrile copper(I) hexafluorophosphate.

Prepare the glassware by letting sit overnight in DI water. Test the pH of the DI water; pH should be about ~ 5.5-6.5. After 24 hours, dry the glassware in a drying oven (or overnight on a rack) for an additional 24 hours. These steps are critical. Without it, the pH may be too basic forcing more Cu^{2+} to form over $Cu(0)$. See the Pourbaix diagram for copper in water. The ideal region for pH is the blue box. Be aware, this diagram is for copper in an aqueous solution (boxes not identified are oxide phases) but it serves as a fairly accurate guide for intercalation in acetone.
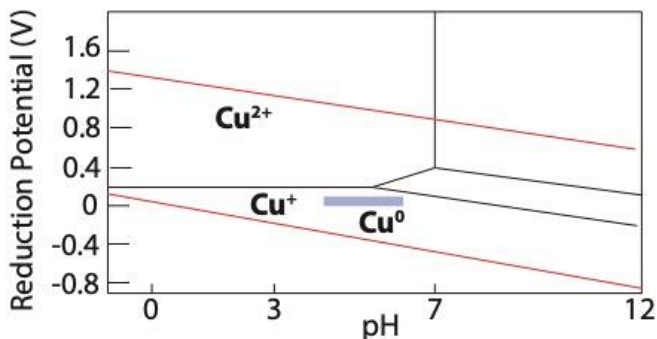
Fig 7. Pourbaix Diagram of copper in water. Blue is the ideal pH region for copper intercalation.

The tetrakisacetonitrile copper hexafluorophosphate precursor powder should be a white to yellow color. Bluish powder means that your source has been exposed to too much water and should not be used.

Setup the reflux apparatus as shown in Fig 1. There is no need to use an air-free setup. Heat a solution of 0.01 g tetrakisacetonitrile copper hexafluorophosphate in 5 mL acetone in the round-bottom flask to just below reflux (48°C). Once heated, drop in the 2D material, free or suspended on a substrate, into the round bottom flask. Keep heating just below reflux for 4 hours. After 4 hours, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone will help remove any other salt impurities that may end up on the substrate.

The reaction solution should be a light yellow color with a tiny amount of whitish precipitate after 4 hours. A blue color means that the solution was too basic during the reaction and too much Cu^{2+} was formed and not enough $Cu(0)$. If the solution is allowed to sit and cooled to room temperature after the intercalation reaction, the solution should develop a yellow/white/blue powder precipitate (which is a copper – and sometimes contaminated with Si from the glass - PF_6 compound). With time, a solution allowed to sit will turn blue. This is the Cu^{2+} coming out of its solvent shell and not complexed with the PF_6. The copper 2+ during the reaction will be solvated in a solvent shell as shown in the example with acetone below.

$$2\ [Cu(CH_3CN)_4]^+ + 6\ C_3H_6O \rightarrow [Cu(C_3H_6O)_6]^{2+} + Cu + 8\ CH_3CN$$
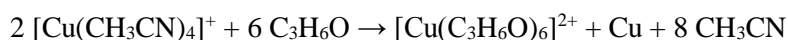
The following table can be used as an approximate time for reaction and amount of precursor to achieve the desired percent intercalated. Note this will be different in different materials.

Cu +1	acetone	time	~ intercalated in Bi_2Se_3
0.14 g	5 mL	10 min	30-50 atm % $\pm$ 20%
0.07 g	5 mL	10 min	20-40 atm % $\pm$ 20%
0.01 g	5 mL	10 min	10 atm % $\pm$ 10%
0.01 g	5 mL	4 hr	60 atm % $\pm$ 5%
0.01 g	5 mL	30 min	25-40 atm % $\pm$ 15%
0.01 g	5 mL	10 min	5-10 atm % $\pm$ 5%

Note that with 0.14 g tetrakisacetonitrile copper hexafluorophosphate in 5 mL acetone, this intercalation reaction can be done in about 10 mins with a large distribution of intercalant.

