

**New Main-Group-Element-Rich nido-Octahedral Cluster  
System: Synthesis and Characterization of  
[Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>3</sub>-As)μ<sub>3</sub>-EFe(CO)<sub>4</sub>(2)]**

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# A New Main Group Element-rich *nido*-Octahedral Cluster System: Synthesis and Characterization of $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]$

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ABSTRACT. A series of clusters of the form  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]$  where E is either P or As were synthesized from  $[\text{Et}_4\text{N}]_2[\text{HAS}\{\text{Fe}(\text{CO})_4\}_3]$  and  $\text{ECl}_3$ .  $\text{AsCl}_3$  gives the As-only compound;  $\text{PCl}_3$  produces compounds having two As atoms with one P atom, or one As atom and two P atoms and can exist as two possible isomers, one of which is chiral. The  $\text{As}_2\text{P}$  and  $\text{AsP}_2$  clusters co-crystallize and their structure as determined by single-crystal X-ray

diffraction is given along with the structure of the As-only cluster. Analytical data as well as DFT calculations support the formation and geometries of the new molecules.

## Introduction

Transition metal organometallic clusters have proven to have a very rich structural chemistry, which can be rationalized within the framework of the so-called Wade-Mingos electron counting rules.<sup>1</sup> This delocalized bonding formalism, originally developed for boron hydride clusters,<sup>2</sup> was, with the help of the isolobal analogy,<sup>3</sup> extended to transition metal clusters as well as to main group clusters and hybrid systems made of both main group elements and transition metals. In the latter case, the validity of the isolobal analogy is sometimes borderline because of the mismatch of the main group element and transition metal orbitals, leading to deviations from the Wade-Mingos rules.<sup>4-6</sup> This specific feature, together with the potential for skeletal isomerism arising from the metal/main group chemical heterogeneity, renders the structural chemistry of mixed main group/transition metal clusters particularly diverse and original from the point of view of bonding.

In our pursuit of single-source precursors to metal pnictide phases, we have explored routes to combine phosphorus and arsenic with iron in single source precursors with the goal of producing  $\text{Fe}_x(\text{As}_{1-y}\text{P}_y)$  ( $x = 1 - 3$ ;  $y = 0 - 1$ ) and related heterometallic compounds for their important electronic, magnetic, and magneto-caloric effects.<sup>7-13</sup> We have been particularly interested in  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Fe}(\text{CO})_4\}_3]$  ( $[\text{Et}_4\text{N}]_2[\mathbf{I}]$ ) as a starting material because it can be prepared cleanly in very high yields without using volatile arsine or organoarsenic compounds.<sup>14</sup> Starting with  $[\text{Et}_4\text{N}]_2[\mathbf{I}]$ , a series of compounds was prepared that included  $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}(\text{CO})_4\}\{\text{Fe}_2(\text{CO})_7\text{H}\}]$ ,  $[\text{Et}_4\text{N}][\{\text{Fe}_3(\text{CO})_{10}\}\text{As}\{\text{Fe}(\text{CO})_4\}]$ ,  $[\text{Et}_4\text{N}][\{\text{H}_2\text{Fe}_3(\text{CO})_9\}-$

