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Assembly and Stabilization of \( \{E(\text{cyclo-P}_3)_2\} \) (\( E = \text{Sn, Pb} \)) as a Bridging Ligand Spanning Two Triaryloxi niobium Units \( \dagger \)

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Complexes (THF)\(_{n-1}\)E[\( P_n\text{Nb(ODipp)}_3 \)]\(_{2}\) (\( E = \text{Sn, Pb}; \text{Dipp} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3 \)) were isolated (>90%) from the salt metathesis of [\( \text{Na(THF)}_3 \)]\([\text{P}_3\text{Nb(ODipp)}_3 ] \) with \( E^{2+} \) salts. The reaction of (THF)Sn[\( P_n\text{Nb(ODipp)}_3 \)] with pyridine-N-oxide was investigated as a method to deposit a new \( \text{SnP}_3 \) phase. Additionally, the neutral complex \( P_3\text{Nb(ODipp)}_2(\text{py})_2 \) was prepared from [\( \text{Na(THF)}_3 \)]\([\text{P}_3\text{Nb(ODipp)}_3 ] \) in the presence of pyridine and salts of coordinating cations (Mg(II), Sn(II), Pb(II), Ge(II), Hg(II) and Ag(I)) in benzene. \( P_3\text{Nb(ODipp)}_2(\text{py})_2 \) was found to successfully produce \( \text{AsP}_3 \) upon treatment with AsCl\(_3\). The characterization of complexes (THF)\(_{n-1}\)Sn[\( P_n\text{Nb(ODipp)}_3 \)]\(_{2}\), (THF)\(_2\)Pb[\( P_n\text{Nb(ODipp)}_3 \)]\(_{2}\), and \( P_3\text{Nb(ODipp)}_2(\text{py})_2 \), 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.\(^1\)\(^-\)\(^3\) For example, it has been recently shown that better control over the morphology of tin phosphide particles, interesting as anodic\(^4\)\(^-\)\(^7\) and photocatalytic materials,\(^7\) could be achieved using solvothermal and mechanochemical synthetic methods\(^8\) than with traditional ones that involve heating the constituent elements together at high temperatures.\(^9\) The successful synthesis of molecular arsenic phosphide \( \text{AsP}_3 \) from the triple salt metathesis reaction of AsCl\(_3\) with the cyclo-\( P_3 \)\(^{\text{2-}} \)transfer reagent [\( \text{Na(THF)}_3 \)]\([\text{P}_3 \text{Me(THF)}_3 \])\(_{2}\); \( \text{Me} = \text{C}_6\text{H}_5 \),\(^10\)\(^-\)\(^11\) 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 “GeP\(_n\)\(^{\text{2-}} \)” and “SnP\(_n\)\(^{\text{2-}} \)”, isoelectronic and expected to be isostructural with the reported \( \text{AsP}_3 \) and \( \text{SbP}_3 \) tetrahedra.\(^10\) Quickly learned that when treating the [\( \text{Na(THF)}_3 \)]\([\text{I-P}_3 \]) complex with germanium or tin(II) salts, only a partial salt metathesis reaction occurred and the cyclo-\( P_3 \) 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 stabilized by coordination to niobium was formed quantitatively (along with 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 \( 2\text{P}_3 \) (\( 2 = \text{Nb(ODipp)}_2(\text{py})_2 \)) – a neutral cyclo-\( P_3 \)\(^{\text{2-}} \) transfer reagent (see Scheme 1).

Assembling the “\( \text{EP}_n \)” (\( E = \text{Sn, Pb} \)) metallophosphide ligand

Treating a bright orange solution of [\( \text{Na(THF)}_3 \)]\([\text{I-P}_3 \]) (2 equiv) in tetrahydrofuran (THF) with tin or lead dichloride (1 equiv) resulted in the quantitative formation of the complexes (THF)\(_{n-1}\)Sn[\( P_n\text{Me(THF)}_3 \)]\(_{2}\) and (THF)\(_2\)Pb[\( P_n\text{Me(THF)}_3 \)]\(_{2}\), 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). \(^1\)H and \(^31\)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-\( P_3 \) units. The \(^31\)P NMR spectra of the complexes in benzene display broad singlet resonances at \(-219 \text{ ppm} \) (\( \Delta v/2 = 185 \text{ Hz} \)) for the tin phosphide and at \(-212 \text{ ppm} \) (\( \Delta v/2 = 180 \text{ Hz} \)) for the lead phosphide, shifting to \(-202 \text{ ppm} \) for both species in THF. These values are upfield of \(-200 \) and \(-158 \text{ ppm} \), the chemical shifts of the [\( \text{Na(THF)}_3 \)]\([\text{I-P}_3 \]) salt in benzene and THF, respectively, but downfield of \(-235 \text{ ppm} \), the chemical shift observed for the \( \text{SnIV} \) complex \( \text{Ph}_3\text{SnP}_3\text{Nb(ODipp)}_3 \) in benzene.\(^11\) Empirically, we note that the upfield shift for the \(^31\)P NMR chemical shift of the [\( \text{I-P}_3 \)] unit correlates with an increase of the interaction of the cyclo-\( P_3 \) 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 (THF)\(_{n-1}\)Sn[\( P_n\text{Me(THF)}_3 \)]\(_{2}\) and (THF)\(_2\)Pb[\( P_n\text{Me(THF)}_3 \)]\(_{2}\) indicate the loss of the local \( C_{3v} \) symmetry of the \( 1\text{-P}_3 \) moieties observed in solution (see Figures \( 1 \) and \( 2 \)). With one THF molecule coordinated, the tin atom in (THF)\(_{n-1}\)Sn[\( P_n\text{Me(THF)}_3 \)]\(_{2}\) bridges almost symmetrically two \( 1\text{-P}_3 \)
units by interacting with one P vertex of each of the [NbP3] 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, 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. 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 (THF)2Pb[1-P3]2 interacts with each [NbP3] unit through mainly one Pb–P interaction of 2.843(1) Å, slightly longer than the mean Pb–P interaction reported in the CCDC database, 2.75 Å. Perturbation of the [NbP3] tetrahedra by Sn and Pb atom to the cyclo-P3 units is best reflected in the elongation of the Nb–P interatomic distances from an average of 2.51 Å in [Na(THF)3][1-P3] to 2.55 Å in (THF)Sn[1-P3]2 and 2.56 Å in (THF)2Pb[1-P3]2.

