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Examination of indium triphospholyls as precursors for nanoparticle syntheses

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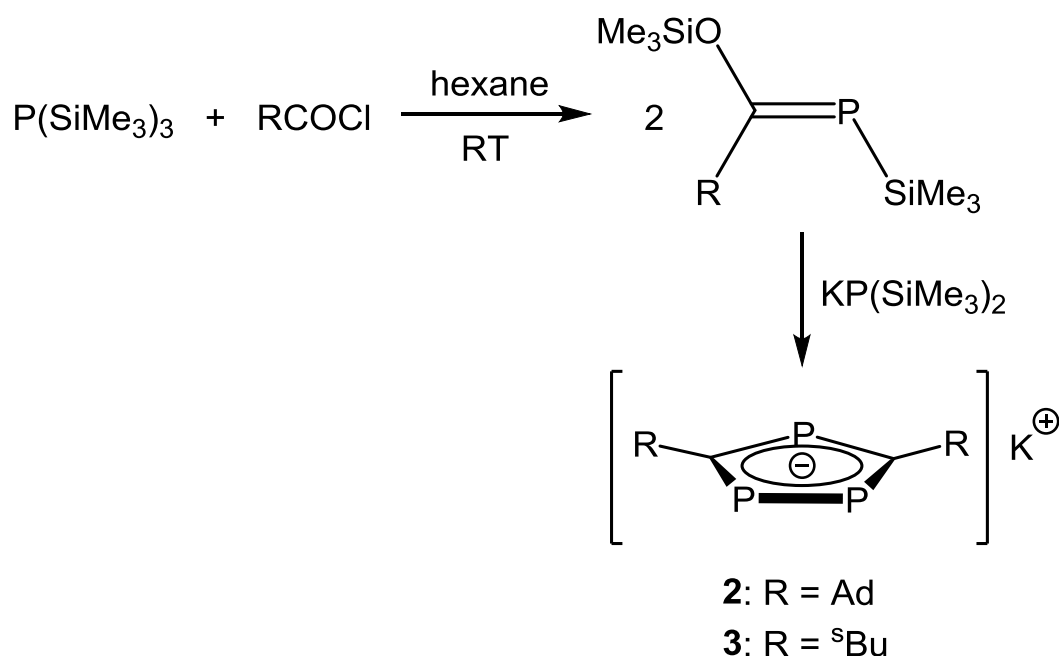
Abstract: The synthesis and characterization of the new compounds $K(P3C2R2)$ ($R = Ad$ (2), sBu (3)) and $In(P3C2R2)$ ($R = Ad$ (4), Mes (5)) are described. Further, the synthesis of indium nanoparticles via a single-source precursor approach using $In(1,2,4-P3C2tBu2)$ (1) as precursor is reported. These nanoparticles were characterized by TEM, HRTEM, EDX, XRD, NMR and optical spectroscopies.

Introduction

Indium-based (nano)materials are of high technological significance in modern electronics. Representative devices incorporating indium are transparent conducting electrodes (indium tin oxide),[] photodetectors (indium and indium gallium arsenide)[] or phosphors (indium phosphide) as used e.g. in the last generation of TV screens.[] The race toward miniaturization and the implementation of devices at nanoscale has spotlighted the question of an efficient synthesis protocol for nanoparticles (NPs).[] The rational design of synthetic procedures to control the size, shape and composition of NPs is one of the ultimate goals. In this context, the choice of precursor is of central importance and it is associated with many issues (nucleation/growth balance, size, shape, ...), including the material purity with the potential generation of polluting side products.[,] In the case of metal indium NPs, typical precursors are indium compounds at the oxidation state of +III and required reducing agents as hydrides, alkali metals, or alkalides.[] However, the potential contamination by salt by-products makes separation and purification processes more difficult.[7] Using the organometallic complex $[In(\eta^5-C5H5)]$, we developed a protocol based on soft conditions (room temperature, no strong reducing agent), relying on the low oxidation state (+I) of indium leading to high quality $In(0)$ NPs.[] In the same vein, but in the context of the synthesis of InP NPs, the appropriate choice of the indium precursor avoids detrimental side reactions while allowing the preparation of high quality nano-objects. For instance, the high energy indium precursor $tris(N,N'$ -diisopropylacetamidinato)indium(III) is reactive at temperatures low enough (150 °C) to prevent the oxidation of the resulting InP particles.[,] However, this synthesis, as many others, relies on a multisource precursor approach which includes the use of highly reactive $P(SiMe_3)_3$ as phosphorus

