Properties and Reactivity Patterns of AsP₃: An Experimental and Computational Study of Group 15 Elemental Molecules

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Properties and Reactivity Patterns of AsP₃: An Experimental and Computational Study of Group 15 Elemental Molecules

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Abstract

Facile synthetic access to the isolable, thermally robust AsP₃ molecule has allowed for a thorough study of its physical properties and reaction chemistry with a variety of transition-metal and organic fragments. The electronic properties of AsP₃ in comparison with P₄ are revealed by DFT and AIM approaches and are discussed in relation to the observed electrochemical profiles and the phosphorus NMR properties of the two molecules. An investigation of the nucleus independent chemical shifts revealed that AsP₃ retains spherical aromaticity. The thermodynamic properties of AsP₃ and P₄ are described. The reaction types explored in this study include the thermal decomposition of the AsP₃ tetrahedron to its elements, the synthesis and structural characterization of [(AsP₃)FeCp*(dppe)][BPh₄] (dppe = 1,2-bis(diphenylphosphino)ethane), 1, selective single As–P bond cleavage reactions, including the synthesis and structural characterization of AsP₃(P(N(Pr)₂)N(SiMe₃)₂)₂, 2, and activations of AsP₃ by reactive early transition-metal fragments including Nb(H)(η²-Bu(H)C=NAr)(N[CH₂Bu]Ar)₂ and
Mo(N[3Bu]Ar)₃ (Ar = 3,5-Me₂C₆H₃). In the presence of reducing equivalents, AsP₃ was found to allow access to [Na][E₃Nb(ODipp)₃] (Dipp = 1,2-diisopropylphenyl) complexes (E = As or P) which themselves allow access to mixtures of AsₙP₄₋ₙ (n = 1–4).

**Introduction.**

White phosphorus, P₄, is of interest as a soluble, molecular form of this element obtained industrially via the thermal method of phosphate rock reduction. P₄ is the primary precursor to most P-containing compounds.¹ Melting without decomposition at 44 ºC, pure P₄ is a white, waxy substance that presents no difficulties in terms of isolation, storage, and handling, as long as oxygen is excluded.¹,² On the other hand, yellow arsenic, As₄, is thermally and photochemically unstable in the condensed phase, reverting readily to the metallic form.² As such, its chemistry and application in industry is not well developed. Recently, the interpnictide molecule AsP₃ was synthesized in pure form and was shown to be robust, isolable, and as easy to handle as P₄ itself.³

Though only recently isolated and studied as a pure material, AsP₃ has long been contemplated by inorganic chemists in both academic and industrial settings. Ozin was the first to observe AsP₃ as one component of a hot gas phase mixture of arsenic and phosphorus vapors using Raman spectroscopy, inspiring chemists to speculate on the stability of the AsP₃ heteroatomic tetrahedron.⁴ The physical properties of solid and liquid arsenic-phosphorus phases have been described in some detail,⁵,⁶ but our understanding of the nature and properties of the tetraatomic tetrahedra AsₙP₄₋ₙ (n = 1 – 3) is far from complete. AsP₃ has been suggested as an impurity in white phosphorus as prepared industrially.⁷ The apatite mineral used in the industrial production of P₄ is known to contain a small percentage of As for P substitution (0.003 – 0.03%) which is not removed prior to reduction and likely leads to some amount of AsP₃ impurity in industrially prepared P₄.⁸,⁹ With our discovery of a selective, niobium-mediated synthesis of AsP₃ and the present work, we are elucidating both the physical and chemical properties of this small molecule that bridges the gap between the soluble, molecular forms of the elements phosphorus and arsenic.
The present work delivers an overview of the synthesis and properties of AsP₃ as well as a detailed picture of the structural and electronic properties of AsP₃ as deduced by experiment, Density Functional Theory (DFT),¹⁰ and Bader’s Atoms in Molecules (AIM)¹¹ analysis. Also described herein are reactivity studies of AsP₃ with transition-metal complexes and with main-group element systems, for comparison with related data on P₄ reactivity, and to show that under the proper conditions, AsP₃ serves as a soluble As⁰ source. The utility of AsP₃ for the synthesis of mixed arsenic-phosphorus ligands that would be difficult to synthesize by other means will also be highlighted.

**Results and Discussion**

**Synthesis and Physical Properties of AsP₃.**

The industrial synthesis of elemental phosphorus has remained essentially unchanged for over a century and consists of heating phosphate rock in excess of 1400 ºC with coke and gravel.¹⁹ White phosphorus can also be prepared from red phosphorus by thermolysis at elevated temperature, similar to the synthesis of yellow arsenic from metallic arsenic.² White phosphorus has become difficult to obtain for research purposes in the United States, and both white and red phosphorus are classified by the DEA as List I federally regulated substances.¹² Anionic cyclo-P₃ complexes of niobium have proven to be

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**Scheme 1**

![Diagram of reactions involving AsP₃ and other compounds.](image)
effective as $P_3^{3-}$ transfer agents, and when combined with an $E^{3+}$ source ($E = P$, As, Sb), we have shown that access to $P_4$, $AsP_3$, and $SbP_3$ is possible.$^{3,13-15}$ Specifically in the case where $E = As$, treatment of $[Na][P_3Nb(ODipp)_3]$ ($Dipp = 2,6$ diisopropylphenyl) with 1 equiv of $AsCl_3$ affords $AsP_3$ in greater than 70% isolated yield as shown in Scheme 1, i.$^3$ This reaction provides the first solution-phase synthesis of an interpnictide $As_nP_{4-n}$ ($n = 1$ – 3) tetrahedron.

Transition-metal chalcogenide chemistry provides us with a family of reactions bearing close relation to our synthesis of $AsP_3$. Namely, treatment of $Y_2X_2$ ($Y = S$, Se, Te; $X = Cl$ or Br) with $S_5TiCp_2$ results in formation of $Y_2S_5$ and $X_2TiCp_2$.$^{16-18}$ The first example of such a reaction ($Y = S$, $X = Cl$) comes from a 1968 report by Schmidt and coworkers (Scheme 1, ii)$^{16}$ When $Y = Se$ or Te, this reaction is an illustrative example of the solution synthesis of a heteroatomic interchalcogenide using transfer of $S_5^{2-}$ from an early transition metal center to an $M_2^{2+}$ fragment; a close analogy to the solution synthesis of a heteroatomic interpnictide using transfer of $P_3^{3-}$ from an early transition metal center to an $As^{3+}$ fragment.

The physical properties of $AsP_3$ have been probed by a variety of methods. $AsP_3$ readily sublimes under vacuum at $60$ ºC and melts without decomposition at $72$ ºC.$^3$ $AsP_3$ has been shown to be thermally stable in refluxing toluene solution for more than one week.$^3$ Raman spectroscopy obtained on solid samples of $AsP_3$ shows four resonances at 313 ($a_1$), 345 ($e$), 428 ($a_1$), and 557 ($e$) cm$^{-1}$, consistent with calculated stretching modes for this $C_{3v}$ symmetric molecule.$^3$ High-resolution, electron-impact mass spectroscopy on a solid sample of $AsP_3$ has provided a mass of 167.8426 m/z.$^3$ A solution molecular weight determination of $AsP_3$ gives a molecular weight of $167 \pm 5$ m/z (95% confidence level) confirming that the molecule also exists in the monomeric form when in solution. Finally, phosphorus NMR spectroscopy shows a single sharp resonance at $-484$ ppm in benzene solution.$^3$ This shift is 36 ppm downfield of that for elemental phosphorus in the form of $P_4$ (discussed below).

