A Nuclear Magnetic Resonance Study of the Binding of Trimethylphosphine Selenide to Cadmium Oleate

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Supporting Information

ABSTRACT: We report an NMR study on the binding of trimethylphosphine selenide (Se=PMe₃) to cadmium oleate (Cd(OA)₂) in CDCl₃ and toluene- d_8 . At room temperature in CDCl₃, Se=PMe₃ binds to Cd(OA)₂ in 1:1 ratio with a binding constant of 20 ± 3 as determined by NMR titration. The Cd-bound and free Se=PMe₃ are in fast exchange on the NMR time scale at room temperature and gives only one ³¹P NMR peak. At ca. 190 K, three ³¹P NMR peaks were observed for a toluene- d_8 solution of 1:1 mixture of Cd(OA)₂ and Se=PMe₃. These three peaks were tentatively assigned to free Se=PMe₃ (9.0 ppm), 1:1 (19.5 ppm), and 2:1 complex between Se=PMe₃ and Cd(OA)₂ (18.8 ppm).



INTRODUCTION

The coordination chemistry of trialkylphosphine chalcogenide plays a key role in the synthesis of group II-VI and IV-VI semiconductor nanostructures.¹⁻¹² Several studies suggested that the coordination of trialkylphosphine chalcogenide precedes the monomer production in the synthesis of CdSe and PbSe nanocrystals.^{2,4–7} Binding of phosphine chalcogenide to metal precursors (e.g., cadmium carboxylate and lead carboxylate) was shown to activate the chalcogenide for its subsequent release of the chalcogen atom, which leads to the production of monomer.^{2,4,5,7,11} In many cases, the rate of monomer production was shown to be the rate-limiting step of the nanocrystal synthesis and plays a key role in the nucleation and shape evolution of the nanocrystals.⁵ In other related studies, the structure of phosphine was shown to have a strong impact on the reactivity of precursors by Ruberu et al. and Owen et al.^{5,13} Finally, the impact of chalcogen exchange on the nanocrystal synthesis has also been reported.^{8,13}

The coordination chemistry between phosphine chalcogenides and cadmium salts has been reported by several studies.^{14–17} Dean and co-workers have shown that $R_3P=E$ and $R_2P(Se)(CH_2)_nP(Se)Ph_2$ (R = phenyl, cyclohexyl; n = 1, 2,3; E = S, Se) bind to CdX₂ (X = SbF₆ and AsF₆) in liquid SO₂.¹⁶ At 209 K, a solution of 4.1: 1 mixture of Ph₃PSe and Cd(SbF₆)₂ gave well-resolved ³¹P NMR peaks for the free and metal-bound phosphine chalcogenide. For the metal bound Ph₃PSe, its ²J_{Cd-P} was observed to be 48 Hz; its ¹J_{P-Se} (585 Hz) was significantly smaller than that of free R₃P==E (655 Hz). At room temperature or at 209 K but in the presence of excess metal ion, fast ligand exchange was observed, as indicated by the absence of coupling between P and Cd atoms. These results as well as additional ¹¹³Cd NMR studies support the formation of [Cd(Ph₃PSe)₄]²⁺ complex at low temperature.^{15,17}

Although these early studies provided important insight into the coordination chemistry of phosphine chalcogenides, the systems they studied are very different from those used in the syntheses of group II–VI nanocrystals. These early studies focus on the coordination of phosphine chalcogenides to CdX_2 (X = SbF₆ and AsF₆) in liquid SO₂ while semiconductor nanocrystal synthesis typically uses cadmium carboxylate and a hydrocarbon solvent.^{1,2,4,7} While SbF₆⁻and AsF₆⁻ bind weakly to metal ions and can be readily displaced by common ligands,¹⁸ carboxylate is a much stronger ligand for Cd²⁺.³ Therefore, it is likely that the presence of carboxylate could affect the coordination of trialkylphosphine chalcogenide to Cd²⁺.

