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# Single-pot synthesis of zinc nanoparticles, borane (BH<sub>3</sub>) and *closo*-dodecaborate $(B_{12}H_{12})^{2-}$ using LiBH<sub>4</sub> under mild conditions<sup>†</sup>

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Reduction of ZnCl<sub>2</sub> using LiBH<sub>4</sub> in mesitylene yielded zinc nanoparticles (Zn-NPs), borane (BH<sub>3</sub>) and *closo*-dodecaborate (B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup>. The BH<sub>3</sub> evolved gas was trapped as Ph<sub>3</sub>P:BH<sub>3</sub> adduct while *closo*-(B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup> was extracted by methanol and characterized from spectral data.

**Introduction** The chemical syntheses of metal nanoparticles (NPs) generally provides a less energy consuming alternative route to physical methods. Carefully chosen reducing and stabilizing molecules help to synthesize NPs, whose purity is the same as that obtained through chemical vapour deposition (CVD) or any other physical methods.<sup>1</sup> Further, if easily removable, volatile and synthetically useful side products are produced during NPs synthesis, it will embellish the interest for further advancement. In this paper we report an enticing method of chemical synthesis for zinc nanoparticles (Zn-NPs) and simultaneous production of borane (BH<sub>3</sub>) and *closo*-dodecaborate  $(B_{12}H_{12})^{2^-}$  in a single reaction.

The Zn-NPs and its composites are expected to find wide applications in several areas including biomedical, antibacterial coatings, cosmetology, catalysis, lubrication, and solar cells.<sup>2</sup> They were also tested as an ingredient to shorten the ignition delay time of explosive materials, and as a catalyst for the decomposition of ammonium perchlorate in a propellant composition.<sup>3</sup> Few physical methods, including laser ablation and electrodeposition, are known to produce Zn-NPs.<sup>4</sup> Still chemical synthetic methods are appealing because of the possibility of obtaining nanoparticles as a solution or suspension.<sup>5</sup> Therefore, with an intention of finding a new synthetic route to Zn-NPs, we chose reducing zinc chloride (ZnCl<sub>2</sub>) using lithium borohydride (LiBH $_4$ ) in mesitylene as solvent. The results obtained from this reaction are described in this paper.

# **Results and discussion**

# Zinc nanoparticles (Zn-NPs)

In a typical synthetic procedure (Scheme 1), the  $\text{ZnCl}_2$  was reduced by  $\text{LiBH}_4$  in deoxygenated mesitylene. The reaction mixture was refluxed under a static nitrogen atmosphere. Gas evolution was observed during the reaction. When the gas evolution ceased and increasing amounts of a black-grey residue was observed (~24 h) the reaction mixture was allowed to cool to room temperature. The solid residue obtained was filtered through a glass frit and washed with 20–30 mL portions of ice cold dry methanol to remove LiCl and other side products of the reaction. The grey coloured residue was dried under vacuum and finally designated as Zn-NPs (yield: 80–90%).

In recent reports, it was described that when LiBH<sub>4</sub> and NaBH<sub>4</sub> were thermally decomposed they yielded lithium and sodium salts of  $(B_{12}H_{12})^{2-}$ , respectively.<sup>6</sup> It is also well known that the oxidation of NaBH<sub>4</sub> by I<sub>2</sub> would evolve the BH<sub>3</sub> gas, and this method has been well utilized in organic synthesis.<sup>7</sup> Further, the same reaction was modified<sup>8</sup> to prepare various salts of  $(B_{12}H_{12})^{2-}$  with good yields. In this context, it is interesting to find the possible boron-containing product from a reaction wherein LiBH<sub>4</sub> is used as the reducing agent. Also, it would be useful if we could isolate one or more boranes from such a reaction involving LiBH<sub>4</sub> and ZnCl<sub>2</sub>. Since such boron-containing compounds were anticipated to be side products in



**Scheme 1** Reduction of zinc chloride by lithium borohydride (the reaction is not balanced for either stoichiometry or charge).

