White phosphorus as single source of "P" in the synthesis of nickel phosphide†

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White phosphorus, P_4, was reacted in a stoichiometric manner with Ni(0) complexes or particles to produce nanoparticles of nickel phosphide.

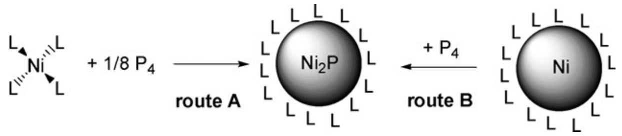
White phosphorus, P_4, is the most widely employed starting precursor for all the chemistry pertaining to phosphorus derivatives. It serves as a phosphorus carrier for the elaboration of most phosphines *via* the intermediacy of either PCl_3 or PH_3. However, apart from these well-known basic transformations, P_4 has only rarely been used in more elaborate processes. Its reactivity towards transition metals has been studied with the ultimate goal of devising metal catalyzed transformations to phosphorus derivatives, without having to handle highly toxic PH_3 gas for instance. The development of such processes has been hampered by the often uncontrollable reactivity of P_4 with metal precursors. Indeed, coordination of one to four phosphorus centers and insertions into one to several of the P–P bonds of P_4 are highly competitive processes. In some instances however, using carefully designed metal complexes, with strongly bound ligands, one of these processes may be favored.[1]

From another standpoint, some synthetic approaches toward nanocrystalline transition metal phosphides have been developed very recently. This interest is driven by the wide range of applications found for these species (catalytic, electronic, or magnetic applications).[2] Three different routes stand out as the most reliable. Firstly, the solvothermal reaction starting from a phosphate precursor may lead to different derivatives depending on the decomposition temperature.[3] This procedure typically requires very high temperatures. Secondly, the highly sensitive phosphine derivative $P(SiMe_3)_3$ may be hydrolyzed *in situ* to form highly toxic PH_3 which in turns reacts with a metal precursor.[4] This method was used in particular for the synthesis of the highly desirable semi-conductor InP, albeit only in mg quantities.[5] Lastly, several groups have used both the coordinating behavior of TOP (tri-*n*-octylphosphine) and its ability to act as a "P atom" donor, through thermal decomposition at around 330 °C, to form several metal phosphides such as Ni_2P or FeP.[6] However this latter method requires the use of large amounts, well over stoichiometry, of the TOP solvant/ligand in an uncontrolled process.

Taking into account the known chemistry of P_4, we postulated that the reaction between a metal center in a formal "zero" oxidation state, bearing labile ligands, and P_4 would result in successive metal-insertions in P–P bonds to lead to the desired "metal phosphide" in a stoichiometric manner. As a proof of the validity of our concept, we present here the first results in the synthesis of a model species, Ni_2P. Two different strategies were envisioned for the source of Ni(0): the first relies on monometallic organometallic precursors (route A, Scheme 1) and the second uses Ni(0) nanoparticles (route B, Scheme 1).

Before trying to stabilize nanoparticles of Ni_2P made by either one of these routes, it had to be verified that the reaction could indeed be carried out in the bulk (route A, without stabilizing ligands L). Thus, in a first attempt, $[Ni(COD)_2]$ complex dissolved in toluene, was reacted at room temperature with a stoichiometric amount of P_4 (also in toluene).‡ It resulted in the instantaneous precipitation of a black solid, insoluble in all common solvents (Scheme 2). NMR characterization of the supernatant solution showed the absence of both the starting compounds, (P_4 in the ^{31}P NMR spectrum and $[Ni(COD)_2]$ in the ^{1}H NMR spectrum) indicating a quantitative reaction. A thermal treatment (300 °C, 1 h) of this solid suspended in TOPO (tri-*n*-octylphosphine oxide), resulted in the formation of highly insoluble nanocrystalline Ni_2P as shown both by X-ray powder diffraction (see Fig. 1) and TEM, although the TEM pictures showed a binomial type population (from a drop of the soluble part). Most importantly, this first experiment established the feasibility of our approach.

