Mysteries of TOPSe Revealed: Insights into Quantum Dot Nucleation

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Materials and Methods:

All compounds were used as received unless otherwise noted. CdO (99.99%), oleic acid (90% tech. grade), 1-octadecene (90% tech. grade), PbO (99.9+%), Selenium shot (99.999%), diphenylphosphine (98%; DPP), triethylphosphine (99%, TEP), trioctylphosphine (90% tech. grade; TOP) and anhydrous toluene (99.8%) were purchased from Sigma-Aldrich. Meanwhile, trioctylphosphine (97%; TOP), tri-isopropylphosphine (98%; TIPP) and di-isopropylphosphine (98%; DIPP) were purchased from the Strem chemical company. Toluene- d_8 was purchased from Cambridge Isotope Labs. All solvents were dry and degassed, using three freeze-pump-thaw cycles, for all NMR experiments.

NMR spectra were recorded on a Bruker Avance 500 (500 MHz for ^{1}H; 202 MHz for ^{31}P and 125.65 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to an internal standard TMS (0 ppm for ^{1}H and ^{13}C) and external standard H_3PO_4 (0 ppm for ^{31}P).

Synthesis of starting materials:

Cadmium (II) oleate: $Cd(C_{18}H_{33}O_2)_2$
$Cd(oleate)_2$ was produced by combining 0.642 g CdO (5 mmol) with 3.96 mL oleic acid (12.5 mmol, 90% tech grade, Aldrich) and 10 mL 1-octadecene (90% tech. grade, Aldrich). The above contents were heated to 220 °C in a 50 mL 3-neck flask with flowing N_2. After solvation of the red CdO solid the contents were heated for an additional hour then cooled to room temperature. Acetone was added to precipitate $Cd(oleate)_2$ as a white and waxy solid which was then isolated by centrifugation.

Lead (II) oleate: $Pb(C_{18}H_{33}O_2)_2$
$Pb(oleate)_2$ was synthesized by combining 1.12 g PbO (5 mmol) with 3.96 mL oleic acid (12.5 mmol) and 10 mL 1-octadecene. The remaining procedure was identical to the method detailed above for $Cd(oleate)_2$. FTIR characterization confirmed the identity and purity of both the lead and cadmium products.[1]

Trioctylphosphine selenide: $SeP(C_8H_{17})_3$
30 mL of trioctylphosphine (67 mmol) and 5.29 g Se^0 (67 mmol) were combined and stirred overnight in a nitrogen filled glovebox. This yielded a viscous solution and was used without further purification unless noted. $^{31}P\{^1H\}$(toluene-d_8, δ ppm): 36.8 ($^1J_{P\text{-}Se}$ = 711 Hz). Numerous impurities are observable and shown in Figure S3.

Diphenylphosphine selenide: $SePPh_2H$

1.58 g Selenium shot (20 mmol) was combined with 3.48 mL diphenylphosphine (20 mmol) with 25 mL anhydrous toluene in a one-neck flask in a nitrogen filled glove-box. A stir bar was added and the flask was sealed with a septum and removed from the glove-box. The septum was removed and the flask was quickly connected to a water-cooled condenser with a slight flow of nitrogen. The solution was brought to reflux for 16 hrs yielding a slightly-yellowed clear solution. Toluene was removed by rotary evaporation until a white solid precipitated from solution. The solid was re-crystallized from a hot toluene solution yielding diffraction quality crystals. ^1H(toluene-d_8, δ ppm): 7.23 (d, $^1J_{H-P}$) = 456 Hz. $^{31}P\{^1H\}$(toluene-d_8, δ ppm): 7.5 ($^1J_{P-Se}$ = 768 Hz). ^{31}P(toluene-d_8, δ ppm): 7.5 (d, $^1J_{P-H}$ = 457 Hz).

Tri-isopropylphosphine selenide: $SeP(C_3H_7)_3$

500 μL of tri-isopropylphosphine (2.6 mmol), 0.205 g Se^0 (2.6 mmol), and 2.5 mL anhydrous toluene were combined in a nitrogen filled glovebox and stirred together at RT overnight. Volatiles were removed in vacuo leaving a white solid which was recrystallized from hot toluene. $^{31}P\{^1H\}$(toluene-d_8, δ ppm): 69.7 ($^1J_{P-Se}$ = 714 Hz).

Triethylphosphine selenide: $SeP(C_2H_5)_3$

2.0 mL triethylphosphine (13.6 mmol) and 1.10 g Se^0 (14.0 mmol) were combined with 20 mL anhydrous toluene in a nitrogen filled glovebox and stirred overnight. Excess Se^0 solid was removed by filtration and the solid product was isolated after rotary evaporation of toluene. Triethylphosphine selenide was purified by recrystallization from hot acetone followed by filtration and washing with cold acetone. $^{31}P\{^1H\}$(toluene-d_8, δ ppm): 43.5 ($^1J_{P-Se}$ = 716 Hz).

Triphenylphsophine Selenide: $SeP(C_6H_5)_3$

0.734 g triphenylphosphine (2.8 mmol) and 0.25 g Selenium (3.17 mmol) were combined and stirred overnight in 10 mL of anhydrous toluene in a nitrogen filled glovebox. Excess Se^0 was removed by filtration. Toluene was removed from the reaction mixture by rotary evaporation leaving a white solid, triphenylphosphine selenide, which was recrystallized from hot toluene. Isolated crystals were washed with cold acetone. $^{31}P\{^1H\}$(toluene-d_8, δ ppm): 35.9 ($^1J_{P-Se}$ = 762 Hz).

Reaction between pure tertiary phosphines and $Pb(oleate)_2$

36.9 mg $Pb(oleate)_2$ (48 μmol) was combined with 23.0 mg TIPPSe (48 μmol) and dissolved in a total of 600 μL toluene-d_8 in a J-Young NMR tube. The reaction was heated to 120 °C and monitored periodically by optical absorption and ^{31}P NMR over a period of five hours. No reaction was evident by either optical absorption or ^{31}P NMR. Upon addition of 7 μL diisopropylphosphine (48 μmol) the solution quickly turned from colorless to black indicative of PbSe QD formation. Analogous reactions were performed with triethylphosphine selenide and triphenylphosphine selenide with identical results.