Herein, we report a ³¹P NMR study of the coordination of Se=PMe₃ to Cd(OA)₂ in CDCl₃ and toluene- d_8 . Cd(OA)₂ is one of the most commonly used cadmium precursors for the synthesis of group II–VI nanocrystals.^{1,19} In addition to understanding their coordination chemistry, another major goal of this study is to probe the kinetics and thermodynamics associated with the formation of the coordination complex. This information is critical to modeling the kinetics of nanocrystal nucleation and growth but has been long missing in the literature.^{20,21}

RESULTS AND DISCUSSION

Binding of Se=PMe₃ to Cd(OA)₂ at Room Temperature. ³¹P NMR spectroscopy is a sensitive tool to probe the coordination of Se=PMe₃ to metal ions because metal binding causes a large change in its ³¹P chemical shift.^{16,17} The ³¹P NMR spectrum of Se=PMe₃ in toluene- d_8 gives a sharp singlet at 5.74 ppm (Figure 1A) with characteristic ⁷⁷Se satellites (¹J_{P-Se} = 720 Hz). In the presence of Cd(OA)₂, the ³¹P chemical shift of Se=PMe₃ increased along with a decrease in the ¹J_{P-Se} and both spectroscopic changes increase with

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Figure 1. ³¹P{¹H} spectra (toluene- d_{sv} , $T = 293 \pm 1$ K) of (A) pure Se=PMe₃ ($\delta = 5.74$ ppm, ¹ $J_{P-Se} = 720$ Hz), (B) 4: 1 mixture of Se=PMe₃: Cd(OA)₂ ($\delta = 9.49$ ppm ¹ $J_{P-Se} = 676$ Hz), (C) 1: 1 mixture of Se=PMe₃: Cd(OA)₂ ($\delta = 11.54$ ppm, ¹ $J_{P-Se} = 648$ Hz), (D) 0.2: 1 mixture of Se=PMe₃: Cd(OA)₂ ($\delta = 16.14$ ppm, ¹ $J_{P-Se} = 586$ Hz), and (E) ca. 1: 1 mixture Se=PMe₃ and Cd(OTf)₂ ($\delta = 21.28$ ppm, ¹ $J_{P-Se} = 533$ Hz). Note: spectrum E was taken in CD₂Cl₂ due to solubility reasons; similar chemical shift was observed in acetone- d_6 for a ca. 1: 1 mixture of Se=PMe₃ and Cd(OTf)₂ (see Experimental Section).

increasing Cd: Se ratio (Figure 1B–D); a similar downfield shift was also observed in the ⁷⁷Se spectra (Figure S1, Supporting Information). For a sample having a 5: 1 ratio of Cd(OA)₂ and Se=PMe₃, the ³¹P NMR peak shifted to δ = 16.14 ppm and the ¹J_{P-Se} decreased to 586 Hz. In no cases did we observe satellite peaks that could be assigned to coupling to ¹¹¹Cd or ¹¹³Cd. The downfield shift of ³¹P and ⁷⁷Se NMR peaks and the decrease in ¹J_{P-Se} are consistent with the binding of Se=PMe₃ to Cd(OA)₂. ^{16,17} The fact that we observed only a single ³¹P peak and the absence of Cd satellites both suggest that the exchange between metal-bound and free Se=PMe₃ is faster than the NMR time scale, ^{16,17} in our case, ca. 1 μ s to 100 ms.²²

To evaluate the role of oleate on the binding of Se=PMe₃ to Cd^{2+} , we also prepared a 1:1 mixture of Se=PMe₃ and cadmium triflate $(Cd(OTf)_2)$. The ³¹P NMR spectrum of this mixture is shown in Figure 1E. It can be seen that $Cd(OTf)_2$ produced the largest downfield shift (to 21.28 ppm) and the largest decrease in ¹J_{P-Se} (to 533 Hz) in this series of experiments. This result suggests that the binding of Se=PMe₃ to $Cd(OTf)_2$ is significantly stronger than to $Cd(OA)_2$, as expected due to the fact that triflate is a much weaker Cd ligand than oleate.¹⁸

Binding Stoichiometry and Equilibrium Constant at Room Temperature. To evaluate the binding stoichiometry between Se=PMe₃ and Cd(OA)₂, we used the method of continuous variation, also known as the Job's method.²³ Briefly, we prepared a series of solutions of Se=PMe₃ and Cd(OA)₂ in CDCl₃ in which we kept their total molar concentration constant but varied their mole fractions (χ_{Se} and χ_{Cd}). At room temperature, the ³¹P NMR chemical shift of Se=PMe₃ is a weighted average of that of metal-bound and free species and therefore is a function of the solution composition. Addition of $Cd(OA)_2$ will induce an increase in the ³¹P chemical shift relative to that of pure Se=PMe₃ ($\Delta\delta$). To determine the binding stoichiometry, the product of $\Delta\delta$ and χ_{Se} is plotted against χ_{Se} ; the maximum of the plot would correspond to the stoichiometry of the complex. As shown in Figure 2, a clear maximum was observed at 50% mole fraction of Se=PMe₃, suggesting the formation of a 1:1 complex at room temperature (eq 1).

