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# Assembly and Stabilization of $\{E(\text{cyclo-P}_3)_2\}$ ( $E = \text{Sn, Pb}$ ) as a Bridging Ligand Spanning Two Triaryloxyniobium Units<sup>†</sup>

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Complexes  $(\text{THF})_{0-2}E[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$  ( $E = \text{Sn, Pb}$ ;  $\text{Dipp} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ) were isolated (>90%) from the salt metathesis of  $[\text{Na}(\text{THF})_3][\text{P}_3\text{Nb}(\text{ODipp})_3]$  with  $E^{2+}$  salts. The reaction of  $(\text{THF})\text{Sn}[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$  with pyridine-*N*-oxide was investigated as a method to deposit a new  $\text{SnP}_6$  phase. Additionally, the neutral complex  $\text{P}_3\text{Nb}(\text{ODipp})_2(\text{py})_2$  ( $\text{py} = \text{pyridine}$ ) was prepared from  $[\text{Na}(\text{THF})_3][\text{P}_3\text{Nb}(\text{ODipp})_3]$  in the presence of pyridine and salts of coordinating cations ( $\text{Mg}(\text{II})$ ,  $\text{Sn}(\text{II})$ ,  $\text{Pb}(\text{II})$ ,  $\text{Ge}(\text{II})$ ,  $\text{Hg}(\text{II})$  and  $\text{Ag}(\text{I})$ ).  $\text{P}_3\text{Nb}(\text{ODipp})_2(\text{py})_2$  was found to successfully produce  $\text{AsP}_3$  upon treatment with  $\text{AsCl}_3$ . The characterization of complexes  $(\text{THF})_{0-1}\text{Sn}[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$ ,  $(\text{THF})_2\text{Pb}[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$  and  $\text{P}_3\text{Nb}(\text{ODipp})_2(\text{py})_2$ , including their solid state structures, is discussed.

## Introduction

Metallophosphides are attractive materials especially for their potential to function as electron reservoirs, but exploring and exploiting their properties hinges on improving the synthetic methods to control their composition, morphology and structure.<sup>1-3</sup> For example, it has been shown recently that better control over the morphology of tin phosphide particles, interesting as anodic<sup>4-6</sup> and photocatalytic materials,<sup>7</sup> could be achieved using solvothermal and mechanochemical synthetic methods<sup>8</sup> than with traditional ones that involve heating the constituent elements together at high temperatures.<sup>9</sup> The successful synthesis of molecular arsenic phosphide  $\text{AsP}_3$  from the triple salt metathesis reaction of  $\text{AsCl}_3$  with the *cyclo-P*<sub>3</sub><sup>3-</sup> transfer reagent  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$ , ( $\mathbf{1} = \text{Nb}(\text{ODipp})_3$ ,  $\text{Dipp} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ),<sup>10,11</sup> made us wonder if the same molecular strategy could be used to prepare new molecular or metastable phases of bulk main group phosphides, in particular those of group 14 elements.

To start, we explored the possibility of preparing the unknown anions “ $\text{GeP}_3^-$ ” and “ $\text{SnP}_3^-$ ”, isoelectronic and expected to be isostructural with the reported  $\text{AsP}_3$  and  $\text{SbP}_3$  tetrahedra.<sup>10</sup> We quickly learned that when treating the  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  complex with germanium or tin(II) salts, only a partial salt metathesis reaction occurred and the *cyclo-P*<sub>3</sub> unit remained coordinated to niobium. In the case of germanium no well-defined new germanium containing species could be isolated, but interestingly, in the case of tin a complex featuring an unusual  $[\text{SnP}_6]$  metallophosphide ligand and stabilized by coordination to niobium was formed quantitatively (along with  $\text{NaCl}$ ); this behavior is also replicated by lead. Herein we show that this metallophosphide ligand can be liberated from the niobium coordination sphere using an oxygen-atom transfer reagent, or can facilitate the formation

of complex  $\mathbf{2-P}_3$  ( $\mathbf{2} = \text{Nb}(\text{ODipp})_2(\text{py})_2$ ) – a neutral *cyclo-P*<sub>3</sub><sup>3-</sup> transfer reagent (see Scheme 1).