source. $P(\text{SiMe}_3)_3$ depletes very quickly during the synthesis of NPs leaving no molecular phosphorus precursor available for monomer production during the growth stage.[] Accordingly, growth proceeds via Ostwald ripening, leading to increased polydispersity and to the difficulty of synthesizing large InP nanocrystals (NCs). The use of single-source precursors (SSPs) can potentially provide several key advantages such as delivering the different elements simultaneously.[] Moreover, the existence of preformed bonds can lead to a material with fewer defects and/or better stoichiometry control. However, this route has been very little exploited for InP NP synthesis. To the best of our knowledge, only O'Brien et al. took advantage of the decomposition of the In(III) SSP $\text{In}(\text{PtBu}_2)_3$. [] However, the obtained 7 nm NPs are poorly crystallized and have a crystalline core of ca. 2.5 nm surrounded by an amorphous shell. Interestingly, Nixon et al. mentioned that the triphospholyl indium(I) complex $\text{In}(1,2,4\text{-P}_3\text{C}_2\text{tBu}_2)$ (1) is a suitable precursor for bulk crystalline indium phosphide, without, however, giving any detailed results.[] The research on the rational design of precursors for InP NPs synthesis is thus still in its early stages and acquiring additional knowledge (structure-reactivity relationship) is thus highly desirable. Herein, we report the synthesis and characterization of the novel triphospholyl compounds $(\text{In})(1,2,4\text{-P}_3\text{C}_2\text{R}_2)$ ($\text{R} = \text{Ad}, \text{Mes}$). Additionally, we present our efforts to prepare indium-based NPs using $\text{In}(1,2,4\text{-P}_3\text{C}_2\text{tBu}_2)$ 1 as SSP.

Over the last two decades, the use of triphospholyl as ligand has become more widespread because of the strong similarities between the polyphospholyl anions and their much more widely studied cyclopentadienyl analogues.[] So far, the 1,2,4-triphospholyl anions $(1,2,4\text{-P}_3\text{C}_2\text{R}_2)^-$ with $\text{R} = \text{tert-butyl (tBu)}$, [] isopropyl (iPr) , [] mesityl (Mes) , [] trimethylsilyl [] and phenyl (Ph) [] were reported. We present the synthesis of the new 1,2,4-triphospholyl salts with sec-butyl (sBu) and adamantyl (Ad) substituents.



Scheme 1: General synthesis of potassium salts of triphospholyls.

The potassium salts $\text{K}(1,2,4\text{-P}_3\text{C}_2\text{R}_2)$ ($\text{R} = \text{Ad}$ (2), sBu (3)) are synthesized by the reaction of potassium bis-(trimethylsilyl)phosphanide, $\text{K}(\text{P}(\text{SiMe}_3)_2)$ with the corresponding phosphalkene $\text{Me}_3\text{SiO}(\text{R})\text{C}=\text{P}(\text{SiMe}_3)$ (Scheme 1).[16] The ^{31}P NMR spectrum of the isolated product showed, a

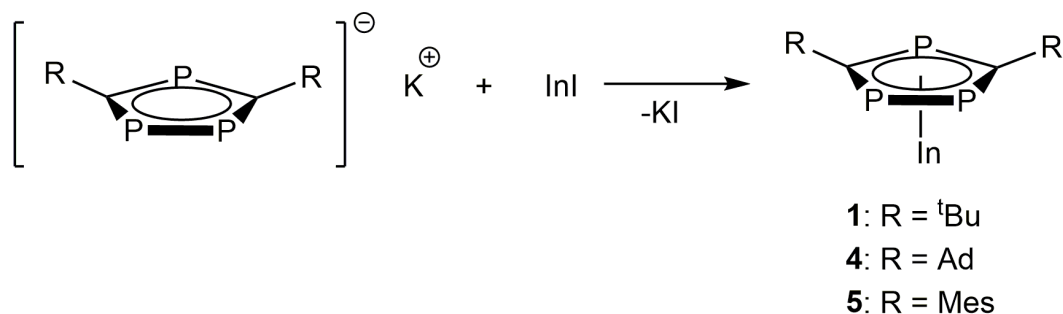
doublet at $\delta = 244.6$ ppm ($2J_{PP} = 48$ Hz) and surprisingly two triplets at $\delta = 248.1$ ppm ($2J_{PP} = 48$ Hz) and $\delta = 248.0$ ppm ($2J_{PP} = 48$ Hz) instead of one expected triplet. An explanation for this are the chirality centers in the sBu groups, causing three possible isomers of compound 3, two enantiomers and a meso form (see SI). The observed ^{31}P NMR spectrum can therefore be explained by two overlapping AB2 patterns originating from these isomers (simulated ^{31}P NMR spectra can be found in the SI). In comparison, all previously reported derivatives (1,2,4-P3C2R2)- reveal a doublet and a triplet with similar coupling constants, except for (1,2,4-P3C2iPr2)- which shows a higher order AB2 pattern.[17] The yields and NMR chemical shifts of these derivatives are given in Table 1. The values of the new compounds are in the expected range.

