Phase-Programmed Nanofabrication: Effect of Organophosphite Precursor Reactivity on the Evolution of Nickel and Nickel Phosphide Nanocrystals

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Abstract
A better understanding of the chemistry of molecular precursors is useful in achieving more predictable and reproducible nanocrystal preparations. Recently, an efficient approach was introduced that consists of fine-tuning the chemical reactivity of the synthetic molecular precursors used, while keeping all other reaction conditions constant. Using nickel phosphides as a research platform, we have studied how the chemical structure and reactivity of a family of commercially available organophosphite precursors (P(OR)₃, R = alkyl or aryl) alter the preparation of metallic and metal phosphide nanocrystals. Organophosphites are a versatile addition to the pnictide synthetic toolbox, nicely complementing other available precursors such as elemental phosphorus or trioctylphosphine (TOP). Experimental and computational data show that different organophosphite precursors selectively yield Ni, Ni₁₂P₅, and Ni₂P and that these phases evolve over time through separate mechanistic pathways. Based on our observations, we propose that nickel phosphide formation requires organophosphite coordination to a nickel precursor, followed by intramolecular rearrangement. We also propose that metallic nickel formation involves outer sphere reduction by uncoordinated organophosphite. These two independent pathways are supported by the fact that preformed Ni nanocrystals do not react with some of the most reactive phosphide-forming organophosphites, failing to evolve into nickel phosphide nanocrystals. Overall, the rate at which organophosphites react with nickel(II) chloride or acetate to form nickel phosphides increases in the order P(OMe)₃ < P(OEt)₃ < P(OnBu)₃ < P(OCH₂tBu)₃ < P(OiPr)₃ < P(OPh)₃. Some organophosphites, such as P(OMe)₃ or P(OiPr)₃, transiently form zerovalent, metallic nickel, while this is the only persistent product observed with the bulky organophosphite P(O-2,4-tBu₂C₆H₄)₃. We expect that these results will alleviate the need for time-consuming testing and random optimization of several different reaction conditions, thus enabling a faster development of these and similar pnictide nanomaterials for practical applications.

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ABSTRACT: A better understanding of the chemistry of molecular precursors is useful in achieving more predictable and reproducible nanocrystal preparations. Recently, an efficient approach was introduced that consists of fine-tuning the chemical reactivity of the synthetic molecular precursors used, while keeping all other reaction conditions constant. Using nickel phosphides as a research platform, we have studied how the chemical structure and reactivity of a family of commercially available organophosphite precursors (P(OR), R = alkyl or aryl) alter the preparation of metallic and metal phosphide nanocrystals. Organophosphites are a versatile addition to the pnictide synthetic toolbox, nicely complementing other available precursors such as elemental phosphorus or trietylphosphine (TOP). Experimental and computational data show that different organophosphite precursors selectively yield Ni, Ni₈P₅, and Ni₃P and that these phases evolve over time through separate mechanistic pathways. Based on our observations, we propose that nickel phosphide formation requires organophosphite coordination to a nickel precursor, followed by intramolecular rearrangement. We also propose that metallic nickel formation involves outer sphere reduction by uncoordinated organophosphite. These two independent pathways are supported by the fact that preformed Ni nanocrystals do not react with some of the most reactive phosphide-forming organophosphites, failing to evolve into nickel phosphide nanocrystals. Overall, the rate at which organophosphites react with nickel(II) chloride or acetate to form nickel phosphides increases in the order P(OEt)₃ < P(OnBu)₃ < P(OCH₂tBu)₃ < P(OiPr)₃ < P(OPh)₃. Some organophosphites, such as P(O-Me)₃ or P(OiPr)₃, transiently form zerovalent, metallic nickel, while this is the only persistent product observed with the bulky organophosphite P(O-2,4-tBu₂C₆H₄)₃. We expect that these results will alleviate the need for time-consuming testing and random optimization of several different reaction conditions, thus enabling a faster development of these and similar pnictide nanomaterials for practical applications.

