

Mechanistic Study of the Role of Primary Amines in Precursor Conversions to Semiconductor Nanocrystals at Low Temperature**

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Abstract: Primary alkyl amines (RNH_2) have been empirically used to engineer various colloidal semiconductor nanocrystals (NCs). Here, we present a general mechanism in which the amine acts as a hydrogen/proton donor in the precursor conversion to nanocrystals at low temperature, which was assisted by the presence of a secondary phosphine. Our findings introduce the strategy of using a secondary phosphine together with a primary amine as new routes to prepare high-quality NCs at low reaction temperatures but with high particle yields and reproducibility and thus, potentially, low production costs.

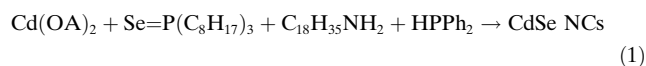
Colloidal semiconductor nanocrystals (NCs) have exhibited emerging potential in biological imaging, solid-state lighting, and photovoltaics.^[1–3] After years of efforts, the current state-of-the-art in NC synthesis is principally empirical; with a large body of literature, there is only a poor comprehension of mechanistic details. Among the various high-temperature recipes developed in the past 15 years, the reaction of $M(OOCR)_n + E=PR_3 \rightarrow ME$ NCs represents a general approach to binary colloidal metal chalcogenide (ME) semiconductor NCs, where $M(OOCR)_n$ symbolizes metal carboxylates and $E=PR_3$ stands for tertiary phosphine chalcogenides.

Primary alkyl amines RNH_2 have been used as beneficial additives. They were suggested to function as surface ligands via coordination and/or hydrogen bonding that stabilize the NCs and affect their optical properties,^[4–9] and/or as a component in the reaction medium that shapes nucleation/growth during the formation of semiconductor NCs including CdS ,^[10] $CdSe$,^[11–14] $CdTe$,^[15] $ZnSe$,^[16,17] ZnS ,^[17] PbS ,^[18] $PbSe$,^[19] InP ,^[20,21] $CuInS_2$,^[22] and $CuInSe_2$.^[23] However, the fundamen-

tal chemistry that involves the amine during the conversion of NC precursors at low temperature to NCs is still largely unknown. And one of the reasons is related to the fact that commercial tri-*n*-octylphosphine ($P(C_8H_{17})_3$ or TOP) contains dioctylphosphine ($HP(C_8H_{17})_2$),^[24] which has been identified to be an active impurity in the synthesis of NCs,^[25,26] and was found in commercial tri-*n*-octylphosphine oxide ($O=P(C_8H_{17})_3$) at high temperature.^[27]

In order to improve the low-temperature nucleation/growth of colloidal NCs with high particle yield and reproducibility, commercial diphenylphosphine ($HPPH_2$ or DPP) has been employed as an additive (but without the presence of a primary amine in 1-octadecene (ODE)).^[24–26,28–32] For the reaction of $M(OOCR)_n + E=PR_3 + HPPH_2 \rightarrow ME$ NCs, recently, diphenylphosphine selenide ($Se=PPh_2H$ or $SeDPP$) has been suggested to be the Se precursor rather than tri-*n*-octylphosphine selenide ($Se=P(C_8H_{17})_3$ or $SeTOP$), due to the Se exchange of $Se=P(C_8H_{17})_3 + HPPH_2 \rightleftharpoons P(C_8H_{17})_3 + Se=PPh_2H$.^[25,26] Being much more reactive than $Se=P(C_8H_{17})_3$, $Se=PPh_2H$ is most likely the chalcogenide precursor that reacts with the metal precursor, such as cadmium oleate ($Cd(OOCC_{17}H_{33})_2$ or $Cd(OA)_2$). Indeed, the use of $HPPH_2$ successfully promotes low-temperature nucleation/growth with enhanced particle yield and reproducibility, but only when the molar ratio of $M(OOCC_{17}H_{33})_2$ to $Se=P(C_8H_{17})_3$ is high.^[26,29–32] This requirement was argued that the strong coordination between $P(C_8H_{17})_3$ and $Cd(OOCC_{17}H_{33})_2$ assists the formation of $Se=PPh_2H$ from Equilibrium $Se=P(C_8H_{17})_3 + HPPH_2 \rightleftharpoons P(C_8H_{17})_3 + Se=PPh_2H$ which is heavily weighted toward $Se=P(C_8H_{17})_3$.^[26]

The present study addresses our mechanistic rationalization of the intriguing mystery: how primary amines modulate the precursor conversion at low temperatures to NCs in the presence of a secondary phosphine. Due to the inescapable presence of $HP(C_8H_{17})_2$ as an active impurity in commercial $P(C_8H_{17})_3$, Equation (1) presents our model reaction system



to investigate the chemistry of the precursor conversion at low temperature in ODE, with both oleylamine ($C_{18}H_{35}NH_2$ or OLA) and $HPPH_2$ used. From Reaction (1), ^{31}P NMR detected phosphorous-containing compounds which were $Ph_2P(Se)-NHC_{18}H_{35}$ (58 ppm and $J_{P-Se} = 775$ Hz, **1**), $Ph_2P-NHC_{18}H_{35}$ (42 ppm, **2**), Ph_2P-PPh_2 (–14 ppm, **3**), and $C_{17}H_{33}COO-PPh_2$ (99 ppm, **4**) (Scheme 1). Also, the temporal evolution of clusters/NCs was monitored by absorption