**Electronic Structure of $AsP_3$.**

The electrochemical profiles of $AsP_3$ and $P_4$ have been compared using cyclic voltammetry in THF solution (Figure 1). $P_4$ has a single broad reduction event with onset at $-1.3$ V vs Fc/Fc$^+$. This is
the only observable reduction feature in the \( \text{P}_4 \) cyclic voltammogram (CV) and possibly indicates formation of the \( \text{P}_4 \) radical anion followed by irreversible bond rupture.\(^{19}\) Scanning cathodically, the CV of \( \text{AsP}_3 \) displays a similarly broad irreversible reduction event with onset at \(-1.0\) V vs Fc/Fc\(^+\), which likely is a result of the more easily generated \( \text{AsP}_3 \) radical anion followed by bond rupture. The earlier onset of reduction for \( \text{AsP}_3 \) suggests that the LUMO of \( \text{AsP}_3 \) is lower in energy than the LUMO of \( \text{P}_4 \) by approximately 10 kcal mol\(^{-1}\). The calculated molecular orbitals for \( \text{P}_4 \) and \( \text{AsP}_3 \) show that the LUMO of \( \text{AsP}_3 \) is lower in energy by 4.9 kcal mol\(^{-1}\) (Figure 2). Scanning anodically from the rest potential, no observable oxidation events are initially observable in the solvent window of the experiment. Upon reduction however, both the \( \text{AsP}_3 \) and \( \text{P}_4 \) solutions show a single oxidation wave. Repeated scanning causes the oxidation events to grow in intensity and shift slightly in potential, suggesting that they are a result of electropolymerization or some other complicating process. The observed stabilization of the \( \text{AsP}_3 \) LUMO renders reduction chemistry more facile and is certainly a contributor to the enhanced reactivity of \( \text{AsP}_3 \) as compared to \( \text{P}_4 \).

Figure 1. Cyclic Voltammogram of \( \text{P}_4 \) (blue) and \( \text{AsP}_3 \) (red).

0.25 M [NBu\(_4\)][PF\(_6\)] in THF at 20 °C, sweep rate 300 mV s\(^{-1}\), referenced vs Fc/Fc\(^+\), \( \text{AsP}_3 \) purified by sublimation (red), \( \text{P}_4 \) purified by recrystallization (black).
Closer scrutiny of the molecular orbital diagrams of AsP$_3$ and P$_4$ gives additional insight into the differences of these two related molecules (Figure 2). We find that the HOMO-LUMO energy gap of AsP$_3$ is smaller in magnitude by 0.40 eV as compared to that for P$_4$ (Figure 2). The lower energy HOMO-LUMO gap of AsP$_3$ is manifest experimentally in the $^{31}$P NMR spectrum. Based on the electron density distribution in AsP$_3$, it might be expected that the presence of the more electropositive As atom would increase the electron density at the phosphorus nuclei causing the remaining three phosphorus atoms to be more shielded and resonate at higher field relative to P$_4$. This, however, is not the case. In benzene solution, P$_4$ resonates at $-520$ ppm in the $^{31}$P NMR spectrum while the phosphorus atoms of AsP$_3$ resonate at $-484$ ppm. A decomposition of the NMR shielding terms, as calculated with ADF, reveals that the paramagnetic shielding term is the dominant contributor to the chemical shift (Table 1). The paramagnetic shielding term of AsP$_3$ is more negative by approximately 40 ppm. This decrease in the paramagnetic term arises from greater coupling of the virtual and occupied orbitals due to the

![Molecular orbital diagrams for AsP$_3$ (left) and P$_4$ (right). Both diagrams were calculated using C$_{3v}$ symmetry to allow for direct comparison of the calculated orbitals.](image)

**Figure 2.** Molecular orbital diagrams for AsP$_3$ (left) and P$_4$ (right). Both diagrams were calculated using C$_{3v}$ symmetry to allow for direct comparison of the calculated orbitals.
decrease in the HOMO-LUMO gap (HLG). Thus, it is the HLG, not the electron density at P, that is responsible for the observed chemical shift difference between P$_4$ and AsP$_3$.

**Table 1.** NMR shielding tensors for AsP$_3$ and P$_4$.

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<th>$\sigma_{\text{dia}}$</th>
<th>$\sigma_{\text{para}}$</th>
<th>$\sigma_{\text{SO}}$</th>
<th>HLG</th>
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<td>954.694</td>
<td>-151.744</td>
<td>17.372</td>
<td>4.58 eV</td>
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<tr>
<td>P$_4$</td>
<td>953.301</td>
<td>-111.418</td>
<td>16.116</td>
<td>4.98 eV</td>
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An additional electronic property of note for comparison between P$_4$ and AsP$_3$ is the degree of spherical aromaticity harbored by these clusters. Hirsch and coworkers have previously applied the concept of spherical aromaticity to a variety of $T_d$ cage molecules including P$_4$ by calculating the nucleus-independent chemical shift (NICS) at the cage critical point. The NICS value for P$_4$ is known by this method to be large and negative, indicative of spherical aromaticity and large diamagnetic ring currents in the cluster. Following location of the cage critical points in P$_4$ and AsP$_3$, we find that the NICS value calculated for P$_4$, $-59.444$, is only one unit more negative than that found for AsP$_3$, $-58.230$. This indicates that despite the lowering in molecular symmetry upon going from P$_4$ to AsP$_3$, a great deal of spherical aromaticity is retained. The retention of spherical aromaticity is partially due to the fact that AsP$_3$, like P$_4$, maintains closed shell $\sigma$ and $\pi$ subsystems resulting in symmetrically distributed angular momenta (Figure 2).

That the degree of spherical aromaticity in AsP$_3$ is not diminished relative to P$_4$ implies that the presence of the single As atom does not greatly perturb the charge distribution. There are two limiting views of the charge distribution in AsP$_3$: one view is that AsP$_3$ contains an As$^{3+}$ ion supported by a P$_3^{3-}$ unit, while an alternative view is that AsP$_3$ contains neutral P atoms and a neutral As atom. Calculations using the AIM method have suggested that the phosphorus atoms of AsP$_3$ harbor a very slight negative charge of $-0.04 \ e$ and the arsenic atom makes up the balance, having a slight positive charge of $+0.12 \ e$. Table 2 compiles the charge descriptions given by the AIM method, as well as the Hirshfeld and Voroni Deformation Density methods. All three methods give generally good agreement of the assigned charges and support the description that AsP$_3$ contains a neutral As atom and three neutral P atoms. This
charge distribution informs our description of AsP$_3$ as a soluble, molecular combination of these two elements. This analysis is in agreement with more simple interpretations based on Pauling electronegativities (P, 2.19 and As, 2.18), as well as with more complicated theoretical descriptions (Supporting Information Figure 1S).$^{27,28}$

Table 2. Calculated atomic charges for AsP$_3$.

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<th>Hirshfeld (e)</th>
<th>Voroni (e)</th>
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<td>As</td>
<td>+0.126</td>
<td>+0.0461</td>
<td>+0.051</td>
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<tr>
<td>P</td>
<td>−0.042</td>
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In order to obtain a more quantitative depiction of the As–P and P–P bond energies in AsP$_3$, we investigated the heats of atomization of AsP$_3$, As$_2$P$_2$, As$_3$P, P$_4$, and As$_4$, in order to calculate average bond energies for these species.$^{27}$ Bond energies are computed as an energy difference between the molecule and the single atoms. The individual atoms are computed as spherically symmetric and spin-restricted.$^{29}$ In order to accurately represent the true atomic ground state, we calculated the fragment energy of a single P atom with three $\alpha$ spins ($^4S$ ground state).$^{29}$ After correction for the true atomic
ground state and for the zero point energy of the molecule, we obtained reliable and accurate heats of atomization as shown in Table 3. These data permit estimation of the bond dissociation energies; for example, the P$_4$ molecule is composed of six P–P bonds, so division of the heat of atomization of P$_4$ by six gives an estimate of the P–P bond energy. Our calculations put the P–P bond energy of P$_4$ at 47 kcal mol$^{-1}$, which compares favorably with the 47 kcal mol$^{-1}$ obtained from experimental values. Using this energy for the P–P bonds, we can extend our method to AsP$_3$. Following subtraction of 3 P–P single bond energies from the heat of atomization we computed for AsP$_3$, we are left with 3 As–P bonds; with an estimated bond dissociation energy of 41 kcal mol$^{-1}$ each. Similarly, the As–As bonds of As$_4$ were found to have bond dissociation energies of 36 kcal mol$^{-1}$. Keeping the P–P and As–As bond energies constant, extraction of P–As bond energies from the heats of atomization of As$_2$P$_2$ and As$_3$P give the same value of 41 kcal mol$^{-1}$ (Table 3). In summary, our calculations indicate that the As–P bonds of AsP$_3$ are 6 kcal mol$^{-1}$ weaker than the P–P bonds of P$_4$ (and 5 kcal mol$^{-1}$ stronger than the As–As bonds of As$_4$). This is in agreement with our observations of the enhanced reactivity of these bonds (vide infra) relative to P$_4$ as well as reported values for typical P–P, P–As, and As–As single bond strengths.