Things to be aware of:
- The substrate matters. A silicon substrate without much of an oxide layer can mediate electroless deposition of copper. This will be seen as dendritic looking copper on the substrate. If this shows up, the intercalation reaction was unsuccessful.
- If the reaction solution is turning bright blue within ten minutes of starting, there are ways to save it. Add a tiny drop (uL or less) of nitric acid to the reaction. Note that this is adding an acid to an organic which generates a lot of hydrogen! This can be very dangerous so use this only if desperate. If it turns blue after an hour or so, don't worry too much about it.
- Make sure to prep the glassware and check the pH before proceeding. This is pretty much the one thing that can kill the reaction.

Deintercalation: Zero-valent copper can be deintercalated by a comproportionation redox reaction through the use of a Cu^{2+} salt.

$$Cu^0 + Cu^{2+}(aq) \rightleftharpoons 2Cu^+(aq)$$
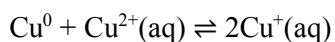
$Cu(0)$ can be deintercalated by $CuCl_2$. Care must be taken to use a salt that isn't hydrated. Hydrated salts, such as copper nitrate hydrate, will prohibit the deintercalation by preventing the comproportionation reaction.

The setup in Fig 1 or the setup in Fig 3 can be used for deintercalation. Place the 2D material in the round bottom flask or the bottom of a beaker. Add a solution of 0.002 g of $CuCl_2$ dissolved in 5 ml HPLC grade acetone and keep the solution with sample at room temperature for 3 hours. Afterwards, remove the substrate/sample and rinse with acetone to remove excess $CuCl_2$ and CuCl. The use of acetone (which is a relatively hard base by hard/soft acid base theory) with a Cu^{2+} salt can promote some cation exchange between the cation such as Bi^{3+} and the Cu^{2+} in addition to the comproportionation which leads to defects in the material. While the amount of defects created is small, the cation exchange reaction can be prevented through addition of a soft base.

Deintercalation without exchange can be performed by placing the substrate in a round bottom flask or beaker (Fig 1 or Fig 3) followed by addition of a solution of 0.001 g $CuCl_2$ dissolved in 0.5 ml acetone with 10 ml of trioctylphosphine. Keep the substrate in solution at room temperature for one hour. Remove and rinse with acetone. Cation exchange between Cu^{2+} and Ge^{2+}, Mo^{4+}, W^{4+}, In^{3+}, Nb^{4+} in acetone is not favored so the deintercalation of Cu in MoS_2, BN, graphite and other layered chalcogenides does not require addition of a soft base.

Fe.

$$Fe(CO)_5 + \Delta \rightarrow 5CO + \textbf{Fe(0)}$$
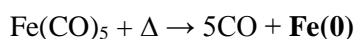
This one shouldn't work because iron pentacarbonyl doesn't decompose until about 220°C, but it does. Make sure there is a lot of light on the solution because it appears that photodissociation of iron pentacarbonyl helps this reaction proceed.

This reaction requires an air-free setup. Follow the procedure for chromium above or use a Schlenk line as shown in Fig 3.

Place the 2D material in the round-bottom flask, evacuate and flushed with N_2 gas. In a glovebox, create two stock solutions. **Stock solution 1** should be 5 mL of anhydrous acetone. **Stock solution** 2 should be created from 0.01 g of iron pentacarbonyl dissolved in 3mL of air free acetone. Inject the first stock solution of anhydrous acetone into the round-bottom flask and heat to just below reflux (~45-48C). Dropwise, inject in the iron (solution 2) over the course of 1.5 hours. After all solution has been injected, allow the mixture to sit just below reflux for 1 more hour. Remove substrates or material from the solution and rinsed with hot acetone and hot ethanol, exposing to air at this point is okay.

Ideally, and if the reaction is done to perfection, the solution should remain transparent. Sometimes under excess light, it is possible to crash out all the iron – which will appear as a dark black or red precipitate once exposed to air. This is rare to get. Rinse the substrate or material with ethanol and acetone (25 °C).