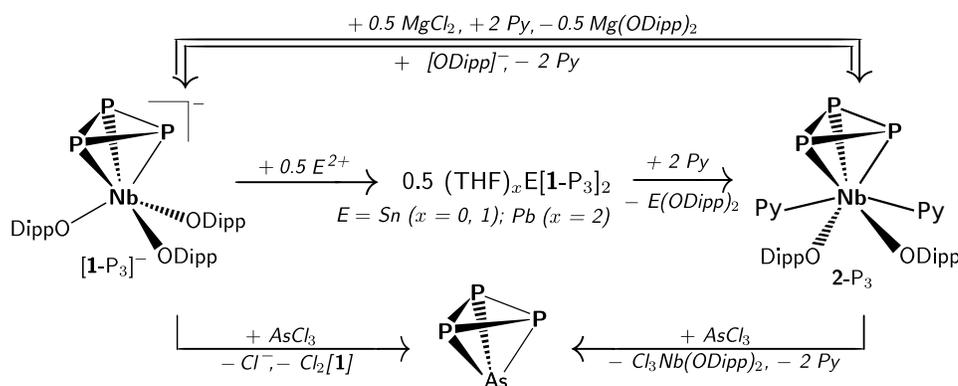
## Assembling the “EP<sub>6</sub>” ( $E = \text{Sn, Pb}$ ) metallophosphide ligand

Treating a bright orange solution of  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  (2 equiv) in tetrahydrofuran (THF) with tin or lead dichloride (1 equiv) resulted in the quantitative formation of the complexes  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  and  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$ , respectively (see Scheme 1), as well as sodium chloride. *n*-Pentane extraction of the residue obtained upon removing the volatile materials from the crude reaction mixture allowed the selective dissolution of the metal phosphide complex, and facilitated its isolation as a spectroscopically pure material, dark red in the case of tin (94% yield) and maroon in the case of lead (96% yield). <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic analysis of the two complexes at 21°C indicated that in solution they are  $C_{3v}$  symmetric, suggestive of fluxional coordination of the tin and lead atoms to the *cyclo-P*<sub>3</sub> units. The <sup>31</sup>P NMR spectra of the complexes in benzene display broad singlet resonances at –219 ppm ( $\Delta\nu_{1/2} = 185$  Hz) for the tin phosphide and at –212 ppm ( $\Delta\nu_{1/2} = 180$  Hz) for the lead phosphide, shifting to –202 ppm for both species in THF. These values are upfield of –200 and –158 ppm, the chemical shifts of the  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  salt in benzene and THF, respectively, but downfield of –235 ppm, the chemical shift observed for the  $\text{Sn}^{\text{IV}}$  complex  $\text{Ph}_3\text{SnP}_3\text{Nb}(\text{ODipp})_3$  in benzene.<sup>11</sup> Empirically, we note that the upfield shift for the <sup>31</sup>P NMR chemical shift of the  $[\mathbf{1-P}_3]$  unit correlates with an increase of the interaction of the *cyclo-P*<sub>3</sub> unit with the coordinated cation, in the order  $\text{Na}^+ < \text{Pb}^{2+} < \text{Sn}^{2+} < \text{Ph}_3\text{Sn}^+$ .