Table 1: ^{31}P NMR data and yields of various 1,2,4-triphospholyl salts.

M(1,2,4-P3C2R2);	$^{31}\text{P}\{^1\text{H}\}$ [ppm]		Yield [%]
R = tBu, M = K	256	248	47
R = SiMe ₃ , M = Li	327	316	a)
R = Mes, M = K	266.4	261.7	44
R = iPr, M = K	247.6	244.7	48
R = Ph, M = Na	274.7	253.9	76
R = Ad, M = K (2)	248,7	241	57
R = sBu, M = K (3)	248.1, 248.0	244.6	29

a) no yields are given.

Cloke, Nixon and coworkers described the metathesis reaction of InI and the potassium triphospholyl salt containing the tBu substituent,[16] which we also follow in our approach. In the following, we discuss our results of the reactions of K(1,2,4-P3C2R2) (R = Mes, iPr, sBu (3), Ad (2)) with InI (Scheme 2). Unfortunately, for the reaction of InI with K(1,2,4-P3C2R2) (R = iPr or sBu (3)) at various temperatures, no evaluable results were obtained due to non-reacting or decomposition, when higher reaction temperatures were used. For the reaction of the adamantyl derivative 2 with InI, a reaction temperature of 110 °C is needed to conduct the metathesis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the residue, obtained after filtration of the reaction mixture and removal of the solvent, shows a low-field shift to 249.5 ppm for the doublet and to 254.7 ppm for the triplet in comparison to the starting material. In the Direct Insertion Probe–Mass Spectrometry (DIP-MS) (EI, 70 eV) of the reaction mixture (after filtration), the molecular ion peak of In(1,2,4-P3C2Ad2) (4) is found at 502.0605 m/z, indicating that the desired product 4 was formed, which, however, could unfortunately not be proven further. During and after the reaction, a white precipitate occurred. After filtration, a further precipitate is formed over time even at higher or lower temperatures. This white solid is insoluble in the usual polar or nonpolar solvents and the results of the elemental analysis do not match compound 4. Therefore, we could not clearly confirm if this solid is a decomposition or an agglomeration product. A possible similar agglomerate for In(C5H5) was already described.[]



Scheme 2: Salt metathesis of 1,2,4-triphospholyls.

Moreover, we targeted to synthesize In(1,2,4-P3C2Mes2) (5) by the reaction of K(1,2,4-P3C2Mes2) with InI. During the modified synthesis of K(1,2,4-P3C2Mes2),^[18] we realized that also K(1,3-P2C3Mes3) is formed as a byproduct in a ratio of about 15%. In the ³¹P{¹H} NMR spectra of the reaction mixture, a sharp singlet at 175.1 ppm was observed, which could be assigned to K(1,3-P2C3Mes3). In comparison, the signal for K(1,3-P2C3iPr3) appears at 159.6 ppm.^[17] Since it was not possible to separate the two compounds, the mixture of the diphospholyl and the triphospholyl salts was further reacted with InI. The suspension of both educts was refluxed in toluene for 5.5 hours and, after workup, a yellow powder remained. Yellow plate-like crystals of In(1,2,4-P3C2Mes2) (5) suitable for X-ray structure analysis and unidentifiable yellow crystals[] could be isolated from a saturated dichloromethane solution at -30°C in a crystalline yield of 40%. Despite multiple attempts to separate the crystal mixture, analytically pure 5 could unfortunately not be obtained.