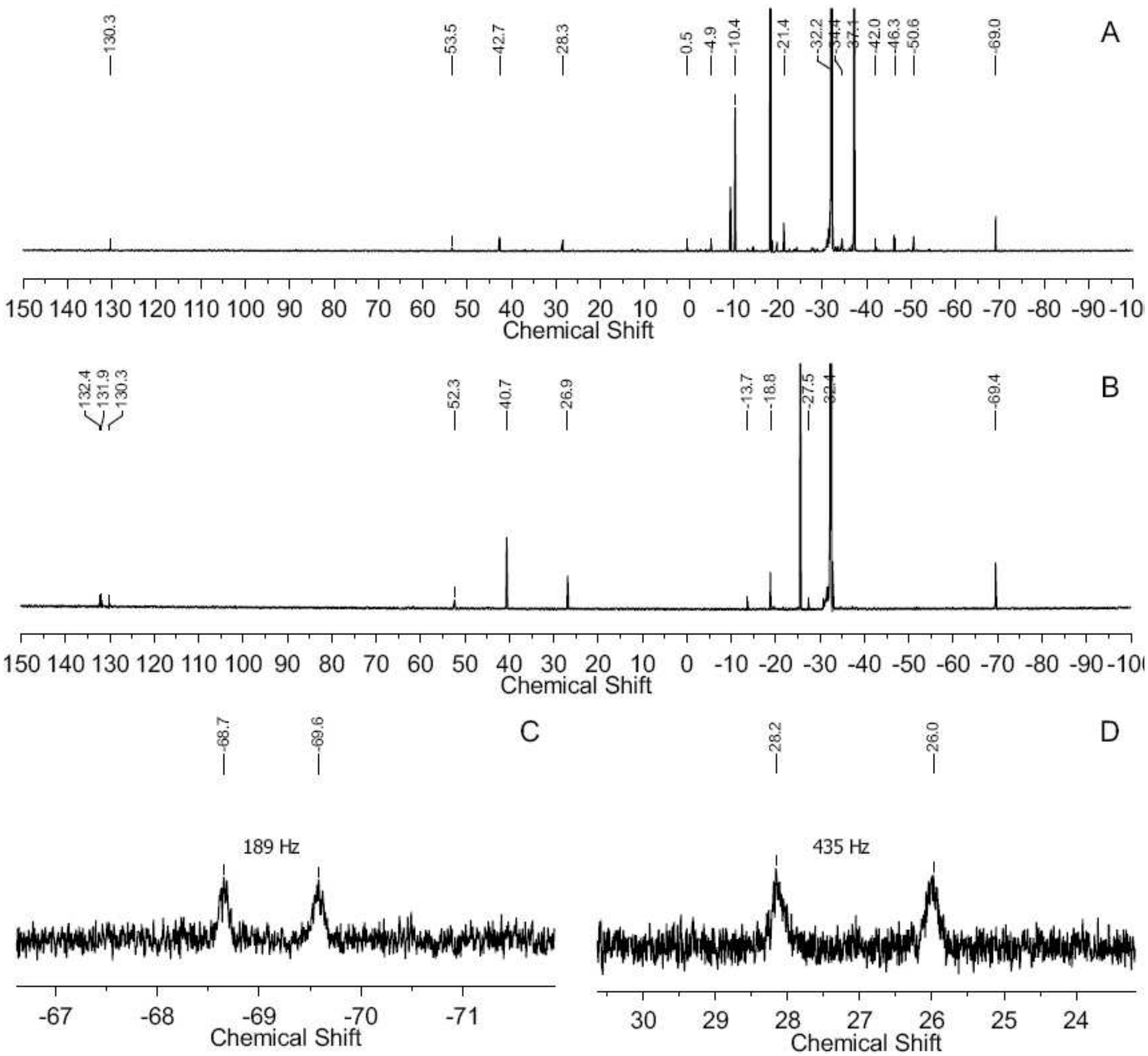


Figure S1. $^{31}P\{^{1}H\}$ NMR for A.) Aldrich technical grade 90% TOP B.) Strem 97% TOP. ^{31}P NMR of observed P-H containing compounds C.) DOP and D.) DOPO.

Trioctylphosphine (TOP) is commercially available but generally impure with numerous unidentified impurities. Two notable and identifiable components are dioctylphosphine (DOP) and dioctylphosphine oxide (DOPO).

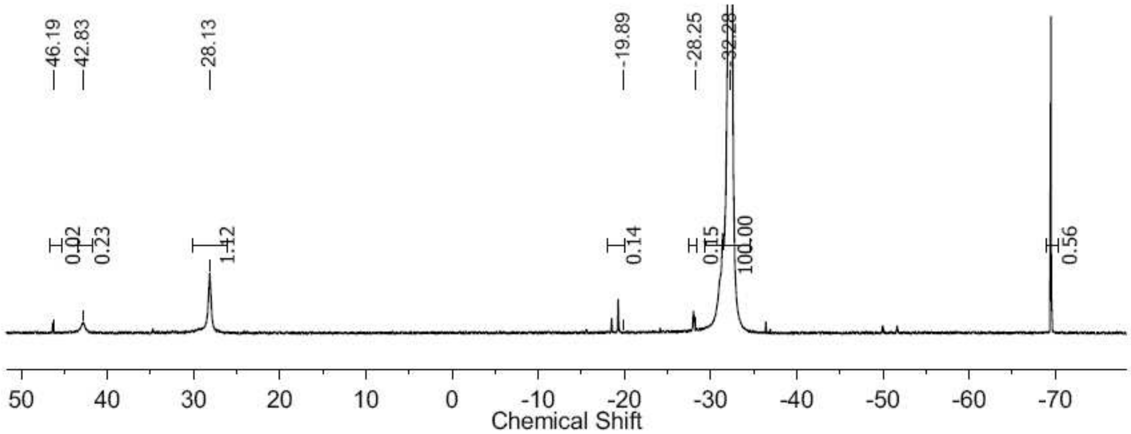


Figure S2. $^{31}P\{^{1}H\}$ NMR of tributylphosphine. Dibutylphosphine (δ – 69.5 ppm) is easily observed in neat solution.

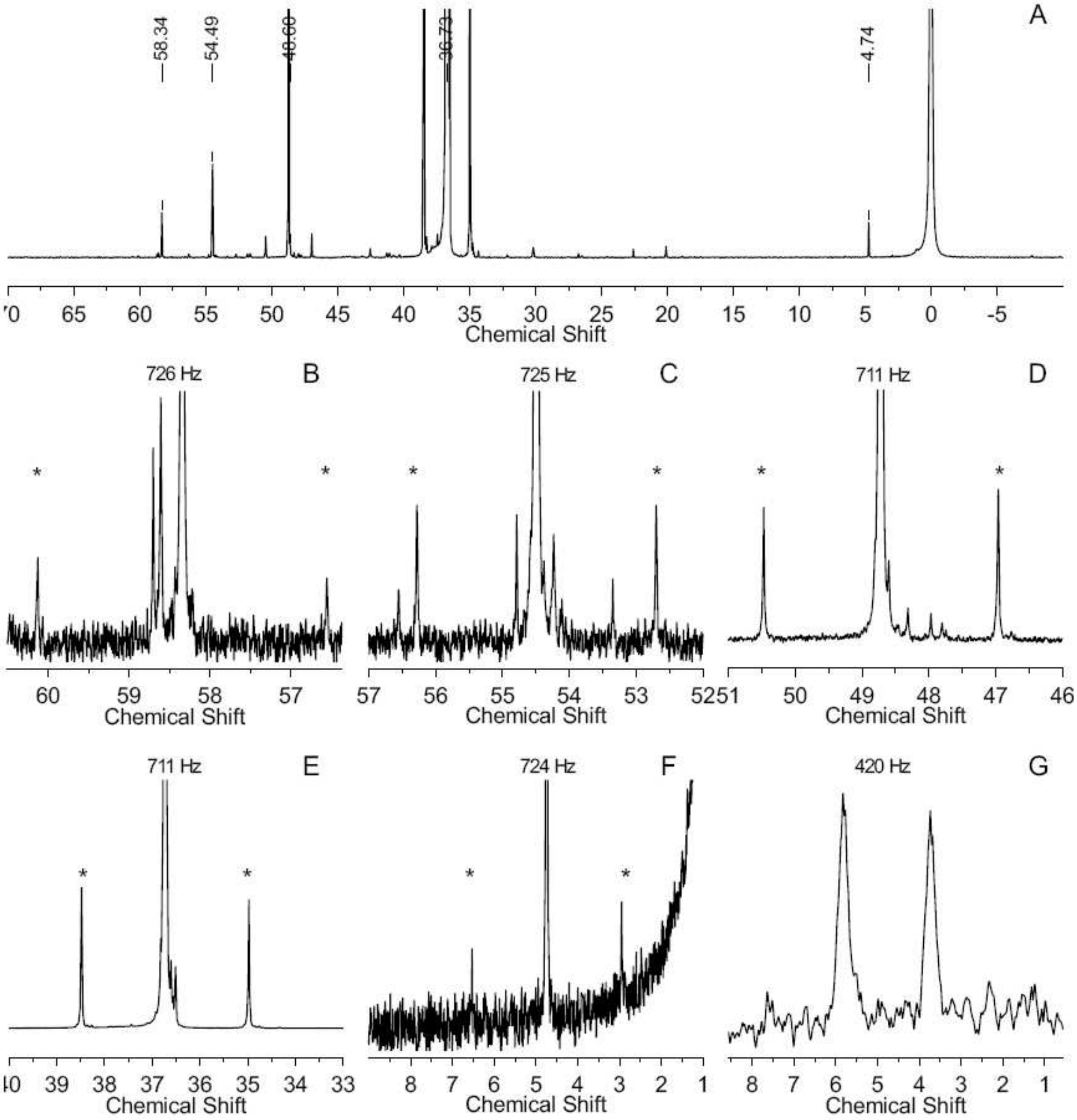


Figure S3. A.) ^{31}P{^{1}H} NMR of neat TOPSe B.) , C.) , D.) , represent unidentified phosphorus (V) compounds possessing strong $^{1}J_{\text{P-Se}}$ coupling E.) TOPSe F.) DOPSe G.) ^{31}P of DOPSe resonance exhibiting a 420 Hz $^{1}J_{\text{H-P}}$ coupling. The astericks highlight ^{77}Se satellites. It is likely that the Se-containing species in panels B, C and D represent three possible alkoxy derivatives of TOPSe. A phosphoric acid standard is shown at 0.0 ppm and added as an internal standard to the NMR tube within a flame sealed capillary.