The solid-state structures of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  and  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$  indicate the loss of the local  $C_{3v}$  symmetry of the  $\mathbf{1-P}_3$  moieties observed in solution (see Figures 1 and 2). With one THF molecule coordinated, the tin atom in  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  bridges almost symmetrically two  $\mathbf{1-P}_3$

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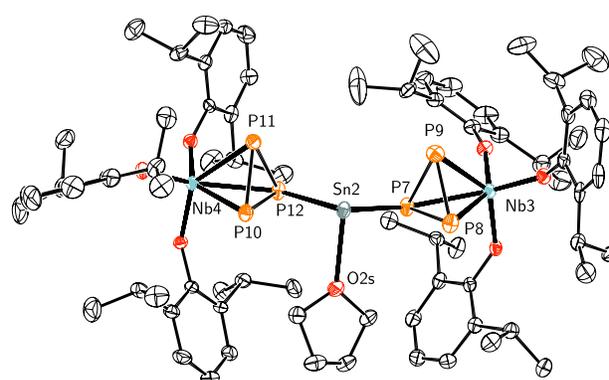


**Scheme 1** Synthesis of complexes  $(\text{THF})_x E[\mathbf{1-P}_3]_2$  ( $E = \text{Sn}, \text{Pb}; x = 0-2$ ) and  $\mathbf{2-P}_3$  from the reported salt  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$ . Both  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  and  $\mathbf{2-P}_3$  can transfer the *cyclo-P*<sub>3</sub> unit to arsenic and form  $\text{AsP}_3$ .

units by interacting with one P vertex of each of the  $[\text{NbP}_3]$  tetrahedra. The P–Sn interatomic distances of 2.683(1) and 2.672(1) Å respectively are close to 2.62 Å, the mean value for a P–Sn single bond reported in the CCDC database,<sup>12</sup> but longer than 2.51 Å, the calculated value for a single P–Sn bond based on the sum of the covalent radii of the elements.<sup>13</sup> The almost orthogonal P12–Sn2–P7 angle of 92.23(4)° is suggestive of *p*-orbital involvement in the bonding interactions necessary for Sn(II) to complete its octet. With two THF molecules satisfying its coordination sphere, the lead atom in  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$  interacts with each  $[\text{NbP}_3]$  unit through mainly one Pb–P interaction of 2.843(1) Å, slightly longer than the mean Pb–P interaction reported in the CCDC of 2.75 Å.<sup>12</sup> The perturbation of the  $[\text{NbP}_3]$  tetrahedra by Sn and Pb coordination to the *cyclo-P*<sub>3</sub> units is best reflected in the elongation of the Nb–P interatomic distances from an average of 2.51 Å in  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  to 2.55 Å in  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  and 2.56 Å in  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$ .

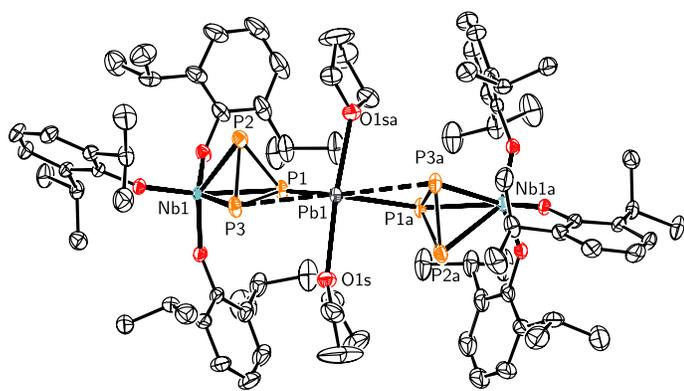
Examples of molecular species in which tin or lead have an all-phosphorus coordination environment are rare and include cage compounds such as  $[\text{Sn}_{10}(\text{tBuP})_4]$  and  $[\text{Pb}_7(\text{tBuP})_7]$ ,<sup>14,15</sup> which in addition to E–P bonds (averaging 2.57 Å for Sn), also contain metal-metal interactions. Other relevant examples are the isomorphous metallopolyphosphides  $[\text{SnP}_{15}]^{3-}$  and  $[\text{PbP}_{15}]^{3-}$ , which could be isolated in low yields by the salt metathesis of the Zintl anions  $\text{K}_3\text{P}_7$  and the element diiodide, in a 2:1 ratio.<sup>16</sup> X-ray analysis of these anions established their overall geometry, best described as two nortricyclic P<sub>7</sub> units connected by an  $\mu^2, \eta^2, \eta^2$ -[PE] bridge, but crystallographic disorder of the P and E atoms precluded any discussion of bond metrical parameters. Another noteworthy instance of tetrel incorporation in all-phosphorus ligands is the formation of the triatomic, aromatic *cyclo-EP*<sub>2</sub> ( $E = \text{Ge}, \text{Sn}, \text{Pb}$ ) between two niobium centers by salt metathesis involving the terminal niobium phosphide  $[\text{PNb}(\text{N}[\text{CH}_2^t\text{Bu}]\text{Ar})_3]^-$  ( $t\text{Bu} = \text{tert-C}_4\text{H}_9$ ,  $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$ ) with  $E^{2+}$  salts in a 2:1