From the calculated values for heats of atomization and the known heats of formation of the As and P atoms at 0 K, we are able to extract estimated heats of formation at 0 K for As$_n$P$_{4-n}$ by summation of the experimental heats of formation of the constituent atoms followed by subtraction of the calculated heats of atomization (Table 3). As would be expected, there is a monotonic increase in the standard heats of formation with increasing $n$ (Table 3, Figure 3). This trend in heats of formation begins to shed light on the thermodynamic stability of these tetrahedral pnictogen molecules and shows that upon increasing the arsenic content there is a significant price to pay for formation of As$_n$P$_{4-n}$ from the elements in their standard states.
<table>
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<th>Bond Energy Calculated $^b$ kcal mol$^{-1}$</th>
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<td>284</td>
<td>P–P 47</td>
<td>17</td>
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<td>$\text{AsP}_3$</td>
<td>266</td>
<td>P–P 47</td>
<td>32</td>
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<td>As–P 41</td>
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<tr>
<td>$\text{As}_4$</td>
<td>220</td>
<td>As–As 36</td>
<td>68</td>
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$^a$ Heat of atomization = |total bonding energy $\text{As}_n\text{P}_{4-n}$| $-|n \text{ (energy }^4\text{S As atoms)} + (4-n \text{ (energy }^4\text{S P atom)}| - |Zero point energy|

$^b$ Heat of atomization / 6; $^c$ $\Delta_fH_0^o = \sum(\Delta_fH_0^o \text{ constituent atoms}) / 6$ – Heat of atomization

**Reactivity Studies.**

A series of reactivity studies have been carried out with $\text{AsP}_3$. The reactions chosen have previously been successfully carried out with $\text{P}_4$ and include thermolysis, adduct formation, single bond cleavage reactions by transition metal and organic radicals, and molecule activation with $\text{Nb(H)}(\eta^2$-$^1\text{Bu(H)}\text{C=NAr})(\text{N[CH}_2^2\text{Bu]}\text{Ar})_2$ ($\text{Ar} = 3,5-$Me$_2$C$_6$H$_3$), $\text{Mo(N[}^2\text{Bu]}\text{Ar})_3$, and $\text{Cl}_2\text{Nb(ODipp)}_3$ under reducing conditions. In looking at such a class of reactions we hope to compare the reactivity patterns of $\text{P}_4$ and $\text{AsP}_3$ in light of their contrasting physical and electronic properties as elucidated in the theoretical studies.

**Thermolysis of $\text{AsP}_3$.**

Amorphous red phosphorus was first obtained in 1848 by heating $\text{P}_4$ in the absence of air for several days at high temperatures, and is now made on a commercial scale of 7000 tons per year by a similar thermal conversion process. Red phosphorus is much less toxic and much less reactive than monomeric white phosphorus and it is extensively used in the production of matches, flame retardants, and phosphide materials for semiconductor applications. Semiconductor applications account for a majority of red phosphorus consumption, with aluminum phosphide production accounting for over...
24% of the total consumption. Much of this aluminum phosphide is further alloyed with species such as gallium arsenide to tune the semiconductor band gap.\textsuperscript{1,2}

Polymeric forms of P/As alloys are exceedingly rare.\textsuperscript{33,34} Intrigued by the possibility of a “red AsP\textsubscript{3},” phase wherein one out of every four sites in red P would be occupied by an As atom, we subjected AsP\textsubscript{3} to the same conditions under which P\textsubscript{4} converts to red P. Heating a sealed tube containing white AsP\textsubscript{3} to 300 °C for 36 h resulted in apparent segregation of the elements, producing amorphous metallic arsenic and amorphous red phosphorus, as determined by Raman spectroscopy (diagnostic for red P\textsuperscript{35}), powder XRD analysis (diagnostic for amorphous metallic As\textsuperscript{36}), and EDS elemental analysis of the bulk material (Figure 4). The EDS elemental map shown in Figure 4 shows distinct regions where only phosphorus (red) and only arsenic (green) are sequestered; however, there are some regions (yellow) where the two species may be found together, suggestive of incomplete separation. Repetition of this experiment on a variety of scales gave highly reproducible results.

\textbf{Figure 4.} Thermal decomposition of AsP\textsubscript{3} to metallic arsenic and red phosphorus. A). Raman spectra of the product of heating AsP\textsubscript{3} (black) and an authentic sample of red phosphorus (red). B). Powder XRD data for the product of heating AsP\textsubscript{3}. C). Photographs of the reaction vessel before heating (bottom) and after heating (top). D). Elemental mapping by EDS analysis using an SEM microscope.
Thermal decomposition of AsP$_3$ to the elements is quite surprising and the mechanism by which this occurs is not known. One possibility is that under thermal conditions four molecules of AsP$_3$ disproportionate to give rise to three molecules P$_4$ and one molecule of As$_4$, which themselves then revert to red phosphorus and metallic arsenic. From our calculated heats of formation (Figure 2), we can get an estimate for the heat of disproportionation of four molecules of AsP$_3$ to give three molecules of P$_4$ and one molecule of As$_4$. In so doing we find that the process is downhill by 7.42 kcal mol, suggesting that the kinetic stability of AsP$_3$ is quite important in its isolability, as thermodynamically it is only metastable. An alternative mechanism might involve the formation of “red AsP$_3$”, which is not itself thermally robust, reverting to red phosphorus and metallic arsenic. It may be speculated that an alternative to the thermal pathway may yet be successful in leading to a red polymeric form of AsP$_3$, and preliminary studies on AsP$_3$ polymerization by radical initiators and UV light are under way.

**Coordination chemistry of AsP$_3$.**
In our initial report on the facile synthesis of AsP₃, we used the complex \((\mu-N_2)[Mo(CO)_3(P'iPr_3)_2]\) to complex the AsP₃ tetrahedron and to provide a structural glimpse of the intact tetrahedron (Scheme 2, i). Unfortunately, the AsP₃ adduct, \((AsP₃)Mo(CO)_3(P'iPr_3)_2\) was unstable above 0 °C and for that reason was difficult to work with. Additionally, accurate determination of the As–P interatomic distances in \((AsP₃)Mo(CO)_3(P'iPr_3)_2\) was hampered by a 70:30 disorder between the As atom and one of the two non-complexed P atoms in the tetrahedron. Thus, we sought to synthesize a more thermally stable adduct of AsP₃ and hoped to obtain accurate metrical parameters from an ordered crystal structure.

The precursor FeCp*(dppe)Cl, which had been reported to form a stable P₄ adduct, has allowed us to realize this goal. Treatment of dark green FeCp*(dppe)Cl with 1 equiv of AsP₃ in THF results in a gradual color change to brown over 20 minutes. Subsequent treatment of the reaction mixture with 1 equiv of NaBPh₄ results in an immediate color change to bright magenta. Following removal of the NaCl byproduct, \([(AsP₃)FeCp*(dppe)][BPh₄]\), 1, was isolated in 80% yield by recrystallization of the

![Figure 5. Solid-state structure of complex 1 shown with 50% probability thermal ellipsoids. A). View of the \([(AsP₃)FeCp*(dppe)]^+\) core. B). View of the asymmetric unit. Hydrogen atoms and CH₂Cl₂ solvent residues omitted for clarity.](image-url)
crude solids from 1:1 Et$_2$O:THF (Scheme 2, ii). X-ray diffraction quality crystals of 1 were grown from a mixture of THF and CH$_2$Cl$_2$ at −35 °C over the course of several days. The X-ray structure of 1 (Figure 5) displays a fully ordered AsP$_3$ tetrahedron in an η$^1$ binding mode at a phosphorus vertex (Table 1S). The solid-state structure of 1 is consistent with the solution-state configuration of the AsP$_3$ unit as assigned by NMR spectroscopy (Supporting Information Figure 2S). The P12–As1 and P12–P13,14 distances in 1 are 2.283(2) Å and 2.183(3) Å, respectively, and are noticeably shorter than typical P–As and P–P single bonds. The other As–P and P–P bonds are noticeably longer with As1–P13 at 2.334(2) Å, As1–P14 at 2.336(2) Å, and P13–P14 at 2.231(3) Å. The shortened bond lengths to P12 are the effect of rehybridization that occurs upon AsP$_3$ binding to the Fe center, producing greater 3s character in the bonding molecular orbitals of this four-coordinate phosphorus atom. It is noteworthy that the Fe1-P12 interatomic distance of 2.172(2) Å is significantly shorter than the Fe-phosphine bond distances at 2.233(2) Å and 2.242(2) Å.