INTRODUCTION

A better understanding of the chemistry of molecular precursors is useful in achieving more predictable and reproducible nanocrystal preparations, and thus in producing more desirable nanocrystalline properties. Recently, we and others demonstrated an efficient approach to manipulate the outcome of nanocrystal preparations that consists of replacing the synthetic molecular precursors used while keeping all other conditions constant. ¹⁻⁷ This simple but powerful approach requires investigating the effect of chemical group substitution on the relative rates of decomposition of the molecular precursors, which directly impact their relative rates of nanocrystal nucleation and growth. The direct results of these types of studies are working scales of chemical reactivities for families of closely related molecular precursors (for example, phosphine chalcogenides,² disubstituted dichalcogenides,¹ thioureas³), each one of which obviates the need for much more time-consuming testing and optimization of several different reaction conditions or of unrelated precursors at random. Here, we expand and generalize this chemical reactivity approach to the controllable synthesis of metal phosphides as an entry into the more general field of pnictide (M−V, M = metal) nanomaterials.

The most common phosphorus precursors used to synthesize nanocrystalline metal phosphides are triphenylphosphine (PPh₃), trietylphosphine (TOP) and its oxide (TOPO), red and white phosphorus (P₄), phosphates (R₃PO₄, R = alkyl or metal cation), and single source precursors such as [Ni(Se₂PR₂)₂]₈⁻²⁴. Other less explored precursors include hypophosphites (MH₂PO₂, M = metal or ammonium cation)²⁵⁻³⁶ and the organophosphite P(OEt)₃.³⁵ Also known as phosphite esters or simply phosphites (P(OR), R = alkyl or aryl), organophosphites are particularly appealing as synthetic precursors because they are highly reactive and potentially tunable with group (R) substitution, while also being readily commercially available and fairly inexpensive. This contrasts
with other available alternatives which, while synthetically also useful, are unsupported and not tunable (Pₐ) or require relatively high reaction temperatures in excess of 320–340 °C (TOP). 18−19 In this work, we explore how the structure and reactivity of a significantly expanded family of easily accessible organophosphites affects the synthesis of nickel phosphate nanocrystals.

Nanostructured nickel phosphides garnered a lot of recent interest because of their unique optoelectronic properties and applications. 36 Nanocrystalline nickel phosphides are catalytically active in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions, 77 and in the hydrogen evolution reaction (HER), where they benefit from low overpotentials and some of the largest cathodic densities among nonprecious metal catalysts. 84−85 Nanocrystalline nickel phosphides are also of interest as electrodes for lithium ion batteries. 49 Several methods exist for the synthesis of nickel phosphate nanocrystals (mostly Ni₃P and Ni₄P₃), including chemical vapor deposition, 50 solution-phase (colloidal) synthesis, 16,51 solvothermal synthesis, 77 electrosynthesis, 78 hydrothermal synthesis, 79 solid-state synthesis, 80 microwave synthesis, 81 and temperature-programmed phosphate reduction. 82 These methods yield nickel phosphate nanocrystals with various morphologies. 83 Their exact phase and composition obtained is affected by the Ni to P ratio, 84,85 counteranions, 86, voltage (in case of electrosynthesis), 86 the identity and concentration of surfactants, 87 the reaction solvent(s), 89 time, and temperature. 90 Some methods call for fine-tuning and optimization of multiple factors in order to achieve satisfactory levels of phase and composition control. 91−95 Organophosphites offer a distinctive system where the control of phase composition can be achieved under a single set of directly comparable (identical) reaction conditions and linked to the chemical structure, bonding, and reactivity of closely related molecular precursors. Here, we demonstrate that organophosphate precursor reactivity controllably affects the composition and phase evolution of nickel (Ni) and nickel phosphate (Ni₃P and Ni₄P₃) nanocrystals.

### EXPERIMENTAL SECTION

**Materials.** Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 99.9%), trimethyl phosphate (P(OMe)₃, 97%), triethyl phosphate (P(OEt)₃, 98%), tri-n-butyl phosphate (P(OnBu)₃, 94%), trimethylphosphite (P(OMe)₃, 97%), tri-isopropyl phosphite (P(OiPr)₃, 94%), triphenylphosphite (P(OPh)₃, 97%), and trioctylamine (C₈H₁₇-N₃, 80–90%) were used as received and handled under an inert (dry-N₂ or Ar) atmosphere inside a glovebox or with a Schlenk line.