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spectroscopy, and density functional theory (DFT) calculations were performed to evaluate the structures, Gibbs free energies, and frontier orbitals of our proposed intermediates. Due to the presence of the two nitrogen-containing compounds **1** and **2**, the role of the amine in the precursor conversion is significantly different from that without the presence of a secondary phosphine.^[4] Upon the presence of the secondary phosphine and the primary amine, $\text{Se=PPh}_2\text{H}$ instead of $\text{Se=P(C}_8\text{H}_{17})_3$ is postulated to be the Se precursor which coordinates to the Cd precursor $\text{Cd(OOCC}_{17}\text{H}_{33})_2$. Following the release of two acids from the resulting $(\text{C}_{17}\text{H}_{33}\text{COO})_2\text{Cd(Se=PPh}_2\text{H})_2$ (**B**), $\text{Ph}_2\text{PSe-Cd-SePPh}_2$ (**E**) develops and reacts with the amine leading to $\text{Ph}_2\text{PSe-Cd-SeNHC}_{18}\text{H}_{35}$ (**I**) + HPPH_2 or $\text{HC}_{18}\text{H}_{35}\text{N-Cd-SePPh}_2$ (**H**) + $\text{Se=PPh}_2\text{H}$. **I** and **H** give out **1** and **2**, respectively, in addition to CdSe. This mechanism involves numerous Se exchange reactions (such as $\text{E} + \text{HPPH}_2 \rightleftharpoons \text{G} + \text{Se=PPh}_2\text{H}$), and reversible substitution of small ligand molecules, the amine, phosphine, and acid (around metal chalcogenide centers such as $\text{E} + \text{C}_{18}\text{H}_{35}\text{NH}_2 \rightleftharpoons \text{I} + \text{PPh}_2\text{H}$ in which the amine participates in the cleavage of one Se-P bond of **E**). Our mechanistic study suggests that the reactant amount affects dominant reaction pathways leading to NCs at low temperature and the four phosphorous-containing compounds detected.

Figure 1 presents our ^{31}P NMR spectra collected from four mixtures at room temperature, where the mixtures of $2\text{Cd(OA)}_2 + 1\text{SeTOP}$ (a) and $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 8\text{C}_{18}\text{H}_{35}\text{NH}_2$ (b) are relatively similar to the published

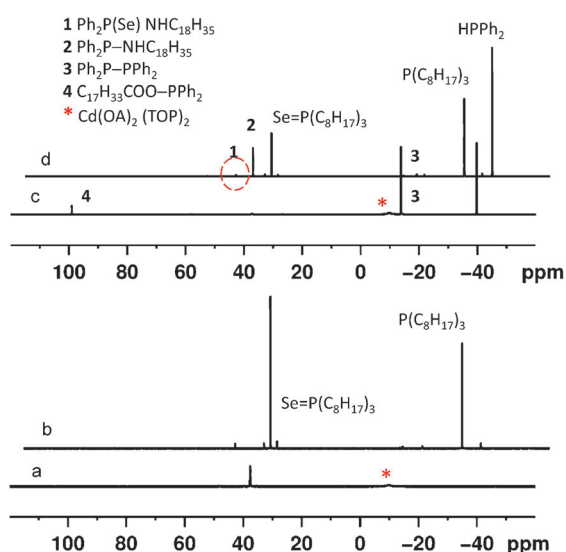


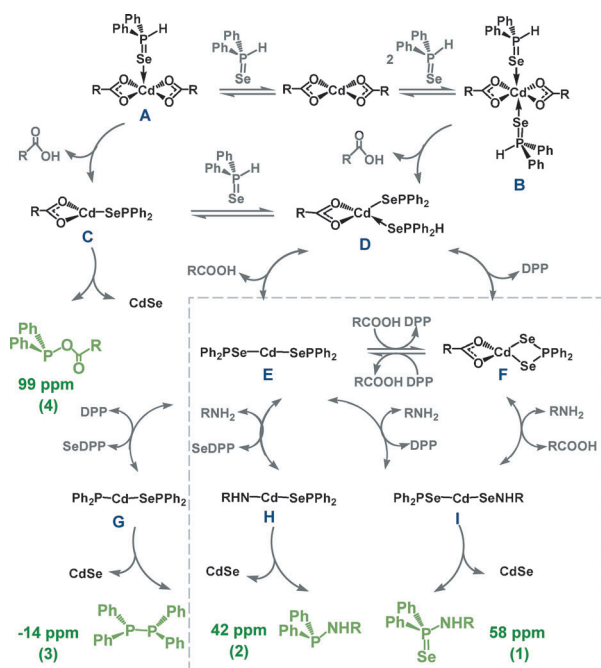
Figure 1. The ^{31}P NMR spectra acquired from four reaction mixtures (a–d) at room temperature. Commercial 90% TOP was used to prepare $\text{Se=P(C}_8\text{H}_{17})_3$ with a 1 Se-to-2.2 TOP molar ratio. The presence of the amine $\text{C}_{18}\text{H}_{35}\text{NH}_2$ slows down the consumption of $\text{Se=P(C}_8\text{H}_{17})_3$ in $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 8\text{C}_{18}\text{H}_{35}\text{NH}_2$ (b) as compared to that in $2\text{Cd(OA)}_2 + 1\text{SeTOP}$ (a), and the consumption of $\text{Se=P(C}_8\text{H}_{17})_3$ in $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 2\text{HPPH}_2 + 8\text{C}_{18}\text{H}_{35}\text{NH}_2$ (d) as compared to that in $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 2\text{HPPH}_2$ (c). Importantly, compounds **1** and **2** were detected from (d), suggesting that the amine participates the precursor conversion with additional pathways as compared to those in (c).^[26,34]

