White phosphorus and metal nanoparticles: a versatile route to metal phosphide nanoparticles†

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P_4 reaction with metal NPs (In, Pb, Zn) provides an easy access to the corresponding metal phosphide NPs in a soft and stoichiometric reaction. Size-influence on the reactivity is investigated in the case of indium.

Molecular reactivity of P_4 (the most reactive allotrope of phosphorus) toward transition metal fragments has attracted much attention in the previous four decades because of its room-temperature reactivity.[1] P_4 may behave as a "classical" phosphine ligand *via* coordination of the lone pair(s) at phosphorus in well-designed organometallic complexes.[2] Alternatively, the initial P_4 tetrahedron may be deeply transformed in the coordination sphere, providing complex species incorporating various P_n moieties (from P_1 to P_{12}), opening routes to P_4 functionalization in solution under mild conditions.[3] The key feature for these low-temperature activations of P_4 is the use of its molecular form (in solution) and a carefully designed molecular reactant (transition metal complexes or organic species). Surprisingly, this enhanced reactivity has been very rarely exploited in the field of nanomaterials.[4] Indeed, while some studies report the use of P_4 in the synthesis of metal phosphide nanoparticles (NPs),[5] it is generally added as a solid in hydrothermal conditions, at high temperature for days, as a source of PH_3.[5,6] Alternative 'P' donors have also been used in relatively mild conditions, such as $P(SiMe_3)_3$,[7] TOP (tri-*n*-octylphosphine)[8] or PPh_3.[9]

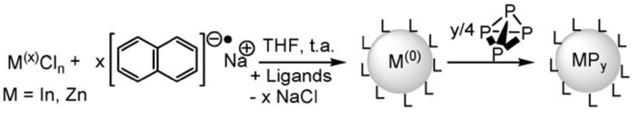
In this work, we demonstrate that soluble metal NPs (from groups 12 to 14: Zn, In and Pb) successfully substitute M(0) complexes which are not accessible in these cases, for the activation of the whole P_4 molecule, in a controlled and stoichiometric reaction. The M(0) NPs provide a versatile access to highly desirable metal phosphide NPs, which exhibit relevant properties in the fields of catalysis,[5d,10] luminescence,[11] magnetic applications,[10b,12] and electrodes for lithium batteries.[13] Our approach could, in principle, be extended to most metals. The influence of the size of the particles on the kinetics of the reaction is also presented herein.

Very few synthetic procedures are known for Zn NPs, because they are readily oxidized by oxygen ($E°(Zn) = -0.76$ V). This can only be prevented by surface passivation[14] which makes them unreactive. The synthesis of In NPs is also quite challenging and usually yield large NPs (> 10 nm),[15] even though smaller In NPs (5 nm) could be obtained by Chaudret *et al.*[16] The above mentioned syntheses of either small sized NPs of Zn or In did not suit our purposes in terms of stabilizing the ligand system and we devised a novel strategy toward these NPs based on a strong reduction.

It is actually known in inorganic/organometallic chemistry that strong one-electron reducing agents are able to transform in a stoichiometric manner, oxidized transition metal complexes into stable M(0) complexes provided that appropriate ligands are also bound to the metal center.[17] We extended this strategy to the challenging synthesis of metal NPs (In, Zn) by promoting a strong nucleation rate using Na/naphthalenide and insuring surface stabilization with trialkyl-phosphine/amine ligands. In the field of NPs, this reducing agent has been used once on $SiCl_4$,[18] and very recently for Pt containing alloys.[19] The fast reduction of $InCl_3$ and $ZnCl_2$ by stoichiometric amounts of sodium naphthalenide in the presence of an excess of ligand (either trioctylphosphine or trioctylamine) was carried out at room temperature (Scheme 1). This reaction yielded M(0) NPs species together with NaCl (which was observed by XRD after centrifugation of the crude mixture) as the expected byproduct of the reduction. In both cases a brown colloidal suspension of highly reactive M(0) NPs was obtained.

Because of their extremely fast reactivity toward either O_2 or H_2O, their complete characterization was then not attempted. However, TEM observations of the crude mixtures showed the presence of small NPs (TOP as surface ligand). In the case of indium, the NPs appeared to be in the 2–7 nm range with some larger aggregates (up to 10 nm) (Fig. 1, left). The NPs appeared smaller in the case of Zn (1–5 nm) (ESI†).

In a second step, without treatment, these NPs were reacted with P_4 at room temperature showing a reactivity comparable to that of M(0) complexes, because of their high surface-to-volume



Scheme 1 Synthetic pathway for InP and Zn_3P_2 NPs.