**Synthesis. Phosphiite Addition Solution.** Inside a glovebox filled with dry N₂, the phosphite precursor [0.40 mmol: 0.05 mL of P(OMe)₃, 0.07 mL of P(OEt)₃, 0.11 mL P(OnBu)₃, 117 mg of P(OCH₂Bu)₃, 0.10 mL of P(OiPr)₃, 0.11 mL of P(OPh)₃, or 259 mg of P(O-2,4-tBu₂C₆H₄)₃] was thoroughly dissolved in ODE (1.00 g, 1.27 mL).

**Nanocrystal Synthesis: General Procedure.** Inside a three-neck flask, NiCl₂·6H₂O (26 mg, 0.10 mmol) or Ni(OAc)₂ (18 mg, 0.10 mmol), oleylamine (270 mg, 1.00 mmol, 0.33 mL), and ODE (5.00 g, 6.34 mL) were degassed under a vacuum at 80 °C for 1 h, refilled with Ar, and heated to 275 °C. After 5 min, the organophosphate addition solution (above) was quickly injected and kept at this temperature while stirring. Aliquots were taken out after 1, 10, and 30 min reactions. The mixture was allowed to cool to room temperature, and nanocrystalline products were isolated by twice washing with toluene and centrifugation at 4900 rpm for 5 min. Thermal analysis (TGA/DSC) experiments showed that typical yields of nanocrystalline phases (without organics) ranged between 44 and 58% (see Supporting Information).

**Control Experiments.** Ni nanocrystals were synthesized with P(O-2,4-Bu₄C₆H₄)₃ using the general synthetic procedure above. The nanocrystals were isolated and purified thrice by washing with toluene and centrifugation at 4900 rpm for 5 min, before drying under a dynamic vacuum. The general synthetic procedure was then repeated replacing Ni nanocrystals for the nickel precursor.

**Characterization. Optical Characterization.** Absorption spectra were measured with a photodiode array Agilent 8453 UV−Vis spectrophotometer.

**Structural Characterization.** Powder X-ray Diffraction (XRD) was measured using Cu Ka radiation on a Scintag XDS-2000 diffractometer. Transmission Electron Microscopy (TEM) was conducted on carbon-coated copper grids using a FEI Tecnai G2 F20 field emission scanning transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line to line resolution <0.10 nm). Particle dimensions were measured manually and/or with ImageJ for >50–100 particles. Averages are reported ± one standard deviation.

**Computations. Organophosphate Precursors.** We modeled homolytic and heterolytic P−O and C−O bond cleavage in organophosphites by optimizing the geometries of whole molecule and separate molecular fragments under similar methods and basis sets. The general process is illustrated as AB → A + B, where the cleavage energy (assumed to correspond to the bond strength) was calculated as ΔEₓₐ + ΔEₐₜ − ΔEₓₐ. The multiplicities of the different molecular fragments were monitored for spin contamination through their S² values. Homolysis involves triplet multiplicity, while heterolysis involves singlet multiplicity. The calculated total energy (ΔE), electronic energy with zero-point energy correction (ΔEₑₑ), change in enthalpy (ΔH), and change in Gibbs free energy (ΔG) were then connected to 298.15 K and 1 atm (gas phase). We also calculated the Gibbs free energy (ΔG) with the nonpolar solvent of cyclohexane and the polar solvent water by carrying out a single point energy correction with the aforementioned optimized geometries. The solvated Gibbs free energies (ΔG) follow the same patterns of those reported in the gas phase (see Supporting Information). All calculations were carried out using the Gaussian 03 package running on the CenterOS based Linux cluster at the Department of Chemistry, Prairie View A&M University. The Tao−Perdew−Staroverov−Scuseria (TPSS) method implemented in Gaussian 03 was used for all geometry optimizations, solvation modeling, and frequency calculations. As a new generation of density functional, TPSS matches or even exceeds in accuracy almost all prior functionals, including the most popular functional-B3LYP with hybrid exchange functionals. For example, TPSS recognizes relatively weak interactions (such as agostic interactions), while B3LYP significantly underestimates them. Because hydrogen atoms in the modeling system do not play significant roles in our study, the 6-311G(d) (basis set) was used for all elements in the modeling system. Not applying polarization functions on the H's far from the phosphorus center atom does not significantly degrade computational precision and accuracy, while significantly accelerating the calculations. All structures were fully optimized and frequency analyses performed to ensure minima were achieved, with zero imaginary vibrational frequencies derived from vibrational frequency analysis. Thermodynamic functions, including enthalpies, entropies, and free energies, were calculated at 298.15 K and 1 atm. The Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) was applied to compute aqueous solvation Gibbs free energies for all compounds (see Supporting Information available).