system without the use of HPPH_2 .^[4] The mixtures of $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 2\text{HPPH}_2$ (c) and $2\text{Cd(OA)}_2 + 1\text{SeTOP} + 2\text{HPPH}_2 + 8\text{C}_{18}\text{H}_{35}\text{NH}_2$ (d) correspond to our targeted system with the use of a secondary phosphine HPPH_2 . For the four mixtures, commercial 90% TOP was used to synthesize 1M SeTOP with a 1 Se-to-2.2 TOP molar ratio; 1M SeTOP has been widely used since 1993.^[33] It is evident that the amine slowed down the consumption of SeTOP in the two systems, with and without HPPH_2 . Also, the two broad peaks around -10 ppm in Mixtures a and c, labeled by two red stars and assigned to $\text{Cd(OA)}_2(\text{TOP})_2$,^[26] did not show up in Mixtures b and d. Thus, Mixtures b and d exhibit some similarity, regarding the reduced interaction between TOP and $\text{Cd(OOCC}_{17}\text{H}_{33})_2$ and the slowed down consumption of SeTOP by the presence of $\text{C}_{18}\text{H}_{35}\text{NH}_2$. At the same time, the rate of the consumption of SeTOP in Mixture d [Reaction (1)] is much higher than that in Mixture b; the disappearance of $\text{Se=P(C}_8\text{H}_{17})_3$ at 80°C was evident for Mixture d but not for Mixture b (Figure S1A in the Supporting Information). Accordingly, Mixture d should be more practical for the synthesis of semiconductor NCs at low temperature with enhanced particle yield and synthetic reproducibility (Figure S1B and S1C). The effect of the amount of the amine on nucleation and growth is monitored and presented in Figure S1D.

The mechanism of the precursor conversion in Mixture d should be significantly more complicated than that of Mixture c. With the detection of $\text{Ph}_2\text{P(Se)-NHC}_{18}\text{H}_{35}$ (58 ppm and $J_{\text{P-Se}} = 775$ Hz, **1**), $\text{Ph}_2\text{P-NHC}_{18}\text{H}_{35}$ (42 ppm, **2**), and $\text{Ph}_2\text{P-PPh}_2$ (-14 ppm, **3**) from Mixture d, and $\text{C}_{17}\text{H}_{33}\text{COO-PPh}_2$ (99 ppm, **4**) and **3** from Mixture c, it is easy to understand that the presence of the amine leads to additional reaction paths in the precursor conversion. Compound **3** and **4** were reported from the syntheses of PbSe ,^[25] CdSe ,^[14,26,34,35] ZnS ,^[36] ZnSe ,^[36] and ZnSeS NCs.^[36] The chemical shift for **1** is similar to that reported for $\text{Ph}_2\text{P(Se)-NHC}_{12}\text{H}_{25}$ (57 ppm, $J_{\text{P-Se}} = 775$ Hz), which was monitored from a mixture of $\text{Cd(OOCPh)}_2 + \text{Se=PPh}_2\text{H} + \text{C}_{12}\text{H}_{25}\text{NH}_2$.^[14] To the best of our knowledge, **2** has never been reported from the synthesis of semiconductor NCs and the mechanism of precursor conversion in Reaction (1) has never been addressed, although primary amines have been widely used as additives in the synthesis of semiconductor NCs.^[5–23,37]

To verify the assignment of compounds **1** and **2**, we performed two reactions of $\text{Ph}_2\text{P(Se)Cl}$ and Ph_2PCl with $\text{C}_{18}\text{H}_{35}\text{NH}_2$, respectively, as presented in Figure S2. Also, Figure S2 indicates that the Se exchange equilibrium between **1** and **2**, that is, $\text{1} + \text{HPPH}_2 \rightleftharpoons \text{2} + \text{Se=PPh}_2\text{H}$, is weighted heavily toward **1**, similar to $\text{Se=P(C}_8\text{H}_{17})_3 + \text{HPPH}_2 \rightleftharpoons \text{P(C}_8\text{H}_{17})_3 + \text{Se=PPh}_2\text{H}$ which is weighted heavily toward SeTOP.^[25,26] For the reaction of **2** + HPPH_2 at room temperature, no **3** was detected. Trace amounts of **2** and HPPH_2 were detected from the reaction of **3** + $\text{C}_{18}\text{H}_{35}\text{NH}_2$ at 100°C . Thus, these four phosphorus-containing compounds were all independently synthesized.^[26,34] The chemical shift for **2** is comparable to what was reported for $\text{PPh}_2\text{P-NHR}$ (where $\text{R} = \text{Et}$, 40.4 ppm; $\text{R} = n\text{Pr}$, 40.9 ppm).^[38]

Scheme 1 addresses our proposed mechanism of the precursor conversion to NCs in Reaction (1), with $\text{R} =$



Scheme 1. The plausible mechanism proposed for the precursor conversion in Reaction (1). This mechanism starts with $\text{Se}=\text{PPh}_2\text{H}$ -coordinated $\text{Cd}(\text{OA})_2$, **A** and **B** which result in **C** and **D** after acid release, respectively. CdSe stands for the cluster/NC, the formation of which is accompanied by the four P-containing compounds which were detected by ^{31}P NMR spectroscopy. With their chemical shift indicated, the four P-containing compounds are labeled by bold green numbers. Those intermediates labeled by bold letters (**C** to **I**) were studied by DFT (shown in Scheme S1 and S2 for their bond lengths and frontier orbitals). The amine-related reactions are highlighted in the dashed-line box with the products of CdSe and Compounds **1** and **2**.