 $Se=PMe_3 + Cd(OA)_2 = (OA)_2Cd(Se=PMe_3)$ (1)



Figure 2. Job plot suggesting a 1:1 binding stoichiometry between $Se=PMe_3$ and $Cd(OA)_2$.

By using a similar approach, we have also determined the equilibrium constant of eq 1 by NMR titration. In this case, we varied the ratios of $Cd(OA)_2$ and Se=PMe₃ and recorded their



Figure 3. ${}^{31}P{}^{1}H$ NMR spectra (243 MHz, 298 K, CDCl₃) of Se= PMe₃ upon addition of Cd(OA)₂ showing the progressive downfield shift of Se=PMe₃ resonance.

³¹P NMR spectra at 298 K (Figure 3). Because the measured ³¹P chemical shift is a weighted average of the bound and unbound Se=PMe₃, we can calculate the concentration of bound and unbound Se=PMe₃ if the chemical shift of the pure species is known. In this case, the chemical shift of free Se=PMe₃ can be measured directly; a 1:1 mixture of Cd(OTf)₂ and Se=PMe₃, which has a ³¹P chemical shift of 21.3 ppm, is a good approximation of the Cd-bound Se=PMe₃ because triflate is a weak ligand and can be easily displaced by Se=PMe₃. From the calculated concentrations, we then determined the equilibrium constant for eq 1 to be 20.2 ± 3.1. At 298 K, this equilibrium constant corresponds to a free energy change of $-(7.4 \pm 0.4)$ kJ·mol⁻¹.

Low-Temperature NMR Studies. Variable temperature (VT) NMR spectroscopy was carried out in order to gain additional insight into the binding dynamics between Se= PMe_3 and $Cd(OA)_2$. For these experiments, we prepared three toluene- d_8 solutions having different Cd: Se ratios: 4:1 (sample A), 1: 1 (sample B), and 1: 4 (sample C). Their ³¹P{¹H}spectra were recorded in the range of 190 to 296 K and a subset of them are shown in Figure 4.



Figure 4. Selected ³¹P VT-NMR spectra (toluene- d_8) of a mixture of 1 equiv of Cd(OA)₂ and (A) 0.25 equiv, (B) 1 equiv, and (C) 4 equiv of Se= PMe₃.

All three samples gave a single ³¹P resonance at room temperature. Upon cooling, all samples showed a slight downfield shift and significant peak broadening; the Se satellites disappeared at ca. 240 K. At ca. 200 K, the single resonance evolved into two at ca. 19 and 9 ppm. The temperature at which this peak splitting occurs appears to increase with decreasing Se:Cd ratio, being 194 K, 200 K, and 217 K for sample A, B, and C, respectively. Upon further cooling, additional changes were observed for the newly emerged peak at 19 ppm. For sample A, the peak remained broad; however, for sample B and C, the peak at 19 ppm split into two that are separated by 0.7 ppm (e.g., for sample B, the two peaks are located at 19.5 and 18.8 ppm). The relative intensity of the two peaks depends on the Cd: Se ratio, with excess Se increasing the high field (lower ppm) peak. On the other hand, the peak at 9 ppm remained as a sharp singlet at 190 K. For sample A, the signal-to-noise ratio was too low to determine if there were Se satellites. For samples B and C, however, Se satellite peaks were clearly visible at ca. 190 K with a ${}^{1}J_{Se-P}$ = 708 and 692 Hz for sample B and C, respectively.