stoichiometry.<sup>17</sup>



**Fig. 1** Solid-state molecular structure of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  with ellipsoids at the 50% probability level and rendered using PLATON.<sup>18</sup> Hydrogen atoms and the disordered solvents ( $\text{Et}_2\text{O}$ ) were omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn2–P12 2.683(1), Sn2–P10 2.929(1), Sn2–P11 3.386(2), Sn2–P7 2.672(1), Sn2–P8 3.216(1), Sn2–P9 3.270(1), P11–Nb4 2.549(1), P10–Nb4 2.518(1), P12–Nb4 2.580(1), P9–Nb3 2.542(2), P8–Nb3 2.560(1), P7–Nb3 2.533(1), P11–P12 2.192(2), P12–P10 2.234(2), P10–P11 2.176(2), P9–P8 2.174(2), P8–P7 2.206(2), P7–P9 2.201(2), P12–Sn2–P7 92.23(4), P10–Sn2–P8 171.09(4).

Interested in the interaction of naked group 14 cations with the  $\mathbf{1-P}_3$  moiety, we wondered if THF incorporation could be circumvented by use of a weakly coordinating solvent. Heating a bright orange slurry of  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  (2 equiv) and  $\text{SnCl}_2$  (1 equiv) in benzene to 70 °C for 3 h resulted in the formation of a new species, which was isolated in 94% yield as a maroon powder.  $C_{3v}$  symmetric in solution, the product displayed a single, relatively sharp signal in its  $^{31}\text{P}$  NMR spectrum at –226 ppm ( $\Delta\nu_{1/2} = 9$  Hz) in benzene, upfield of that of the  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  complex. X-ray analysis con-

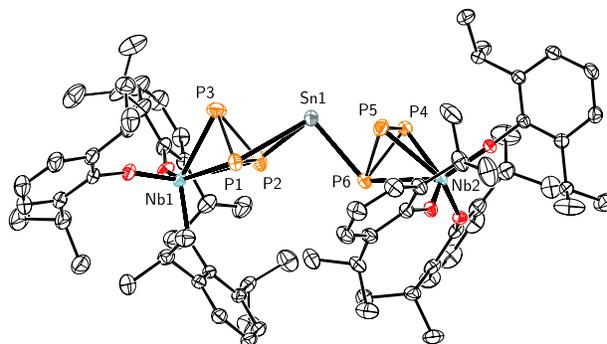


**Fig. 2** Solid-state molecular structure of  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$  with ellipsoids at the 50% probability level and rendered using PLATON.<sup>18</sup> Hydrogen atoms and the disordered solvent ( $\text{C}_6\text{H}_6$ ) were omitted for clarity. Selected interatomic distances (Å) and angles ( $^\circ$ ): Pb1–P1 2.8434(6), Pb1–P3 3.1375(6), Pb1–P2 3.6390(7), Pb1–O1s 2.592(2), Nb1–P2 2.5402(6), Nb1–P3 2.4999(7), Nb1–P1 2.5843(6), P1–P2 2.185(1), P2–P3 2.177(1), P3–P1 2.2101(8), P3–Pb1–P1 43.02(2).