Fractional Distillation of neat TOPSe

10 mL of neat TOPSe was added to a one-neck flask and equipped with a short-path distillation head and receiving flask. The flask was evacuated to 50 mTorr and slowly heated. Fraction A was collected starting at a temperature of 185ºC for a total of 2.0 mL. Two additional 2.0 mL fractions were collected at 190 and 195 °C. The remaining ~4.0 mL in the round-bottom flask represents fraction C. ^{31}P NMR was used to calculate the purity of TOPSe in each fraction. Sample B was produced by making a 1.0 M solution of TOPSe dissolved in TOP and represents a routinely utilized Se source for QD growth in literature methods.

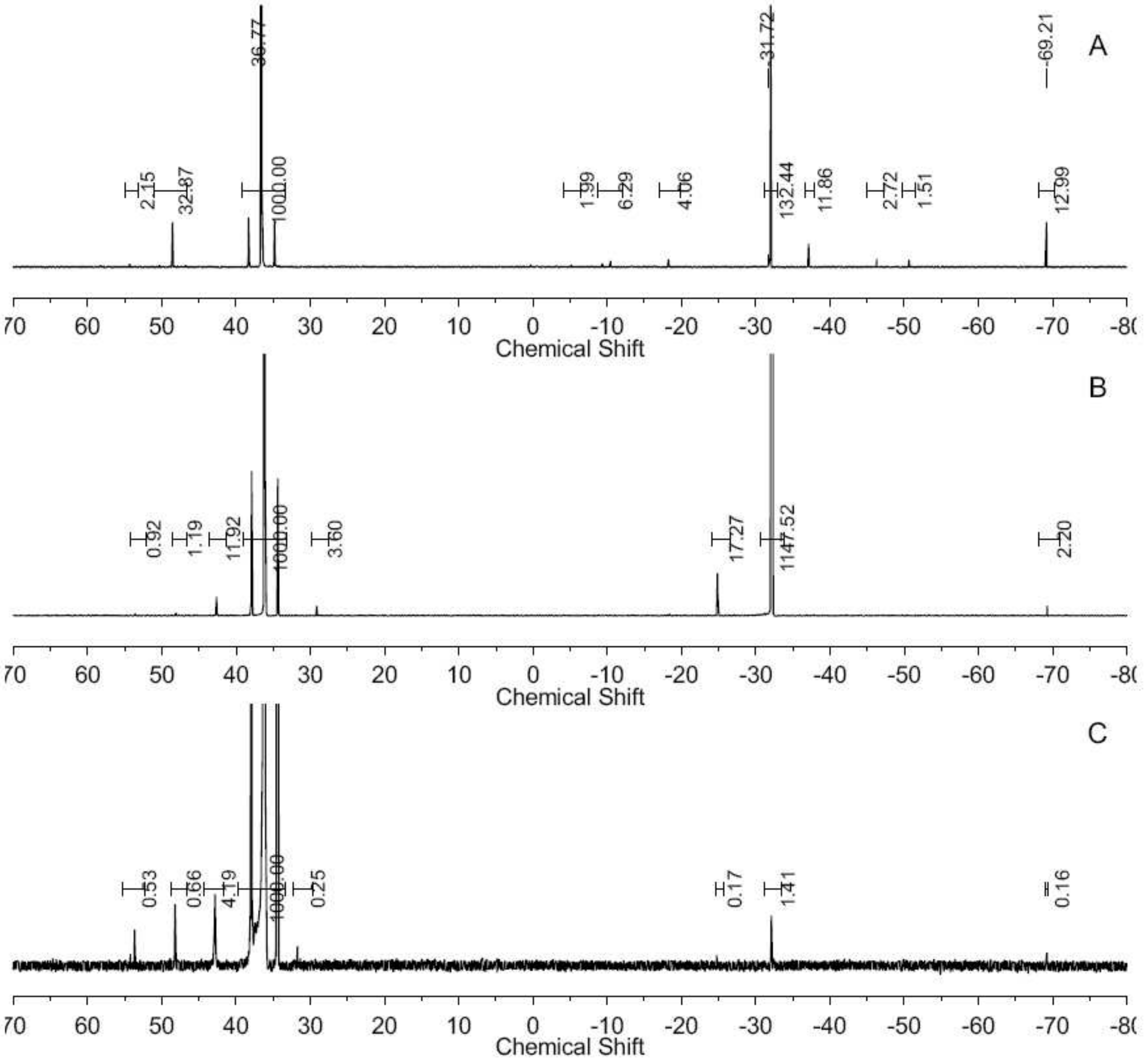


Figure S4. Panels A and C represent ^{31}P{^{1}H} NMR for TOPSe samples with varying purity produced from vacuum distillation of neat TOPSe made using technical grade TOP. Panel B represents 1.0 M TOPSe produced by dissolving selenium powder in TOP.

The following lists the major phosphorus containing components present in each phosphine source used for PbSe growth in Figure S5. These numbers are the result of the ^{31}P integrations shown in Figure S4.

A: 82.7% TOPSe, 11.0% TOP and 1.1 % DOP
B: 45.0% TOPSe, 53.6% TOP and 0.1% DOP
C: 99.3% TOPSe, 0.14% TOP and 0.02% DOP

PbSe MSC synthesis using distilled TOPSe

104 mg PbO (0.47 mmol), 0.59 mL oleic acid (1.9 mmol) and 1.4 mL octadecene were combined in a 3-neck flask and heated under nitrogen to 150 °C until the previously yellow solid had completely dissolved producing Pb(oleate)$_2$. The solution was cooled to 40 °C where 1 mmol of TOPSe was injected (concentration was corrected for by the purity of the phosphine source by dilution with octadecene) and monitored by optical absorption (Figure S5).

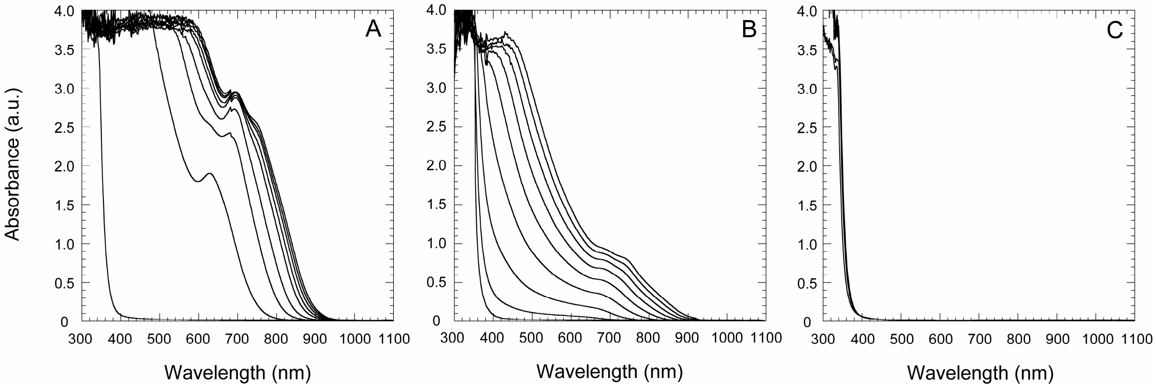


Figure S5. Absorbance monitored at regular intervals for reactions between Pb(oleate)$_2$ and TOPSe of varying purity. Panels A, B and C correspond to the TOPSe sources shown in Figure S4. A direct comparison between experiments after 40 minutes of reaction was shown in the main text as Figure 1. Experimental conditions were chosen to best observe the negligible growth of the unreactive pure TOPSe source in panel C. Unfortunately, these conditions resulted in the production of a significant amount of PbSe MSCs for the experiment shown in panel A and caused the absorbance to saturate near 600 nm.