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our reaction, it could be also possible to monitor the reaction and products by <sup>11</sup>B NMR spectral analysis. As expected, a few boron-containing compounds were also formed in the above reaction, as observed from the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of the methanol extracts. However, we were able to isolate only BH<sub>3</sub> gas and  $[B_{12}H_{12}]^{2-}$  from the above reaction (*vide infra*).

The large surface to volume ratio makes the metal nanoparticles highly susceptible to surface oxidation and aggregation.<sup>9</sup> Therefore, some surfactants or polymers are widely used to protect and stabilize metal nanoparticles. In order to circumvent both problems we intended to protect the Zn-NPs using poly(vinylpyrrolidone) (PVP). It is also interesting to note at this juncture that the polymer stabilized Zn-NPs were tested as an antibacterial coating and in corrosion protection.<sup>10</sup> To obtain polymer protected nanoparticles, we have conducted the above synthesis of Zn-NPs in the presence of PVP also. This reaction yielded Zn-NPs stabilized in polymer (Zn-PVP-NPs). The reactions were performed aiming at a 1:0.5 weight ratio of Zn-NPs to PVP. However, the actual ratio would vary slightly based on the extent of the completeness of the reduction reaction and possible loss of polymer during washing. It is believed that PVP stabilizes the nanoparticles by donating its lone pair of electrons to the metal atoms on the surface of the particles.<sup>11,12</sup>

#### Characterization of Zn-NPs

The PXRD patterns (Fig. 1) obtained for the Zn-NPs, with and without PVP, were compared with that of JCPDS (#87-0713) and were found to be in good agreement with the reported PXRD pattern of hexagonal Zn. Thermogravimetric (TG–DTA) analyses (Fig. 2 and Fig. S1, ESI†) of both Zn-NPs and Zn-PVP-NPs were also carried out. In both cases, sharp endothermic peaks were observed around 415 and 417.5 °C, respectively, in the DTA curve, corresponding to the melting point of zinc. Such a small difference in the melting points of free nanoparticles and nanoparticles in a matrix has been thoroughly studied and was explained based on Gibbs-Thomson equation.<sup>13</sup> In the DTA curve of the side products, a sharp endothermic peak corresponding to the melting point of lithium chloride was observed. Because no other inorganic



Fig. 1 PXRD pattern of Zn-NPs in polymer (PVP) matrix



Fig. 2 DTA curve of Zn-NPs and Zn-PVP-NPs.

salt having such a high melting point was possible from our reaction, the data confirmed the formation of lithium chloride as one of the side products (Fig. S2, ESI<sup>†</sup>). In the FT-IR spectrum (Fig. S3, ESI<sup>†</sup>) of the Zn-PVP-NPs, the carbonyl stretching frequency of PVP was observed. A slight shift in the frequency from pure PVP was observed (1660 cm<sup>-1</sup> was shifted to 1650 cm<sup>-1</sup>), which can be ascribed to the coordination of the oxygen atoms of PVP to atoms on the surface of the Zn-NPs.<sup>14</sup>

#### Microscopic investigations

Investigation of the NPs by FESEM (Fig. 3) showed that most of the uncoated Zn-NPs were cubic, while Zn-PVP-NPs were irregular flakes. The FESEM picture of the Zn-NPs obtained immediately after the reaction showed smaller particles (50–100 nm), while bigger particles were observed (750 nm–1  $\mu$ m) in pictures taken after a few days (Fig. S4, ESI†). This may be due to the kinetic instability of the metal nanoparticles, leading to aggregation which is a common phenomenon in the absence of any surfactant.<sup>15</sup> However, the sizes of the Zn-PVP-NPs were in the range of 50–100 nm, indicating the prevention of aggregation by a polymer. The prevention of the particle size growth might have been due to the atoms on the surface of Zn-NPs being coordinated by lone pair electrons of the oxygen and nitrogen atoms present in PVP. This coordination on the surface was evidenced from the FT-IR spectrum,