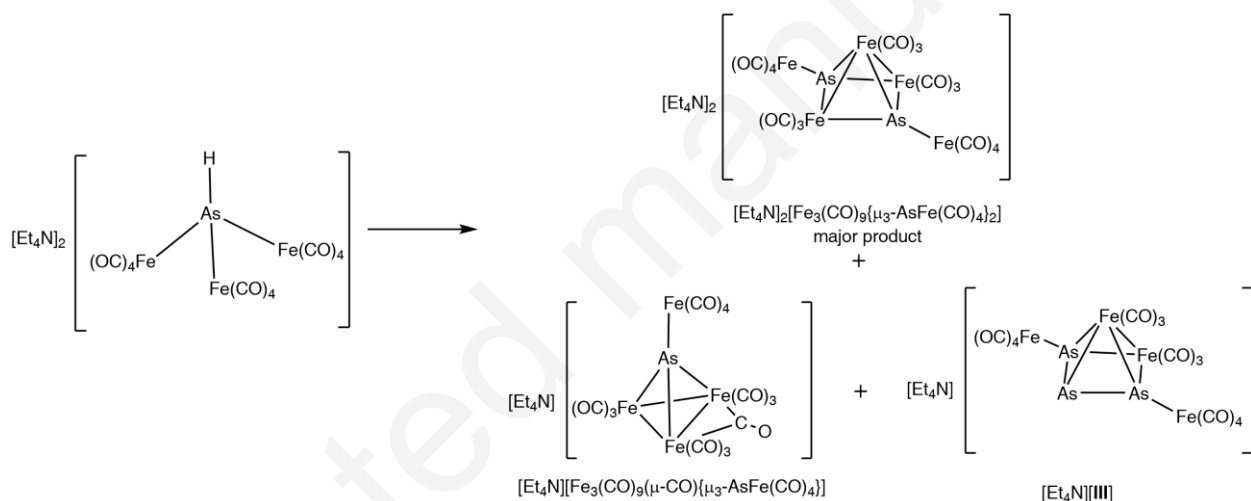
$\text{As}\{\text{Fe}(\text{CO})_4\}$ ],  $[\text{Et}_4\text{N}][\text{As}\{\text{HFe}_2(\text{CO})_7\}\{\text{FeMn}(\text{CO})_8\}]$ ,  $[\text{As}\{\text{Fe}_2(\text{CO})_8\}\{\text{FeMn}(\text{CO})_8\}]$ ,  $[\{\text{H}_2\text{Fe}_3(\text{CO})_9\}\text{As}\{\text{Mn}(\text{CO})_5\}]$  and  $[\text{Et}_4\text{N}][\{\text{Fe}_3(\text{CO})_{10}\}\text{As}\{\text{Mn}(\text{CO})_4\text{Br}\}]$  by using various oxidants in the absence or presence of  $\text{Mn}(\text{CO})_5\text{Br}$ .<sup>15</sup> As an additional strategy we have examined the addition of  $\text{ECl}_3$  to  $[\text{Et}_4\text{N}]_2[\text{I}]$  as a means of introducing additional main-group elements into the cluster framework. Herein we report the synthesis, structures and theoretical descriptions of a series of compounds  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]$  where E is either As or P. These compounds possess a previously unobserved *nido*-octahedral  $\text{E}_3\text{M}_2$  core.

## Results and Discussion

### *Synthesis and Characterization*

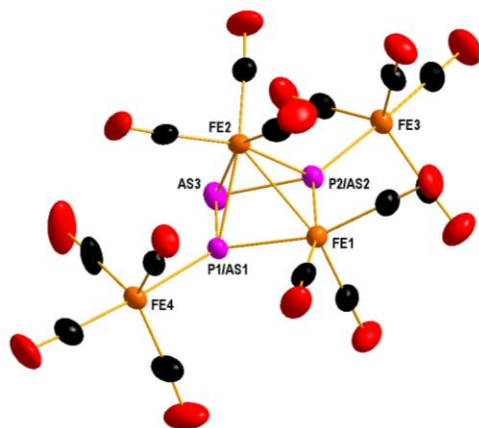
Immediately upon reaction of  $[\text{Et}_4\text{N}]_2[\text{I}]$  with  $\text{ECl}_3$  (E = P, As) in the presence of triethylamine, a blanketing mist forms in the flask above the reaction solution with rapid bubbling. The color transitions from a deep brick-red to a yellow-brown over the course of the addition and maintains this color for approximately 20 minutes. Then the mist disappears and the solution color transitions to a deep orange-red. The IR of the solution in the first 20 minutes suggests a complex mixture of products. For E = As, the spectrum at 30 min primarily shows the CO stretching bands associated with the known  $[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$ , the major product of the reaction (Scheme 1). Extraction of the crude product with diethyl ether yielded small amounts of  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$ ,  $[\text{Et}_4\text{N}][\text{II}]$ , along with  $[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\mu_3\text{-AsFe}(\text{CO})_4\}]$ .<sup>15</sup> In contrast, for E = P, the IR spectrum after 30 min largely resembled that of  $[\text{Et}_4\text{N}][\text{II}]$  and was proven to contain a mixture of P and As in the flanking positions (*vide infra*). These was the only isolated product and is designated collectively as  $[\text{Et}_4\text{N}][\text{III}]$ . That spectrum showed little change over the following 24 hours as well.

To probe the course of the  $\text{PCl}_3$  reaction further, ESI/MS of the crude product from that reaction dissolved in acetonitrile contains anions with the formulation  $[\text{Fe}_4(\text{CO})_{14}\text{As}_2\text{P}]^-$ ,  $[\text{Fe}_4(\text{CO})_{14}\text{AsP}_2]^-$ ,  $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]^{2-}$ ,  $[[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]]^-$  (another *nido*-octahedral cluster), as well as  $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-PFe}(\text{CO})_4\}\{\mu_3\text{-AsFe}(\text{CO})_4\}]^{2-}$ , the previously unknown mixed pnictogen anion, both as the dianion and paired with the cation as  $[[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9\{\mu_3\text{-PFe}(\text{CO})_4\}\{\mu_3\text{-AsFe}(\text{CO})_4\}]]^-$  (See **1a**, Supporting Information).<sup>14</sup> Interestingly the  $\text{As}_3$  compound was not detected.