We then turned our attention to obtaining soluble nanoparticles of Ni_2P, which requires, as a prerequisite, the selection of a ligand that allows the kinetic stabilisation of the growing species and prevents their aggregation. TOP, which already proved to be a competent ligand for the stabilization of nanoparticles of Ni_2P synthesized at high temperature, was



Scheme 1 Reactions of P_4 towards Ni(0) precursors.

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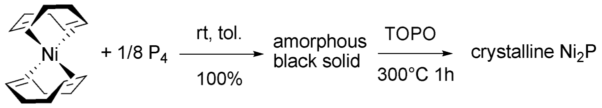


Scheme 2 Bulk synthesis of Ni_2P from $[Ni(COD)_2]$.

used in a mechanistic study of route A. The reaction of the $[Ni(COD)_2]$ complex with 10 equivalents of TOP was carried out at room temperature (Scheme 3), and followed by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum of the crude mixture showed the co-existence of three phosphorus containing species: a sharp signal for the homoleptic $[Ni(TOP)_4]$ complex (δ_P = −4.2 ppm), a broad signal for the free TOP (δ_P = −33.3 ppm), and a sharp singlet (δ_P = 10.7 ppm) corresponding to a previously unknown complex. The two complexes are formed in an approximate 1 : 2 ratio, respectively (as attested by integration of the respective signals). Suspecting that this latter complex could be the mixed $[Ni(COD)(TOP)_2]$ complex, we synthesized it quantitatively from the reaction of $[Ni(COD)_2]$ with only two equivalents of TOP, and characterized it by ^{31}P and ^1H NMR spectroscopies.

Because of the long alkyl chains it was reluctant to crystallize, but final proof of the structure was obtained with the analogous $[Ni(COD)(PBu_3)_2]$ complex (δ_P = 10.3 ppm) using a similar procedure (see ESI†). The reaction of the mixture with a stoichiometric amount of P_4 at room temperature was then followed by $^{31}P\{^1H\}$ NMR spectroscopy. Again, the reaction is very fast, being complete within a few minutes. The spectrum showed the lack of signal for P_4 (at −524 ppm) and the complete disappearance of the starting Ni complexes with the concomitant release of TOP (signal at −33.3 ppm), as well as a weak, very broad signal at around 0 ppm. However, precipitation of Ni_2P particles proved to be impossible, suggesting the formation of very small species or soluble cluster type complexes. A thermal process was then performed in order to grow larger particles.

A second route (route B, Scheme 1) was also devised, starting from preformed nickel nanoparticles. It has been reported in the literature that thermal decomposition of a Ni(II) precursor, $[Ni(acac)_2]$, at 215 °C in the presence of large amounts of either TOP, TOPO or OA (oleylamine) resulted in the formation of Ni(0) nanoparticles.[7] We reasoned that starting from a more reactive, already in the "right" oxidation state, Ni(0) precursor, the reaction would occur at much lower temperature.[8] Indeed, thermal decomposition of $[Ni(COD)_2]$ at 100 °C in the presence of 10 equivalents of TOPO or OA led to the formation of the desired monodisperse Ni(0) NPs (Scheme 4, Fig. 2b and c). The same procedure using TOP did not lead to the formation of Ni NPs but to the above described mixture of complexes, despite a long heating period at 100 °C. However, in order to test the second route, Ni(0) particles were prepared from $[Ni(acac)_2]$ and TOP at 215 °C (Scheme 4, Fig. 2a). It may be noted here that the analogous reaction performed at 215 °C with the Ni(II) precursor $[Ni(acac)_2]$, and 10 TOPO only led to agglomerated particles, whereas with 10 TOP they remained isolated.