Fig. 3 FESEM image of (a) Zn-NPs with scale bar 1  $\mu m.$  (b) Zn-PVP-NPs with scale bar 1  $\mu m.$ 



Fig. 4 TEM and HRTEM images of the Zn-PVP-NPs with scale bars 100 nm and 5 nm, respectively. FFT of a single nano crystal is also shown.

as discussed earlier. This phenomenon could have been the reason for smaller sized particles compared to free nanoparticles.<sup>16</sup> The advantage of stabilization of the nanoparticles using a polymer is that it can protect them from oxidation and also from aggregation.

The TEM images of the Zn-PVP-NPs (Fig. 4 and Fig. S5,  $ESI^{\dagger}$ ) also confirmed the formation of irregularly shaped flakes with sizes ranging 50–100 nm. Fast Fourier Transformations (FFT) of HRTEM showed the orientation of the (0 0 2) plane matching with PXRD. The restriction of the growth of the particles by the polymer chains could be the probable reason for the irregular shape of the nanoparticles, otherwise they could have grown to a particular shape.

The elemental composition of both Zn-NPs and Zn-PVP-NPs specimens were determined by EDX (energy dispersive X-ray spectrometry) on SEM, FESEM and TEM. The EDX spectra (Fig. S7 and S8, ESI<sup>†</sup>) showed a strong peak corresponding to zinc. The weight percentage of zinc in all the EDX spectra was consistent. Due to surface oxidation, a peak corresponding to the oxygen appeared in the EDX spectrum of Zn-NPs without a polymer coating, indicating the requirement for surface protection.

# Isolation of BH<sub>3</sub>

Lithium borohydride (LiBH<sub>4</sub>) and lithium aluminium hydride (LiAlH<sub>4</sub>) are well known hydride sources for use as reducing agents in synthetic chemistry. Studying the fate of a reagent used in the synthesis and side products formed from such reagent, assists in understanding the reaction pathway. For example, in recent reports, when AlCl<sub>3</sub> was reduced by LiAlH<sub>4</sub>, lithium chloride and alane formation was observed.<sup>17</sup> Alane further decomposed at higher temperatures to yield aluminium nanoparticles.<sup>18</sup> However, the fate of boron from LiBH<sub>4</sub> in a reduction reaction has not been understood much.

Since there was a probability for the formation of one or more boranes in our reactions, it is essential to identify each of the products from the reaction mentioned in the Scheme 1. Indeed, when we probed the evolved gas from our reaction we were able to identify the  $BH_3$ . It was shown that triphenylphosphine (PPh<sub>3</sub>) easily reacts with borane to form a triphenylphosphine–borane adduct.<sup>19</sup> Hence, in order to confirm the formation of  $BH_3$ , the same reaction was performed in the



**Fig. 5** ORTEP diagram showing crystal structure of the  $Ph_3P:BH_3$  complex. Phenyl hydrogens are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P1-B1 = 1.924(3), P1-C1 = 1.814(3), P1-C7 = 1.84(3), P1-C14 = 1.811(3), B1-H1A = 0.960, B1-H1B = 0.960, B1-H1C = 0.960, C7-P1-B1 = 112.261(16), C14-P1-B1 = 113.88(16), C1-P1-B1 = 111.83(15), C14-P1-C7 = 104.85(12), C7-P1-C1 = 106.62(12), C14-P1-C1 = 106.86(12), P1-B1-H1A = 109.5, P1-B1-H1B = 109.5, P1-B1-H1C = 109.5, H1A-B1-H1C = 109.5, H1A-B1-H1B = 109.5, H1B-B1-H1C = 109.5.