Scheme 1. Reaction products from treatment of  $[\text{Et}_4\text{N}]_2[\text{I}]$  with  $\text{AsCl}_3$ .

The structures of both the  $\text{As}_3$  and  $\text{As}_x\text{P}_y$  compounds (**Figure 1**) were determined by single crystal X-ray diffraction. Interestingly, in the case of the mixed P-As system there was a non-statistical distribution of P and As over the flanking sites.

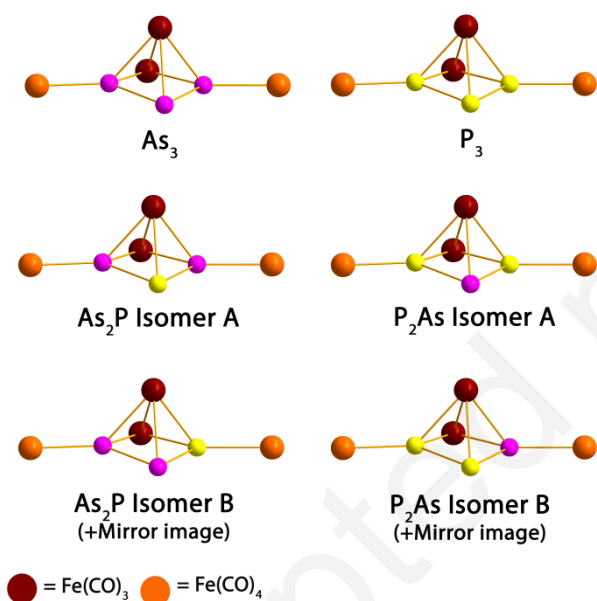


**Figure 1.** Structure of the anion  $[\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]^-$ , **[III]**<sup>-</sup>, as determined by single-crystal X-ray Diffraction. Ellipsoids given at 50% probability.

As shown in **Figure 2**, six different compounds are possible, of which two (As-As-P and P-P-As) exist as enantiomers. The X-ray refinement showed those crystals to be composed of a mixture of several of the compositional isomers of **[III]**<sup>-</sup> wherein the flanking “E” sites were a mixture of arsenic and phosphorus, with 50% and 66% P at the two  $\text{Fe}(\text{CO})_4$ -bound positions. That the two sites refined to different values was especially surprising given the centrosymmetric nature of the space group. The central, naked main group atom refined to essentially only As and was fixed completely as that element. The overall composition indicated by the refinement was  $\text{As}_{1.83}\text{P}_{1.17}$ .

The related  $\text{M}_3\text{E}_2$  *nido*-octahedral compounds have been known for some time.<sup>16–30</sup> and the compounds reported here may be viewed as an isolobal replacement of  $\text{Fe}(\text{CO})_3^-$  by P or As.  $[\text{Et}_4\text{N}][\text{II}]$  and  $[\text{Et}_4\text{N}][\text{III}]$  are electron precise, and the core electron count of each is consistent with that predicted by Wade-Mingos’s rules for a *nido*-octahedron with seven skeletal electron pairs distributed across five vertices.<sup>1</sup> *Nido*-octahedra in an  $\text{M}_2\text{E}_3$  configuration in which E, taken generally as any nonmetal, are unknown outside a handful of structures with a carbon at the

bridging “E” vertex.<sup>31–39</sup> In those structures, the idealized square-pyramidal geometry is highly distorted and the bridge-carbon bears an alkyl or phosphine group. Anions [II]<sup>-</sup> and [III]<sup>-</sup> are related to the metallated polyphosphine structural class of which there are numerous examples,<sup>30,40,41</sup> but this is the first time this unit has been observed as part of an octahedral cluster. Moreover, with its mixed P/As ligand composition, [III]<sup>-</sup> is related to a small collection of structures in which the pnictogens are found at mixed positions as ligands in metallated systems.<sup>42–47</sup>



**Figure 2.** The various  $[\text{Fe}_2(\text{CO})_6(\mu_3\text{-E})]\{\mu_3\text{-EFe}(\text{CO})_4\}_2^-$  compounds possible with an  $\text{Fe}_2\text{E}_{3-x}\text{E}'_x$  core, namely  $\text{As}_3$ ,  $\text{P}_3$ ,  $\text{As}_2\text{P}$  (isomers A and B) and  $\text{AsP}_2$  (isomers A and B).