**As–P bond cleavage reactions.**

The estimated 6 kcal mol$^{-1}$ difference in energy between the As–P bonds and the P–P bonds in AsP$_3$ suggests that reactions resulting in selective As–P bond cleavage may be possible. Several systems are known to promote radical opening of the P$_4$ tetrahedron to produce substituted tetraphosphabicyclobutane structures. A noteworthy example of this reaction type was reported by
Lappert and coworkers and uses (P(N(Pr)2)N(SiMe3)2)2 as a source of the phosphorus radical •P(N(Pr)2)N(SiMe3)2, which was shown to activate P4 to produce the corresponding 1,4-bis(phosphido)tetrabiphosphabicyclobutane. While activation of P4 by (P(N(Pr)2)N(SiMe3)2)2 requires somewhat harsh conditions (refluxing in toluene for 1.5 h), the corresponding reaction with AsP3 is rapid at room temperature. Upon mixing (P(N(Pr)2)N(SiMe3)2)2 with 1 equiv of AsP3 in toluene the initially colorless reaction mixture turns bright yellow. NMR spectroscopic analysis of the crude reaction mixture shows clean and quantitative conversion to AsP3(P(N(Pr)2)N(SiMe3)2)2 (set of isomers), 2, in which a single As–P bond has been selectively cleaved, as assigned by 31P NMR spectroscopy (Scheme 3, i and Figure 3S). Recrystallization of the crude reaction mixture from n-hexane/Et2O gave crystalline 2 in 88% yield. X-ray crystallographic analysis on a single crystal of 2 confirmed the selective As–P bond cleavage as shown in Figure 6 and Table 2S. The geometrical parameters of the arsatriphosphabicyclobutane core of 2 are nearly isomorphous with the all-phosphorus analog as reported by Lappert and coworkers. A discussion of accurate P–P and As–P bond lengths is precluded by disorder in the crystal structure of 2. Notably, there is a positional disorder of As1 and P1, but there is no As component to the P2 or P3 positions.

Figure 6. Solid-state structure of compound 2 with 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity.
The bright green Ti(III) reagent Ti(N[\textit{t}Bu]Ar)\textsubscript{3} (Ar = 3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) has proven to be a potent metalloradical and one-electron reductant since its first synthesis by reduction of the corresponding C\textsubscript{3}Ti(N[\textit{t}Bu]Ar)\textsubscript{3} complex in 1995.\textsuperscript{39-43} Given the facile radical opening of the AsP\textsubscript{3} tetrahedron with (P(N(\textit{i}Pr)\textsubscript{2})N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}, we hypothesized that Ti(N[\textit{t}Bu]Ar)\textsubscript{3} would be a good candidate for forming a 1,4-bis(metallo)arsatriphospha bicyclobutane. In fact, Ti(N[\textit{t}Bu]Ar)\textsubscript{3} does react with AsP\textsubscript{3} to generate the desired 1,4-bis(metallo)arsatriphosphabicyclobutane, AsP\textsubscript{3}(Ti(N[\textit{t}Bu]Ar)\textsubscript{3})\textsubscript{2}, 3-AsP\textsubscript{3}, in which a single As–P bond has been cleaved selectively; however, the reaction does not go to completion. Instead, an equilibrium is established between AsP\textsubscript{3}, Ti(N[\textit{t}Bu]Ar)\textsubscript{3}, and 3-AsP\textsubscript{3} (Scheme 3, ii). This equilibrium was studied by \textsuperscript{31}P NMR spectroscopy at a variety of concentrations and temperatures. In all cases the equilibrium favored the reactants, with 3-AsP\textsubscript{3} never accounting for more than 30% of the reaction mixture (Figure 4S, 14S, 15S).\textsuperscript{44} The analogous reaction with P\textsubscript{4} likewise gave an equilibrium mixture, but the 1,4-bis(metallo)tetraphosphabicyclobutane product, P\textsubscript{4}(Ti(N[\textit{t}Bu]Ar)\textsubscript{3})\textsubscript{2}, 3-P\textsubscript{4}, never accounted for more than 5% of the reaction mixture under identical conditions. Although no intermediates were detected in these equilibria, the systems did not conform to the simple equilibrium expression, $K_{eq} = \frac{3}{[Ti(N[\textit{t}Bu]Ar)\textsubscript{3}]^2[EP\textsubscript{3}]}$ (E = As, P), suggesting that more complicated processes are at work. It should be noted that the concentration of Ti(N[\textit{t}Bu]Ar)\textsubscript{3} was obtained by subtraction of 2[3-E\textsubscript{4}] from [Ti(N[\textit{t}Bu]Ar)\textsubscript{3}]\textsubscript{0}. In direct competition reactions, the tendency of Ti(N[\textit{t}Bu]Ar)\textsubscript{3} to react with EP\textsubscript{3} (E = P, As) to form the radical-opened bicyclobutane derivatives, 3-AsP\textsubscript{3} and 3-P\textsubscript{4}, revealed a measurable preference for edge-opening of AsP\textsubscript{3}, (Figure 14S and 15S), consistent with heightened reactivity for AsP\textsubscript{3} over P\textsubscript{4} (vide supra). One hypothesis for why Ti(N[\textit{t}Bu]Ar)\textsubscript{3} is unsuccessful at driving the radical cleavage of either P\textsubscript{4} or AsP\textsubscript{3} fully to 3-EP\textsubscript{3} (E = P, As) is centered upon the unfavorable loss in entropy inherent in forming a single product molecule from three reactant molecules. The interaction between the hard titanium(IV) metal center and the soft phosphorus (or arsenic) center does not provide a large enough enthalpic contribution to counterbalance the entropic losses incurred.

Formation of $\mu_2$:$\eta^2$:$\eta^2$-E\textsubscript{2}Nb\textsubscript{2} complexes (E = As, P).
The activation of white phosphorus by early-transition-metal complexes has been a prolific area of investigation in recent years.\textsuperscript{45-48} Included among these are niobium complexes bearing three monoanionic ligands. This class of complexes has given rise to a wide array of \( P_n \) ligands (\( n = 1 – 8 \)).\textsuperscript{3,45,49,50} The metallaziridine(hydride) derivative, \( \text{Nb}(\text{H})(\eta^2 \cdot \text{Bu}(\text{H})\text{C}=\text{NAr})(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_2 \) (\( \text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3 \)), was found to react with 0.25 equiv of white phosphorus to quantitatively give rise to the corresponding \( (\mu_2:\eta^2,\eta^2-P_2)[\text{Nb}(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_3]_2 \) complex, which has a diagnostic phosphorus NMR resonance at 399 ppm in \( \text{C}_6\text{D}_6 \). Because of the high efficiency of this reaction it seemed to be an ideal candidate for reactivity tests with \( \text{AsP}_3 \), with an eye towards formation of \( (\mu_2:\eta^2,\eta^2-P_2)[\text{Nb}(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_3]_2 \) and \( (\mu_2:\eta^2,\eta^2-\text{AsP})[\text{Nb}(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_3]_2 \) in a 1:1 ratio. In fact, treatment of bright yellow \( \text{Nb}(\text{H})(\eta^2 \cdot \text{Bu}(\text{H})\text{C}=\text{NAr})(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_2 \) with a slight excess (0.35 equiv) of \( \text{AsP}_3 \) results in clean and complete conversion to the expected 1:1 green mixture of products, \( (\mu_2:\eta^2,\eta^2-P_2)[\text{Nb}(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_3]_2 \), 4-P, and \( (\mu_2:\eta^2,\eta^2-\text{AsP})[\text{Nb}(\text{N}[\text{CH}_2\text{Bu}]\text{Ar})_3]_2 \), 4-AsP, over the course of 90 min (Scheme 4). \( ^{31}\text{P} \) NMR spectroscopic analysis of the crude reaction mixture shows exclusively two resonances in a 2:1 ratio at 399 and 438 ppm, respectively (Figure 5S). Assignment of the resonance at 438 ppm to 4-AsP was corroborated by DFT NMR shielding calculations.\textsuperscript{28} This reaction provides access to a rare AsP ligand bridging two niobium metal centers and future work with 4-AsP will be aimed at identifying reactions in which the AsP unit is released.\textsuperscript{51-53}
Formation of terminal E≡M complexes (E = As, P).