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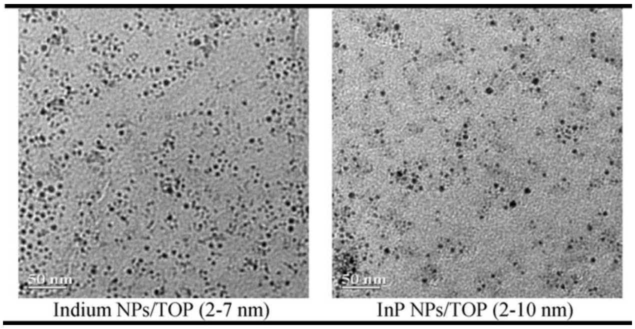


Indium NPs/TOP (2-7 nm) InP NPs/TOP (2-10 nm)

Fig. 1 As-synthesized NPs obtained by $InCl_3$ reduction, and InP NPs obtained after reaction of the In NPs with P_4.

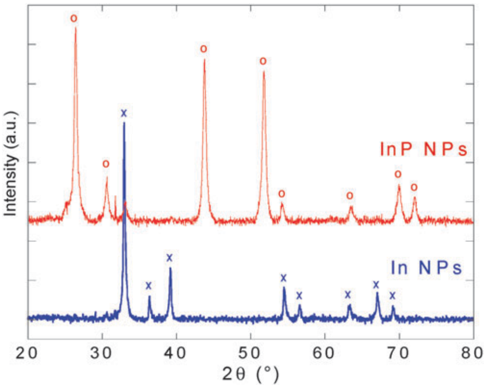
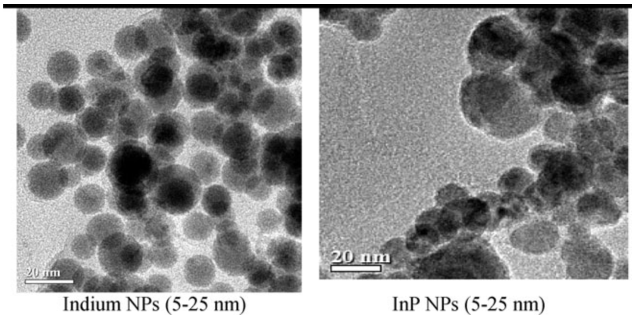


Fig. 2 XRD on InP NPs (top, circles from JCPDS 03-065-2889) obtained from isolated In NPs (bottom, crosses from JCPDS 03-065-9682).



Indium NPs (5-25 nm) InP NPs (5-25 nm)

Fig. 3 TEM observations of 'large' In and InP NPs.

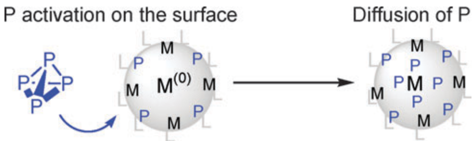
ratio. Indeed, the reaction, followed by ^{31}P NMR spectroscopy, showed the disappearance of P_4 (singlet at −521 ppm) within a few minutes, without the appearance of any signal. This correlates with a stoichiometric reaction of P_4 at room temperature with the In NPs, yielding InP NPs. Similarly, 1/6 equiv. of P_4 were added on the solution of Zn NPs at room temperature to form Zn_3P_2. TEM observations on the NPs synthesized with TOP show particles in the 2–10 nm range for InP (Fig. 1, right) and 1–5 nm for Zn_3P_2 (ESI†). Note that TEM analysis of TOA-capped NPs shows slightly larger particles and aggregates (ESI†), indicating that the surface stabilization by the amine is poorer than by the phosphine. Elemental analysis (EDS on a MEB) was conducted on the TOA-capped NPs in both cases, after centrifugation and extensive washing of the NPs. It indicated ratios of 1.0 : 1.0 for In : P, in agreement with a stoichiometric reaction of white phosphorus on the metal NPs, and 3.0 : 1.7 for Zn : P, slightly off the theoretical ratio.

The kinetics of the oxidation of M(0) NPs appears to depend on the outmost importance on their size. Indeed, the works of Chaudret *et al.* and Feldmann *et al.* had demonstrated different kinetics of oxidation,[15a,16] from instantaneous oxidation in the first case (5 nm NPs), and a resistance for a couple of hours in the other case (diameter > 10 nm), while other works do not mention oxidation of the particles (50 nm NPs).[15b] A similar kinetic behavior in their reaction with P_4 was expected, which prompted us to study larger systems: In, to provide a direct comparison, and Pb.