$\text{C}_{17}\text{H}_{33}$ for RCOOH or RCOO and $\text{R} = \text{C}_{18}\text{H}_{35}$ for RNH_2 and NHR . This mechanism starts with $\text{Cd}(\text{OA})_2$ which is placed in the top middle part. With $\text{Se}=\text{PPh}_2\text{H}$ instead of $\text{Se}=\text{P}(\text{C}_8\text{H}_{17})_3$ as the Se precursor, $\text{Se}=\text{PPh}_2\text{H}$ -coordinated $\text{Cd}(\text{OA})_2$, $(\text{C}_{17}\text{H}_{33}\text{COO})_2\text{Cd}(\text{Se}=\text{PPh}_2\text{H})$ (**A**) and $(\text{C}_{17}\text{H}_{33}\text{COO})_2\text{Cd}(\text{Se}=\text{PPh}_2\text{H})_2$ (**B**) are developed first. Following the release of acid, $\text{C}_{17}\text{H}_{33}\text{COOCd}-\text{SePPh}_2$ (**C**) and $\text{C}_{17}\text{H}_{33}\text{COOCd}-\text{SePPh}_2(\text{Se}=\text{PPh}_2\text{H})$ (**D**) are formed, respectively. From **D**, the release of additional acid or HPPH_2 results in $\text{Ph}_2\text{PSe}-\text{Cd}-\text{SePPh}_2$ (**E**) and $\text{C}_{17}\text{H}_{33}\text{COOCdSe}_2\text{PPh}_2$ (**F**), respectively. The reactions of the amine with **E** or **F** to **1** and **2** are highlighted in one dashed-line box. Note that the two important intermediates **E** and **F** are connected by $\text{E} + \text{C}_{17}\text{H}_{33}\text{COOH} \rightleftharpoons \text{F} + \text{HPPH}_2$.

Scheme 1 shows the reaction products, namely the CdSe NCs and the four phosphorus products identified by ^{31}P NMR spectroscopy. $\text{Ph}_2\text{PSe}-\text{CdSe}-\text{NRH}$ (**I**), $\text{RHN}-\text{CdSe}-\text{PPh}_2$ (**H**), $\text{Ph}_2\text{P}-\text{CdSe}-\text{PPh}_2$ (**G**), and **C** are proposed to be the immediate precursors of the four identified phosphorous-containing products, **1**, **2**, **3**, and **4**, respectively. The present study suggests that the formation of **C** could be dominated by the **B** to **D** to **C** Path, as compared to the **A** to **C** Path. The latter was first proposed in 2010 via one SeDPP coordination and the former in 2013 via two SeDPP coordination.^[25,26]

Similarly to the phosphorous-containing products, **I** and **H** can be linked by $\text{I} + \text{PPh}_2\text{H} \rightleftharpoons \text{H} + \text{Se}=\text{PPh}_2\text{H}$; also, **G** and **C** can be associated by $\text{G} + \text{RCOOH} \rightleftharpoons \text{C} + \text{PPh}_2\text{H}$.^[34] Scheme 1 is consistent with previous reports^[5,6,14,25,26,34] and with the observations presented in Figure 1–3 and S1–S4.

Scheme S1 presents our DFT study of the key intermediates proposed in Scheme 1 at temperature of 298.15 K. It is worthy of notice that, to explore reaction mechanisms, contemporary DFT calculations represent a pragmatic compromise between detailed calculations of quantum mechanics at high levels and assessments by chemical intuition. The former are not feasible at present, whereas the latter can not reliably distinguish between plausible intermediates. Fortunately, DFT is able to assist in the differentiation of alternative pathways. The intermediates in Scheme 1 are relatively low in free energy, as compared to their isomers (Scheme S1). For example, $\text{Ph}_2\text{PSe}-\text{CdSe}-\text{NRH}$ (**I**) is ca. 30 kJ mol^{-1} lower than $\text{HRN}-\text{CdSe}_2\text{PPh}_2$, $\text{RHN}-\text{CdSe}-\text{PPh}_2$ (**H**) is ca. 25 kJ mol^{-1} lower than $\text{Ph}_2\text{P}-\text{CdSe}-\text{NRH}$, and $\text{Ph}_2\text{PSe}-\text{CdSe}-\text{PPh}_2$ (**E**) is ca. 63 kJ mol^{-1} lower than $\text{Ph}_2\text{P}-\text{CdSe}_2\text{PPh}_2$.

In principle, intermediate **E** could also be formed from the reaction of $\text{Cd}(\text{Se}_2\text{PPh}_2)_2$ (**5**) + HPPH_2 with the release $\text{Se}=\text{PPh}_2\text{H}$.^[34] Figure 2 shows ^{31}P NMR spectra of **5** (a), **5** + 1 equivalent (equiv) of HPPH_2 (b, simplified as **5** + 1 HPPH_2 and such simplification applies to the rest of the reactions), **5** + $16 \text{ C}_{18}\text{H}_{35}\text{NH}_2$ (c), $1 \text{ Se}=\text{PPh}_2\text{H} + 1 \text{ C}_{18}\text{H}_{35}\text{NH}_2$ (d), **5** + $16 \text{ C}_{18}\text{H}_{35}\text{NH}_2 + 1 \text{ HPPH}_2$ (e), and **5** + $16 \text{ C}_{18}\text{H}_{35}\text{NH}_2 + 4 \text{ HPPH}_2$ (f). Intriguingly, the grow-in of **3** and $\text{Se}=\text{PPh}_2\text{H}$ from the (b) mixture of **2** + HPPH_2 , together with the detection of **1** and **3** from the (e) and (f) mixtures of **5** + $\text{C}_{18}\text{H}_{35}\text{NH}_2 + \text{HPPH}_2$, provides supportive evidence for the formation of **E** and its conversion to **1** via **I** and to **3** via **G** as proposed in Scheme 1, with reaction $\text{E} + \text{RNH}_2 \rightleftharpoons \text{I} + \text{PPh}_2\text{H}$ and reaction $\text{E} + \text{HPPH}_2 \rightleftharpoons \text{G} + \text{Se}=\text{PPh}_2\text{H}$. Also, no **2** was detected from the (e) and (f) mixtures, which corroborates that the equilibrium, $\text{1} + \text{HPPH}_2 \rightleftharpoons \text{2} + \text{Se}=\text{PPh}_2\text{H}$ is weighted toward **1**, and **2** has its own immediate precursor **H**.