P₄ degradation to P₁ units has been observed in the treatment of the reactive Mo(III) precursor Mo(N[³Bu]Ar)₃ with 0.25 equiv of P₄ to give the P≡Mo(N[³Bu]Ar)₃ complex." Access to the arsenide congener of P≡Mo(N[³Bu]Ar)₃ is also afforded by the corresponding reaction with As₄, however, this experiment is challenging as As₄ is unisolable." A soluble, isolable source of As⁰ would be preferable to obtain a stoichiometric transformation to the terminal arsenide complex, and AsP₃ proves to be an effective source of a single As⁰ equivalent. Treatment of Mo(N[³Bu]Ar)₃ with a slight excess of AsP₃ (0.29 equiv) results in formation of a 1:3 mixture of As≡Mo(N[³Bu]Ar)₃, 5-As, and P≡Mo(N[³Bu]Ar)₃, 5-P, over the course of 1 h (Scheme 5). The ¹H NMR spectroscopic features for 5-As and 5-P are coincident, but the corresponding ¹³C NMR spectroscopic features are distinct and reveal that the reaction cleanly forms 5-As and 5-P in a 1:3 ratio (Figure 6S). Interestingly, it was found that in 1:1 competition experiments of AsP₃ and P₄ with Mo(N[³Bu]Ar)₃, there is no selectivity for reaction with AsP₃ over P₄ (Figure 16S). This is a striking example of a reaction in which AsP₃ does not give enhanced reactivity over P₄, and is an interesting case. The reaction of AsP₃ with Mo(N[³Bu]Ar)₃ gives us clear proof that AsP₃ functions experimentally as a soluble source of As⁰ and P⁰ and also provides motivation for future studies in the synthesis of precise 3:1 mixtures of metal phosphides and metal arsenides for materials applications." "

Formation of cyclo-E₃ complexes (E = As, P), As₂P₂, and As₃P.

Our original synthesis of AsP₃ involved treatment of an anionic niobium cyclo-P₃ complex with AsCl₃ to obtain the tetraatomic tetrahedron. Since that discovery, we have been interested in preparing

Scheme 5
other anionic cyclo-E₃ compounds, in particular an anionic cyclo-As₂P complex. Such a species could, in principle, be used to synthesize the previously unexplored tetraatomic interpnictides As₂P₂ and As₃P by treatment of the cyclo-As₂P derivative with the appropriate ECl₃ reagent (E = P, As). Strides in this direction have been made by investigating the reaction between AsP₃ and Cl₂Nb(ODipp)₃ in the presence of a reducing agent.³⁵⁻⁹ Combining AsP₃ with Cl₂Nb(ODipp)₃ in a 1:1 ratio in THF followed by treatment with Na/Hg amalgam gives rise to a mixture of [Na][P₃Nb(ODipp)₃], ⁶-P₃, [Na][AsP₂Nb(ODipp)₃], ⁶-AsP₂, [Na][As₂PNb(ODipp)₃], ⁶-As₂P, and, presumably, [Na][As₃Nb(ODipp)₃], ⁶-As₃, over the course of 30 min. Evidence for formation of ⁶-P₃, ⁶-AsP₂, and ⁶-As₂P in a 10:5:1 molar ratio (76% yield from Cl₂Nb(ODipp)₃) is provided by the clean appearance of three singlets in the ³¹P NMR spectrum of the crude reaction mixture, spaced as expected for sequential As-doping of the cyclo-P₃ complex (vide supra) at −206 (⁶-P₃), −167 (⁶-AsP₂), and −132 ppm (⁶-As₂P) (Figure 7S). From the considerable concentration of the unexpected ⁶-As₂P (and from subsequent analysis, vide infra), we propose that ⁶-As₃ is also present in low concentration. Treatment of this crude reaction mixture with AsCl₃ with the exclusion of light rapidly generated a reaction mixture containing Cl₂Nb(ODipp)₃(THF) and the tetraatomic interpnictides AsP₃, As₂P₂, As₃P, as well as As₄ (Scheme 6).⁶⁰ The presence of the four tetrahedral molecules is confirmed by ³¹P NMR spectroscopy and by GC-MS (Table 4, Figure 7 and Figures 8S – 13S). It is of note that the ratio of As to P atoms in the final product
mixture is 1 to 1.6, which is very near the 1 to 1.3 ratio that we would expect (¾ AsP₃ + AsCl₃) over the course of the two reactions. This is an important observation that implies that there is no selective loss of As or P atoms during the synthesis. We are currently investigating alternative syntheses of As₂P₂ and As₃P for exploration of these molecules as pure substances.

Table 4. NMR and GC-MS data for synthesis of AsP₃, As₂P₂, As₃P, and As₄.

<table>
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<tr>
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<th>P₄ (internal standard)</th>
<th>AsP₃</th>
<th>As₂P₂</th>
<th>As₃P</th>
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<td>³¹P Shift (ppm)</td>
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<td>Calculated ³¹P Shift (ppm)</td>
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<td>−482</td>
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<td>−424</td>
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<td>GC-MS retention time a</td>
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<td>300</td>
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<tr>
<td>GC-MS area (a.u.)</td>
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<td>30475</td>
<td>11348</td>
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<td>~1977</td>
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<tr>
<td>Yield b</td>
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<td>49% c</td>
<td>39% d</td>
<td>50% e</td>
<td>2% f</td>
</tr>
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</table>

a GC-MS data were collected using an Agilent 6890N network GC system with an Agilent 5973 Network mass selective detector and an Rtx-1 column from Restek. b Yields of AsP₃, As₂P₂, and As₃P are calculated from the corresponding starting concentration of 6-E₃; in each case the theoretical yield is 100%; for As₄ the yield is calculated from the starting concentration of Cl₂Nb(ODipp)₃ making the theoretical yield << 100%. c GCMS yield from 6-AsP₃; d GCMS yield from 6-As₂P₂; e GCMS yield from Cl₂Nb(ODipp)₃

Conclusions and Future Directions.

For the first time, the reaction chemistry of the interpnictide compound AsP₃ has been investigated. In the presence of Lewis acidic metal fragments, adduct formation is selective for binding at a single phosphorus vertex, and reducing main group and transition metal species effect radical cleavage reactions where a single As–P bond is selectively cleaved. Furthermore, AsP₃ can be used to prepare otherwise difficult to access mixed As/P molecules, both as free entities, in the case of the mixed interpnictides AsₙP₄₋ₙ (n = 1-3), or as coordinated ligands, in the case of 4-AsP. The electronic and structural features that render AsP₃ distinct from P₄ are consistent with the reactivity patterns that have emerged. In particular, we have been able to distinguish between the vertices of the AsP₃ molecule in the formation of compounds 1 and 2. DFT calculations have provided us insight into the electronic structure of this unique tetraatomic molecule and have provided us with estimates of important thermodynamic parameters. We are currently investigating the use of AsP₃ in the synthesis of solid-state, mixed arsenide-phosphide materials as well as a “red AsP₃” phase, both of which may be of
interest for the development of novel semiconductor materials. Future work will target the directed synthesis of the new interpnictides As$_2$P$_2$ and As$_3$P reported herein as well as further unveil the diverse reaction chemistry of AsP$_3$.