We assign the peak at 9 ppm to free Se=PMe₃ based on the following evidence: its chemical shift and ${}^{1}J_{Se-P}$ are close to those measured for pure Se=PMe₃ (Figure 1A); the small difference could be attributed to temperature and the effect of ligand exchange. In addition, its intensity also increased with increasing amount of Se=PMe₃ in the solution. The two peaks near 19 ppm were assigned to Cd-bound Se=PMe₃. The fact that their relative intensity also depends on the Cd: Se ratio suggests that the high field peak and low field peak could correspond to coordination complexes having 1:2 and 1:1 Cd/ Se ratios, respectively. However, this assignment will require additional study to confirm. Although our result suggests the formation of both 1:1 and 1:2 complexes at <200 K, it is worth noting that the Job plot (Figure 2) clearly indicated the formation of 1:1 complex at room temperature. This should not come as a surprise given that low temperature will favor molecular association processes.

Kinetics and Thermodynamics of the Formation of Coordination Complex. From the VT-NMR data, we can estimate the rate of exchange between bound and free Se= PMe₃. Specifically, at the coalescence temperature, which is defined as the temperature at which the two exchanged NMR

peaks merge into one, eq 2 can be used to estimate the exchange rate: $^{\rm 24}$

$$k = \frac{1}{\sqrt{2}}\pi\Delta\nu\tag{2}$$

Here *k* is the exchange rate constant, $\Delta \nu$ is the difference in the chemical shift of the bound and free Se=PMe₃ (in Hz). In our experiment, the coalescence temperature is estimated to be around 220 K for the sample with 1:1 Cd:Se ratio (Figure 2B). The $\Delta \nu$ value was measured to be 2.1 × 10³ Hz from the spectrum taken at 193 K. The exchange rate constant was thus calculated to be $4.7 \times 10^3 \text{ s}^{-1}$ at 220 K. Note that eq 2 assumes that the two exchanged species are of equal population, which is not strictly the case in our experiments. Therefore, the calculated exchange rate constant should be considered as an order-of-magnitude estimate. Nevertheless, from this rate constant and the corresponding temperature, the activation free energy of the exchange process can be estimated by the following equation to be 38 kJ·mol⁻¹, where T_C is the coalescence temperature and R is gas constant.²⁵

$$\Delta G^{\ddagger} = R \times T_{\rm C} \times \left[22.96 + \ln \left(\frac{T_{\rm C}}{\Delta \nu} \right) \right]$$

Using the same VT-NMR data, we have also calculated the $\Delta H_{\rm R}$ and $\Delta S_{\rm R}$ of the complex formation by analyzing the temperature dependence of the binding equilibrium for sample B (Cd: Se = 1: 1) in the range of 248–290 K. In the analysis, we only considered the formation of 1:1 complex; this simplification is justified because the Job plot indicates that such complex is formed at room temperature. Noting that the Cd/Se ratio is 1 in this case, the equilibrium constant (*K*) for eq 1 can be expressed by the following equation:

$$K = \frac{f}{C_0 (1 - f)^2}$$
(3)

where C_0 is the overall concentration of Se=PMe₃ and *f* is the molar fraction of Cd-bound Se=PMe₃. After taking the logarithm of both sides of eq 3 and recognizing that

$$\Delta H_{\rm R} - T\Delta S_{\rm R} = -RT \ln K$$

we obtained

$$-\frac{\Delta H_{\rm R}}{RT} + \frac{\Delta S_{\rm R}}{R} + \ln C_0 = \ln \frac{f}{(1-f)^2}$$

Thus plotting $\ln(f/(1 - f)^2)$ against 1/T will give a straight line (Figure 5), and from the slope and intercept we obtained



Figure 5. Thermodynamic analysis of Se=PMe₃ binding to $Cd(OA)_2$. Please see text for an explanation of the terms.

 $\Delta H_{\rm R} = (-14.5 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1} \text{ and } \Delta S_{\rm R} = (-27.5 \pm 1.2) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. These values predict $\Delta G_{\rm R} = (-6.3 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K, in good agreement with the result $(-(7.4 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1})$ obtained from the NMR titration experiment.

CONCLUSION

In conclusion, we have studied the coordination of Se=PMe₃ to Cd(OA)₂ in CDCl₃ and toluene- d_8 . Our result indicates that Se=PMe₃ binds to Cd(OA)₂ in 1:1 ratio at room temperature with a binding constant of 20 ± 3. The ΔH_R and ΔS_R of the complex formation were calculated from the temperature dependence of the equilibrium constant to be (-14.5 ± 0.4) kJ·mol⁻¹ and (-27.5 ± 1.2) J·mol⁻¹·K⁻¹, respectively. The Cdbound and free Se=PMe₃ are in fast exchange at room temperature at the NMR time scale but can be resolved by ³¹P NMR at T < 220 K. At ca. 190 K, ³¹P NMR data suggests the formation of complexes having 1:1 and 2:1 ratio of Se=PMe₃ to Cd(OA)₂.