firmed the identity of the new tin phosphide as a  $C_1$  symmetric  $\text{Sn}[\mathbf{1-P}_3]_2$  complex (see Figure 3). In the absence of a coordinating solvent, the Sn atom in  $\text{Sn}[\mathbf{1-P}_3]_2$  satisfies its octet by interacting with a total of three phosphorus atoms through three long interactions of 2.8014(7), 2.7541(9) and 2.7009(7) Å. In  $\text{Sn}[\mathbf{1-P}_3]_2$  the tin atom is effectively sandwiched between two staggered *cyclo*- $\text{P}_3$  rings, an environment reminiscent of that experienced by tin in extended phosphides. In particular, within the corrugated layers of  $\text{SnP}_3$ , a tin atom bridges three puckered  $\text{P}_6$  rings with an interatomic distance Sn–P of 2.662(3) Å, and interacts with three additional phosphorus atoms from a neighboring layer with long Sn–P interatomic distances of 2.925(3) Å.<sup>19</sup> Analogous to what was observed in the case of the  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  complex, the Nb–P interactions of the  $[\text{NbP}_3]$  tetrahedra are slightly weaker than in the parent  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  salt, with Nb–P interatomic distances averaging 2.56 Å. Interestingly, addition of THF to a benzene solution of  $\text{Sn}[\mathbf{1-P}_3]_2$  does not lead to the formation of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$ , but to a mixture of unidentified species with no detectable  $^{31}\text{P}$  NMR signal and with broad features observed in the  $^1\text{H}$  NMR spectrum.

### Releasing “ $\text{SnP}_6$ ” from a molecular precursor

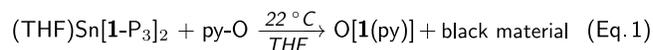
Interested in forming new molecular or bulk main group phosphides, we explored releasing the metallophosphide  $[\text{SnP}_6]$  ligand from the coordination sphere of niobium. The reaction of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  with an oxygen atom transfer agent may liberate the bridging  $[\text{SnP}_6]$  cluster and effect the formation of the previously reported oxo dimer  $\{\text{ONb}(\text{ODipp})_3\}_2$ .<sup>20</sup>



**Fig. 3** Solid-state molecular structure of  $\text{Sn}[\mathbf{1-P}_3]_2$  with ellipsoids at the 50% probability level and rendered using PLATON.<sup>18</sup> Hydrogen atoms and the disordered solvent ( $\text{C}_6\text{H}_6$ ) were omitted for clarity. Selected interatomic distances (Å) and angles ( $^\circ$ ): P1–Sn1 2.8014(7), P2–Sn1 2.7541(9), P6–Sn1 2.7009(7), P5–Sn1 3.0184(7), P4–Sn1 2.9867(7), P1–P2 2.2073(9), P1–P3 2.1920(9), P3–P2 2.190(1), P6–P5 2.2118(9), P5–P4 2.1849(9), P4–P6 2.2070(9), Nb1–P3 2.5374(7), Nb1–P1 2.5679(7), Nb1–P2 2.5846(8), Nb2–P6 2.5905(7), Nb2–P5 2.5409(7), Nb2–P4 2.5442(7), P3–P1–Sn1 77.81(3), P2–Sn1–P6 101.07(2), P1–Sn1–P5 120.23(2).

This strategy was previously used to release the  $[\text{Ph}_3\text{SnP}_3]$  unit from the  $\text{Ph}_3\text{SnP}_3\text{Nb}(\text{ODipp})_3$  complex with transfer to 1,3-cyclohexadiene.<sup>11</sup>