With an As/P ratio of 1.83 to 1.17 indicated by the crystal data and only two compositional isomers possible, the implied percentages of 83% of the As<sub>2</sub>P isomer and 17% of the AsP<sub>2</sub> isomer could be estimated. The composition of the crystals as a mixture of the As<sub>2</sub>P and AsP<sub>2</sub> isomers is further supported by the analytical data; the As<sub>2</sub>P:AsP<sub>2</sub> ratio of 4.88:1 predicts C/H/N percentages of 28.76%, 2.20% and 1.52%, respectively. Elemental analysis gave 29.35% C, 2.31 %H, and 1.66% N.

The <sup>31</sup>P-NMR data is also consistent with the isomer distribution. As one molecule of the AsP<sub>2</sub> isomer has two equivalent P atoms, its shift should have twice the signal as one molecule of the As<sub>2</sub>P isomer; the crystal and MS data predict two signals integrating to a ratio of 1:0.4. Experimentally, <sup>31</sup>P-NMR of the crystals showed two signals: a shift at 323.5 ppm integrating to one unit and a shift at 307.2 ppm integrating to 0.32 units, respectively, in good agreement with the X-ray data.

<sup>31</sup>P NMR data obtained for the crude reaction mixture show the two additional peaks at 147.5 and 153.90 ppm as compared to the solution NMR of the recrystallized sample. While the previously mentioned signals at 307 and 323 ppm respectively can be attributed to the As-As-P and P-As-P signals, the 147.5 and 153.9 signals could be attributed to phosphorus at the bridging position. It may also be that one among the 147.5 and 153.9 signals can be attributed to the phosphorus atom in [Et<sub>4</sub>N]<sub>2</sub>[Fe<sub>3</sub>(CO)<sub>9</sub>{μ<sub>3</sub>-PFe(CO)<sub>4</sub>}{μ<sub>3</sub>-AsFe(CO)<sub>4</sub>}], identified in the ESI/MS of the crude product. For comparison, white phosphorus (P<sub>4</sub>) shows one signal at ~-525 ppm.<sup>48</sup> Theoretical calculations (Table 1) support a ~327-389 ppm location for the flanking phosphorus atoms and a ~185-287 ppm location for the bridging phosphorus atoms. While the expected phosphorus-phosphorus couplings were not directly observed, such couplings may be too broad



to be observed. Among other examples of mixed P/As metallated ligand systems, there are only a few documented instances of P-P coupling.<sup>42,49</sup>

[Et<sub>4</sub>N][**III**] is not susceptible to protonation. Treatment with the super acid HSO<sub>3</sub>CF<sub>3</sub> was insufficient to protonate the bridging pnictogen atom. Efforts to alkylate and metallate the bridge pnictogen with ethyl bromide and Mn(CO)<sub>5</sub>Br were also unsuccessful, probably because of steric crowding at this position.

### *Theoretical Studies*

Full geometry optimizations of the various compounds shown in **Figure 2** have been carried out by DFT calculations at the PBE0/Def2TZVP level (see Computational Details). Relevant computed NMR data are given in Table 1 and energetic data are provided in Table 2. In the case of the As<sub>2</sub>P and AsP<sub>2</sub> systems, the more stable isomers were found to be isomers B and A, respectively, *i.e.*, those for which the naked main-group atom is arsenic, in full agreement with the X-ray data for which this position is found to be of 100% As occupation (see above).

The free energy preference for these isomers is not very large (4.4 and 2.7 kcal/mol, respectively) but it appears to be enough for avoiding the isolation of the other isomers. In the case of the less stable isomers (as well as in the P<sub>3</sub> species) the naked phosphorus atom is negatively charged (NPA charge range: -0.02/-0.05), suggesting it should be subject to electrophilic attack. This is not the case when phosphorus is bonded to an Fe(CO)<sub>4</sub> group nor for naked arsenic (range: +0.06/+0.14). This is in line with the fact that naked phosphorus atoms are rare in main-group transition-metal organometallic cluster chemistry.

**Table 1.** DFT-computed  $^{31}\text{P}$  NMR chemical shifts (ppm) of the P-containing compounds of **Figure 2**. The atom numbering corresponds to that of Figure 1.

	<b>P(1)</b>	<b>P(3)</b>	<b>P(2)</b>
<b>P<sub>3</sub></b>	327	185	327
<b>As<sub>2</sub>P (isomer A)</b>	-	287	-
<b>As<sub>2</sub>P (isomer B)</b>	-	-	389
<b>AsP<sub>2</sub> (isomer A)</b>	364	-	364
<b>AsP<sub>2</sub> (isomer B)</b>	-	234	357

**Table 2.** DFT-computed HOMO-LUMO gaps and relative energies between the various compounds of **Figure 2**.  $\Delta E^0$  = ZPE-corrected energy,  $\Delta G$  = free energy,  $\Delta H$  = enthalpy.