Our study highlights the usefulness of NMR spectroscopy in understanding the kinetic and thermodynamics of processes relevant to the synthesis of CdSe nanocrystals. Among other things, understanding the binding kinetics and thermodynamics will allow us to quantify the degree of activation of chalcogen precursors by the metal. Such information will be useful to design new precursor pairs that offer targeted reactivity and to match precursors for the synthesis of multicomponent nanocrystals.^{13,26} Given that similar precursor combinations have been used in the synthesis of other nanocrystals (e.g., CdS and CuInSe₂),^{26–28} we expect that the approaches outlined here may be useful in the mechanistic studies of these material systems as well.

EXPERIMENTAL SECTION

Unless otherwise noted all operations were performed under an atmosphere of dry nitrogen using Schlenk and vacuum techniques, or in a nitrogen filled glovebox.

Chemicals. Selenium powder (Aldrich, \geq 99.5%), CdO (99.5%, Aldrich), trioctylphosphine (TOP, 97%, Aldrich), trimethylphosphine (99%, Strem), oleic acid (Aldrich, 90%), trifluoromethanesulfonic acid (98%, Aldrich) were used as received. NMR samples were prepared in CDCl₃ or toluene-*d*₈

that were previously degassed, dried with 4 Å molecular sieves and stored in a glovebox. Acetone- d_6 and CD_2Cl_2 (1 mL ampules, Aldrich) were used as received.

Solution NMR spectra were obtained on Bruker Avance III 500 MHz and Bruker Avance III 600 MHz spectrometers. Chemical shift values are given in ppm. ¹H and ¹³C chemical shifts are referenced to TMS, and for ³¹P spectra 85% H₃PO₄ was used as external reference; ⁷⁷Se shifts were referenced to the lock signal. ³¹P NMR spectra were acquired with inverse gated decoupling. Coupling constants (*J*) are given in Hertz (Hz). The temperature of the NMR spectrometer was calibrated with methanol and ethylene glycol standards.

Cadmium Triflate, Cd(OTf)₂. This compound was synthesized by dissolving CdO in triflic acid following literature procedures.^{29–31} Briefly, Cd(OTf)₂ in the form of a white powder was prepared by carefully mixing cadmium oxide (2.55 g, 20 mmol), triflic acid (4 mL, 45 mmol) and H₂O. The mixture was gently heated at 45 °C for 22 h resulting in a solution which was subsequently concentrated by heating. Anhydrous diethyl ether was added dropwise to obtain a precipitate. The precipitate was washed several times with ether and stored in an oven at 140 °C.

Se=PMe₃. This compound was synthesized as we previously reported.^{2,4} Briefly, trimethylphosphine (2.50 g, 32.86 mmol) was added to a vial and cooled to -30 °C. Se powder (2.725 g, 34.51 mmol) was then added slowly to the vial inside a glovebox. The mixture was stirred for 24 h at room temperature to give a white precipitate. CH₂Cl₂ (5 mL) was added to dissolve the white precipitate and unreacted Se was removed by filtration. Addition of hexane and slow evaporation at reduced pressure gave white microcrystals which were stored in a glovebox. ¹H NMR (500.16 MHz, CDCl₃, r.t.) δ = 1.93 [d(13.3), 9H, CH₃]. ¹³C(¹H) NMR (125.77 MHz, CDCl₃, r.t.) δ = 23.08 [d(49.1), CH₃]. ³¹P{¹H} NMR (202.47 MHz, CDCl₃, r.t.) δ = 8.77 (¹J_{P-Se} = 682 Hz)

Cadmium Oleate, Cd(OA)₂. This compound was prepared by dissolving CdO in oleic acid and subsequent precipitation with acetone.^{2,4} In a typical synthesis, CdO (1.036 g, 8.07 mmol) was added to 10.2 mL of oleic acid (32.2 mmol, 90% tech grade, Aldrich) in a 3-neck flask. The mixture was degassed at 100 °C and then heated at 190 °C until a colorless solution was observed. The solution was cooled to room temperature and acetone was added to precipitate Cd(OA)₂ as a white solid, which was filtered off and dried *in vacuo* overnight to remove acetone.