### RESULTS AND DISCUSSION

**General Observations.** The basic reaction we studied consists of injecting an organophosphate precursor into a solution containing a nickel(II) source (chloride or acetate)
and oleylamine in 1-octadecene (ODE) at 275 °C (Scheme 1). We specifically chose these parameters so that we could directly compare the molecular precursors under conditions where they all reacted (see Experimental Section for details). Aliquots were taken from the mixture after 1, 10, and 30 min reactions and the contents characterized by optical and, after precipitation, XRD patterns and representative TEM images (after 30 min reaction) of nanocrystals obtained by reacting nickel(II) chloride in oleylamine and octadecene at 275 °C. The results from our precursor screening, including powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) data for selected precursors (additional data are available from the Supporting Information). All results, summarized in Table 1, are fully reproducible, as the same products are observed every time that a given set of experimental conditions was repeated (for example, see Figure S1).

Our experimental observations show that different organophosphate precursors consistently lead to the formation of metallic nickel or nickel phosphides or both and that these phases evolve over time (Figure 2). It is clear that the chemical structure and reactivity of the specific molecular organophosphate precursor used exert a significant influence on the ease (rate) of formation as well as on the selectivity toward different nickel-containing nanocrystals. The results of these reactions are independent of the exact nickel(II) precursor used; for example, NiCl₂ and Ni(OAc)₂ produce the same product(s) after similar reaction times (Figure S2). This could be important for applications, as halides can poison the catalytic activity of nickel phosphides.

**Evolution of Nickel Phosphides.** Under the conditions studied (Scheme 1 above), the organophosphate precursors P(OMe)₃, P(OEt)₃, P(OnBu)₃, P(OCH₂tBu)₃, P(OiPr)₃, and P(OPh)₃ lead to nanocrystalline Ni₁₂P₅ or Ni₃P or both. In the cases where it is observed, formation of the nickel-rich tetragonal Ni₁₂P₅ phase precedes the formation of the hexagonal Ni₃P phase, the latter being the final product after 30 min at 275 °C in most of these cases. The subsequent phase transformation from Ni₁₂P₅ to Ni₃P is significantly slower in the case of the P(OCH₂tBu)₃ precursor (complete after 90 min), possibly because it is relatively bulky, with a Tolman cone angle θ of 180° (Table 2). Generally, primary aliphatic organophosphates such as P(OMe)₃ and P(OCH₂tBu)₃ are the slowest to react with the nickel(II) precursor (Figures 1a,b and 2), whereas the aromatic phosphate P(OPh)₃ is the fastest to react with the nickel(II) precursor (Figures 1c and 2). At early reaction times (1–10 min), some primary alkyl phosphites, P(OMe)₃, P(OEt)₃, and P(OnBu)₃, form a minor, transient crystalline impurity ("A") that is characterized by a broad X-ray diffraction at ca. 2θ = 47°. Because it roughly matches one of the main diffractions of either Ni₁₂P₅ or Ni₃P, we speculate this peak may correspond to poorly diffracting nickel phosphide nuclei, perhaps with significant preferred orientation (Figure 1a). However, we are at present unable to unambiguously characterize this phase.

Extensive TEM analysis of the 30 min reaction products showed a strong correlation between organophosphate precursor reactivity and the size and morphology of nickel phosphide nanocrystals. The most reactive phosphide-forming precursors such as P(OPh)₃ lead to dense (nearly solid or void-free) and relatively small (ca. 17–37 nm) Ni₃P nanocrystals (Figure 1c and Table 1). In contrast, the least reactive phosphide-forming precursors such as P(OMe)₃ yield hollow and relatively larger (ca. 49–55 nm) Ni₃P nanocrystals (Figure 1a and Table 1). The presence and formation of such nanocrystal voids following a phase transformation is widely attributed to the Kirkendall effect. During the conversion from Ni₁₂P₅ to Ni₃P, nickel ions diffuse outward and phosphide ions diffuse inward, migrating toward and away from the reactive nanocrystal surface, respectively. Highly reactive precursors such as P(OPh)₃ are very efficient at generating phosphide ions, which can then quickly diffuse inward toward the nanocrystal interior, thus counterbalancing

![Figure 1](image-url)
the outward diffusion of nickel ions and resulting in dense (solid or void-free) Ni$_2$P nanocrystals. In contrast, less reactive precursors such as P(OMe)$_3$ are not as efficient sources of phosphide ions; outward diffusion of nickel ions dominates in this case, resulting in the formation of hollow Ni$_2$P nanocrystals.