Treatment of a solution of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  (1 equiv) in  $\text{Et}_2\text{O}$  with pyridine-*N*-oxide (py-O, 2 equiv) in THF effected the immediate formation of a pale yellow supernatant and a fine black suspension, which was precipitated with  $\text{Et}_2\text{O}$  and collected by suction filtration on a sintered frit. Isolated in 69% yield, the species contained in the yellow filtrate was identified and structurally characterized as the pyridine adduct of the niobium oxo monomer,  $\text{O}[\mathbf{1}(\text{Py})]$ . Interestingly, when  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  was treated with py-O in the presence of excess 1,3-cyclohexadiene (20–100 equiv) no soluble phosphorus containing species was observed to form, in contrast to the observation reported in the case of the  $\text{Ph}_3\text{SnP}_3\text{Nb}(\text{ODipp})_3$  complex.<sup>11</sup>



The black particles collected from the reaction appeared crystalline and displayed a metallic shine. Insoluble in common laboratory solvents (e.g. toluene, THF, pyridine, dimethylformamide) they slowly turned yellow upon exposure to air. Powder diffraction analysis revealed the presence of a few, broad features<sup>21</sup> and indicated that no metallic Sn or any known tin phosphides were present.<sup>9,19,22–24</sup> Energy-dispersive X-ray spectroscopy analysis of this material indicated an even distribution of tin and phosphorous throughout the sample, with an average ratio of Sn:P of 1:5.4. In ad-

dition to tin and phosphorus, combustion elemental analysis of this black solid indicated variable carbon content, from 16 to 27%, possibly stemming from coordinated THF or intercalated ODipp-containing species. Solid state  $^{31}\text{P}$  NMR analysis using Cross Polarization Magic-Angle spinning revealed the presence of a broad signal around 13 ppm, this being located in a  $^{31}\text{P}$  NMR region characteristic to Hittorf-type bonding in violet phosphorus (see section S.2).<sup>25</sup> Interestingly, heating this material to temperatures of 250–290 °C led to the formation of  $\text{P}_4$  and either  $\text{Sn}_4\text{P}_3$  or  $\text{SnP}$ , well characterized tin phosphides.<sup>9,19,22–24</sup>

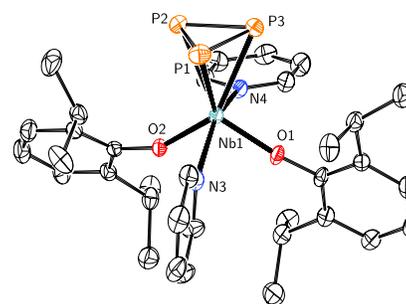
These preliminary characterization data seem to indicate that the black material produced by releasing the  $[\text{SnP}_6]$  ligand from  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  contains a new phosphorus-rich tin phosphide, but an improved procedure for its preparation and further characterization data will be needed to establish the details of its structure and chemical formula.

### A neutral *cyclo-P*<sub>3</sub> niobium transfer reagent

Exposing red solutions of  $(\text{THF})\text{Sn}[\mathbf{1-P}_3]_2$  and  $(\text{THF})_2\text{Pb}[\mathbf{1-P}_3]_2$  complexes to pyridine immediately effected a color change to bright green, and the formation of a single new species with a  $^{31}\text{P}$  NMR chemical shift of –78 ppm, containing ODipp and pyridine ligands in a ratio of 1:1, as determined by  $^1\text{H}$  NMR spectroscopy. Its identity as the neutral *cyclo-P*<sub>3</sub> niobium *bis*-ODipp complex  $\mathbf{2-P}_3$ , was elucidated using X-ray diffraction (see Figure 4). Effectively a salt elimination process with formation of  $\text{Sn}(\text{ODipp})_2$  and the neutral  $\mathbf{2-P}_3$  complex, similar transformations also took place when pyridine and salts of Ge(II), Hg(II), Ag(I) or Mg(II) were added to solutions of  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$ . A convenient synthesis of  $\mathbf{2-P}_3$ , isolated in 95% yield as a bright green solid, was devised using  $\text{MgCl}_2$  as a stoichiometric reagent (see Scheme 1). Interestingly, complex  $[\text{Ag}][\mathbf{1-P}_3]$ , formed in the salt metathesis of  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  (1 equiv) with  $\text{AgOTf}$  (1 equiv) displays an intriguing quintet centered around –243 ppm in the  $^{31}\text{P}$  NMR spectrum. This NMR feature suggests that in solution  $[\text{Ag}][\mathbf{1-P}_3]$  aggregates into a tetramer,<sup>26,27</sup> a hypothesis supported also by a Diffusion Ordered NMR spectroscopy experiment (see SI).<sup>28</sup>