Reaction between secondary phosphines and M(oleate)$_2$

DPP + Pb(oleate)$_2$

100 μL DPP (0.57 mmol) and 0.22 g Pb(oleate)$_2$ (0.57 mmol) were combined with 500 μL toluene-d$_8$ and flame sealed in a NMR tube under vacuum. The sample was heated in an oil bath at 140 °C while measuring both ^{1}H and ^{31}P NMR at specific time intervals.

DPP + Cd(oleate)$_2$:

An analogous experiment was performed with 25 μL DPP (0.14 mmol) and 0.14 g Cd(oleate)$_2$ (0.21 mmol) in 600 μL toluene-d$_8$. However no reaction was observed to occur at 140 °C after several days of heating.

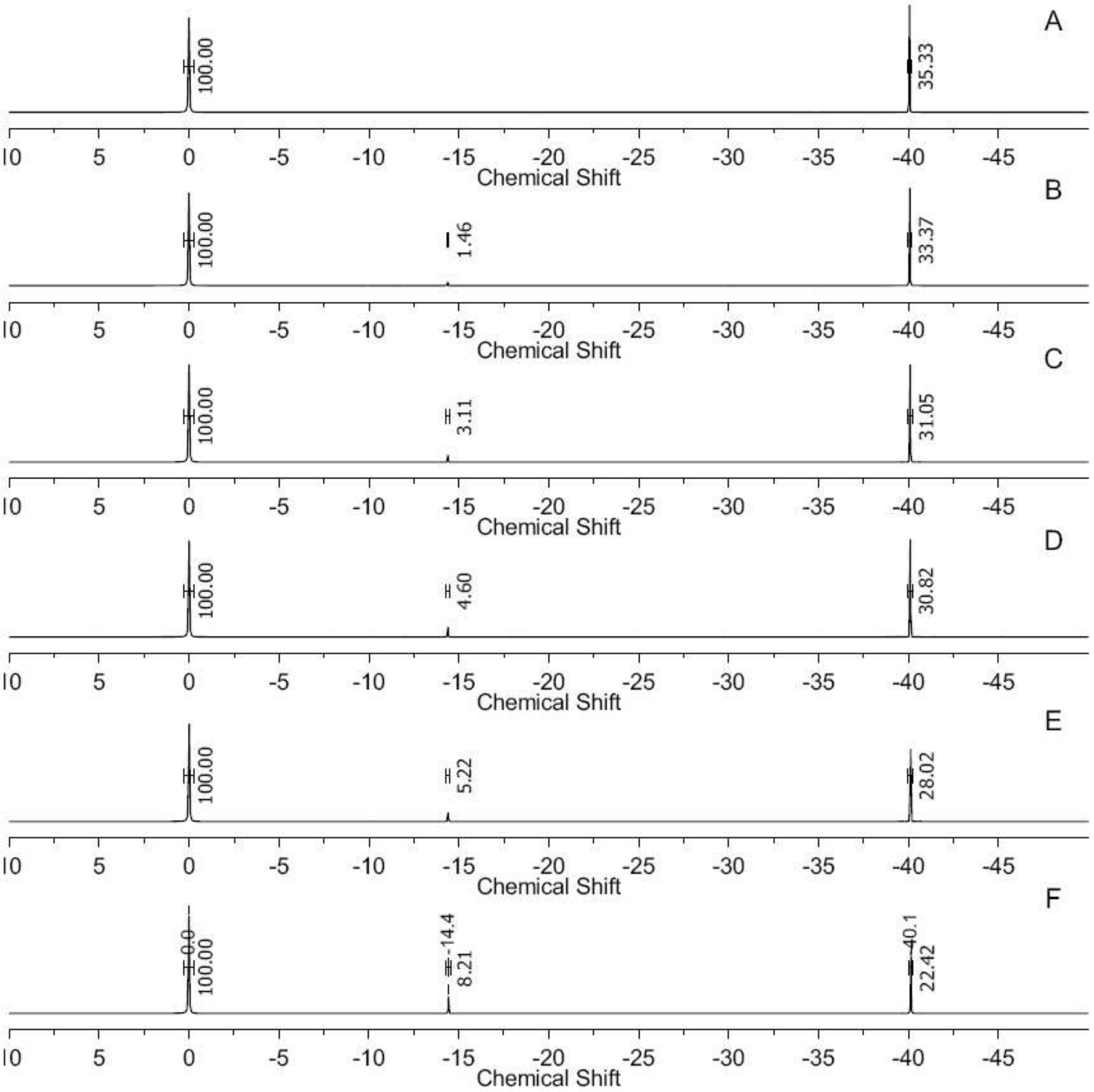


Figure S6. $^{31}P\{^1H\}$ NMR at specific time intervals for the reaction between diphenylphoshphine and Pb(oleate)$_2$ in a flame-sealed NMR tube heated to 140 °C. A phosphoric acid internal standard (δ 0.0 ppm) was included into the NMR tube in a flame-sealed capillary. A.) Prior to heating, B.) 10 min, C.) 20 min, D.) 40 min, E.) 60 min, F.) 240 min. The formation of **12** (δ – 14.4 ppm) is shown at the expense of DPP (**7**, δ – 40.1 ppm).