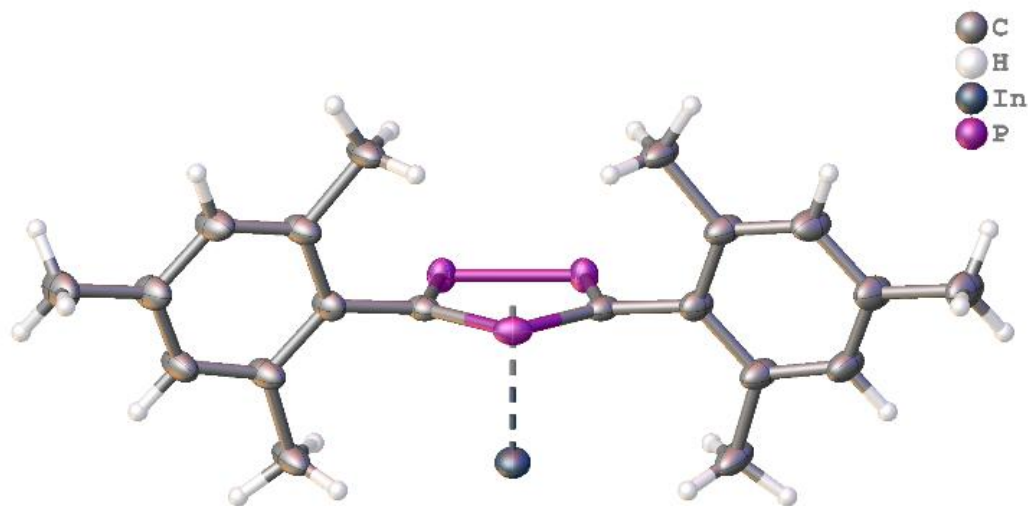


Figure 1: Molecular structure of 5. Ellipsoids are drawn at 50 % probability level. Selected bond lengths [Å]: P2-P2' 2.1208 (13), P2-C1 1.755(2), P1-C1 1.748(3), In1-P1 3.0340(8), In1-P2 3.0268(6).

The ³¹P{¹H} NMR spectrum of the crystal mixture in thf-d₈ shows the expected AB₂ pattern for 5 associated with an η⁵-ligated, 1,2,4-substituted P₃C₂ ring (triplet at 276.8 ppm and a doublet at 274.8 ppm, 2J_{P-P} = 43.2 Hz). The ¹H NMR spectrum shows three singlets at 2.22 ppm, 2.25 ppm and 6.87 ppm for the protons of the Mes group. Additionally, the ³¹P{¹H} NMR spectrum displays a singlet at 184.7 ppm, indicating the formation of In(1,3-P2C3Mes3), as expected owing to the impurities of K(1,3-P2C3Mes3) in the starting material of K(1,2,4-P3C2Mes2). This compound could

not be separated from 5, due to a similar solubility. The ratio of this side product ranges from 10 to 18%. The elemental analysis of the crystal mixture proves the presence of the diphosphylyl in the same ratio as detected by ^{31}P NMR.