The solubility of **5** in ODE at room temperature is remarkably low (Figure 2a, without $\text{C}_{18}\text{H}_{35}\text{NH}_2$). After heating at 100°C , the suspension exhibited one phosphorus resonance at 12.0 ppm with $J_{\text{P-Se}} = 480 \text{ Hz}$. In the presence of one equivalent of HPPH_2 (Figure 2b), there was little change at room temperature but small amounts of $\text{Se}=\text{PPh}_2\text{H}$ and **3** were detected at 80°C . With excess $\text{C}_{18}\text{H}_{35}\text{NH}_2$ (Figure 2c), a clear solution was formed immediately at room temperature that exhibited one phosphorus resonance at 21.3 ppm with $J_{\text{P-Se}} = 559 \text{ Hz}$. Little change was seen after this transparent solution was heated at 120°C , 140°C , and 160°C , indicating a high thermal stability for amine-coordinated **5**, in addition to its enhanced solubility. $\text{Se}=\text{PPh}_2\text{H}$ reacted readily with the amine (Figure 2d), resulting in the formation of **6** ($\text{Ph}_2\text{PSe}_2\text{NRH}_3$, where $\text{R} = \text{C}_{18}\text{H}_{35}$, 22.4 ppm and $J_{\text{P-Se}} = 609 \text{ Hz}$) and HPPH_2 .^[34,39]

At room temperature, while **5** exhibited little reactivity toward HPPH_2 (Figure 2b), amine-coordinated **5** displayed appreciable reactivity toward HPPH_2 , producing more **1** than **3** from the mixture with 1 equiv of HPPH_2 (Figure 2e) and more **3** than **1** from the mixture with 4 equiv of HPPH_2

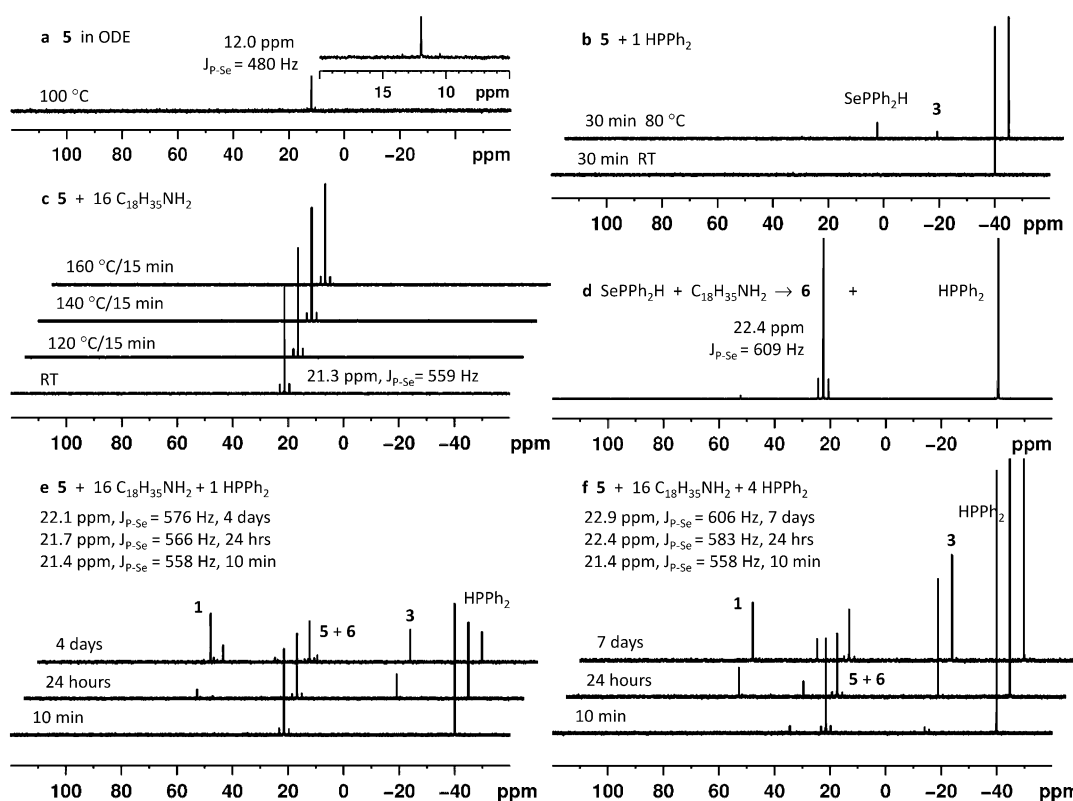


Figure 2. ^{31}P NMR study of the six mixtures (a–f) indicated without the presence of $\text{Cd}(\text{OA})_2$ to explore **E**. The detection of **3** and $\text{Se}=\text{PPh}_2\text{H}$ from Mixture b is noteworthy, together with **1** and **3** from Mixtures e and f. Scheme S2 presents our proposed mechanism of the precursor conversion in these three mixtures, involving the formation of **E** from Compound **5** via its reaction with HPPH₂.