	<b>As<sub>2</sub>P (isomer A)</b>	<b>As<sub>2</sub>P (isomer B)</b>	<b>AsP<sub>2</sub> (isomer A)</b>	<b>AsP<sub>2</sub> (isomer B)</b>
$\Delta E^0$ (kcal/mol)	5.3	0.0	0.0	3.5
$\Delta G$ (kcal/mol)	4.4	0.0	0.0	2.7
$\Delta H$ (kcal/mol)	5.3	0.0	0.0	3.7
$\Delta E_{\text{HOMO-LUMO}}$ (eV)	3.99	4.03	4.17	4.06

Mechanistic Considerations:

The mechanism by which these new clusters are formed is clearly complicated and must involve recombination of a variety of E, E{Fe(CO)<sub>4</sub>} and/ or E{Fe(CO)<sub>4</sub>}<sub>2</sub> fragments, which

furthermore could be either neutral or charged. As described previously, there are several pathways by which  $[\text{Et}_4\text{N}]_2[\text{I}]$  can react. These include abstraction of  $\text{H}^\bullet$ ,  $\text{H}^-$  or  $\text{H}^+$ . Importantly,  $[\text{I}]^{2-}$  bears a hydride at the arsenic center, allowing a possible aminolysis reaction with  $\text{PCl}_3$  and concomitant  $\text{HCl}$  evolution.<sup>50</sup> Furthermore,  $[\text{I}]^{2-}$  is dianionic, making nucleophilic displacement at the P center with elimination of  $[\text{Et}_4\text{N}]\text{Cl}$  feasible, and electron transfer is also possible. Direct oxidation of the metal center by  $\text{EX}_3$  could occur too. For example, von Seyerl *et al.* showed that  $\text{AsCl}_3$  reacted with  $\text{Cr}(\text{CO})_5\text{THF}$  to yield the unsaturated arsinidene CIAs  $\{\text{Cr}(\text{CO})_5\}_2$ <sup>51</sup> while Huttner reported that  $\text{PCl}_3$  reacts with  $\text{Fe}_2(\text{CO})_9$  to yield  $[\{\text{Fe}_2(\text{CO})_8\}(\mu_4\text{-P})\{\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})\}]$ .<sup>52</sup> Furthermore, Markó and coworkers noted that  $\text{Co}_2(\text{CO})_8$  reacts with  $\text{PBr}_3$  or  $\text{PI}_3$  to give  $[\text{Co}_3(\text{CO})_8\text{P}]_3$ .<sup>53</sup> The same authors noted that  $\text{RPCl}_2$  and  $\text{Co}_2(\text{CO})_8$  gave  $\text{Co}_3(\text{CO})_9\text{PR}$  along with  $\text{CoCl}_2$ .<sup>54</sup>

Various observations leading to spirocyclic or spiked tetrahedral structures were already postulated in the earlier report. These same pathways could explain the route to  $[\text{Et}_4\text{N}][\text{III}]$  as well. This discussion is more speculative and, since multiple products are formed, a variety of these pathways may be operating simultaneously. In some ways, having both As and P present in the bridging position would have made the mechanistic discussion easier, as that would imply a completely random combination of  $\text{E}\{\text{Fe}(\text{CO})_x\}_y$  fragments. Steric crowding may prevent formation of  $[\text{Fe}_2(\text{CO})_6\{\text{E}\{\text{Fe}(\text{CO})_4\}_3}]^-$  explaining the lack of an  $\text{Fe}(\text{CO})_4$  group on the central main group atom. Loss of an  $\text{Fe}(\text{CO})_4$  group would occur more readily from As than P, which is consistent with the lack of negative charge found at the As atom in the DFT calculations.

The appearance of the thick mist above the reaction solution upon introduction of  $\text{PCl}_3$  could result from  $\text{HCl}$  formation to produce an intermediate such as  $[\{(\text{CO})_4\text{Fe}\}_3\text{AsPCl}_2]^{2-}$  with an As-P bond. Reduction of the  $\text{PCl}_2$  by iron carbonyl fragments suggests an intriguing possibility - the

intermediacy of a multiply bonded species such as  $(\text{CO})_4\text{Fe}-\text{E}\equiv\text{E}'-\text{Fe}(\text{CO})_4$ . Both  $\text{E} = \text{E}' = \text{P}$  and  $\text{E} = \text{As}$ ,  $\text{E}' = \text{P}$  could exist. Addition of an  $[\text{As}\{\text{Fe}(\text{CO})_x\}_2]^-$  fragment across the multiple bond could explain the preference for P at the end positions and the presence of only As in the central location.