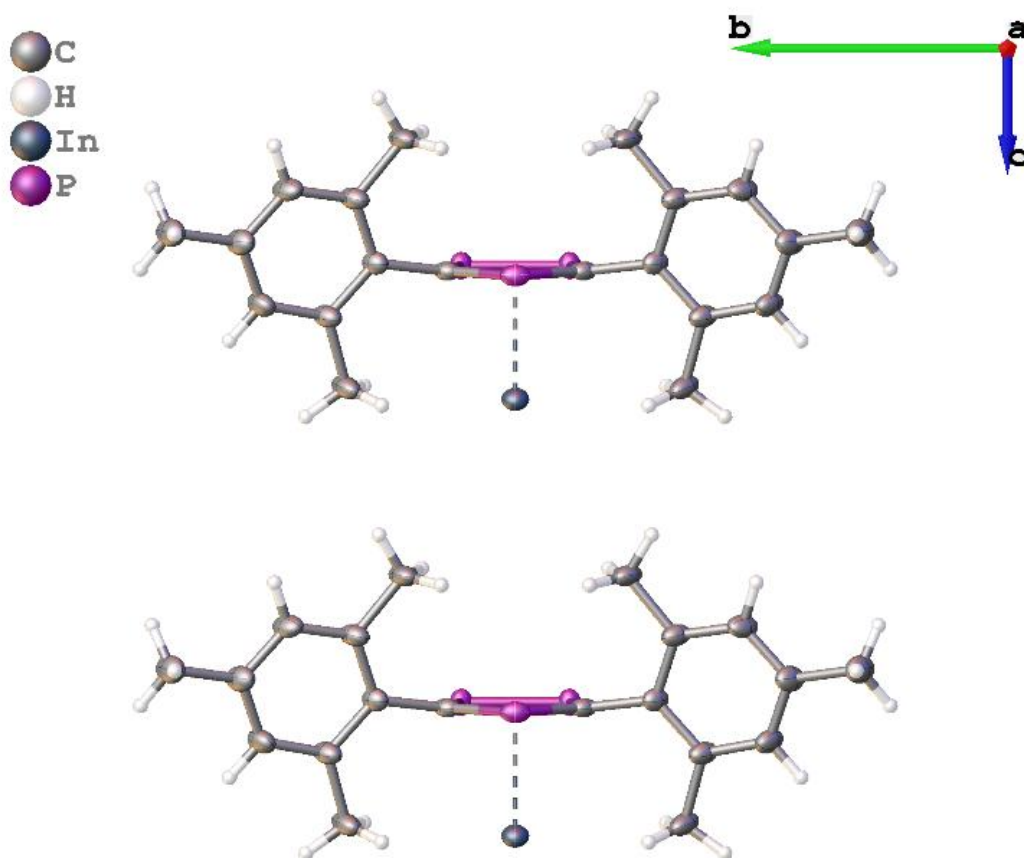


Figure 2: Crystal packing of 5, view along the a-axis. Ellipsoids are drawn at 50% probability level.

The molecular structure of 5 is depicted in Figure 1. The indium atom is η^5 -coordinated by the planar P3C2 ring of the 1,2,4-triphospholyl ligand. In contrast to the related triphospholyl compound 1, where the half-sandwich units are linked into chains by weak interactions between the indium centers and adjacent P3C2 rings,[16] 5 represents a monomeric compound. In 5, the distance of the indium atom to the next ring is with 6.239 Å much longer than in 1 (3.526 Å).[16] This difference is attributed to the larger steric bulk of the Mes units, which are tilted by 78.9° to the ring and could block significantly the intermolecular interactions (Figure 2). The bond lengths within the P3C2 ring are with P1-C1 1.748 (3) Å, C1-P2 1.755 (2) Å, P2-P2' 2.1208 (13) Å similar to those of [Cp*Fe(1,2,4-P3C2Mes2)] with P1-C1 1.761 (3) Å, C1-P2 1.777 (3) Å, P2-P2' 2.118 (1) Å.[18] The indium centroid distance in 5 amounts to 2.563 Å, which is comparable to the value of 2.598 Å found for 1.[16]

The Direct Exposure Probe–Mass Spectrometry (DEP-MS) (EI, 70 eV) clearly shows the molecular ion peak of 5 at 470.01572 m/z. Additionally, fragment peaks for In⁺ (114.90653 m/z), P3C2Mes2⁺ (355.10411 m/z), InP2CMes⁺ (307.94952 m/z), P2CMes⁺ (193.03999 m/z) and P≡CMes⁺ (162.06477 m/z) are found, indicating that 5 decomposes under the conditions of the mass spectrometry into the phosphalkyne P≡CMes and InP2CMes.

Further, we intended to investigate the ability of 1 as a single-source precursor for the generation of NPs. In order to gain insight into the suitability of this precursor for nanomaterial production,

thermal gravimetric analyses (TGA) were performed (Figure S11). Several steps of decomposition occur, starting at a temperature of 225 °C. The corresponding weight loss of 46% indicates a segregation of a tBuCP unit and an isobutene moiety, followed by an HCP elimination at higher temperatures. At 325 °C, the decomposition results formally in InP, suggesting that 1 could be relevant for the InP synthesis. We then focused on the investigation of the decomposition behaviour of the single-source precursor 1 in solution. Compound 1 (1eq) was dissolved in mesitylene and transferred into a Fisher-Porter autoclave with hexadecylamine (HDA) (1eq) and oleic acid (OIA) (1eq). This solution was stirred at 150 °C for one hour. The yellow solution turns black and a fine, black powder evolves. The synthesized particles feature micrometric dimensions, as can be observed in Transmission Electron Microscopy (TEM) pictures (Figure S12), some of them displaying an elongated shape. The powder diffraction pattern of the sample indicates the presence of indium phosphide and elemental indium. However, the content of indium phosphide in this mixture is low, compared to that of indium (Figure 3). However, it is known that molecular compounds of indium in the +1 oxidation state are prone to disproportionation and that they can be easily reduced,[] which might explain the high In ratio in the formed particles. In accordance with that, we had already shown before the cyclopentadienyl analogue [In(η^5 -C₅H₅)] to lead to the synthesis of spherical indium NPs or indium nanowhiskers in soft conditions.[8] The preparation of microparticles with 1 suggests that the synthesis is governed by a growth regime here precluding the stabilization of NPs.