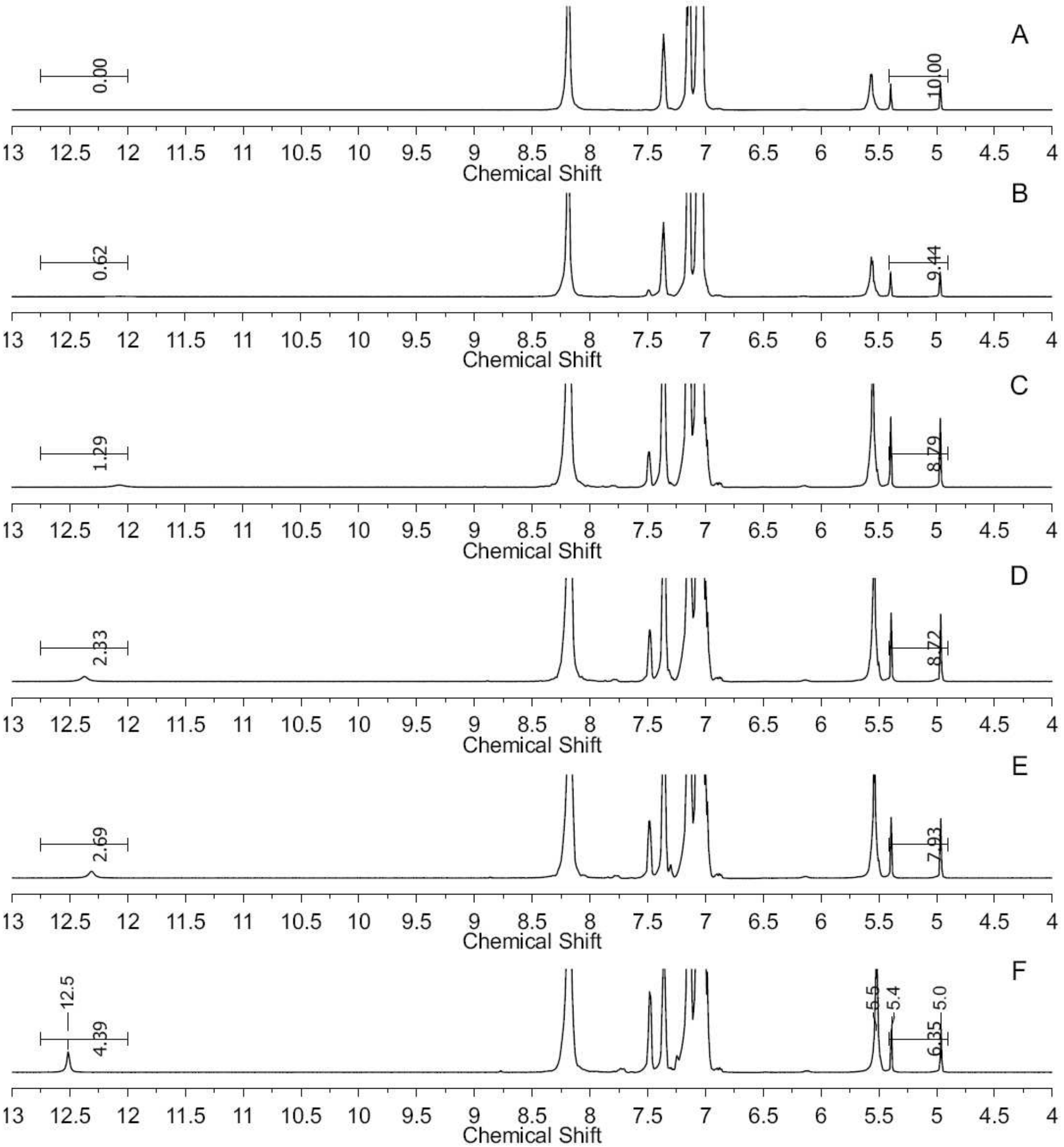


Figure S7. ^{1}H NMR at specific time intervals for the reaction between diphenylphoshphine and Pb(oleate)$_2$ in a flame-sealed NMR tube heated to 140 °C. The integrations for the DPP doublet at 5.2 ppm are set based on the calibrated ^{31}P{^{1}H}signals for DPP from Figure S6 and highlight the steady growth of oleic acid (**2**, δ 12.5 ppm) at the expense of DPP (**7**, d, δ 5.2 ppm) .

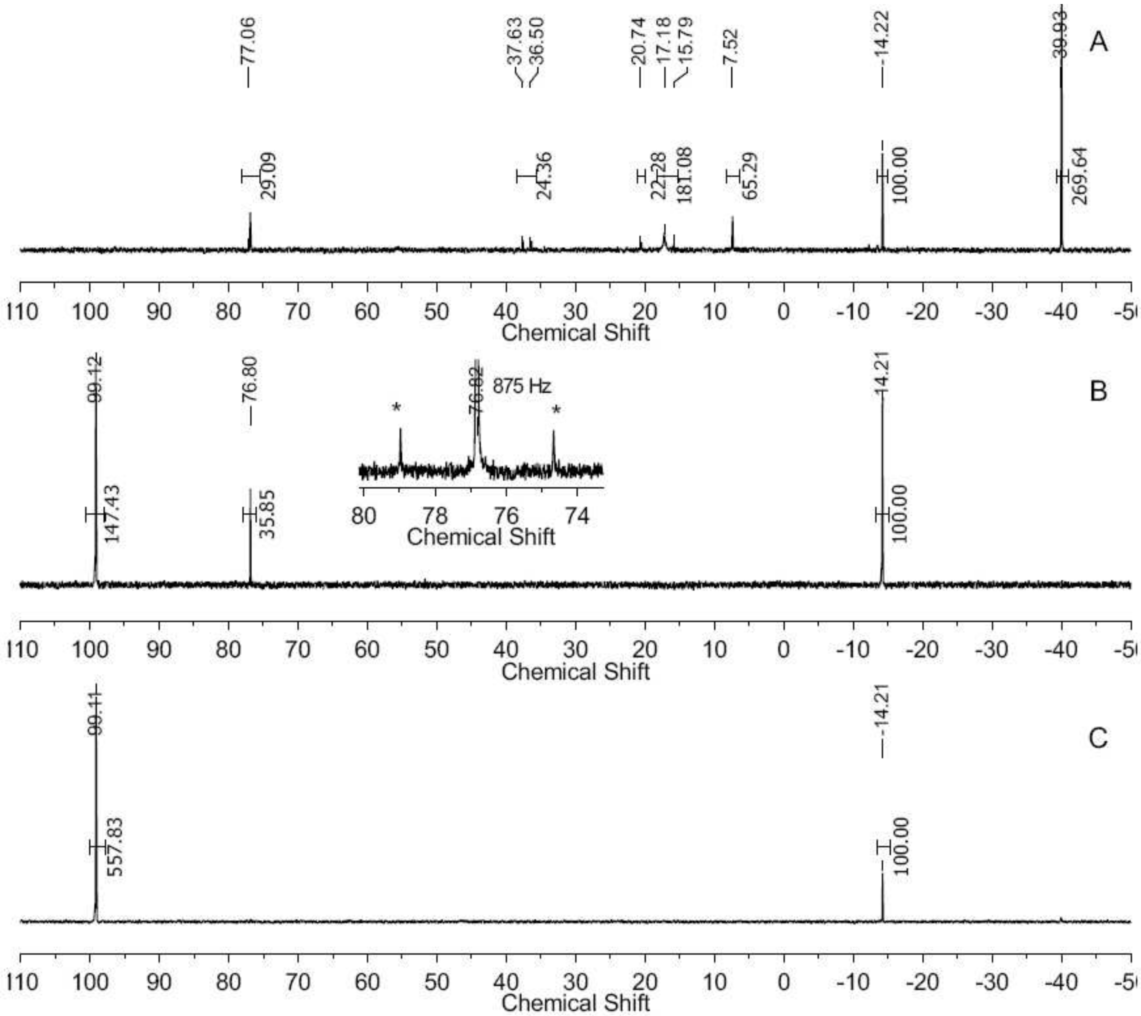


Figure S8. $^{31}P\{^{1}H\}$ NMR for the reaction between DPPSe and Cd(oleate)$_2$ with varying reagent ratios (DPPSe:Cd(oleate)$_2$ A.) 2.0:1.0, B.) 1.0:1.0, C.) 1.0:2.0. NMR were recorded ~ 10 minutes after combination of the two reagents at room temperature. The inset on panel B is for the resonance resulting from 9-Octadecenoxydiphenylphosphine selenide (**8**) with easily observed ^{77}Se satellites(*).

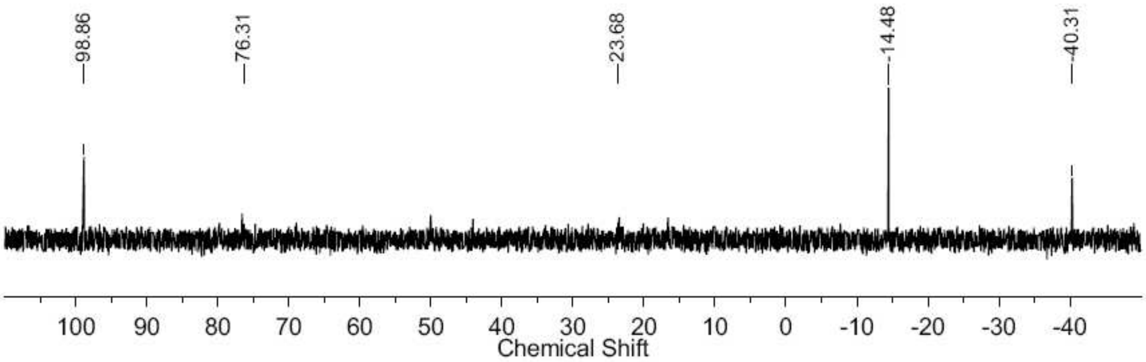


Figure S9. $^{31}P\{^{1}H\}$ NMR for the reaction between DPPSe and Pb(oleate) ~ 10 minutes after combination at room temperature with a 1:1 initial reagent ratio. Identical resonances can be observed for reactions between DPPSe and both Cd(oleate)$_2$ and Pb(oleate)$_2$.