The appearance of  $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$  in the reaction solution (**1b**, Supporting Information) implies an oxidative process is taking place, but its structural similarity to the  $\text{E}_3\text{M}_2$  compound suggested that it could be an intermediate in the formation of **[III]**<sup>-</sup>. To test this hypothesis,  $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$  was treated with  $\text{PCl}_3$  (**1c**, Supporting Information). This led to the formation of small amounts of the  $\text{AsP}_2$  compound, but also the  $\text{P}_3$  variant, unseen in the original reaction of  $[\text{Et}_4\text{N}]_2[\text{I}]$  with  $\text{PCl}_3$  after 48 hours of reaction time (**1b**, Supporting Information). This would suggest vertex substitution is possible, but the low yield indicates it is not the prevailing mechanism for the formation of the  $\text{AsP}_2$  and  $\text{As}_2\text{P}$  variants.

We cannot rule out the possibility that the isolation of  $[\text{Et}_4\text{N}][\text{III}]$  may be a matter of the stability of the products; the less stable species generated in the  $\text{PCl}_3$  addition process may simply decompose leaving the observed mixture of products.

## Conclusions

The tendency of  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Fe}(\text{CO})_4\}]$ ,  $[\text{Et}_4\text{N}]_2[\text{I}]$ , to react with  $\text{PCl}_3$  to form the mixed P/As  $[\text{Et}_4\text{N}][\text{III}]$  is similar to the manner in which  $[\text{Et}_4\text{N}]_2[\text{I}]$  forms  $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$  as the majority product upon treatment with one equivalent of a one-electron oxidant. Both products share square-pyramidal cores, with the former bearing an  $\text{M}_2\text{E}_3$  core and the latter an  $\text{M}_3\text{E}_2$  core. This would suggest  $\text{PCl}_3$  interacts in an oxidative manner with

[Et<sub>4</sub>N]<sub>2</sub>[I], ultimately supplying neutral phosphorus atoms to the recombining fragments to form the core. These P atoms are found at the flanking positions of the core. If P atoms do take the bridge position during the M<sub>2</sub>E<sub>3</sub> core formation, the clusters in which they are incorporated are unstable and may be subject to electrophilic attack.

In the case of [Et<sub>4</sub>N]<sub>2</sub>[I] reacting with AsCl<sub>3</sub>, [Et<sub>4</sub>N][{Fe<sub>3</sub>(CO)<sub>10</sub>}As{Fe(CO)<sub>4</sub>}] is the majority product with a small amount of [Et<sub>4</sub>N][II] formed. The appearance of the latter suggests that the reactivity of [Et<sub>4</sub>N]<sub>2</sub>[I] towards AsCl<sub>3</sub> mirrors at least in part its reactivity with PCl<sub>3</sub> although another pathway, perhaps the same observed for the formation of [Et<sub>4</sub>N][{Fe<sub>3</sub>(CO)<sub>10</sub>}As{Fe(CO)<sub>4</sub>}] from the reaction of [Et<sub>4</sub>N]<sub>2</sub>[I] with hydride abstraction agent [CPh<sub>3</sub>][BF<sub>4</sub>] may be involved.<sup>15</sup>

With these clusters, the structural diversity exhibited by the metal carbonyls expands further. The cluster series reported herein also points to the possibility of other M<sub>2</sub>E<sub>3</sub> clusters. A reexamination of some of the known M<sub>3</sub>E<sub>2</sub> clusters might yield insights into other instances in which PCl<sub>3</sub> and a suitable starting material might yield an M<sub>2</sub>E<sub>3</sub>-type cluster with metals in addition to iron and main-group elements other than phosphorus and arsenic.

## EXPERIMENTAL

**General Considerations:** All reactions were performed under a dry, oxygen-free argon atmosphere according to standard Schlenk techniques. The solvents dichloromethane, tetrahydrofuran, and ethyl ether were dried with a Pure Process Technology solvent purification system and degassed prior to use. [Et<sub>4</sub>N]<sub>2</sub>[HAs{Fe(CO)<sub>4</sub>}<sub>3</sub>] was prepared according to literature methods.<sup>14</sup> PCl<sub>3</sub> was obtained from Sigma Aldrich, distilled, and stored under argon. Triethylamine was obtained from Sigma Aldrich, dried over KOH, and distilled under argon.