$Fe(CO)_5$	acetone	time	~ intercalated in Bi_2Se_3
0.01 g	Total = 8 mL	2.5 hours	8 atm % $\pm$ 3%

Ge.

$$2GeBr_2 + 150°C \rightarrow \textbf{Ge(0)} + GeBr_4$$
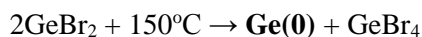
While it is possible to intercalate germanium using tin chloride, given the favorable redox potentials, germanium (II) bromide disproportionates at high temperatures to germanium metal and $GeBr_4$. Thus, an intercalation reaction can be performed by heating the reactants and host to 150^oC. This reaction works with any germanium halide. Buy and use what is cheapest (GeI_2, $GeCl_2$, $GeBr_2$).

This reaction must be done in air-free conditions. Follow the setup according to Cr above or setup the reaction with a Schlenk line as shown in Fig 3. Germanium halides must also be stored in a glovebox and tend to come in a scored glass capsule.

Octadecene is the solvent used for this reaction. It is possible to buy this anhydrous. Or just degass tech grade following procedures outlined above. Store degassed octadecene in a glovebox.

Store the octadecene in a glovebox. Prepare two stock solutions: a solution of 5 mL octadecene (**stock solution 1**) and a solution of 0.01 g $GeBr_2$ in 5 mL degassed octadecene (**stock solution 2**). Use an air-free setup as according to Fig 3 (or following Cr). Place the 2D material or substrate in the round bottom flask, evacuate, and flush with N_2. Under N_2, inject the **stock solution 1** of octadecene into the round bottom flask and heat to 170^oC. Dropwise over the course of 1.5 hours, inject in the **stock solution 2** of ~5mM $GeBr_2$ dissolved in 5 mL of degassed octadecene. Afterwards, remove the substrate with exposure to air and rinse repeatedly with acetone to remove excess octadecene and germanium bromide. Best to just make a bath of warm acetone and drop the substrate into it and wait about 3 minutes. Repeat as desired to intercalate more Ge.

$GeBr_2$	octadecene	time	~ intercalated in Bi_2Se_3
0.01 g	Total = 10 mL	1.5 hrs	5 atm % $\pm$ 3%

In.

$$3InCl \leftrightarrow InCl_3 + 2In(0)$$

Indium chloride disproportionates very well in both dimethyl sulfoxide and tetrahdyrofuran. These solvents can be used for intercalation. We have also found that InCl slowly disproportionates in acetone. Indium chloride is air sensitive; intercalation reactions are performed under inert N_2 atmosphere using standard Schlenck techniques. Follow the procedure for Cr or setup on a Schlenk line as in Fig 3.

Place the substrate or 2D materials in the round-bottom flask, evacuate and flush with N_2. In a glovebox, prepare two stock solutions. The first (**solution 1**) should be 3mL of acetone in an air-free septa vial. The second (**solution 2**) should be 0.015 g InCl dissolved in 3mL of air free acetone. Inject **solution 1** of just acetone into the round bottom flask and heat to just below reflux (50 °C). Dropwise, inject **solution 2** over the course of an hour. Let the solution heat for an additional 20-30 mins. Remove the substrate from solution and rinse with hot ethanol and hot acetone (~45 °C).

Notes: This one you can actually be lazy on because InCl disproportionates so slowly in acetone. You can actually inject the entire solution in and reflux for an hour. I advise the slower route for better results.

InCl	acetone	time	~ intercalated in Bi_2Se_3
0.015 g	Total = 6 mL	1.5 hrs	7-17 atm % $\pm$ 10%

Mn.

$$Mn_2(CO)_{10} + \Delta \rightarrow 10CO + 2\mathbf{Mn(0)}$$
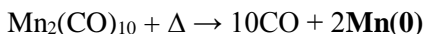
Much like Co and Fe, manganese is intercalated by the decomposition of manganese carbonyl in a solution under inert atmosphere. Again, either use a Schlenk line or use the procedure and setup explained for Cr above.