(Figure 2 f). Scheme S2 presents the chemical mechanism proposed for the precursor conversion to **1**, **3**, and the cluster from **5** in the presence of HPPH₂ and C₁₈H₃₅NH₂. This mechanism is in full agreement with our experimental observations. In the presence of HPPH₂ only and with no C₁₈H₃₅NH₂ (Figure 2 b), only **3** and $\text{Se}=\text{PPh}_2\text{H}$ were developed. In the presence of both HPPH₂ and C₁₈H₃₅NH₂ (Figure 2 e and f), no $\text{Se}=\text{PPh}_2\text{H}$ but **1** was formed, together with **3**. Moreover, the relative amount of **1** to **3** increases when the relative amount of C₁₈H₃₅NH₂ to HPPH₂ increases (such as from Figure 2 f to e). As these two reactions continued, there were changes in the chemical shift from 21.4 to 22.1 ppm for Figure 2 e and to 22.9 ppm for Figure 2 f, together with the change in $J_{\text{P-Se}}$ from 558 to 576 Hz for Figure 2 e and to 606 Hz for Figure 2 f. It is easy to understand this change: a mixture of amine-coordinated **5** (Figure 2 c) and **6** (Figure 2 d) will show only one averaged chemical shift and $J_{\text{P-Se}}$. Thus, the observed change in the chemical shift and $J_{\text{P-Se}}$ can be readily interpreted as an increase in **6** due to the formation of $\text{Se}=\text{PPh}_2\text{H}$ which then reacted with the excess amine. More $\text{Se}=\text{PPh}_2\text{H}$ was produced and thus more **6** was formed from the mixture with 4 equiv of HPPH₂ (Figure 2 f) than from the mixture with 1 equiv of HPPH₂ (Figure 2 e).

Scheme 1 is in full agreement with our previous study which suggests that, for $\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2 + \text{Se}=\text{P}(\text{C}_8\text{H}_{17})_3 + \text{HPPH}_2$, **4** or **3** are favored by RCOOH or HPPH₂, respectively.^[34] Furthermore, Scheme 1 predicts that only **1** will be obtained from **I** via $\text{F} + \text{C}_{18}\text{H}_{35}\text{NH}_2$ or via $\text{E} + \text{C}_{18}\text{H}_{35}\text{NH}_2$.

When HPPH₂ is increased, **E** will increase (from **D** or from **F**); thus, **2** and **3** increase. In order to test the pathways of **F-I-1** and **F-E-I-1**, we designed the reaction of **5** + $\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2$ without or with HPPH₂, based on $\text{5} + \text{Cd}(\text{OA})_2 \rightleftharpoons 2\text{C}_{17}\text{H}_{33}\text{COOCdSe}_2\text{PPh}_2$ (**F**).^[34]

Figure 3 shows ^{31}P NMR spectra collected from the reaction of **5** + $6\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2 + 16\text{C}_{18}\text{H}_{35}\text{NH}_2$ at room temperature and at elevated temperatures (Figure 3 a) and from the 10-minute reactions of **5** + $\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2 + \text{HPPH}_2$ at room temperature (Figure 3 b–d). The effects of the amounts of HPPH₂, C₁₈H₃₅NH₂, and $\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2$ are addressed in Figure 3 b–d, respectively. Without HPPH₂, one phosphorus resonance was monitored at 18.8 ppm with $J_{\text{P-Se}} = 542$ Hz from Figure 3 a reaction of **5** + $6\text{Cd}(\text{OCC}_{17}\text{H}_{33})_2 + 16\text{C}_{18}\text{H}_{35}\text{NH}_2$ at room temperature, and is expected to be the amine-coordinated precursor **F**. When this solution was heated at 120 °C, amine-coordinated **F** disappeared slowly, accompanied by the formation of **1**. Thus, amine-coordinated **F** should be much more reactive than amine-coordinated **5** at elevated temperatures (Figure 2 c). This Figure 3 a reaction provides the very evidence that the amine contributes to the cleavage of Se–P bond of **F** leading to **1** (via **I** obtained from the reaction of $\text{F} + \text{RNH}_2 \rightleftharpoons \text{I} + \text{RCOOH}$).

In the presence of a tiny amount of HPPH₂ with the HPPH₂-to-**5** molar ratio of 0.05, **1** was formed immediately and predominantly as an almost single species at room temperature (Figure 3 b). With more HPPH₂ (1 equiv and