AgPF<sub>6</sub> was obtained from Strem Chemicals and used without further purification. IR measurements were obtained using a Perkin Elmer Spectrum Two FTIR spectrometer. <sup>1</sup>H and <sup>31</sup>P NMR data were recorded on a 500 MHz Bruker spectrometer (202 MHz for <sup>31</sup>P). H<sub>3</sub>PO<sub>4</sub> (85%) was used as the reference standard for the <sup>31</sup>P NMR spectra. ESI mass spectra were obtained on a Bruker Daltonics MicroTOF analyzer equipped with an Agilent 1200 HPLC system.

1a) Synthesis of [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>3</sub>-As){μ<sub>3</sub>-EFe(CO)<sub>4</sub>}]<sub>2</sub>, E = P/As [Et<sub>4</sub>N][**III**]: 1.4 g of (Et<sub>4</sub>N)<sub>2</sub>{H-As(Fe(CO)<sub>4</sub>)<sub>3</sub>} (1.6 mmol) was dissolved in 20 mL of DCM or THF at room temperature. To this solution 0.5 mL of triethylamine was added (3.6 mmol) with stirring. After 5 minutes, a solution of 0.14 mL of PCl<sub>3</sub> (1.6 mmol) in 20 mL DCM or THF was added dropwise (2 mL/min) and the mixture stirred overnight. The following day, the solution was reduced to dryness *in vacuo* and 60 mL dry, degassed Et<sub>2</sub>O was added. This was allowed to stir for 3 h whereafter the solution was filtered and stored in a refrigerator at -10 °C for 3 weeks. Rhombohedral red crystals of [Et<sub>4</sub>N][**III**] grew along the walls of the flask above and below the solution level. Yield 225 mg, 15% (Based on As). IR, ν<sub>CO</sub> (DCM) 2064 (vw), 2032 (vs), 2019, (s), 1983 (w), 1960 (w), and 1935 (m) cm<sup>-1</sup>. <sup>31</sup>P-NMR (500 MHz, d<sup>6</sup>-acetone):δ 323.54 (1P, s), 307.13 (0.32P, s) ppm. Analysis calc'd for the 83% As<sub>2</sub>P/17% AsP<sub>2</sub> mixture determined by X-ray analysis and <sup>31</sup>P-NMR (C/H/N)= (28.76%/H = 2.20%/N = 1.52%). Found (C/H/N)= (29.49%/2.31%/1.66%). ESI-MS (m/z, (relative %)) 752.5 ([Fe<sub>2</sub>(CO)<sub>6</sub>AsP<sub>2</sub>{Fe(CO)<sub>4</sub>}]<sub>2</sub>)<sup>-</sup> calcd for Fe<sub>4</sub>AsP<sub>2</sub>C<sub>14</sub>O<sub>14</sub> 752.39 (35.5), 796.5 ([Fe<sub>2</sub>(CO)<sub>6</sub>As<sub>2</sub>P{Fe(CO)<sub>4</sub>}]<sub>2</sub>)<sup>-</sup> calcd for Fe<sub>4</sub>As<sub>2</sub>PC<sub>14</sub>O<sub>14</sub> 796.34 (64.5).

1b) Synthesis of [Et<sub>4</sub>N][Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>3</sub>-As){μ<sub>3</sub>-AsFe(CO)<sub>4</sub>}]<sub>2</sub>: 1.380 g of (Et<sub>4</sub>N)<sub>2</sub>{H-As(Fe(CO)<sub>4</sub>)<sub>3</sub>} (1.6 mmol) was dissolved in 20 mL of DCM or THF at room temperature. To this solution 0.5 mL of triethylamine was added (3.6 mmol) with stirring. After 5 minutes, a solution

of 0.14 mL of  $\text{AsCl}_3$  (1.6 mmol) in 20 mL DCM or THF was added dropwise (2 mL/min) and the mixture stirred overnight. The following day, the solution was reduced to dryness *in vacuo* and 60 mL dry, degassed  $\text{Et}_2\text{O}$  was added. This was allowed to stir for 3 h whereafter the solution was filtered and stored in a refrigerator at  $-10\text{ }^\circ\text{C}$  for 3 weeks. Brownish rhombs of product were obtained as a mixture with crystals of  $[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\mu_3\text{-AsFe}(\text{CO})_4\}]$ . Yield Trace, not isolated.  $\nu_{\text{CO}}$  (DCM) 2062 (vw), 2030 (vs), 2014, (s), 2001 (m), 1980 (w), 1960 (w), and 1936 (w)  $\text{cm}^{-1}$ . ESI-MS (m/z, (relative %)) 840.4 (4)  $[\text{Fe}_2(\text{CO})_6\text{As}_3\{\text{Fe}(\text{CO})_4\}_2]^-$  calcd for  $\text{Fe}_4\text{As}_3\text{C}_{14}\text{O}_{14}$  840.29..