**Experimental Details.**

**General Considerations.** All manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N$_2$. All solvents were obtained anhydrous and oxygen-free by bubble degassing (N$_2$) and purification through columns of alumina and Q5. Deuterated solvents were purchased from Cambridge Isotope Labs. Benzene-$d_6$ and toluene-$d_8$ were degassed and stored over molecular sieves for at least 2 d prior to use. Celite 435 (EM Science) were dried by heating above 200 °C under a dynamic vacuum for at least 24 h prior to use. AsP$_3$, $^4$Mo(N[']Bu]Ar)$_3$, $^{63}$Ti(N[']Bu]Ar)$_3$, $^{43}$Cl$_2$Nb(ODipp)$_3$, $^{61}$Nb(H)(η$^2$-Bu(H)C=NAr)(N[CH$_2$Bu]Ar)$_3$, $^{3,37,38,40,59,61,62}$ (PN(Pr)$_2$N(SiMe$_3$)$_2$)$_2$, $^{41}$ and FeCp*(dppe)Cl, $^{40}$ were synthesized according to reported methods. All

![Figure 7. GC-MS chromatogram following treatment of in situ generated 6-P$_3$, 6-AsP$_2$, 6-As$_2$P, and 6-As$_3$ with AsCl$_3$. P$_4$ added as an internal standard.](image.png)
glassware was oven-dried at temperatures greater than 170 °C prior to use. NMR spectra were obtained on Varian Inova 500 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C₆D₆ (¹H = 7.16 ppm, ¹³C = 128.06 ppm) or (CD₃)₂CO (¹H = 2.05 ppm, ¹³C = 29.84 ppm). ³¹P NMR spectra were referenced externally to 85% H₃PO₄ (0 ppm). Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN. UV-Vis spectra were obtained on a Hewlett Packard 845x series UV-Vis system equipped with a tungsten lamp. GC-MS data were collected using an Agilent 6890N network GC system with an Agilent 5973 Network mass selective detector and an Rtx-1 column from Restek. MALDI-TOF MS data were collected on a Bruker OmniFlex instrument and data were processed using the Bruker FlexControl software package. For Raman studies, an Invictus solid state laser at 785 nm, manufactured by Kaiser Optics, was routed through fiber optic cables to a Hololab series 5000 Raman Microscope. The Raman scattering was observed via 180° reflectance through the objective of the Raman microscope. Each spectrum was corrected for dark current and cosmic ray interference using the Hololab software. Powder diffraction data were collected on a PANalytical X’Pert Pro multipurpose diffractometer equipped with a 1.8 kW sealed tube X-ray source using Mo Ka radiation (λ = 0.71073 Å) and equipped with high-speed Bragg Brentano optics. Scanning electron microscopy was performed on a JEOL JSM-5910 instrument using a JEOL BEI detector and a Rontec EDX system for elemental analysis and mapping.

**Thermolysis of AsP₃.** AsP₃ (100 mg) was loaded into a thick walled glass tube. The tube was sealed under vacuum. The tube was wired to a thermocouple probe and the probe and tube were wrapped completely with heating tape. The heating tape was set to heat at 290 – 300 °C for 40 h. After this time the apparatus was cooled and the heating tape was removed. The white–yellow AsP₃ had been converted to a red-black material as well as a metallic shiny material which had sublimed partially up the tube. Raman spectroscopy of the bulk material through the tube revealed complete consumption of the AsP₃ tetrahedron. The tube was scored and broken open. The contents of the tube were removed and placed on a zero background silicon 510 surface for powder diffraction. Powder diffraction data: broad peaks
centered around 18 °, 32 °, 58 °, and 90 ° 20. The product mixture was then also analyzed by Raman spectroscopy and EDS using a JEOL SEM microscope. Raman spectroscopy results: broad and weak resonance at 280 cm\(^{-1}\), sharp and intense resonance at 320 cm\(^{-1}\), broad and intense resonances extending from 340 cm\(^{-1}\) to 500 cm\(^{-1}\). SEM data: in a 50 μm × 50 μm region, elemental composition analysis gave Phosphorus 74.01% (error 0.66%) and Arsenic 25.98% (error 0.76%).

\[(\text{AsP}_3\text{FeCp}^*(\text{dppe})][\text{BPh}_4],\] 1. FeCp*(dppe)Cl (144 mg, 0.230 mmol, 1 equiv) was dissolved in 8 mL of THF and was transferred to a vial containing solid AsP\(_3\) (43 mg, 0.256 mmol, 1.1 equiv) and a stir bar. The reaction mixture was allowed to stir for 30 minutes during which time the originally green reaction mixture went slightly orange (subtle change). At this point NaBPh\(_4\) (79 mg, 0.230 mmol, 1 equiv) was added resulting in immediate formation of a bright magenta-purple color. The reaction mixture was allowed to stir an additional 10 min. At this point the reaction mixture was concentrated and \(n\)-pentane was added to help precipitate the salt. The reaction mixture was filtered through a plug of Celite and the volatile components were concentrated to 5 mL. Et\(_2\)O (3 mL) was added and the purple solution was placed in the freezer to induce precipitation. After 30 min, a copious magenta precipitate had formed. This precipitate was isolated atop a frit resulting in 198 mg (0.183 mmol) of material (80% yield). X-ray diffraction quality crystals were grown from a Et\(_2\)O/CH\(_2\)Cl\(_2\) (1:1) solution at −35 °C. \(^1\)H NMR (20 °C, acetone-\(d_6\), 500 MHz): \(\delta = 1.48\) (15H, s, Cp*-Me), 2.61 (2H, m, dppe-CH\(_2\)), 2.75 (2H, m, dppe-CH\(_2\)), 6.77 (m, 8H, Ar), 6.91 (m, 12H, Ar), 7.34 (br, 8H, Ar), 7.50 (br, 4H, Ar), 7.61 (br, 8H, Ar).

\(^{31}\)P\(\{^1\)H\}\) NMR (20 °C, acetone-\(d_6\), 202.5 MHz): \(\delta = -450\) (2P, d, \(J_1 = 245\) Hz, non-Fe bound P), −261 (1P, tt, \(J_1 = 245\) Hz, \(J_2 = 37\) Hz, Fe-bound P), 89 (2P, d, \(J_2 = 37\) Hz, dppe-P). \(^{13}\)C\(\{^1\)H\}\) NMR (20 °C, acetone-\(d_6\), 125.8 MHz): \(\delta = 10.6\) (s, Cp*-Me), 29.5 (t, dppe-CH\(_2\)), 90.7 (s, Cp*-ring), 122.8 (Ar), 126.6 (Ar), 129.6 (Ar), 131.7 (Ar), 133.2 (Ar), 137.6 (Ar), 164.9 (Ar), 165.7 (Ar). UV-Vis: 494 nm (\(\epsilon = 590\) M\(^{-1}\) cm\(^{-1}\)), 543 nm (\(\epsilon = 480\) M\(^{-1}\) cm\(^{-1}\)). MALDI-TOF MS: 757.0318 m/z ([AsP\(_3\)FeCp* (dppe)]\(^+\)), 589.2216 m/z ([FeCp*(dppe)]\(^+\)), 319.1650 m/z ([BPh\(_4\)]\(^-\)). Elem. Anal. Calcd. for C\(_{60}\)H\(_{59}\)AsBFeP\(_3\): C 66.94, H 5.52, P 14.39; Found: C 66.87, H 5.61, P 13.98.
As$_3$P$_3$(P(N(iPr)$_2$)N(SiMe$_3$)$_2$)$_2$, 2. (P(N(iPr)$_2$)N(SiMe$_3$)$_2$)$_2$ (190 mg, 0.295 mmol) was dissolved in 10 mL of toluene and was added slowly to a vial containing a solution of As$_3$P$_3$ (54 mg, 0.321 mmol) in 5 mL of toluene. Upon mixing the two colorless reagents the reaction mixture took on a vibrant yellow color. The mixture was stirred for an additional 20 min and an aliquot was withdrawn for NMR analysis which showed clean and complete conversion of the starting materials to As$_3$P$_3$(P(N(iPr)$_2$)N(SiMe$_3$)$_2$)$_2$.

The reaction mixture was taken to dryness under reduced pressure and the resulting residue was dissolved in n-hexane/Et$_2$O (2:1) and recrystallized affording 196 mg (0.261 mmol, 88% yield) of pale yellow crystals of As$_3$P$_3$(P(N(iPr)$_2$)N(SiMe$_3$)$_2$)$_2$ (mixture of diastereomers).