presence of PPh<sub>3</sub>. After reaction, the mesitylene was evaporated under vacuum and the product was extracted with benzene. It was further recrystallized from benzene under low temperature and the crystals were analysed by spectroscopy. Formation of phosphine–borane adduct Ph<sub>3</sub>P:BH<sub>3</sub> was primarily confirmed from multinuclear NMR spectral data.<sup>7c,20,21</sup> Further, pure crystals were obtained by recrystallization from benzene solution and characterized by single crystal X-ray crystallography. However, the structure had already been reported in 1982.<sup>22</sup> The molecular structure of the adduct is shown in the Fig. 5, which provided unambiguous proof of the nature of the material obtained from this reaction. The crystal data and structural refinement details are provided in the ESI.<sup>†</sup>

It is worth mentioning that BH<sub>3</sub>, while being one of the major reagents in organic synthesis, has only a few methods known so far for convenient laboratory scale preparation.<sup>7</sup> The reaction described here provided a single-pot synthetic method for Zn-NPs and BH<sub>3</sub> gas under mild conditions. Therefore, our method is expected to also be a useful addition to synthetic chemistry for the production of BH<sub>3</sub>. The clean PXRD pattern of the Zn-NPs obtained from this reaction suggested that addition of triphenylphosphine to the reaction mixture did not affect the formation of the Zn-NPs.

# Isolation of *closo*-(B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup>

The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of the methanol extracts from the reduction reactions showed a predominant peak corresponding to  $(B_{12}H_{12})^{2-}$  and also a few more boron containing products (Fig. S9, ESI<sup>†</sup>). In order to isolate any borane, after filtering the Zn-NPs from the reaction mixture, methanol extracts were dried to obtain a solid product. This methanol

solution also contained lithium chloride. The possibility existed that  $closo-(B_{12}H_{12})^{2-}$  could be present as a lithium salt, as well as a zinc salt in the same solution. Hence, the product was dissolved again in deionized water and triethylamine was added to convert  $closo-(B_{12}H_{12})^{2-}$  into  $(B_{12}H_{12})(HNEt_3)_2$ . Since this triethylamine salt was not soluble in water, it was isolated easily by filtration (isolated yield: 4-5%). Its formation was confirmed by multinuclear NMR, FT-IR and High Resolution Mass spectral data.<sup>8,23</sup> The attempted isolation of other boranes failed owing to their trace quantity and also probably due to their volatility. It should be mentioned that a number of lower boranes are volatile. Despite the stability of closo- $(B_{12}H_{12})^{2-}$ , there has been only one viable laboratory scale synthetic procedure for the preparation of its salt.<sup>8</sup> Hence the method presented here is worthwhile in that context but has to be optimized for use as an alternative method for the synthesis of higher boranes.

# Conclusion

In conclusion, reduction of zinc(II)chloride yielded three products; *viz.* Zn-NPs, BH<sub>3</sub> and  $(B_{12}H_{12})^{2-}$ . The reaction provided an attractive chemical synthetic route to Zn-NPs and an alternative method to produce BH<sub>3</sub> and  $(B_{12}H_{12})^{2-}$ . The ease with which BH<sub>3</sub> and  $(B_{12}H_{12})^{2-}$  were produced in the presence of ZnCl<sub>2</sub> from LiBH<sub>4</sub> is anticipated to be a valuable addition to synthetic chemistry.

# Experimental

### Materials and synthesis

Zinc(II) chloride, poly(vinylpyrollidone) (molecular weight 10 000), and mesitylene were purchased from the Aldrich and lithium borohydride was purchased from the Acros chemicals. Triphenylphosphine was purchased from the SRL, India. All the chemicals were used as received. Mesitylene was thoroughly deoxygenated using a freeze-pump-thaw method before use.