Setup the reaction as according to Fig 3. Place the 2D material in the round-bottom flask, evacuate and flushed with N_2 gas. In a glovebox, create two stock solutions. **Stock solution 1** should be 5 mL of anhydrous acetone. **Stock solution 2** should be created from 0.01-0.03g of manganese octacarbonyl dissolved in 5mL of air free acetone. Inject the **stock solution 1** of anhydrous acetone into the round-bottom flask and heat to just below reflux (~45-48C). Dropwise, inject in the manganese (**solution 2**) over the course of 2-3 hours (note, go slow). After all solution has been injected, allow the mixture to sit just below reflux for 1 more hour. Remove substrates or material from the solution and rinsed with hot acetone and hot ethanol, exposing to air at this point is okay.

$Mn_2(CO)_{10}$	acetone	time	~ intercalated in Bi_2Se_3
0.01-0.03 g	Total = 10 mL	3 hrs, min.	4 atm % $\pm$ 2%

Mo.

$$Mo(CO)_6 + \Delta \rightarrow 6CO + \mathbf{Mo(0)}$$
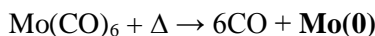
Much like Co, Mn, and Fe, molybdenum is intercalated by the decomposition of molybdenum carbonyl in a solution under inert atmosphere. Again, either use a Schlenk line or use the procedure and setup explained for Cr above. Moly carbonyl has a bad reputation in materials science departments. It is used in organic chemistry classes without concern; beware of this strange safety dichotomy and handle the reaction material by reading the MSDS before proceeding.

Setup the reaction according to Fig 3. Place the 2D material in the round-bottom flask, evacuate and flushed with N_2 gas. In a glovebox, create two stock solutions. **Stock solution 1** should be 5 mL of anhydrous acetone. **Stock solution 2** should be created from 0.01-0.03g of moly carbonyl dissolved in 5mL of air free acetone. Inject **stock solution 1** of anhydrous acetone into the round-bottom flask and heat to just below reflux (~45-48C). Dropwise, inject in the molybdenum (**solution 2**) over the course of 2-3 hours (note, go slow). After all solution has been injected, allow the mixture to sit just below reflux for 1 more hour. Remove substrates or material from the solution and rinsed with hot acetone and hot ethanol, exposing to air at this point is okay. Remove the substrate and rinse with acetone (25 °C).
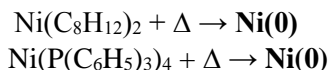
$Mo(CO)_6$	acetone	time	~ intercalated in Bi_2Se_3
0.01-0.03 g	Total = 10 mL	3 hrs, min.	2 atm % $\pm$ 1%

Ni.

$$Ni(C_8H_{12})_2 + \Delta \rightarrow \textbf{Ni(0)}$$
$$Ni(P(C_6H_5)_3)_4 + \Delta \rightarrow \textbf{Ni(0)}$$

Nickel is intercalated by decomposition of nickel(0) coordination compounds. Because these compounds are so sensitive to air, it is necessary to use a Schlenk line or alternative air-free setup. Use Fig 3 or follow the procedure for Cr above. Before beginning, place the 2D material in the round-bottom flask, run nitrogen into the column and flask for ~ 30 mins. Alternatively, if on a Schlenk line, place the 2D materials or substrate in the round bottom flask, evacuate, and flush with N_2 or argon gas.

Prepare two stock solutions in a glovebox. **Stock solution 1** should have 5mL of acetone in a septa vial. **Stock solution 2** should contain 5~10 mM of tetrakis(triphenylphosphine) nickel(0) or bis(1,5-cyclooctadiene) nickel(0) dissolved in 5mL of acetone. For this stock solution, add about 0.01 g of the nickel(0) compound to 5mL of anhydrous acetone in a septa capped vial. Inject in 5mL of air-free acetone (kept in a glovebox and completely free from air) to the flask and heat to reflux. The air free acetone can be placed in a septa capped vial and injected with a syringe that has been flushed with nitrogen three times from the primary flask to prevent any air from getting in. Dropwise, inject the second solution to the flask over the course of 2~3 hours. After completion, wait an additional thirty minutes. Finally, remove substrates or 2D materials from the solution and rinse with acetone in air.