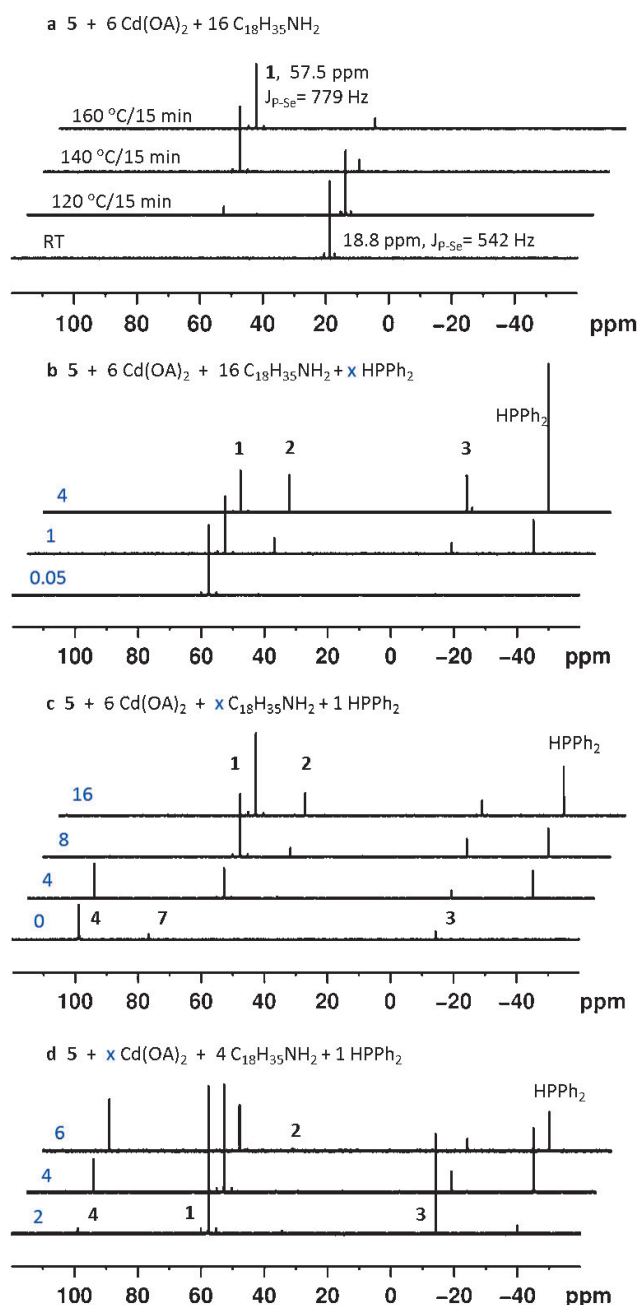


Figure 3. The ^{31}P NMR spectra of the four groups of reaction $5 + \text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2 + \text{HPPH}_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2$ with the feed molar ratios indicated. With $5 + \text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2 \rightleftharpoons 2\text{F}$,^[34] these reactions were designed to investigate the mechanism of the precursor conversion in Reaction (1) shown in Scheme 1. Without the use of HPPH_2 (a), the reaction produced **1** only at elevated temperature such as 120°C (via the Scheme 1 F-I-I pathway). With only a catalytic amount of HPPH_2 (b, 0.05), **1** (and NCs) could be formed at room temperature (via the Scheme 1 F-E-I-I pathway). Clearly, with HPPH_2 at ambient temperature (b–d), the reactant amount influences the reaction paths to **1–4** (Scheme 1).

4 equiv), the yields of **2** and **3** increased, which is in agreement with Scheme 1. Figure 3a and b illustrate that HPPH_2 facilitates low temperature reactions and its amount promotes the reaction paths to **2**, and **3**. Particularly, Figure 3b-0.05 supports the HPPH_2 -assisted reaction pathway of Scheme 1 F-

E-I-1, which involves re-generation of HPPH_2 from **E** to **I**. Furthermore, the fact that this Figure 3b-0.05 reaction proceeded readily at room temperature strongly denotes a relatively low energy path (Scheme 1 F-E-I-1) as compared to the pathway of Scheme 1 F-I-1 which took place at 120°C (as comprehended by Figure 3a). Notably, a catalytic amount of a secondary phosphine lowers the reaction temperature so drastically and assists our discrimination of the pathways of F-I-1 (Figure 3a) and F-E-I-1 (Figure 3b-0.05). When the amount of HPPH_2 is relatively large, **2** (from **H**) and **3** (from **G**) will be produced, in addition to **1**. Accordingly, **E** appears to be a critical intermediate on the route to **1** from **I** and to **2** from **H**, due to its two reactions with $\text{C}_{18}\text{H}_{35}\text{NH}_2$, and to **3** via **G** due to its reaction with HPPH_2 .

Figure 3c reveals that the reaction paths to **4**, **3**, **1**, and/or **2** were affected by the amine amount. When the $\text{C}_{18}\text{H}_{35}\text{NH}_2$ -to- HPPH_2 molar ratio increased from 0, 4, 8, to 16 at room temperature, **4** disappeared while **1** and **2** increased. In the absence of $\text{C}_{18}\text{H}_{35}\text{NH}_2$ at low temperatures, only **3** from **G** and **4** from **C** are produced.^[34] Equilibrium $4 + \text{Se}=\text{P}(\text{H})_2\text{H} \rightleftharpoons 7 + \text{HPPH}_2$ can be found elsewhere, where **7** is $\text{Ph}_2\text{P}(\text{Se})\text{OOC}(\text{C}_{17}\text{H}_{33})_2$ (77 ppm).^[34] Evidently, the presence of $\text{C}_{18}\text{H}_{35}\text{NH}_2$ shifted the dominant reaction path away from Scheme 1 C-4. Such a significant mechanistic impact of the amine amount is, to our knowledge, unprecedented. Figure S3 presents the effect of the amine on the growth of clusters/NCs in six reactions at 35°C . The reactions were $5 + 6\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2 + (0.5 \text{ or } 1)\text{HPPH}_2 + (0, 6, \text{ or } 12)\text{C}_{18}\text{H}_{35}\text{NH}_2$; the three batches in the top and bottom panels have 0.5DPP and 1DPP, respectively. Undoubtedly, the amine amount affects the reaction paths of the precursor conversion and shapes the nucleation and growth.

Figure 3d presents the effect of the amount of $\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2$ for the reactions with the fixed amounts of **5**, $\text{C}_{18}\text{H}_{35}\text{NH}_2$, and HPPH_2 . $\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2$ was prepared from a mixture in ODE with the 1.0CdO-to-2.2 $\text{C}_{17}\text{H}_{33}\text{COOH}$ molar ratio.^[26,34] The increase of $\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2$ led to more $\text{C}_{17}\text{H}_{33}\text{COOH}$ and thus more **4**, because Scheme 1 C-4 pathway became more competitive.^[34] Hence, the ^{31}P NMR study of the Figure 3 reactions fully supports the reaction pathways in Scheme 1, which lead to the four phosphorus compounds, **1**, **2**, **3**, and **4**. Also, the pathways to the formation of their immediate precursors **I**, **H**, **G**, and **C** may be active simultaneously or one may dominate. For example, **1**, **2**, **3**, and **4** were detected concurrently from the $5 + 4\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2 + 4\text{C}_{18}\text{H}_{35}\text{NH}_2 + 1\text{HPPH}_2$ reaction (Figure 3d), while only **1** was detected from the $5 + 6\text{Cd}(\text{OOC}(\text{C}_{17}\text{H}_{33})_2)_2 + 16\text{C}_{18}\text{H}_{35}\text{NH}_2 + 0.05\text{HPPH}_2$ reaction (Figure 3b). Again, the reactant amount dictates the Scheme 1 reaction paths leading to the formation of the CdSe clusters/NCs.