**Evolution of Metallic Nickel.** Some of the organophosphite precursors we screened produce face-centered cubic (fcc) nickel (Ni) nanocrystals. P(OiPr)$_3$ and P(OMe)$_3$ form this phase transiently, with Ni quickly and completely disappearing after 1 and 10 min reaction, respectively (Table 1). Other organophosphites such as P(OEt)$_3$, P(OnBu)$_3$, or P(OCH$_2$tBu)$_3$ could also form Ni transiently, although this was not observed here, likely because we mostly sampled reactions at specific times (1, 10, and 30 min and longer). In the past, the transient formation and disappearance of Ni were used to propose that this was an intermediate phase en route to the formation of nickel phosphides such as Ni$_{12}$P$_5$ and Ni$_2$P (Figure 1d and Table 1).

**Mechanistic Considerations.** Formation of Nickel Phosphides. We have considered up to five potential mechanisms for the initial decomposition of molecular organophosphite
precursors leading to nanocrystalline nickel phosphides \((\text{Ni}_x\text{P}_y)\) in the presence of organophosphites. \(^{118,119}\) Mechanism a requires phosphite coordination to the nickel precursor, followed by an intramolecular rearrangement where the \(\text{P}−\text{O}\) and \(\text{Ni}−\text{X}\) bonds break in a concerted fashion (\(\text{X} = \text{chloride, acetate, or oleylamine derived amide; Scheme 2a}\)). Mechanism b involves homolytic \(\text{P}−\text{O}\) bond cleavage of the free phosphite, followed by reaction with the nickel precursor (Scheme 2b). Mechanisms c and d involve heterolytic \(\text{P}−\text{O}\) bond cleavage in the free phosphite, followed by reaction with the nickel precursor (Scheme 2c and d, respectively). \(^{120}\) Mechanism e involves \(\beta\)-hydride elimination (\(\beta\text{HE})\) to produce \(\text{PH}_3\), which can act as a phosphorus source to generate nickel phosphides (Scheme 2e).

As evidenced by the outcome of reactions using \(\text{P(OOPh)}_3\) (Table 1 and Figure 1c), formation of nickel phosphides under our experimental conditions does not require (is not contingent upon) the presence of \(\beta\)-hydrogens; therefore, we can rule out mechanism e. To address the likelihood that the other mechanisms (a–d) could be involved in our reactions, we performed simple Density Functional Theory (DFT) calculations of the bonds surrounding the reactive \(\text{P(O)}−\) unit. Selected results from these calculations are shown in Table 2 (additional data are available in the Supporting Information). The calculated \(\text{P}−\text{O}\) bond dissociation (homolysis) energies or “BDEs” are only ca. 36–63 kcal/mol (Table 2). For comparison, we estimate that each methylene \(\text{C}−\text{H}\) bond in \(\text{P(OCH}_2\text{tBu)}_3\) has a BDE of 90.72 kcal/mol. In contrast, \(\text{P}−\text{O}\) bond heterolysis energies are much higher, with polarization favoring the movement of electrons toward the more electronegative O atom. Heterolytic \(\text{P}−\text{O}\) bond cleavage is significantly more favorable when phosphonium-alkoxide ion pairs \((\text{P}^+\text{O}−)\) are produced (125–193 kcal/mol) than when phosphide-oxenium \(^{121}\) ion pairs \((\text{P}−\text{O}^+)\) are produced (174–290 kcal/mol, Table 2). Thus, while they may be important in other systems (different phosphide or metal precursors), \(^{120}\) pathways involving \(\text{P}−\text{O}\) bond heterolysis are clearly too energy intensive and demanding to be viable in our reactions, which strongly argues against mechanism c and, in particular, against mechanism d.
An important point when considering the homolytic mechanism b, as well as the heterolytic mechanisms c and d, is that these do not require precoordination of the phosphite precursor to the nickel center. If b or c or d were operative, one would predict (and should fully expect) that a bulky phosphite would react just as easily as a nonbulky one, at a rate that is simply commensurate with its relative P−O bond energy. Critically, this is not observed experimentally. The most sterically encumbered (bulkiest) phosphite that we studied, $P(\text{O}-2,4\text{-tBu}_2\text{C}_6\text{H}_4)\text{3}$ ($\theta = 192^\circ$, Table 2), fails to produce any detectable crystalline nickel phosphide, despite the fact that it has the smallest homolytic and heterolytic P−O energies and, thus, the weakest P−O bond (Table 1). This observation alone allows us to rule out mechanisms b, c, and d and strongly suggests that phosphite coordination is a necessary prerequisite for nickel phosphide formation. Therefore, among the five phosphide-forming mechanisms considered in Scheme 2, we conclude that only mechanism a is consistent with all of our data.