$^1$H NMR (20 °C, benzene-$d_6$, 500 MHz): $\delta$ = 0.43 (36H, br, SiMe$_3$), 1.03 (12H, m, $^t$Pr-Me), 1.20 (6H, m, $^t$Pr-Me), 1.26 (6H, m, $^t$Pr-Me), 3.34 (2H, m, $^i$Pr-CH), 3.48 (2H, m, $^i$Pr-CH).

$^{31}$P{$^1$H} NMR (20 °C, benzene-$d_6$, 202.5 MHz): $\delta$ = −311 (2P, m, P(P$^t$P)As), −148.5 (1P, m, P(P$^t$P)As), 118.5 (1P, m, As bound phosphine), 123 (1P, m, P bound phosphine).

$^{13}$C{$^1$H} NMR (20 °C, benzene-$d_6$, 125.8 MHz): $\delta$ = 5.1 (br, SiMe$_3$), 6.53 (br, SiMe$_3$), 23.6 (m, $^t$Pr-Me), 24.7 (m, $^t$Pr-Me), 48.2 (m, $^i$Pr-CH). Elem. Anal. Calcd. for C$_{24}$H$_{64}$AsN$_4$P$_5$Si$_4$: C 38.39, H 8.59, N 7.46, P 20.62; Found: C 39.42, H 8.78, N 8.26, P 19.27.

**Treatment of As$_3$P$_3$ (and P$_4$) with Ti(N[tBu]Ar)$_3$, Synthesis of 3-P$_4$ and 3-AsP$_3$.** To begin the measurements, As$_3$P$_3$ (15 mg, 0.09 mmol), P$_4$ (11 mg, 0.09 mmol), PPh$_3$ (12 mg, 0.045 mmol), Ti(N[tBu]Ar)$_3$ (68 mg, 0.118 mmol), and toluene (872 mg) were combined and placed in a J-Young style NMR tube. The temperature was varied between 5 °C and 35 °C, allowing the tube to fully equilibrate before taking the final concentration readings. The simplest equilibrium expression was not obeyed, but the product concentration for 3-AsP$_3$ was always higher than for 3-P$_4$. For example, at 20 °C 3-AsP$_3$ and 3-P$_4$ were present in a 7:1 ratio (Figure 14S). These results show that in a 1:1 mixture of As$_3$P$_3$ and P$_4$, a greater percentage of As$_3$P$_3$ undergoes reaction. This experiment was repeated with only As$_3$P$_3$ in the reaction mixture and alternatively with only P$_4$ present to obtain clean NMR spectral data for both 3-AsP$_3$ and 3-P$_4$. $^{31}$P{$^1$H} NMR (As$_3$P$_3$[Ti(N[tBu]Ar)$_3$], 20 °C, benzene-$d_6$, 202.5 MHz): $\delta$ = −275 (2P, d, $J_1$ = 200 Hz, P(P$^t$P)As), −9.6 (1P, t, $J_1$ = 200 Hz, P(P$^t$P)As). $^{31}$P{$^1$H} NMR
Treatment of AsP₃ with Nb(H)(η²-Bu(H)C=NAr)(N[CH₂Bu]Ar)₃, Synthesis of 4-AsP and 4-P₂.

Nb(H)(η²-Bu(H)C=NAr)(N[CH₂Bu]Ar)₃ (113 mg, 0.17 mmol) was dissolved in 5 mL of Et₂O and was added to a vial containing AsP₃ (10 mg, 0.06 mmol) and a stir bar. The reaction mixture was vigorously stirred for 90 min during which time the originally yellow solution took on a deep green color. The volatile components of the reaction mixture were removed under reduced pressure. The resulting green powder was taken up in C₆D₆ for NMR analysis. Recrystallization from Et₂O/C₅ (1:2) afforded 98 mg (82% yield) of a 1:1 mixture of (μ₂:η²,η²-P₂)[Nb(N[CH₂Bu]Ar)₃]₂ and (μ₂:η²,η²-AsP)[Nb(N[CH₂Bu]Ar)₃]₂. 

1H NMR (20 °C, benzene-d₆, 500 MHz): δ = 6.98 (24H, br, o-Ar), 6.59 (12H, s, p-Ar), 4.23 (24H, br, N-CH₂), 2.25 (36H, s, Ar-CH₃, μ₂-P₂), 2.23 (36H, s, Ar-CH₃, μ₂-AsP), 0.97 (54H, s, t-Bu, μ₂-P₂), 0.95 (54H, s, t-Bu, μ₂-AsP). 

31P{¹H} NMR (20 °C, benzene-d₆, 202.5 MHz): δ = 399 (2P, br, μ₂-P₂), 438 (1P, br, μ₂-AsP).

13C{¹H} NMR (20 °C, benzene-d₆, 125.7 MHz): δ = 154.2 (Ar), 138.1 (Ar), 126.6 (Ar), 124.4 (Ar), 73 (N-CH₂), 37.3 (C(CH₃)), 30.3 (C(CH₃), μ₂-P₂), 30.1 (C(CH₃), μ₂-AsP), 22.1 (Ar-CH₃).

Treatment of AsP₃ with Mo(N[¹Bu]Ar)₃, Synthesis of 5-As and 5-P. Mo(N[¹Bu]Ar)₃ (100 mg, 0.16 mmol) was dissolved in 5 mL of Et₂O and was added to a vial containing solid AsP₃ (8 mg, 0.047 mmol). The mixture was stirred for 60 minutes during which time the reaction mixture assumed a dark orange color. The volatile components of the reaction mixture were removed under reduced pressure. The resulting residue was dissolved in C₆D₆ and was taken for NMR analysis. Recrystallization from Et₂O/ n-pentane (1:2) afforded 75 mg (70% yield) of 3:1 PMo(N[¹Bu]Ar)₃ and AsMo(N[¹Bu]Ar)₃. 

1H NMR (20 °C, benzene-d₆, 500 MHz): δ = 6.61 (6H, s, o-Ar), 5.81 (3H, br, p-Ar), 2.04 (18H, s, Ar- Me), 1.66 (27H, s, t-Bu). 

31P{¹H} NMR (20 °C, benzene-d₆, 202.5 MHz): δ = 1216 (1P, br, P≡Mo).