$Ni(C_8H_{12})_2$	acetone	time	~ intercalated in Bi_2Se_3
0.01 g	Total = 10 mL	2.5 hrs, min.	20 atm % ± 3%

Os.
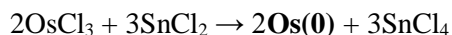
$$2OsCl_3 + 3SnCl_2 \rightarrow 2\textbf{Os(0)} + 3SnCl_4$$

As with Bi above, stannous chloride ($SnCl_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide. The redox potentials of osmium are unknown. This reaction was demonstrated by trial and error.
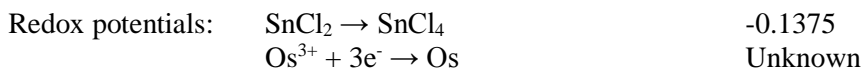
Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375

                      $Os^{3+} + 3e^- \rightarrow Os$ Unknown

:

There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride of 0.014 g of $SnCl_2$ in 5 mL.

Heat a solution of 0.015 g osmium(III) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. Afterwards, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

OsCl$_3$	SnCl$_2$	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.015 g	0.014 g	10 mL	3 hours	5 atm % ± 2%

Pb.

$$PbCl_2 + SnCl_2 \rightarrow \textbf{Pb(0)} + SnCl_4$$
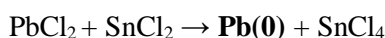
As with Bi and Os above, stannous chloride (SnCl$_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide.

Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375
                        $Pb^{2+} + 2e^- \rightarrow Pb$ -0.1262

                                  Total: 0.0113

This reaction will favor formation of Pb(0) and SnCl$_4$.

There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.01 g of SnCl$_2$ in 5 mL acetone.

Heat a solution of 0.014 g lead(II) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. After, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

PbCl$_2$	SnCl$_2$	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.014 g	0.01 g	10 mL	3 hours	1 atm % ± 1%

Pd.

$$PdCl_2 + SnCl_2 \rightarrow \textbf{Pd(0)} + SnCl_4$$
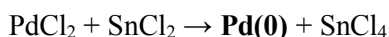
As with Bi, Pb, and Os above, stannous chloride (SnCl$_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide.

Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375
                        $Pd^{2+} + 2e^- \rightarrow Pd$ 0.951

                                  Total: 1.0885

This reaction will favor formation of Pd(0) and SnCl₄ but just barely. The fact that this works was surprising.

There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.01 g of $SnCl_2$ in 5 mL acetone.

Heat a solution of 0.01 g palladium(II) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. Afterwards, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

PdCl₂	SnCl₂	acetone	time	~ intercalated in Bi₂Se₃
0.01 g	0.1 g	5 mL	4 hr	1.76 ± 3%

There is an alternative method that has only barely been explored but shows promise. This one is expensive and perhaps not worth the cost unless you happen to have Pd-DBA sitting around. Palladium may be intercalated through decomposition tris(dibenzylideneacetone) dipalladium(0) [Pd₂(DBA)₃] decomposition. Dissolve 0.01g of Pd-DBA in 5mL of THF. Inject into 5mL of non-dry octadecene with approximately of water heated to 150°C.

Things that don't work: Diol reduction of palladium compounds goes too fast resulting in nanoparticle deposits with no intercalation.

Pt.

$$Pt(P(C_6H_5)_3)_4 + \Delta \rightarrow \textbf{Pt(0)}$$
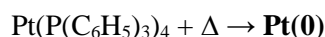
Platinum is intercalated by decomposition of platinum(0) coordination compounds. Because these compounds are so sensitive to air, it is necessary to use a Schlenk line or alternative air-free setup. Use Fig 3 or follow the procedure for Cr above. Before beginning, place the 2D material in the round-bottom flask, run nitrogen into the column and flask for ~ 30 mins. Alternatively, if on a Schlenk line, place the 2D materials or substrate in the round bottom flask, evacuate, and flush with N_2 or argon gas.