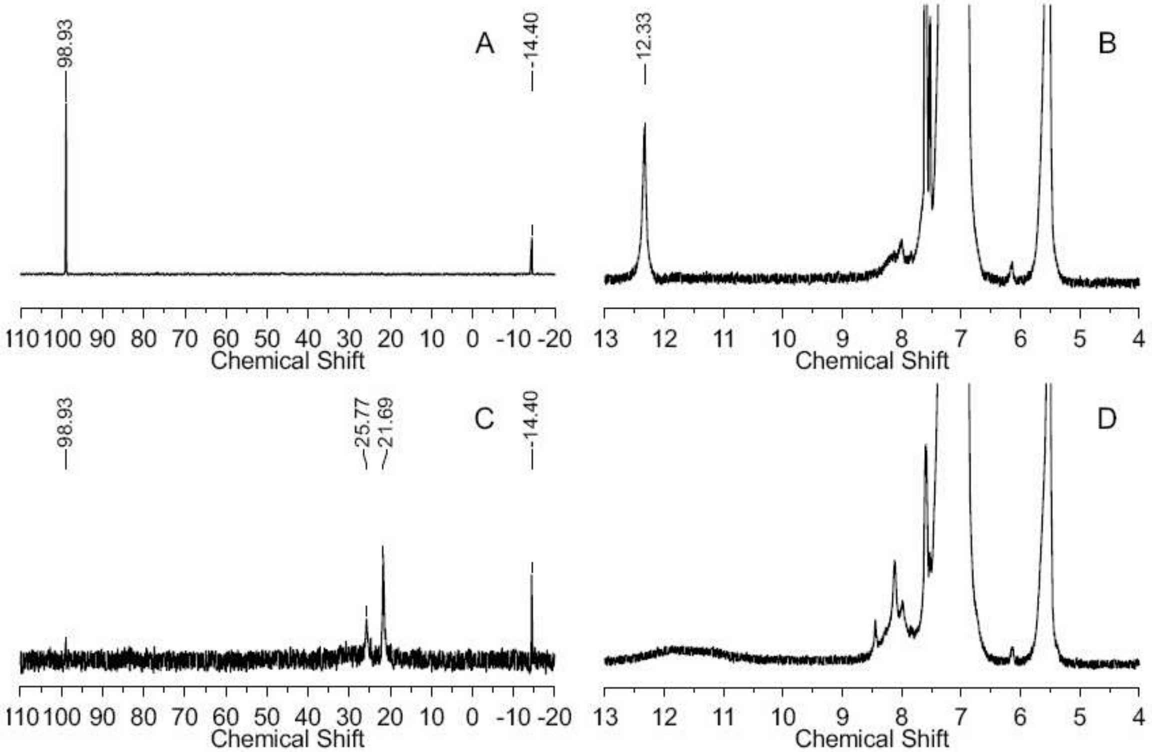
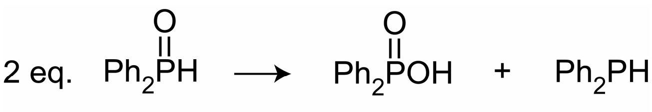


Figure S10. A.) $^{31}P\{^1H\}$ and B.) ^1H NMR for a 1:2 ratio of DPPSe and Cd(oleate)$_2$ 10 min after combination. C.) $^{31}P\{^1H\}$ and D.) ^1H NMR after 24 hrs at room temperature. The resonance for oleic acid (^1H δ12.33 ppm, **2**) and **3** (^{31}P δ 98.9 ppm) disappear between the 24 hrs spanning the top and bottom panels in favor of diphenylphosphine oxide (^{31}P δ 21.6 ppm, **4**) and oleic anhydride **5** (Figure S11).

Post-synthesis, x-ray quality crystals of diphenylphosphinic acid (**13**) were isolated from the reaction mixture by slow solvent evaporation. ^{31}P NMR of this product matched the resonance at 25.7 ppm and likely arises from a bimolecular reaction between two diphenylphosphine oxide molecules.[2]



$$2\text{ eq. } Ph_2\overset{O}{\overset{\|}{P}}H \longrightarrow Ph_2\overset{O}{\overset{\|}{P}}OH + Ph_2PH$$

13

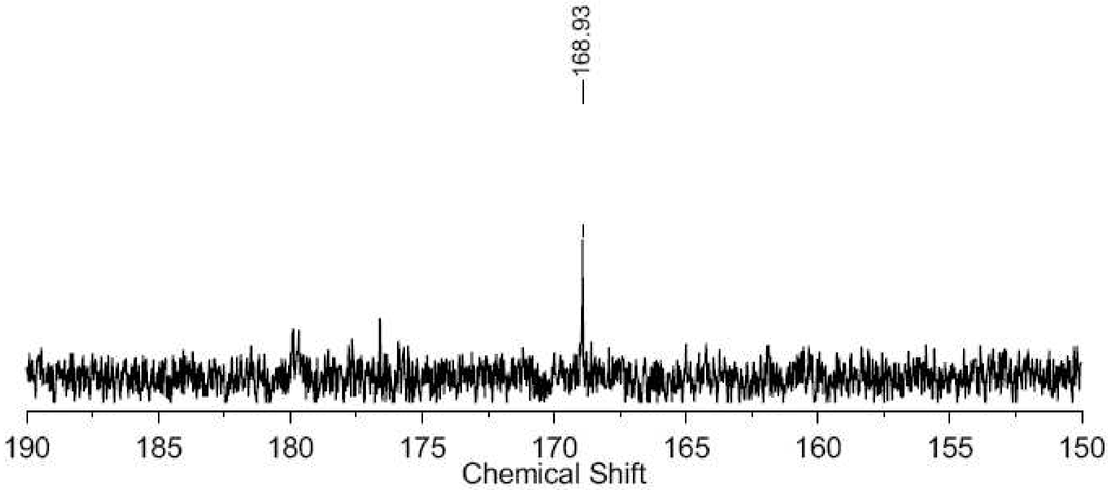


Figure S11. $^{13}C\{^1H\}$ NMR for the same sample shown in Figure S10 panels C and D. This new peak assigned to oleic anhydride (**5**) was only observed after 24 hrs after room temperature combination of DPPSe and Cd(oleate)$_2$.

Solution and Refinement of Crystal Structure for 9.

Crystals of **9** formed as yellow rods with approximate dimensions (0.22 x 0.10 x 0.08 mm^3). A crystals was mounted on a glass fiber and placed on a Bruker SMART APEX II CCD Platform diffractometer under a cold stream of nitrogen at 100.0(1) K. The lattice constraints were obtained from 29063 reflections with values of χ between 1.89 and 36.32°. Cell reduction revealed a triclinic crystal system. The space group was assigned as *P*-1 on the basis of systematic absences and intensity statistics. The structure was solved using SIR97[4] and refined using SHELXL-97.