We synthesized In NPs under nitrogen using a modified single-phase procedure.[15a] (ESI) The isolated black powder was analyzed by powder-XRD, confirming the formation of crystalline In NPs (Fig. 2). TEM observation of the NPs dispersed in hexane showed 5–25 nm spherical NPs. High-resolution images confirmed the crystallinity and structure of the NPs. Importantly, the same spectra were obtained when the isolation of the particles was performed under nitrogen, or in air (*ca.* 15 min for the whole process). Indeed, no shell of $In(OH)_3$ nor In_2O_3 could be observed, suggesting that both the relatively large size of the particles and their coating with oleylamine provided a good kinetic protection against oxidation in air (Fig. 3, left and ESI†).

1/4 equiv. of P_4 in toluene was added to a solution of isolated In NPs in 10 mL of diethylene glycol. ^{31}P NMR spectrum of the solution showed the presence of significant amounts of P_4 (singlet at −521 ppm) indicating that the reaction is not complete at room temperature. Toluene was evaporated under vacuum and the solution was heated at 180 °C for 2 h providing a P_4-free solution as shown by the lack of signal in the ^{31}P NMR spectrum, suggesting complete reaction of P_4 with the NPs. The powder-XRD of the NPs after isolation and washing showed only the InP structure (Fig. 2). TEM observations showed highly crystallized NPs in the same size range as the starting In NPs, suggesting direct insertion of P in the metal template (Fig. 3 and ESI†).

We finally turned our attention to the least reactive species of our series, both because of higher oxidation potential ($E°$(Pb) = −0.13 V) and low surface-to-volume ratio: large Pb NPs. The synthesis of Pb NPs was achieved according to a procedure reported by Aubin *et al.*[20] TEM observations showed polydispersed NPs in the 5–20 nm range (ESI†). The isolated Pb NPs were dispersed in 1-octadecene under an inert atmosphere. We used a low-P stoichiometry (2 Pb for 1 P) because of early reports indicating that only low-phosphorus content alloys are stable.[21] After the addition of a white phosphorus solution in toluene (1/8 equiv. of P_4) at room temperature, the ^{31}P NMR spectrum of the solution showed a singlet at −521 ppm. In fact, no evolution of the peak intensity on a period of 30 min was observed, indicating a slow kinetics of the reaction. The solution was therefore heated at 150 °C for 1 h after which time no more signal in the ^{31}P NMR spectrum was recorded. The NPs were recovered by addition of isopropanol and centrifugation and were washed extensively with isopropanol. Elemental analysis of the NPs by EDS gave the expected Pb : P stoichiometry of 2.0 : 1.0. TEM images revealed polydispersed NPs in the 5–10 nm range (ESI†).



Scheme 2 Proposed metal phosphide formation mechanism.

We investigated the stoichiometric and low-temperature activation of P_4 using soluble metal NPs as reactants. We propose an original synthesis for zinc (groups 12) and indium (group 13) small metal phosphide NPs, based on the strong reduction of a chloride precursor followed by low-temperature, stoichiometric reaction of P_4 on the as-synthesized NPs. This one-pot strategy circumvents the lack of stability of these species toward oxidation. We also showed that crystalline InP particles can be obtained from crystalline In NPs (size and morphology of the starting NPs are preserved), particles in the relevant size range for luminescence and photovoltaic applications. Finally, a kinetic dependence of the reaction of P_4 with M(0) NPs on the size of the particles was observed. While small indium NPs were shown to exhibit a high reactivity at room temperature, reactions involving larger NPs required heating.

This suggests that the mechanism proceeds through reaction on the surface of the NP followed by diffusion of phosphorus in the NP lattice (Scheme 2), the kinetics of which is slowed down in an extended lattice. Finally, we demonstrated here by three examples that M(0) NPs offer a versatile route toward metal phosphide NPs. Detailed studies on the reaction of P_4 toward other metal NPs and on the detailed mechanism of this reaction are underway in our laboratories.

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Notes and references

1 (*a*) M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza and F. Zanobini, *Eur. J. Inorg. Chem.*, 1999, 931; (*b*) M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.*, 2005, **34**, 1038.

2 (*a*) Y. Xiong, S. Yao, E. Bill and M. Driess, *Inorg. Chem.*, 2009, **48**, 7522; (*b*) P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Costantini and P. Stoppioni, *Angew. Chem., Int. Ed.*, 2008, **47**, 4425.

3 (*a*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2007, **129**, 14180; (*b*) M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.*, 2010, DOI: 10.1021/cr900349u; (*c*) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, DOI: 10.1021/cr9003709.