#### Instruments and sample preparation

The pure samples obtained after removing the LiCl completely were used for the characterization. The X-ray diffraction patterns were recorded on Bruker D8 X-ray diffract meter (Cu K $\alpha$  = 1.54 Å) with a scan rate of 6° min<sup>-1</sup>. The <sup>11</sup>B, <sup>31</sup>P, <sup>1</sup>H, NMR spectra were recorded using a Bruker Avance 400 MHz instrument using BF<sub>3</sub>-ether, 85% H<sub>3</sub>PO<sub>4</sub>, and SiMe<sub>4</sub>, respectively, as the standard reference. The Fourier transform infrared (FT-IR) spectra (KBr pellet) were recorded on a Jasco 5300 or Nicolet 380 spectrophotometer. Single-crystal X-ray data collection for the triphenylphosphine borane adduct was carried out at 298(2) K on a Bruker Smart Apex CCD area detector system [ $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å] with graphite monochromator. The data were reduced using SAINTPLUS, and the structure was solved using SHELXS-97 and refined using SHELXL-97.

The structure was solved by direct methods and refined by fullmatrix least-squares cycles on  $F^2$ . All non-hydrogen atoms were refined anisotropically.<sup>24</sup> The TG-DTA analyses were conducted on a Ta Q600 SDT instrument with a standard heating rate 10 °C min<sup>-1</sup> from room temperature to 600 °C under a dynamic nitrogen atmosphere.

The SEM analyses were performed on Philips XL-30 SEM operating at 20 kV. The FESEM analyses were performed on ultra 55 of Carl Zeiss. Samples for SEM and FESEM were prepared on a glass surface by drop casting. The samples were suspended in suitable solvents and sonicated for 1–2 min. Specimens for EDS (energy dispersive X-ray spectrometry) analysis were prepared by dusting the compounds on carbon tape. The TEM analyses were conducted on FEI technai  $G^2$  20 STEM with a 200 kV acceleration voltage. TEM specimens were prepared on carbon coated copper grids with 200 meshes. Samples were suspended in suitable solvents and ultra sonicated for 1–2 min.

# Synthesis of Zn-NPs

The reactants (ZnCl<sub>2</sub>, 10 mmol; LiBH<sub>4</sub>, 20 mmol) were added to the mesitylene (20 mL) which was already placed in a 100 mL two-necked round-bottom flask equipped with a magnetic stirring bar. A reflux condenser with a nitrogen inlet was fitted on the reaction flask. The reaction mixture was refluxed for 24 hours under static nitrogen atmosphere. Gas evolution was observed during the reaction. On completion of the reaction the reaction mixture was allowed to cool to room temperature. The solid residue was filtered through the glass frit and washed with 20–30 mL portions of ice cold dry methanol to remove the LiCl and other side products of the reaction. Further, the black-grey colored residue was dried under vacuum and characterized as Zn-NPs (yield: 80–90%).

# Characterization of (B12H12)(HNEt3)2

After removing the Zn-NPs from the above reaction mixture the methanol extracts were dried to obtain a solid product. The solid was dissolved again in deionized water and then an excess amount of triethylamine was added drop by drop with continuous stirring to maintain the pH around 9-10 at ice cold temperature. Immediately a voluminous precipitate was obtained. To complete the precipitation, the stirring was continued at room temperature overnight. The formation of a colorless solid was observed. This colorless solid was filtered and washed with a small amount of distilled water and dried. Analysis of this solid by spectroscopy confirmed the formation of  $(B_{12}H_{12})(HNEt_3)_2$  salt. NMR: <sup>11</sup>B{<sup>1</sup>H} (CD<sub>3</sub>CN)  $\delta$  -15.31 ppm (s) (Fig. S10, ESI<sup>†</sup>); <sup>11</sup>B -15.33, -16.30 (d, J = 124.5 Hz) (Fig. S10, ESI<sup>+</sup>); <sup>1</sup>H (D<sub>2</sub>O) δ 3.10 (q, 12H, -CH<sub>2</sub>-, *J* = 7.4 Hz), 1.18 (t, 18H, -CH<sub>3</sub>, J = 7.2 Hz), 0.56 to 1.70 [12H, broad poorly resolved, (B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup>] (Fig. S11, ESI<sup>+</sup>); FT-IR: 2482 cm<sup>-1</sup> (strong, B-H stretching) (Fig. S12, ESI<sup>+</sup>). HRMS:  $(M + 23)^+ = 369.41$ (Fig. S13, ESI<sup>†</sup>). Elem. Anal.: Calcd (found) for C<sub>12</sub>H<sub>44</sub>B<sub>12</sub>N<sub>2</sub>: C, 41.63 (41.52); H, 12.81 (12.76); N, 8.09 (8.16) (Fig. S14, ESI<sup>+</sup>). Attempted isolation of other boranes failed owing to their trace quantity.