Job Plot Experiment. The method of continuous variation, also known as Job plot was used to study the stoichiometry of the coordination of Se=PMe₃ to $Cd(OA)_2$.^{23,32} A stock solution of Se=PMe₃ (0.10 M) in CDCl₃ was prepared by dissolving 186 mg of Se=PMe₃ in 12 mL of CDCl₃. A stock solution of cadmium oleate in the same concentration was prepared by dissolving 270 mg of $Cd(OA)_2$ in 4 mL of $CDCl_3$. Both stock solutions were prepared inside a glovebox. A total of 11 NMR samples were prepared by mixing the stock solutions of Se=PMe₃ and Cd(OA)₂ in the following quantities: 0.6 and 0 mL; 0.5 and 0.1 mL; 0.45 and 0.15 mL; 0.4 and 0.2 mL; 0.35 and 0.25 mL, 0.3 and 0.3 mL; 0.25 and 0.35 mL; 0.2 and 0.4 mL; 0.15 and 0.45 mL; 0.1 and 0.5 mL; and 0.05 and 0.55 mL. The NMR spectrum was collected immediately after the sample being prepared to avoid reaction between Se=PMe₃ and $Cd(OA)_{2}$.

Titration Experiments of Se=PMe₃ and Cd(OA)₂ in CDCl₃. The binding of Se=PMe₃ to Cd(OA)₂ was investigated

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by NMR titrations. A stock solution of Se=PMe₃ in CDCl₃ was prepared by dissolving 14 mg of Se=PMe₃ in 6 mL CDCl₃ ([Se=PMe₃] = 0.015 M). A 10 times more concentrated stock solution of cadmium oleate in CDCl₃ was prepared by dissolving 304 mg of Cd(OA)₂ in 3 mL of CDCl₃ ([Cd(OA)₂] = 0.15 M). Both stock solutions were prepared inside a glovebox. A J-Young NMR tube was charged with 0.6 mL of the Se=PMe₃ stock solution and to this NMR tube aliquots of the Cd(OA)₂ stock solution were added. An NMR spectrum was taken after the addition of Cd(OA)₂, and the process was repeated by adding additional Cd(OA)₂ to the solution. The solution was monitored for possible reaction between Se= PMe₃ and Cd(OA)₂, and if such reaction was detected, which was indicated by the formation of O=PMe₃, a fresh sample was prepared.

In order to estimate the chemical shift of Se=PMe₃ coordinated to Cd²⁺, equimolar amounts of Se=PMe₃ and $Cd(OTf)_2$ were combined in CD_2Cl_2 . Although the mixture was not very soluble, a ³¹P resonance of Se=PMe₃ was observed at δ = 21.3 ppm (¹J_{P-Se} = 533 Hz), suggesting that in the system the equilibrium is shifted to the coordination of Se=PMe₃ to cadmium. This is expected from the excellent leaving-group properties of the OTf ligand and the use of a noncoordinating solvent. Similar observations were made when $Cd(OTf)_2$ and Se=PMe₃ were combined in acetone- d_6 , where the system was more soluble. After mixing equimolar amounts of Se=PMe₃ and Cd(OTf)₂, a resonance was observed at δ = 22.94 ppm (${}^{1}J_{P-Se} = 518$ Hz) along with a small amount of precipitate, which disappeared upon the addition of a second equivalent of Se=PMe₃, yielding a colorless solution and one resonance in the ³¹P NMR spectrum at $\delta = 23.10$ ppm (¹ $J_{P-Se} =$ 517 Hz).

VT-NMR Experiments. The following three samples were used in the VT experiments: 88 mg of $Cd(OA)_2$ and 5 mg of Se=PMe₃ dissolved in 1 mL of toluene- d_8 , 22 mg of $Cd(OA)_2$ and 5 mg of Se=PMe₃ dissolved in 1 mL of toluene- d_8 , and 22 mg of $Cd(OA)_2$ and 20 mg of Se=PMe₃ dissolved in 1 mL of toluene- d_8 .

ASSOCIATED CONTENT

S Supporting Information

⁷⁷Se NMR spectra of free trioctylphosphine selenide (TOPSe) and TOPSe with 1 equiv of $Cd(OA)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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