1c) Preparation and Reaction of  $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$  with  $\text{PCl}_3$  and  $\text{Et}_3\text{N}$ : Preparation of  $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$ : 1.4 g of  $[\text{Et}_4\text{N}]_2[\text{HAS}\{\text{Fe}(\text{CO})_4\}_3]$  (1.6 mmol) was dissolved in 20 mL of THF. To this was added dropwise a solution of 0.4 g  $\text{AgPF}_6$  (1.6 mmol) in 20 mL of THF. This was allowed to stir for 1 h and then 0.5 mL of triethylamine was added (3.6 mmol). The resulting solution was allowed to stir for 20 min. FT-IR of the solution after 20 min of stirring showed only the presence of  $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]^{2-}$ . To this solution was then added a solution of 0.14 mL  $\text{PCl}_3$  (1.6 mmol) in 20 mL of THF via cannula. This was allowed to stir for 48 h at room temperature, filtered, and taken to dryness *in vacuo*.

#### ASSOCIATED CONTENT

**Computational details:** Density functional theory geometry optimizations of the five cationic clusters shown in Figure 2 were performed using the Gaussian 09 program,<sup>55</sup> with the PBE1PBE (PBE0)<sup>56-57</sup> hybrid functional and the general Def2TZVP (triple- $\xi$  polarized) basis set from the EMSL Basis Set Exchange Library.<sup>58</sup> Frequency calculations of normal modes of vibration were carried out in order to ascertain that the optimized structure are true minima. The natural

population analysis (NPA) was performed with the NBO 5.0 program.<sup>59</sup> Calculations of the <sup>31</sup>P NMR chemical shifts were performed according to the Gauge invariant atomic orbital (GIAO) method.<sup>60</sup>

### **Supporting Information**

Electronic Supplementary Information (ESI) available: Experimental procedures, ESI-MS data, <sup>31</sup>P-NMR data, and full DFT calculations including computational details, optimized geometries and Cartesian coordinates of the computed clusters, optimized energetic data, and theoretical <sup>31</sup>P-NMR shifts. See DOI: 10.1039/x0xx00000x

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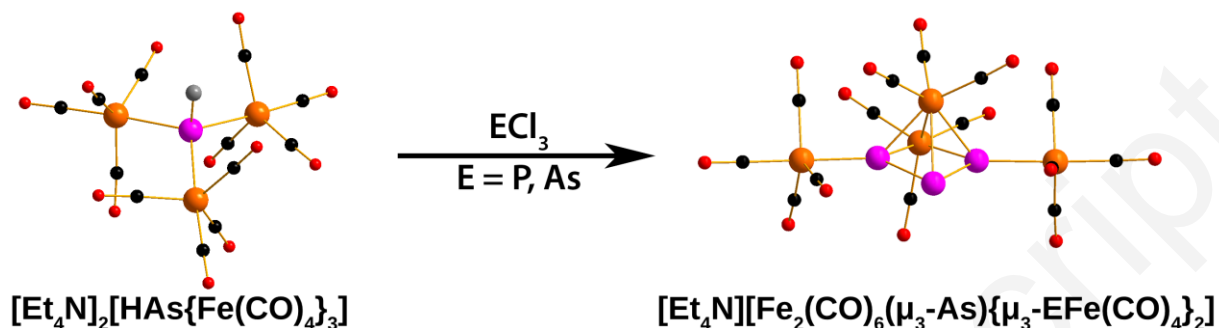
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**Synopsis:** A series of clusters of the form  $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]$  where E is either P or As were synthesized from  $[\text{Et}_4\text{N}]_2[\text{HAs}\{\text{Fe}(\text{CO})_4\}_3]$  and  $\text{ECl}_3$ .  $\text{AsCl}_3$  gives the As-only compound;  $\text{PCl}_3$  produces compounds having two As atoms with one P atom, or two P atoms and one As atom and can exist as two possible isomers, one of which is chiral. The  $\text{As}_2\text{P}$  and  $\text{AsP}_2$  clusters co-crystallize and their structure as determined by single-crystal X-ray diffraction is given along with the structure of the As-only cluster. The new cluster series has a unique square-pyramidal  $\text{M}_2\text{E}_3$  core, structurally analogous to clusters with the well-known  $\text{M}_3\text{E}_2$  core configuration. Analytical data as well as DFT calculations support the formation and geometries of the new molecules.