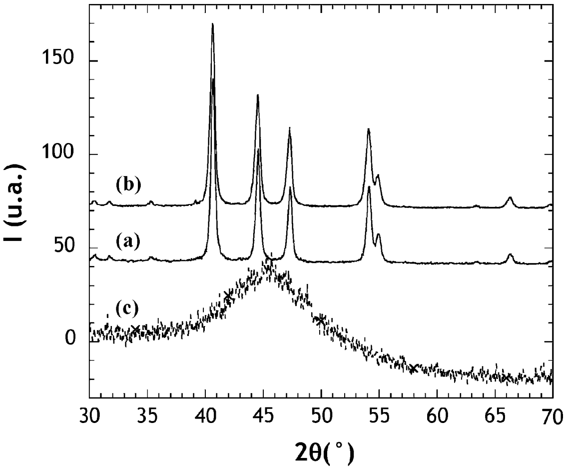
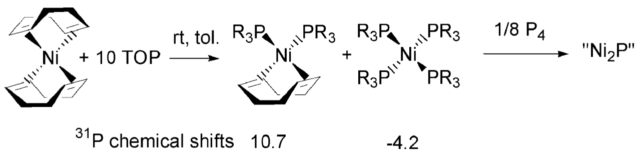


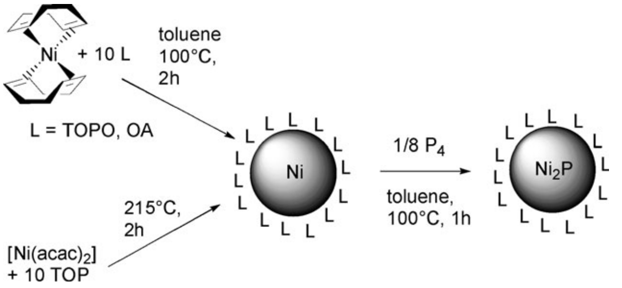
Fig. 1 X-Ray powder diffraction: (a) Ni_2P after thermal treatment at 300 °C for 1 h in TOPO. (b) Ni(0) nanoparticles + P_4, after isolation and thermal treatment at 100 °C for 4 h (solid). (c) Ni_2P before thermal treatment.



Scheme 3 Mechanistic study of the reaction of a Ni(0) complex with P4 in the presence of excess phosphine: **route A**.

The isolated (or not) Ni(0) nanoparticles, stabilized by either TOP or OA were reacted with stoichiometric amounts of P_4 (*vs.* starting Ni complex) at 100 °C for a few hours, leading to the formation of the desired nanoparticles of Ni_2P. X-Ray powder diffraction of the as-synthesized black solid precipitated from the solution showed only featureless peaks, consistent with the formation of nanoparticles of a few nanometres in size (Fig. 2d). A thermal treatment of the crude product at 100 °C for 4 h, allowed the crystallization of the material which the XRD spectrum showed to be Ni_2P, exempt of residual Ni(0) (Fig. 1b). For example, starting from isolated OA stabilized Ni nanoparticles of 6.5 nm (see ESI†), Ni_2P nanoparticles of 4.8 nm were obtained. Most interestingly, our results show that the reaction performed at much lower temperature than usual leads to the desired nanoparticles of Ni_2P.

In conclusion, we present here a new and simple synthesis, as well as stoichiometric, of Ni_2P at low temperature based on the high reactivity of P_4 toward reactive Ni(0) complexes. An extension of this reaction to the reactivity of Ni(0)



Scheme 4 Synthesis of Ni_2P nanoparticles from Ni nanoparticles: **route B**.

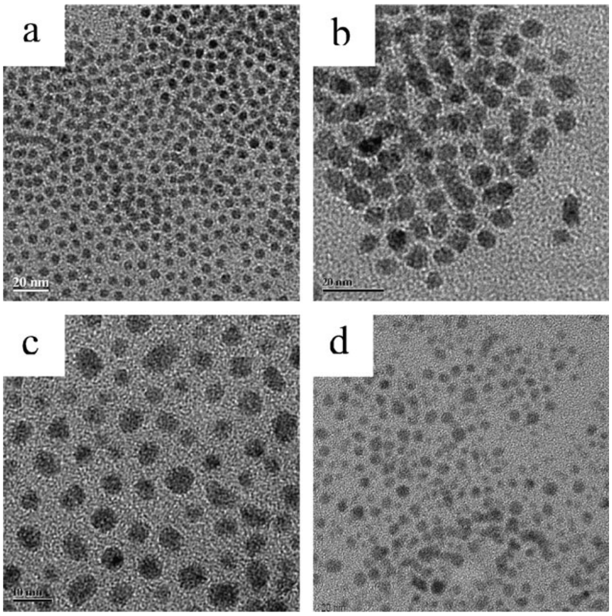


Fig. 2 TEM images for Ni(0) particles stabilized with TOP (a), TOPO (b) or oleylamine (c), and Ni_2P particles stabilized with oleylamine (d).