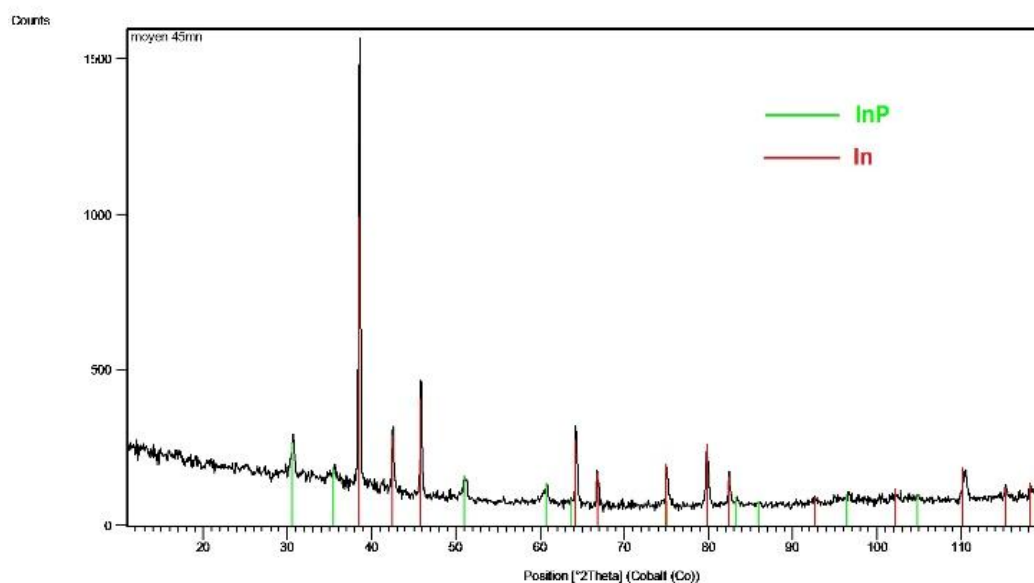


Figure 3: Powder diffraction pattern of the sample prepared from 1 in the presence of one equivalent of HDA and OIA at 150°C.

The same reaction was performed at higher temperature (230 °C). The formation of a black powder which precipitates is also observed (Figure S13). The powder diffraction analysis shows a mixture of bulk In and InP, with the latter being in higher amount than in the sample prepared at 150°C (Figures 3 and S13). The ³¹P Magic Angle Spinning (MAS) NMR spectrum confirms the presence of bulk InP with an intense and broad upfield signal at -137.7 ppm (Figure S14). Additionally, in the ¹³C MAS NMR spectrum, characteristic resonances of oleate and hexadecylamine are found at δ 129.1 and