**Mechanistic Considerations. Formation of Metallic Nickel.**

We next considered the possibility (see above) that a separate pathway may be responsible for the formation of metallic Ni nanocrystals. We concretely evaluated two possible mechanisms (Scheme 3). Mechanism i involves coordination of the phosphite to nickel(II), forming a five-coordinate intermediate that reductively eliminates to produce a Ni(0) phosphite complex,122−125 which then decomposes into zerovalent (metallic) fcc Ni particles (Scheme 3i). This inner sphere reaction and its required intermediates are well-known, having ample precedent in the organometallic literature.126,127 Alternatively, mechanism ii involves direct reduction of nickel(II) to Ni(0) by the free, uncoordinated phosphite (Scheme 3ii). This outer sphere, electron transfer mechanism is supported by the observation that organophosphites can indeed act as reducing agents.128

While the small phosphite $P(\text{OMe})\text{3}$ ($\theta = 107^\circ$, Table 2) and intermediate size phosphite $P(\text{OiPr})\text{3}$ ($\theta = 130^\circ$) transiently produce Ni, it is by far the most sterically encumbered phosphite, $P(2,4\text{-tBu}_2\text{C}_6\text{H}_4)\text{3}$ ($\theta = 192^\circ$), that is the most active in producing crystalline fcc Ni nanoparticles (Scheme 3i). This inner sphere reaction and its required intermediates are well-known, having ample precedent in the organometallic literature.126,127

**Scheme 4**

Building a Chemical Reactivity Scale for Organophosphate Precursors. Having studied the general reactivity and decomposition mechanisms of multiple organophosphate precursors toward nickel(II) chloride (or acetate), we are able to build a chemical reactivity scale for the formation of nickel phosphide nanophases under the conditions we studied. Based on our experimental observations, the ease or rate at which organophosphites react with nickel(II) to form nickel phosphides, only occurring when the binding of a sterically hindered organophosphite to Ni(II) becomes highly unfavorable.

**Decoupling Nickel and Nickel Phosphide Formation.**

As noted above, we have considered two separate mechanistic hypotheses for the evolution of nickel and nickel phosphide nanophases. Our results call into question whether nanocrystalline Ni can really serve as an intermediate during the formation of nickel phosphides, as was reported previously in the literature (albeit, this was for different sets of precursors and reaction conditions compared to those used here).135,67,108 To address this question, we first synthesized Ni nanocrystals as described above using $P(2,4\text{-tBu}_2\text{C}_6\text{H}_4)\text{3}$ (Figure 1d). We then subjected these preformed Ni nanocrystals to some of our most active phosphide-forming organophosphites. As shown in Figure 3, the reaction of isolated, purified Ni nanocrystals with $P(\text{OPh})\text{3}$ and oleylamine in 1-octadecene (ODE) at 275 °C (Scheme 4) does not result in any observable crystalline nickel phosphides. In fact, under these conditions, the Ni nanocrystals simply decompose, forming intractable, amorphous product(s) that is (are) silent by powder XRD. It is important to purify the Ni nanocrystals before running this control reaction, as otherwise some unreacted nickel(II) chloride remains, leading to the very slow formation of some nanocrystalline Ni$_2$P and Ni$_3$P (Figure 3). In summary, we conclude that, under the reaction conditions used here, preformed Ni nanocrystals are not a competent intermediate toward the formation of either Ni$_2$P or Ni$_3$P.
Conclusions