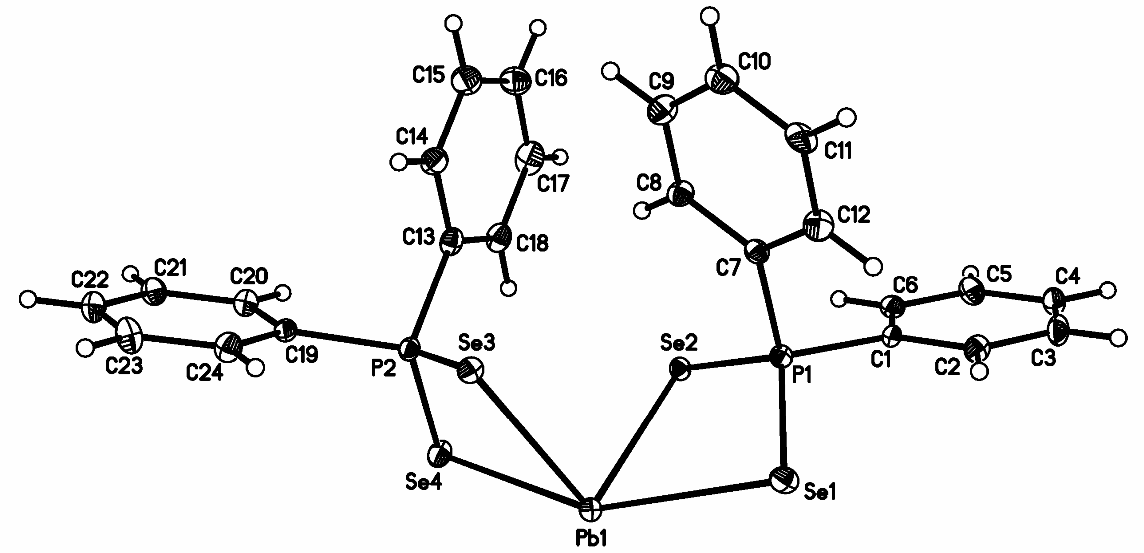
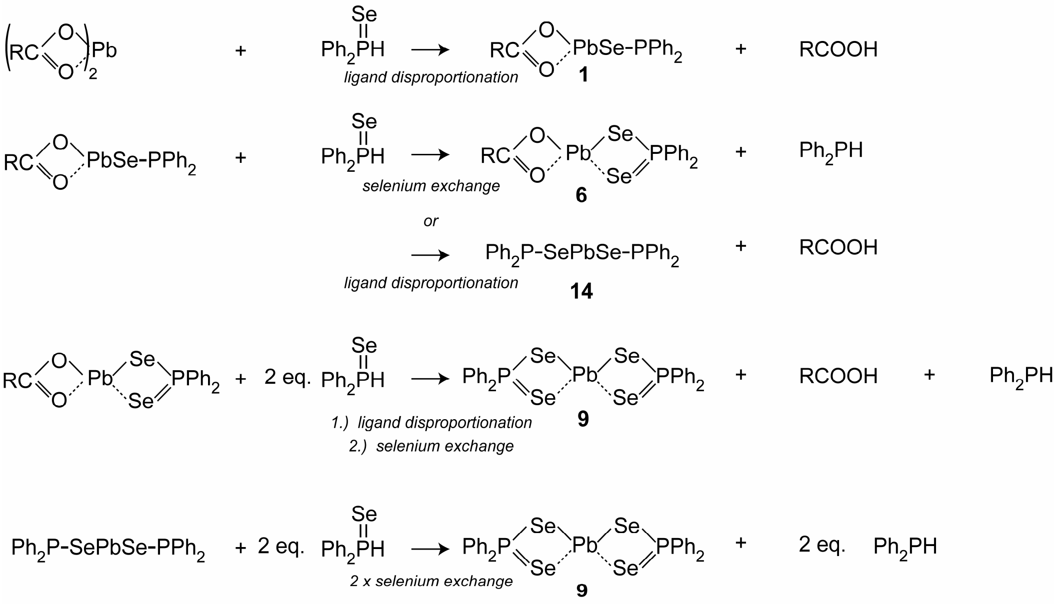


Figure S12. Single crystal X-ray diffraction structure of **9** isolated in high yield from a reaction performed with an excess DPPSe (>5:1; DPPSe:Pb(oleate)$_2$.

Scheme S1. Reaction pathways to **9**



Single crystal of **9** were isolated after several days by slow evaporation of solvent after combining 500 μL of 0.1 M DPPSe (toluene) and 100 μL 0.1 M Pb(oleate)$_2$ (toluene) at room temperature. Unfortunately, no other M-Se species has been isolated from QD reactions most likely due to their highly reactive nature. In **9** there are only two phosphorus nuclei but four selenium atoms. Therefore, selenium exchange must have occurred between an unobserved Pb-Se intermediate (**1**,**6**,**14**) and excess DPPSe. This is supported by the presence of a large quantity of DPP (**7**) in reactions performed with an excess of DPPSe (see Figure S8). Therefore, the identification of **9** represents strong support for the existence of M-Se intermediates such as **1**, **6** and **14** which must precede **9**.

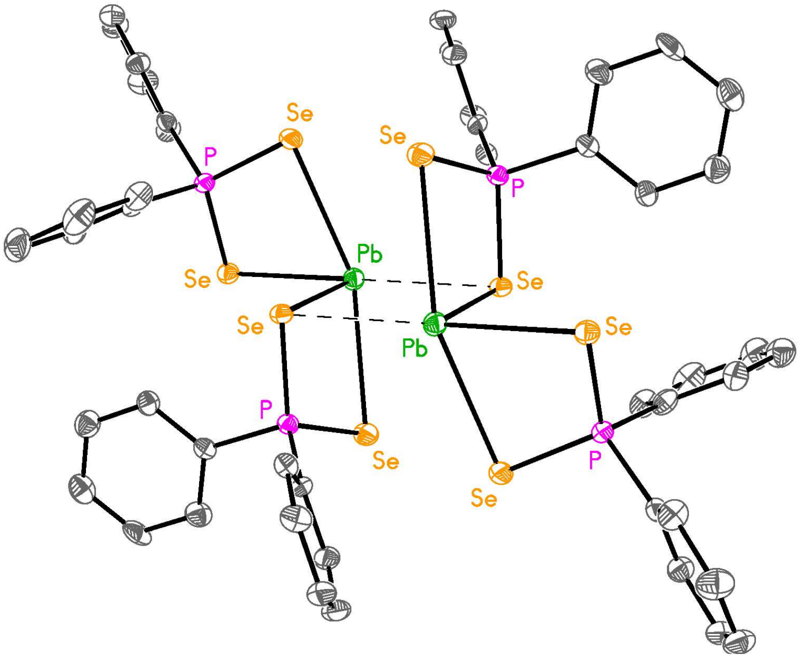


Figure S13. Nearest neighbor orientation for **9** in a single-crystal.

Further, investigation of the packing geometry of two nearest-neighbors of **9** shows the possibility for intermolecular reactions that recreate the octahedral rock-salt crystal structure of bulk PbSe. Bond angles approach 90° for Pb-Se-Pb (90.48°) and Se-Pb-Se (89.52°) very nearly generating a rectangle composed of $(PbSe)_2$ shown at the center of Figure S13. Intermolecular Pb-Se distances (dashed lines) are longer (3.403 Å) than the intramolecular Pb-Se bond distances (2.997 and 3.035 Å). While the intermolecular atomic distances are not short enough to be considered a "bond" this geometry emphasizes the availability of space in **9,** which is expected to translate to related structures (**1**,**6**). It is possible that this geometry represents a transition state for intermolecular metathesis between monomers. Work is currently underway to test this hypothesis, but considering the near-perfect alignment of atoms in this structure it suggests a possible pathway for monomer propagation.

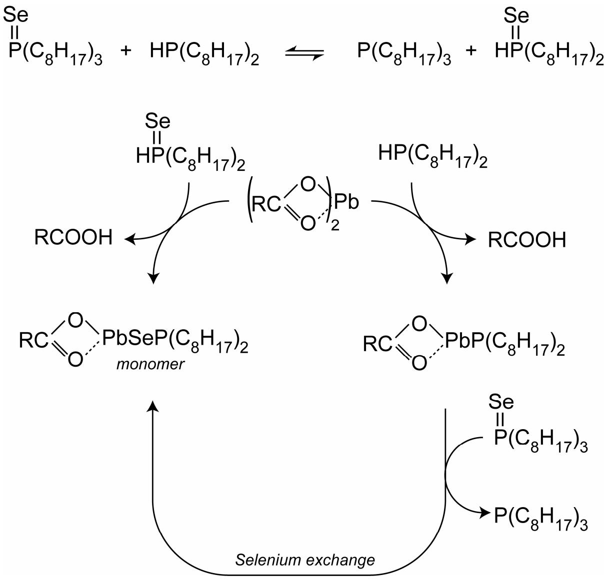


Figure S14. Two coexisting pathways to produce MSe monomer either by direct reaction between secondary phosphine chalcogenides or by a two-step process involving ligand disproportionation and selenium exchange.