41.0 (Figure S15), respectively, suggesting their interaction with the surface of the powder. The TEM analysis of the solid dissolved in the supernatant solution shows the synthesis of roughly spherical NPs with an average size of 6.5 nm (Figures 4 and S16-S17). EDX analysis of the sample shows that In and P are present in a 94:6 ratio (Figure S18), which is unreliable with a homogeneous InP composition in the sample. The UV-vis spectrum of the NPs solution displays a weak absorption at ~700 nm which is consistent with the presence of a small amount of ~6-7 nm InP NPs (Figure S19).[10] However, in the ^{31}P MAS NMR (Figure S20), no metal phosphide signal typical of nanoparticulate InP could be observed in the high-field range.[] Considered together and given the small quantity of phosphorus, this suggests that a mixture of indium phosphide NPs in very minor amounts and metal indium NPs in large proportion was prepared. Consequently, we were not able to image indium phosphide NPs by HRTEM. Instead, the observed amorphous NPs without a fringe pattern (Figure 4) can be assigned to In metal NPs as already seen in previous studies.[8] Crystalline particles were also visible and were identified as In_2O_3 (Figures 4 and S17). As no oxide was evidenced by XRD, their presence on the TEM grid presumably results from the exposure of the sample to air prior to its introduction into the microscope.[8] The ^1H and ^{13}C MAS NMR spectra of the NPs isolated from the solutions suggest that they are stabilized by oleate (Figures S21 and S22). The cross-polarization (CP) ^1H - ^{31}P MAS NMR spectrum also allows for the identification of a phosphorus-based ligand at the surface of the NPs. The CP sequence, for that matter, allows us to infer spatial proximities between species at the interface, as it relies on dipolar coupling between different nuclear spins.[24] While the ^{31}P MAS NMR displays a mixture of phosphorus-containing species, the CP ^1H - ^{31}P MAS one shows only one resonance at 33.6 ppm (Figure S23). This supports the involvement of one sole organophosphorus compound in the coordination sphere of the nanoparticles (presumably a derivative of phosphoric acid or a phosphonate resulting from the reaction of phospholyl moieties with HDA and/or OIA). In contrast to the report by Nixon et al.,[14] our results clearly show that the formation of metal indium is favored here, leading to the formation of indium NPs rather than InP.

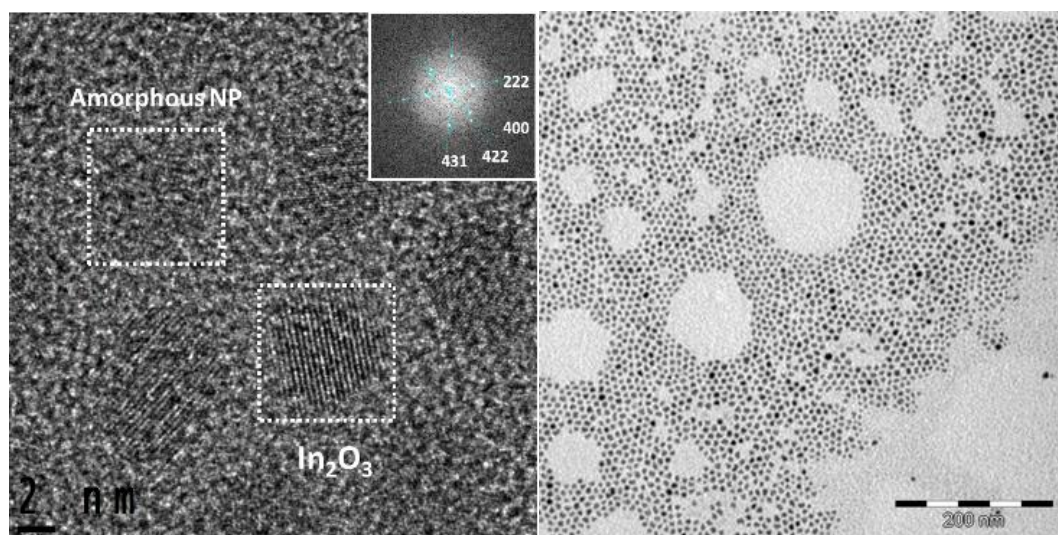


Figure 4: Conventional TEM (left) and HRTEM (right) images of the NPs prepared from 1 in the presence of one equivalent of HDA and OIA at 230°C. The inset in the right panel shows the selected area diffraction pattern taken on the framed In_2O_3 nanocrystal.

In summary, we presented the synthesis and characterization of new triphospholyl salts $K(1,2,4\text{-P}3\text{C}2\text{R}2)$ ($R = \text{Ad}, \text{sBu}$). By salt metathesis of these compounds and of $K(1,2,4\text{-P}3\text{C}2\text{Mes}2)$ with InI , the compounds $\text{In}(1,2,4\text{-P}3\text{C}2\text{R}2)$ ($R = \text{Ad}, \text{Mes}$) could be obtained. While the decomposition of **1** at 150°C led to micronic indium particles, we succeeded in obtaining a nanosize control by increasing the reaction temperature to 230°C , thus favoring the nucleation step instead of the growth step. In both cases, the formation of indium particles is largely favoured instead of indium phosphide. This result is reminiscent of that of $[\text{In}(\eta^5\text{-C}_5\text{H}_5)]$ and stresses the analogy existing between the polyphospholyl complexes and their cyclopentadienyl analogues in the context of NPs synthesis.

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