A critical aspect of the synthesis and application of nanostructured materials is to precisely control their phase, composition, and, consequently, properties. Using a powerful chemical reactivity approach that is well established for metal chalcogenides, we have studied how the structure and reactivity of a family of commercially available organophosphite precursors (P(OR)₃, R = alkyl or aryl) affect the evolution of nickel and nickel phosphide nanocrystals. Our observations show that different organophosphite precursors selectively yield nickel phosphide (Ni₁₂P₅, Ni₂P) or nickel (Ni) nanophases and that these evolve over time through well-defined and separate mechanistic pathways.

In agreement with prior literature reports, we find that the formation of a nickel-rich, kinetic tetragonal Ni₁₂P₅ phase precedes the formation of the final, thermodynamically preferred hexagonal Ni₂P phase. In the specific case of phosphide-forming organophosphites, very reactive precursors such as P(OPh)₃ form small, nearly void-free (dense) nanocrystals, while less reactive precursors such as P(OMe)₃ form large, hollow nanocrystals due to the Kirkendall effect. Some organophosphites such as P(OiPr)₃ and P(OCH₂tBu)₃ yield fcc-Ni transiently, while at least one organophosphite, P(O-2,4-tBu₂C₆H₄)₃, more persistently yields Ni nanocrystals that never evolve into a nickel phosphide phase.

In the specific case of nickel phosphide forming reactions, it is important to note that the observations and discussions in this paper actually deal with two reactions and processes that occur simultaneously, namely the initial decomposition and reaction of organophosphite with Ni₁₂P₅ or Ni₂P under the reaction conditions we used, which is important to note that the observations and discussions in this paper actually deal with two reactions and processes that occur simultaneously, namely the initial decomposition and reaction of organophosphite with Ni₁₂P₅ or Ni₂P under the reaction conditions we used, respectively.

We have carefully considered five and two separate mechanisms for the initial reaction and decomposition of organophosphites and nickel(II) precursors to form nickel phosphide and nickel(0) nanocrystals, respectively. A mechanism requiring organophosphite coordination to the nickel(II) precursor, followed by an intramolecular rearrangement where the P−O and Ni−X bonds break in a concerted fashion (X = chloride, acetate, or oleylamine-derived amide) is consistent with our observations about the formation of nickel phosphides. Another mechanism, involving direct, outer sphere reduction of nickel(II) to Ni(0) by free, uncoordinated organophosphite is consistent with our data on the formation of Ni. Control experiments show that preformed Ni nanocrystals are not competent intermediates in the formation of either Ni₁₂P₅ or Ni₂P under the reaction conditions we used, because they fail to react with some of the most reactive phosphide-forming organophosphites.

Organophosphites are a nice addition to the synthetic toolbox available to pnictide chemists. Other useful phosphide precursors include elemental phosphorus, trioctylphosphine (TOP), and its oxide (TOPO). Unlike elemental phosphorus, which is unsupported, organophosphites are amenable to chemical reactivity fine-tuning via R group substitution with a wide range of aliphatic or aromatic substituents. Unlike TOP or TOPO, which require relatively high reaction temperatures in excess of >320−340 °C, organophosphites can be made more efficient.
or less reactive simply by altering their chemical structure, bonding, and reactivity.

As a direct result of our study, we have built a chemical reactivity scale for organophosphite precursors. The ease or rate at which organophosphites react with nickel(II) dichloride to form nickel organophosphites increases in the order P(OMe)3 < P(OEt)3 < P(OnBu)3 < P(OCH2tBu)3 < P(OiPr)3 < P(OiPr)3. At least two organophosphites, P(OMe)3 and P(OiPr)3, also form nickel nanocrystals transiently, while P(0-2,4-Bu2C6H4)3 only forms nickel nanocrystals, and these persist over time. Other available methods call for fine-tuning and optimizing several reaction conditions in order to achieve satisfactory levels of synthetic control over the phase and composition of metal phosphides. In contrast, we envision our results and approach will enable a faster, more systematic development of these and similar pnictide nanomaterials for practical applications.

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