Synthesis of PbSe QDs

In a nitrogen filled glove box 2.6 mg DPPSe (10 µmol) was dissolved in 2 mL of anhydrous toluene. 12.6 µL of oleic acid (40 µmol) was added to the aforementioned solution after which it was combined with 2 mL of 0.025 M $Pb(oleate)_2$ (50 µmol). The reaction mixture was added to a teflon-sealable 1 cm cuvette and sealed under N_2. The vessel was removed from the glovebox and heated in an 80 °C oil bath. PbSe MSCs predominate at short times but after several minutes QDs are observed to grow. An example spectra is shown after 20 minutes of heating in Figure S15.

Synthesis of CdSe QDs

A 1 mL octadecene solution containing 0.025 M Cd(oleate) (25 µmol) and 630 µmol of oleic acid was heated to 200 °C in a 3-neck flask with flowing N_2. Upon reaching the growth temperature 1 mL of octadecene with 0.025 M DPPSe (25 µmol) and 630 µmol of oleic acid was rapidly injected into the hot Cd-solution immediately inducing a color change from colorless to yellow, indicative of CdSe formation. An example spectra is shown after 10 minutes of heating in Figure S15.

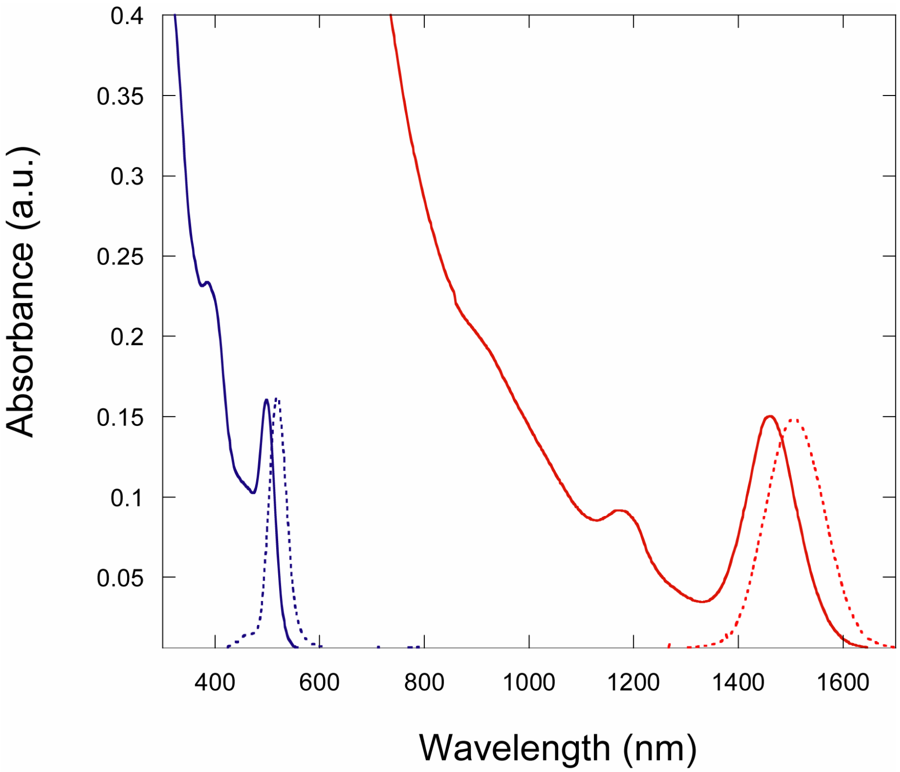


Figure S15. Absorbance (solid) and fluorescence (dotted) for CdSe QDs (blue) and PbSe QDs (red) produced from DPPSe and M(oleate)$_2$ without any post-synthesis processing such as size-selective precipitation.

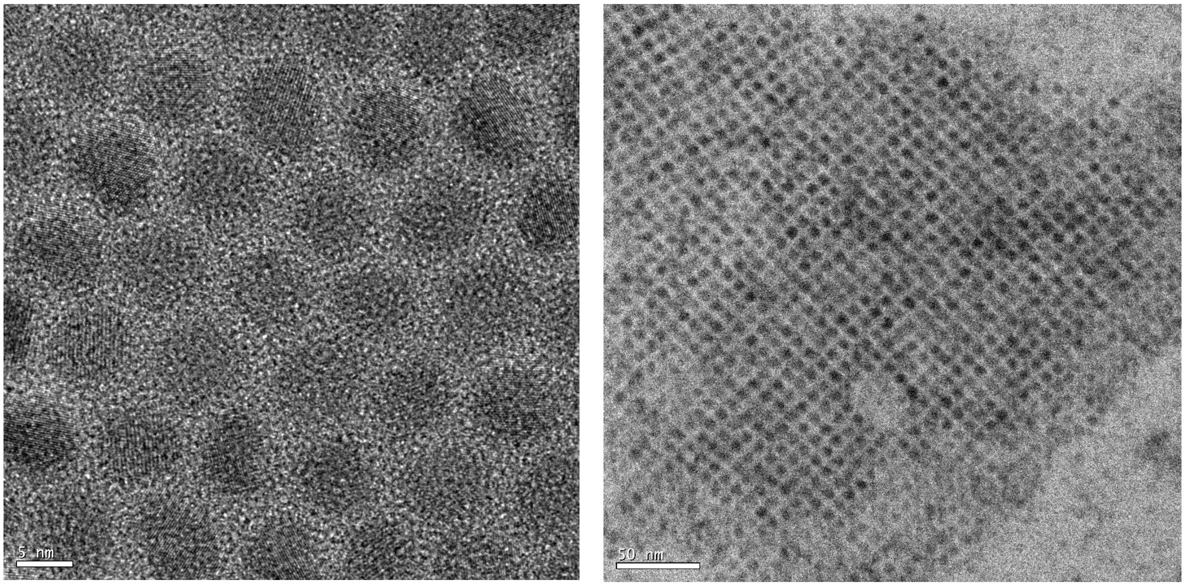


Figure S16. Transmission electron microscopy of PbSe QDs produced from DPPSe and Pb(oleate)$_2$. The spontaneous formation of close-packed arrangements is indicative of the inherent size uniformity resulting from this synthesis. Small spherical PbSe QDs (left) are shown to pack in a hexagonal lattice while larger cubic QDs (right) form into a cubic lattice.

Representative Conversion Yield Calculation

Limiting reagent in this PbSe QD reaction was selenium = 2.25×10^{-6} mol DPPSe

Absorbance Max for PbSe QD sample = 1300 nm

Diameter = $(\lambda_{max}-143.75)/(281.25) = 4.1$ nm

Extinction coefficient (ε) $M^{-1}\ cm^{-1} = (0.03389 * D^{2.53801}) \times 10^5 = 1.22 \times 10^5\ M^{-1}\ cm^{-1}$

From: *ACS Nano* 2009, 3(6), 1518.

C = Absorbance (A) / ε * b = $0.136 / (1.22 \times 10^5\ M^{-1}\ cm^{-1})(1\ cm)$ = **1.1×10^{-6} M QDs**

$1.1 \times 10^{-6}\ M * 3.025 \times 10^{-3}$ L = **3.33×10^{-9} mol QDs**

3.33 mol $\times 10^{-9}$ mol QDs * 6.023×10^{23} QDs / mol QDs = **2.00×10^{15} QDs**

2.00×10^{15} QDs * $3.61 \times 10^{-20}\ cm^3$/QD = **$7.23 \times 10^{-5}\ cm^3$**

$7.23 \times 10^{-5}\ cm^3$ * 1 lattice / $2.29 \times 10^{-22}\ cm^3$ = **3.16×10^{17} lattices**

3.16×10^{17} lattices * 4 Se atoms / lattice = **1.26×10^{18} Se atoms**

1.26×10^{18} Se atoms * 1 mol/ 6.023×10^{23} atoms = **2.10×10^{-6} mol Se**

(2.10×10^{-6} mol Se (QD) / 2.25×10^{6} mol Se (DPPSe))*100 = **93 % Conversion**

References

(1) *J. Am. Chem. Soc.* **2006**, *128* (40), 13032-13033.
(2) *Synthesis* **1987**, *6*, 554-555.