4 S. Carenco, I. Resa, X. Le Goff, P. Le Floch and N. Mézailles, *Chem. Commun.*, 2008, 2568.

5 (*a*) S. Liu, Y. Qian and X. Ma, *Mater. Lett.*, 2008, **62**, 11; (*b*) H. Hou, Q. Peng, S. Zhang, Q. Guo and Y. Xie, *Eur. J. Inorg. Chem.*, 2005, 2625; (*c*) B. M. Barry and E. G. Gillan, *Chem. Mater.*, 2008, **20**, 2618; (*d*) J. Li, Y. Ni, K. Liao and J. Hong, *J. Colloid Interface Sci.*, 2009, **332**, 231.

6 S. Liu, X. Liu, L. Xu, Y. Qian and X. Ma, *J. Cryst. Growth*, 2007, **304**, 430.

7 See, for instance: (*a*) W. E. Buhro, *Polyhedron*, 1994, **13**, 1131; (*b*) R. L. Wells, S. R. Aubuchon, S. S. Kher and M. S. Lube, *Chem. Mater.*, 1995, **7**, 793.

8 See, for instance: (*a*) A. E. Henkes and R. E. Schaak, *Chem. Mater.*, 2007, **19**, 4234; (*b*) J. Park, B. Koo, K. Y. Yoon, Y. Hwang, M. Kang, J.-G. Park and T. Hyeon, *J. Am. Chem. Soc.*, 2005, **127**, 8433.

9 See, for instance: J. Wang, Q. Yang, Z. Zhang and S. Sun, *Chem.–Eur. J.*, 2010, DOI: 10.1002/chem.200902151.

10 (*a*) S. T. Oyama, T. Gott, H. Zhao and Y. Lee, *Catal. Today*, 2009, **143**, 94; (*b*) S. L. Brock and K. Senevirathne, *J. Solid State Chem.*, 2008, **181**, 1552; (*c*) Z. Yao, H. Dong and Y. Shang, *J. Alloys Compd.*, 2009, **474**, L10.

11 (*a*) R. Xie, D. Battaglia and X. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 15432; (*b*) L. Li and P. Reiss, *J. Am. Chem. Soc.*, 2008, **130**, 11588.

12 F. Luo, H. Su, W. Song, Z. Wang, Z. Yan and C. Yan, *J. Mater. Chem.*, 2004, **14**, 111.

13 (*a*) M. G. Kim, S. Lee and J. Cho, *J. Electrochem. Soc.*, 2009, **156**, A89; (*b*) C. Park, Y. Kim and H. Sohn, *Chem. Mater.*, 2009, **21**, 5566; (*c*) F. Gillot, S. Boyanov, L. Dupont, M. Doublet, M. Morcrette, L. Monconduit and J. Tarascon, *Chem. Mater.*, 2005, **17**, 6327; (*d*) S. Boyanov, M. Womes, L. Monconduit and D. Zitoun, *Chem. Mater.*, 2009, **21**, 3684.

14 (*a*) A. Irzh, I. Genish, L. Chen, Y. Ling, L. Klein and A. Gedanken, *J. Phys. Chem. C*, 2009, **113**, 14097; (*b*) H. Amekura, N. Umeda, K. Kono, Y. Takeda, N. Kishimoto, C. Buchal and S. Mantl, *Nanotechnology*, 2007, **18**, 395707; (*c*) G. Canizal, P. Schabesretchkiman, U. Pal, H. Liu and J. Ascencio, *Mater. Chem. Phys.*, 2006, **97**, 321.

15 (*a*) E. Hammarberg and C. Feldmann, *Chem. Mater.*, 2009, **21**, 771; (*b*) N. H. Chou, X. Ke, P. Schiffer and R. E. Schaak, *J. Am. Chem. Soc.*, 2008, **130**, 8140; (*c*) P. Singh, S. Kumar, A. Katyal, R. Kalra and R. Chandra, *Mater. Lett.*, 2008, **62**, 4164.

16 K. Soulantica, A. Maisonnat, M. Fromen, M. Casanove, P. Lecante and B. Chaudret, *Angew. Chem., Int. Ed.*, 2001, **40**, 448.

17 J. E. Ellis, *Inorg. Chem.*, 2006, **45**, 3167.

18 R. K. Baldwin, K. A. Pettigrew, J. C. Garno, P. P. Power, G. Liu and S. M. Kauzlarich, *J. Am. Chem. Soc.*, 2002, **124**, 1150.

19 T. Ghosh, B. M. Leonard, Q. Zhou and F. J. DiSalvo, *Chem. Mater.*, 2010, **22**, 2190.

20 I. Resa, H. Moreira, B. Bresson, B. Mahler, B. Dubertret and H. Aubin, *J. Phys. Chem. C*, 2009, **113**, 7120.

21 J. Pelouze and E. Fremy, *Traité de Chimie générale, analytiques, industrielle et agricole-Tome 3*, Seconde partie, Paris, Masson, 1865.