$C_{2v}$ , symmetric in solution,  $\mathbf{2-P}_3$  is almost  $C_s$  symmetric in the solid state, with the two pyridine molecules coordinated *trans* to each other. With an average Nb–P interatomic distance of 2.52 Å, and P–P bond of 2.19 Å, the  $[\text{NbP}_3]$  tetrahedron in  $\mathbf{2-P}_3$  is only slightly perturbed by the replacement of an ODipp ligand by pyridine. Treatment of  $\mathbf{2-P}_3$  with a source of  $[\text{ODipp}]^-$  anion readily regenerates the  $[\mathbf{1-P}_3]^-$  core (see Scheme 1 and SI).

The neutral *cyclo-P*<sub>3</sub> niobium complex  $\mathbf{2-P}_3$  is uniquely poised to test if sodium chloride formation is a necessary driving force in the synthesis of  $\text{AsP}_3$  from the anionic  $[\mathbf{1-P}_3]^-$



**Fig. 4** Solid-state molecular structure of  $\mathbf{2-P}_3$  with ellipsoids at the 50% probability level and rendered using PLATON.<sup>18</sup> Hydrogen atoms and the co-crystallized solvent (benzene) were omitted for clarity. Selected interatomic distances (Å) and angles (°): Nb1–P1 2.5018(8), Nb1–P2 2.5445(9), Nb1–P3 2.5273(8), P3–P1 2.162(1), P1–P2 2.172(1), P2–P3 2.168(1), Nb1–N3 2.332(3), Nb1–O2 1.960(2), Nb1–N4 2.313(2), Nb1–O1 1.953(2), N3–Nb1–N4 152.40(9), P2–P1–P3 60.02(4), P3–P2–P1 59.78(4).

complex.<sup>29</sup> We found that when treating a solution of the neutral complex  $\mathbf{2-P}_3$  with  $\text{AsCl}_3$ ,  $\text{AsP}_3$  forms in 45% spectroscopic yield along with complex  $\text{Cl}_3\text{Nb}(\text{ODipp})_2$ , suggesting that  $\text{NaCl}$  formation is in fact not essential for this process.

### Conclusions

Devising synthetic methods to assemble main group phosphides from molecular precursors may allow the formation of binary materials with new stoichiometries and interesting emerging properties. Herein we introduced the synthesis of complexes  $(\text{THF})_{0-1}\text{Sn}[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$  and  $(\text{THF})_2\text{Pb}[\text{P}_3\text{Nb}(\text{ODipp})_3]_2$  in which the phosphorus rich metalophosphide ligand  $\{\text{E}(\text{cyclo-P}_3)_2\}$  (E = Sn, Pb) is supported by two niobium alkyoxide platforms. Preliminary studies revealed that releasing the  $\{\text{Sn}(\text{cyclo-P}_3)_2\}$  unit from the coordination sphere of niobium using an oxygen atom transfer reagent led to the formation of a new tin phosphide with an unusually high phosphorus content (P to Sn ratio of ca. 5.4). Further, the neutral complex  $\mathbf{2-P}_3$ , prepared in the pyridine-assisted reaction of  $[\text{Na}(\text{THF})_3][\mathbf{1-P}_3]$  with salts of coordinating cations, was introduced as a new phosphorus transfer reagent and was found to successfully transfer the *cyclo-P*<sub>3</sub> unit to arsenic with formation of the molecular arsenic phosphide  $\text{AsP}_3$ .<sup>10</sup>

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