Examples of molecular species in which tin or lead have an all-phosphorus coordination environment are rare and include cage compounds such as [Sn10(η5-BuP)4] and [Pb7(η5-BuP)2], which in addition to E–P bonds (averaging 2.57 Å for Sn), and 2.56 Å in (THF)Sn[1-P3]2.

Interested in the interaction of naked group 14 cations with the 1-P3 moiety, we wondered if THF incorporation could be circumvented by use of a weakly coordinating solvent. Heating a bright orange slurry of [Na(THF)3][1-P3]2 (2 equiv) and SnCl2 (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. X-ray analysis indicated that the product displayed a single, relatively sharp signal in its 31P NMR spectrum at −226 ppm (Δν1/2 = 9 Hz) in benzene, upfield of that of the (THF)Sn[1-P3]2 complex. X-ray analysis con-
Releasing “SnP₆” from a molecular precursor

Interested in forming new molecular or bulk main group phosphides, we explored releasing the metallophosphide [SnP₆] ligand from the coordination sphere of niobium. The reaction of (THF)Sn[1-P₃]₂ with an oxygen atom transfer agent may liberate the bridging [SnP₆] cluster and effect the formation of the previously reported oxo dimer {ONb(ODipp)₃}₂.¹⁹

This strategy was previously used to release the [Ph₃SnP₃] unit from the Ph₃SnP₃Nb(ODipp)₃ complex with transfer to 1,3-cyclohexadiene.¹¹

Treatment of a solution of (THF)Sn[1-P₃]₂ (1 equiv) in Et₂O 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 Et₂O 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, [O(1(Py))]. Interestingly, when (THF)Sn[1-P₃]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 Ph₃SnP₃Nb(ODipp)₃ complex.¹¹

\[
(\text{THF})\text{Sn[1-P₃]₂} + \text{py-O} \xrightarrow{\text{Et₂O}} \text{O[1(py)]} + \text{black material} \quad (\text{Eq. 1})
\]

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 features²¹ and indicated that no metallic Sn or any known tin phosphides were present.¹⁹,²²–²⁴ Energy-dispersive X-ray spectroscopy analysis of this material indicated an even distribution of tin and phosphorus 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 $^{31}$P NMR analysis using Cross Polarization Magic-Angle spinning revealed the presence of a broad signal around 13 ppm, this being located in a $^{31}$P NMR region characteristic to Hittorf-type bonding in violet phosphorus (see section S.2). Interestingly, heating this material to temperatures of 250–290 °C led to the formation of P$_2$ and either Sn$_4$P$_3$ or SnP, well characterized tin phosphides.9,19,22–24

These preliminary characterization data seem to indicate that the black material produced by releasing the [SnP$_6$] ligand from (THF)Sn$_2$(I-P)$_2$ contains a new phosphorus-rich tin phosphate, 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$_3$ niobium transfer reagent

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

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

The neutral cyclo-P$_3$ niobium complex 2-P$_3$ is uniquely poised to test if sodium chloride formation is a necessary driving force in the synthesis of AsP$_3$ from the anionic [I-P$_3$]$^-$ complex.29 We found that when treating a solution of the neutral complex 2-P$_3$ with AsCl$_3$, AsP$_3$ forms in 45% spectroscopic yield along with complex Cl$_2$Nb(ODipp)$_2$, suggesting that 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 (THF)$_0$–$_1$Sn(P$_2$Nb(ODipp)$_2$) and (THF)$_2$Pb(P$_2$Nb(ODipp)$_2$)$_2$ in which the phosphorus rich metallaphosphate ligand {E(cyclo-P$_3$)$_2$} (E = Sn, Pb) is supported by two niobium alkoxide platforms. Preliminary studies revealed that releasing the {Sn(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 2-P$_3$, prepared in the pyridine-assisted reaction of [Na(THF)$_3$][I-P$_3$] with salts of coordinating cations, was introduced as a new phosphorus transfer reagent and was found to successfully transfer the cyclo-P$_3$ unit to arsenic with formation of the molecular arsenic phosphide AsP$_3$.10

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References

12. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, http://www.ccdc.cam.ac.uk/data_request/cif.
\[
\text{DippO} \quad \text{DippO} \quad \frac{1}{2} \quad \text{DippO} \\
\text{DippO} \\
\text{DippO} \\
\]

\[
\begin{align*}
\text{Nb} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{Sn} & \quad \text{P} & \quad \text{P} & \quad \text{P} \\
\text{THF} & \quad & \quad & \quad & \quad & \quad & \quad & \quad \\
\end{align*}
\]

+ Py-N-O \quad - \text{ONb(ODipp)₃(Py)}

\[
\frac{1}{2} \quad [\text{SnP}_6](\text{THF})_x
\]

Py = pyridine \quad \text{Dipp} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3