13C{¹H} NMR (20 °C, benzene-d₆, 125.7 MHz): δ = 150.6 (Ar, P≡Mo), 150.0 (Ar, As≡Mo), 136.85 (Ar, P≡Mo), 136.80 (Ar, As≡Mo), 130.6 (Ar, As≡Mo), 130.4 (Ar, P≡Mo), 127.7 (Ar), 60.6 (C(CH₃), P≡Mo), 59.8 (C(CH₃), As≡Mo), 34.1 (C(CH₃), As≡Mo), 33.9 (C(CH₃), P≡Mo), 21.5 (Ar-CH₃).
Reduction of Cl\textsubscript{2}Nb(ODipp)\textsubscript{3} in the presence of AsP\textsubscript{3} and Na/Hg followed by treatment with AsCl\textsubscript{3}, Synthesis of 6-P\textsubscript{3}, 6-AsP\textsubscript{2}, 6-As\textsubscript{2}P, 6-As\textsubscript{3}, AsP\textsubscript{3}, As\textsubscript{2}P\textsubscript{2}, As\textsubscript{3}P, and As\textsubscript{4}. Cl\textsubscript{2}Nb(ODipp)\textsubscript{3} (278 mg, 0.40 mmol) was combined with solid AsP\textsubscript{3} (67 mg, 0.40 mmol) and then dissolved in 10 mL of THF. After all the AsP\textsubscript{3} was dissolved a 0.5% Na/Hg amalgam was added. The reaction mixture was allowed to stir for 20 min during which time it assumed a dark orange-brown color. The reaction mixture was taken to dryness. To the residue was added 5 mL of Et\textsubscript{2}O. The resulting residue was filtered to remove any insoluble material. The filtrate was taken to dryness under reduced pressure. The resulting residue was dissolved in a stock solution of P\textsubscript{4} (0.158 mmol total as an internal standard) in C\textsubscript{6}D\textsubscript{6} for NMR analysis. \textsuperscript{31}P NMR (20 °C, benzene-\textit{d}_6, 202.5 MHz): \(\delta = -520 \) (P\textsubscript{4}, s, 0.1581 mmol), \(-206\) (\([\text{Na}][\text{P}_3\text{Nb}(\text{ODipp})_3]\), s, 0.1935 mmol, 48% yield), \(-167\) (\([\text{Na}][\text{P}_2\text{AsNb}(\text{ODipp})_3]\), s, 0.090 mmol, 23% yield), \(-132\) (\([\text{Na}][\text{PAs}_2\text{Nb}(\text{ODipp})_3]\), s, 0.0198 mmol, 5% yield). The total yield of 6-P\textsubscript{3}, 6-AsP\textsubscript{2}, and 6-As\textsubscript{2}P is 76% based on Cl\textsubscript{2}Nb(ODipp)\textsubscript{3}, which is consistent with the yields obtained for the synthesis of 6-P\textsubscript{3} from P\textsubscript{4}.\textsuperscript{3} The NMR tube was returned to the glove box and its contents were taken to dryness. The resulting residue was dissolved in 5 mL of THF and the solution was frozen in the cold well. AsCl\textsubscript{3} (72 mg) was added to this thawing solution (as a stock solution in toluene). The resulting mixture was allowed to stir for 20 min after which time it was filtered through a pad of Celite and concentrated to 1 mL. This sample was placed in an NMR tube (wrapped in Al foil) for analysis. \textsuperscript{31}P{\textsuperscript{1}H} NMR (20 °C, benzene-\textit{d}_6, 202.5 MHz): \(\delta = -520 \) (P\textsubscript{4}, s), \(-484\) (AsP\textsubscript{3}, s), \(-452\) (As\textsubscript{2}P\textsubscript{2}, s), \(-432\) (AsP\textsubscript{3}, s). A portion of the sample was diluted 100-fold with C\textsubscript{6}H\textsubscript{6} and was analyzed by GCMS. GC-MS: P\textsubscript{4} [retention time 7.8 min, parent ion 124 m/z with fragments at 93 (P\textsubscript{3}) and 62 (P\textsubscript{2}), total area 50994], AsP\textsubscript{3} [retention time 8.9 min, parent ion 168 m/z with fragments at 137 (AsP\textsubscript{2}), 106 (AsP), 93 (P\textsubscript{3}), 75 (As), and 62 (P\textsubscript{2}), total area 30475, 49% yield from 6-P\textsubscript{3}], As\textsubscript{2}P\textsubscript{2} [retention time 9.8 min, parent ion 212 m/z with fragments at 181 (As\textsubscript{2}P), 150 (As\textsubscript{2}), 137 (AsP\textsubscript{2}), 106 (AsP), 75 (As), and 62 (P\textsubscript{2}), total area 11348, 39% yield from 6-AsP\textsubscript{2}], As\textsubscript{3}P [retention time 10.6 min, parent ion 256 m/z with fragments at 225 (As\textsubscript{3}), 181 (As\textsubscript{2}P), 150 (As\textsubscript{2}), 106 (AsP), and 75 (As), total area 3176, 50% yield from 6-As\textsubscript{2}P], As\textsubscript{4} [retention time 11.2 min,
parent ion 300 m/z with fragments at 150 (As$_2$) and 75 (As); peaks from neighboring HODipp signal also present, approximate total area 1977, 2% yield from Cl$_2$Nb(ODipp)$_3$].

**X-ray Diffraction Studies.** Diffraction-quality crystals of [(AsP$_3$)FeCp*(dppe)][BPh$_4$] were grown from CH$_2$Cl$_2$/Et$_2$O at −35 °C over the course of several days. Diffraction-quality crystals of AsP$_3$(P(N($^3$Pr)$_2$)N(SiMe$_3$)$_2$)$_2$ were grown from n-hexane/Et$_2$O by cooling at −35 °C over the course of two days. The crystals were mounted in hydrocarbon oil on a nylon loop. Low-temperature (100 K) data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) performing φ and ω scans. A semiempirical absorption correction was applied to the diffraction data using SADABS.$^{63}$ The structures were solved by direct methods using SHELXS$^{64}$ and refined against $R^2$ on all data by full-matrix least squares with SHELXL-97.$^{65}$ All non-H atoms were refined anisotropically. All H atoms were included in the models at geometrically calculated positions and refined using a riding model. The isotopic displacement parameters of all H atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to (1.5 times for methyl groups). All disorders were refined within SHELXL with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances throughout the disordered components. The relative occupancies of disordered components were refined freely within SHELXL. Further details are available in the Supporting Information (Table S1 and a CIF file) and from the CCDC under deposition numbers 730555 (2) and 730556 (1).

**Computational Studies.** All calculations were carried out using ADF 2008.01 from Scientific Computing and Modeling (http://www.scm.com)$^{20,21}$ on a 32-processor Quantum Cube workstation from Parallel Quantum Solutions (http://www.pqs-chem.com). All of the calculations were repeated using the OLYP functionals which are a combination of the OPTX exchange functional of Handy and Cohen used with Lee, Yang, and Parr’s nonlocal correlation function (LYP).$^{66-68}$ In addition, all calculations were carried out using the zero-order regular approximation (ZORA) for relativistic
The basis sets used were quadruple-$\zeta$ with four polarization functions (QZ4P) for As and P in the calculation of $E_4$ tetrahedra ($E = \text{As, P}$) and triple-$\zeta$ with two polarization functions (TZ2P) for all other calculations, as supplied with ADF. Chemical shielding tensors were calculated for the $^{31}\text{P}$ nuclei in the optimized structures by the GIAO method using the ADF package. The functionals, basis sets, and relativistic approximations used were the same as those described above. The isotropic value of the chemical shielding was converted to a chemical shift downfield of 85% phosphoric acid using $\text{P}_4$, white phosphorus, as a computational reference; the computed absolute shielding value of $\text{P}_4$ was correlated with a chemical shift equal to its experimental value ($\sim 520 \text{ ppm}$) in dilute benzene solution. For zero-point energy corrections, frequencies calculations were computed using optimized structures as described above.

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Supporting Information Available. Full crystallographic data on compounds 1 and 2, complete ADF output files, and phosphorus NMR spectra for all reactions can be found in the supporting information document. This information is available free of charge at http://pubs.acs.org.

References.

(7) Willem Schipper, Research and Development, ThermPhos International. Personal communication.
(8) Stow, S. H. Econ. Geol. 1969, 64, 667-671.


(19) The electrochemistry data were collected in 0.25 M [TBA][PF₆] at a scan rate of 300 mV s⁻¹. A 1 mm diameter Pt disk working electrode, curly Pt wire counter electrode, and Ag wire pseudoreference electrode were used for all measurements. All measurements are corrected to Cp₂Fe⁰/⁺ by the addition of Cp₂Fe as an internal standard.


(28) Please see the Supporting Information document for further details.


(44) Concentrations of AsP₃ and 3-AsP₃ were determined by integration against an internal standard (PPh₃). The concentration of Ti(N[′Bu]Ar)₃ was inferred using the equation [Ti(N[′Bu]Ar)₃]ᵣ = [Ti(N[′Bu]Ar)₃]ᵣ - 2[3-AsP₃]ᵣ. This assumes no other degradation pathways are operative during the course of the reaction.


(60) P₄ was used as an internal standard for monitoring purposes. No P₄ was present in the reaction mixture prior to its addition.


(65) Sheldrick, G. M. *SHELXL-97: Program for crystal structure determination; University of Göttingen: Göttingen, Germany, 1997.*


CIF files are available from the Cambridge Crystallographic Database under deposition numbers 730555 (2) and 730556 (1).

Table of Contents Graphic.

TOC Description:
As$_4$, in the solid state, is thermally and photochemically unstable, reverting readily to metallic arsenic. P$_4$, on the other hand, is a key industrial intermediate of commercial importance. The synthesis of the binary compounds As$_n$P$_{4-n}$ represents a way to bridge the knowledge gap between the stable P$_4$ molecule and the fleeting As$_4$ tetrahedron. Herein we report in detail on the physical, electronic, and chemical properties of AsP$_3$ as ascertained by combined theoretical and experimental investigations. We also detail the synthesis and isolation of a number of new molecules derived from AsP$_3$ including [(AsP$_3$)FeCp*(dppe)][BPh$_4$] and AsP$_3$(P(N(Pr)$_2$)N(SiMe$_3$)$_2$)$_2$. The first solution observations of As$_2$P$_2$ and As$_3$P in solution are also reported.