With its fundamental insights and far-reaching implications, Scheme 1 fills a large gap in our knowledge and endorses the use of a primary amine together with a secondary phosphine to promote low-temperature reproducible syntheses of various high-quality binary and alloyed NCs with high particle yields. Being a coordinating ligand, the amine can also be chemically reactive as a hydrogen/proton donor. Our results echo the mechanistic study on the role of $\text{C}_{18}\text{H}_{35}\text{NH}_2$ in the formation of CdSe NCs from the reaction of

$\text{Cd}(\text{OOCCH}_2\text{H}_{33})_2$ and trialkyl phosphine selenide (such as $\text{Se}=\text{P}(\text{C}_8\text{H}_{17})_3$); without the presence of a secondary phosphine, the amine was argued to have no direct contribution to the cleavage of the $\text{Se}=\text{P}$ bond.^[4] In our case, the amine directly participates in the cleavage of the $\text{Se}-\text{P}$ bond such as $\text{Ph}_2\text{PSe}-\text{Cd}-\text{SePPh}_2$ (**E**) + $\text{RNH}_2 \rightleftharpoons \text{Ph}_2\text{PSe}-\text{Cd}-\text{SeNRH}$ (**I**) + HPPH_2 and $\text{C}_{17}\text{H}_{33}\text{COOCdSe}_2\text{PPh}_2$ (**F**) + $\text{RNH}_2 \rightleftharpoons \text{Ph}_2\text{PSe}-\text{Cd}-\text{SeNRH}$ (**I**) + $\text{C}_{17}\text{H}_{33}\text{COOH}$.

In conclusion, we investigated the chemistry of a primary amine during the precursor conversion at low temperature to semiconductor NCs. Our model system is $\text{Cd}(\text{OOCCH}_2\text{H}_{33})_2 + \text{Se}=\text{P}(\text{C}_8\text{H}_{17})_3 + \text{HPPH}_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2$, with the use of both a primary amine $\text{C}_{18}\text{H}_{35}\text{NH}_2$ and a secondary phosphine HPPH_2 added to $\text{M}(\text{OOCR})_n + \text{E}=\text{PR}_3$. Based on our ^{31}P NMR, in-situ absorption spectroscopic studies, and DFT calculations, we proposed a mechanism (shown in Scheme 1) which outlines the reaction pathways to NCs and compounds $\text{Ph}_2\text{P}(\text{Se})-\text{NHC}_{18}\text{H}_{35}$ (58 ppm and $J_{\text{P-Se}} = 775$ Hz, **1**), $\text{Ph}_2\text{P}-\text{NHC}_{18}\text{H}_{35}$ (42 ppm, **2**), $\text{Ph}_2\text{P}-\text{PPh}_2$ (−14 ppm, **3**), or $\text{C}_{17}\text{H}_{33}\text{COO}-\text{PPh}_2$ (99 ppm, **4**). This mechanism involves $\text{Se}=\text{PPh}_2\text{H}$ as the Se precursor, together with a set of equilibria of Se exchange reactions and of metathesis reactions with the reversible exchange of the small molecules, $\text{C}_{18}\text{H}_{35}\text{NH}_2$, HPPH_2 , and $\text{C}_{17}\text{H}_{33}\text{COOH}$. Scheme 1 is supported by our experimental results, such as the detection of **1** to **3** from $\text{Cd}(\text{OOCCH}_2\text{H}_{33})_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2 + \text{Se}=\text{PPh}_2\text{H}$ (Figure S4) and the detection of **1** and **3** from $\text{Cd}(\text{Se}_2\text{PPh}_2)_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2 + \text{HPPH}_2$ (Figure 2). For Reaction $\text{Cd}(\text{Se}_2\text{PPh}_2)_2 + \text{Cd}(\text{OOCCH}_2\text{H}_{33})_2 + \text{C}_{18}\text{H}_{35}\text{NH}_2$, with only a catalytic amount of HPPH_2 (Figure 3b-0.05), NCs together with **1** (via **F-E-I-1**) can be formed at ambient temperature; with no addition of HPPH_2 (Figure 3a), relatively high temperatures (such as 120 °C) are required (via **F-I-1**).

Our mechanistic studies provide more in-depth understanding of the role of primary amines in precursor conversions at low temperature to NCs. The current understanding of the amine and phosphine chemistries, involved in the conversion of precursors to colloidal semiconductor ME NCs, will facilitate the comprehension of the results previously reported in the literature, particularly those about the amine accelerating and retarding effects. These new insights offer strategies for the use of additives to optimize low temperature reactions to produce high-quality semiconductor NCs with improved particle yield and synthetic reproducibility. The additives may include also thiols (RSH), alcohols (ROH), and water, as alternatives to the primary amines and RCOOH. Currently, we are actively exploring these areas. Similarly to the advance of organic syntheses from an empirical art to science in the first half of the 20th century, we believe that mechanism-enabled synthetic control of colloidal semiconductor NCs will be achieved in the first half of the 21st century.^[40]

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