Prepare two stock solutions in a glovebox. Stock solution 1 should have 5mL of acetone in a septa vial. Stock solution 2 should contain 5~10 mM of tetrakis (triphenylphosphine) platinum(0) dissolved in 5mL of acetone. For this stock solution, add about 0.01 g of the platinum(0) compound to 5mL of anhydrous acetone in a septa capped vial. To begin the reaction, inject in 5mL of air-free acetone (kept in a glovebox and completely free from air) to the flask and heat to reflux. The air free acetone can be placed in a septa capped vial and injected with syringe that has been flushed with nitrogen three times from the primary flask to prevent any air from getting in. Dropwise, inject the second solution to the flask over the course of 2~3 hours. After completion, wait an additional thirty minutes. Finally, remove substrates or 2D materials from the solution and rinse with acetone in air.

This one has to be repeated many times to get sizable amounts of platinum intercalated. Also, make sure the lights are on as bright as possible in the hood as it helps for decomposition of the platinum compound.

Pt(P(C$_6$H$_5$)$_3$)$_4$	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.01 g	Total = 10 mL	2.5 hrs min.	1 atm % ± 1%

Rh.
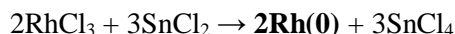
$$2RhCl_3 + 3SnCl_2 \rightarrow \mathbf{2Rh(0)} + 3SnCl_4$$

As with Bi above, stannous chloride (SnCl$_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide.

Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375
                     $Rh^{2+} + 2e^- \rightarrow Rh$ 0.758
   Total: 0.8955

This reaction will favor formation of Rh(0) and SnCl$_4$ but just barely. Repeated intercalation reactions can get more in.

   There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.014 g of SnCl$_2$ in 5 mL.

   Heat a solution of 0.01 g rhodium(III) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. Afterwards, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

RhCl3	SnCl2	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.01 g	0.014 g	Total = 10 mL	3.5 hrs	2 atm % ± 1%

Ru.
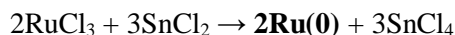
$$2RuCl_3 + 3SnCl_2 \rightarrow \mathbf{2Ru(0)} + 3SnCl_4$$

As with Bi above, stannous chloride (SnCl$_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide.

Redox potentials: $SnCl_2 \rightarrow SnCl_4$ -0.1375
                     $Ru^{2+} + 2e^- \rightarrow Ru$ 0.455
                                         Total: 0.5925

This reaction will favor formation of Ru (0) and SnCl$_4$

This reaction will favor formation of Rh(0) and SnCl$_4$ but just barely. Repeated intercalation reactions can get more in.

There is no need to prepare the glassware before intercalation. Setup the reflux apparatus as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.014 g of SnCl$_2$ in 5 mL.

Heat a solution of 0.01 g ruthenium(III) chloride in 5 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. After, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

RuCl$_3$	SnCl2	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.01 g	0.014 g	Total = 10 mL	3.5 hrs	4 atm % $\pm$ 2%

Sb.
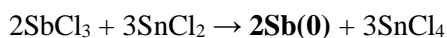
$$2SbCl_3 + 3SnCl_2 \rightarrow \textbf{2Sb(0)} + 3SnCl_4$$

As with Bi above, stannous chloride (SnCl$_2$) is an excellent reducing agent and can be used to reduce many of the metal chlorides to a zero-valent species. The electrochemical redox potential favors oxidation of the tin halide and reduction of the metal halide.

No redox data available.

Notes: This one easily creates nanoparticles so proceed very, very slowly.

There is no need to prepare the glassware before intercalation. Setup the reflux setup as shown in Fig 2. There is also no need to use an air-free setup. Prepare a stock solution of stannous chloride from 0.01 g of SnCl$_2$ in 10 mL acetone.