### Synthesis of Zn-PVP-NPs

The above reaction was carried out in the presence of PVP (0.3269 g). The reactions were performed aiming at a 1:0.5 ratio of Zn-NPs to PVP. After 24 hours, the reaction mixture was allowed to cool to room temperature. The solid residue was filtered through the glass frit and washed with 20–30 mL portions of ice cold dry methanol to remove the LiCl and other side products of the reaction. Further, the black-grey colored residue was dried under vacuum and characterized as Zn-PVP-NPs.

#### Formation of the phosphine-borane complex

The above reduction reaction was carried out in the presence of PPh<sub>3</sub> (20 mmol). After the reaction time, mesitylene was evaporated under vacuum. Then the Ph<sub>3</sub>P:BH<sub>3</sub> adduct was extracted with 25 mL of benzene. It was further recrystallized from benzene under low temperature. The formation of the phosphine-borane complex was primarily confirmed by NMR spectral data. NMR: <sup>11</sup>B{<sup>1</sup>H} (CDCl<sub>3</sub>), broad doublet at  $\delta$  -38.019 and -38.442 ppm ( $J_{B-P}$  = 54.3 Hz); <sup>11</sup>B{<sup>1</sup>H} (THF-d<sub>8</sub>) broad doublet at  $\delta$  –39.64 and –40.07 ppm ( $J_{\rm B-P}$  = 55.2 Hz), (Fig. S15, ESI<sup>†</sup>); <sup>11</sup>B (CDCl<sub>3</sub>)  $\delta$  –37.94 ppm (m) (Fig. S16, ESI<sup>†</sup>);  $^{31}P{^{1}H}$  (CDCl<sub>3</sub>) broad, merged lines at  $\delta$  20.85 and 20.43 ppm  $(J_{P-B} = 68.0 \text{ Hz}); {}^{31}P{}^{1}H{}$  (THF-d<sub>8</sub>) broad, merged lines 20.90 and 20.52 (61.5 Hz) (Fig. S17, ESI<sup>+</sup>). The dissimilarities in the coupling constants are probably due to the line-broadening in the <sup>31</sup>P NMR spectra, which might be induced by the quadrupolar interaction of the two nuclear isotopes (<sup>11</sup>B, I = 3/2, 80.42% naturally abundant and  $^{10}$ B, I = 3, 19.58% naturally abundant) of the adjacent boron leading to poorly resolved lines in <sup>31</sup>P NMR spectra complicating accurate J measurement. Hence it will be reasonable to use the value obtained from the  $^{11}\text{B}$  NMR spectra.  $^{20a,b}$   $^1\text{H}$  (CDCl<sub>3</sub>),  $\delta$  7.62–7.28 (15H, Ph, three set of multiplets), 1.58-1.01, (3H, BH<sub>3</sub>, poorly resolved multiplet) (Fig. S18, ESI<sup>+</sup>). FT-IR: 2245.4 cm<sup>-1</sup> (weak, B-H asymmetric), 2377.6 cm<sup>-1</sup> (strong B-H symmetric), 604.41 cm<sup>-1</sup> (strong B-P stretching) (Fig. S19, ESI<sup>+</sup>). Elem. Anal.: Calcd (found) for C<sub>18</sub>H<sub>18</sub>BP: C, 78.30 (78.32); H, 6.57 (6.41); (Fig. S20, ESI<sup>+</sup>).

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