nanoparticles stabilized by labile ligands (alkylphosphines, phosphine oxides or amines) led to the formation of nanoparticles of Ni_2P. The application of this strategy for the syntheses of several other "metal phosphide" derivatives is currently underway in our laboratories, and results will be reported in due course.

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Notes and references

‡ **Safety Note:** white phosphorus is stable in water but highly flammable and very toxic if swallowed or inhaled. It is incompatible with strong oxidizing agents and strong bases. It is light and heat sensitive. It should be handled accordingly.

Synthesis of [Ni(COD)(PBu$_3$)$_2$]. Over a solution of [Ni(COD)$_2$] (0.45 mmol) in THF (5 mL) tributylphosphine (0.9 mmol) was added. The color of the solution changed from yellow to orange and the solution was stirred 1 h at room temperature. The solvent was removed under vacuum yielding a yellow solid which was crystallized from hexanes. ^1H NMR (C_6D_6, 300 MHz, 25 °C, ppm): 1.04 (6H), 1.49 (8H), 1.68 (4H), 2.40 (4H), 2.60 (4H), 4.55 (4H). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 MHz, 25 °C, ppm): 10.27. X-Ray structure data, $M_t = 285.75$, crystal dimensions $0.30 \times 0.16 \times 0.08$ mm, monoclinic, $C2/c$, $a = 21.777(1)$, $b = 8.967(1)$, $c = 17.218(1)$ Å, $\alpha = 90.00$, $\beta = 90.769(1)$, $\gamma = 90.00°$, $V = 3361.9(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.129$ g cm^{-3}, $\mu = 0.690$ cm^{-1}, $F(000) = 1264$, $\theta_{max} = 30.03°$, hkl ranges: −25 30, −11 12, −20 24, 15 342 data collected, 4911 unique data ($R_{int} = 0.0274$), 4007 data with $I > 2\sigma(I)$, 163 parameters refined, GOF(F^2) = 1.073, final R indices ($R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$, $R1 = 0.0371$, $wR2 = 0.0994$, max/min residual electron density 0.514(0.057)/−0.469(0.057) e Å^{-3}. CCDC 654636.

Synthesis of Ni nanoparticles. A mixture of [Ni(COD)$_2$] (0.5 mmol) and trioctylphosphine oxide (5 mmol) or oleylamine (5 mmol) was stirred magnetically under nitrogen and heated at 100 °C for 2 h. The color of the solution changed from orange to black. After cooling at room temperature, 25 mL of acetone was added to the solution to give a black precipitate, which was separated from the solution by centrifugation (3500 rpm, 10 min), washed several times with acetone and dried under vacuum. The recovered nanoparticles could be redispersed in hexanes.

Synthesis of Ni_2P nanoparticles. To a mixture of Ni nanoparticles (0.5 mmol) and trioctylphosphine oxide (5 mmol) or oleylamine (5 mmol), 0.5 mL of a 0.127 M solution of P_4 in toluene (0.06 mmol) was added. The mixture was stirred under nitrogen at 100 °C for 1 h. After cooling at room temperature, 25 mL of acetone was added to the solution to give a black precipitate, which was washed several times with acetone and dried under vacuum. An XRD spectrum is shown in Fig. 1. A second XRD spectrum is shown after thermal treatment of the solid for 4 h at 100 °C. The X-ray powder diffraction was carried out on the dried samples after a thermal treatment at 100 °C for several hours. The nanoparticles could be redispersed in hexane.

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