Heat a solution of 0.01 g antimony(III) chloride in 10 mL acetone in the round-bottom flask (Fig 1) to just below reflux (48°C). Once heated, drop the 2D material, free or suspended on a substrate, into the round bottom flask. Dropwise, add in the solution of tin(II) chloride very slowly over the course of 3 hours. Keep heating during this time at just below reflux. After 3 hours, and complete injection of the stannous chloride solution, wait an additional 30 – 45 mins with heating. After, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone (~45°C) will help remove any other salt impurities that may end up on the substrate.

| SbCl$_3$	SnCl$_2$	acetone	time	~ intercalated in Bi$_2$Se$_3$
0.01 g	0.01 g	Total = 20 mL	3.5 hrs	20 atm % $\pm$ 8%

Sn.

$$2Sn^{2+} \rightarrow Sn^{4+} + \textbf{Sn(0)}$$

Tin disproportionates in the presence of a tartrate or citrate. These are added as precursors in excess to facilitate disproportion (Table 1).

There is no need to prepare the glassware before intercalation. Setup the reflux setup as shown in Fig 2. There is also no need to use an air-free setup. The following instructions assume the usage of tartaric acid.

Prepare a stock solution of stannous chloride and tartrate from both 0.03 g of $SnCl_2$ and 0.03 – 0.06 g of tartaric acid in 10 mL acetone. Thoroughly agitate the mixture until completely dissolved. Heat the solution in the round-bottom flask to just below reflux (48°C). Once heated, drop in the 2D material, free or suspended on a substrate, into the round bottom flask. Keep heating just below reflux for 4 hours. Afterwards, remove the substrate or 2D crystal from solution and rinse with acetone or ethanol several times. Rinsing with heated acetone will help remove any other salt impurities that may end up on the substrate.

$SnCl_2$	Tart. Acid	acetone	time	~ intercalated in Bi_2Se_3
0.03 g	0.03-0.06 g	10 mL Total	1 hr	20 atm % ± 3%

Deintercalation: Zero-valent copper can be deintercalated by a comproportionation redox reaction through the use of a Sn^{4+} salt.

$$Sn^0 + Sn^{4+}(aq) \rightleftharpoons 2Sn^{2+}(aq)$$
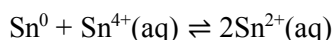
Sn deintercalation should be performed under a nitrogen environment using the Schlenk line technique (or Fig 3) to avoid hydrolysis of $SnCl_4$. Prepare the setup in Fig 2/3. Place the Sn-intercalated samples into a round bottom flask. Evacuate and flush with N_2 several times. Dissolve 0.23 g of $SnCl_4$ in 5 ml anhydrous acetone. Inject the $SnCl_4$ acetone solution into the flask and keep just under reflux (52°C) with N_2 flow for 6 hours. This is a slower reaction but heating expedites tin deintercalation. The material is removed from the flask, rinsed with acetone several times, and dried in air after deintercalation.

W.

$$W(CO)_6 + \Delta \rightarrow 6CO + \textbf{W(0)}$$
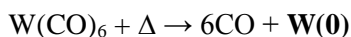
Much like Co, Mn, Mo, and Fe, tungsten is intercalated by the decomposition of tungsten carbonyl in a solution under inert atmosphere. Again, either use a Schlenk line or use the procedure and setup explained for Cr above. Tungsten carbonyl requires a lot higher temperature than the others to decompose the carbonyl groups and it does not decompose as well under light. Thus, octadecene is used rather than acetone.

Degass a stock solution of octadecene as above, in the introduction or under the Ge section.

Setup the reaction as according to Fig 3. Place the 2D material in the round-bottom flask, evacuate and flush with N_2 gas. In a glovebox, create two stock solutions. **Stock solution 1** should be 5 mL of degassed octadecene. **Stock solution 2** should be 10 mM of tungsten hexacarbonyl in 20 mL of degassed octadecene. This is approximately from 0.07 g of tungsten carbonyl dissolved in 20 mL of degassed octadecene. Inject the first stock solution of octadecene into the round-bottom flask and heat to 150-170°C. Dropwise, inject in the tungsten (**solution 2**) over the course of 2-3 hours. After all solution has been injected, allow the

mixture to sit just below reflux for 1 more hour. Remove the substrate and rinse repeatedly with acetone to remove excess octadecene.

$W(CO)_6$	octadecene	time	~ intercalated in Bi_2Se_3
0.01 g	25 mL	3 hours	4 atm % $\pm$ 2%