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

Desmond E. Schipper,^a Djamila Ikhlef,^{b,c} Samila Khalal,^b Jean-Yves Saillard,^b and Kenton H. Whitmire^a

^aDepartment of Chemistry, MS60, Rice University, 6100 Main Street, Houston, TX, 77005, USA.

^bUMR-CNRS 6226 "Sciences Chimiques de Rennes" Université de Rennes 1 35042 Rennes cedex, France. Address here.

^cLaboratoire de Gestion et Valorisation des Ressources Naturelles et Assurance Qualité Université de Bouira 10000 Bouira Algeria

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 ECl_3 . AsCl_3 gives the As-only compound; 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 As_2P and 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

Metal carbonyl clusters have proven to have a rich structural chemistry deriving from a delocalized bonding model whose tenants were elucidated by Wade in his now famous cluster electron counting formalisms developed originally for the boron hydrides.¹ These formalisms were found to be applicable to transition metal systems and also to hybrid systems of main group elements and transition metals, although some exceptional cases arise from mismatch of the main group element and transition metal orbitals, especially for the heavier main group elements.²⁻⁴

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.⁵⁻¹¹ We have been particularly interested in $[\text{Et}_4\text{N}]_2[\text{HAS}\{\text{Fe}(\text{CO})_4\}_3]$ ($[\text{Et}_4\text{N}]_2[\text{I}]$) as a starting material because it can be prepared cleanly in very high yields without using volatile arsine or organoarsenic compounds.¹² Starting with $[\text{Et}_4\text{N}]_2[\text{I}]$, 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 $\text{Mn}(\text{CO})_5\text{Br}$. As an additional strategy we have examined the addition of 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 E_3M_2 core.

Results and Discussion

Synthesis and Characterization

When AsCl_3 was treated with $[\text{Et}_4\text{N}]_2[\text{I}]$ in the presence of triethylamine, the result was the new compound $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$ [**II**] in low yield along with the majority product $[\text{Et}_4\text{N}][\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\mu_3\text{-AsFe}(\text{CO})_4\}]$.¹³ When $[\text{Et}_4\text{N}][\text{I}]$ was instead reacted with PCl_3 , the result was the new compounds $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]$ ($[\text{Et}_4\text{N}][\text{III}]$).¹² The structures of both the As_3 and As_xP_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 $[\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}_2]^-$, **[III]**[−], 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]**[−] 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 $\text{As}_{1.83}\text{P}_{1.17}$.

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 $\text{Fe}_2\text{E}_3\text{-}_x\text{E}'_x$ core, namely As_3 , P_3 , As_2P (isomers A and B) and AsP_2 (isomers A and B).

The related M_3E_2 *nido*-octahedral M_3E_2 compounds have been known for some time.^{14–28} 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.¹ *Nido*-octahedra in an M_2E_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.^{29–37} In those structures, the idealized square-pyramidal geometry is highly distorted and the bridge-carbon bears an alkyl or phosphine group. Anions $[\text{II}]^-$ and $[\text{III}]^-$ are related to the metallated polyphosphine structural class of which there are numerous examples,^{28,38–40} 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, $[\text{III}]^-$ is related to a small collection

of structures in which the pnictogens are found at mixed positions as ligands in metallated systems.^{41–47}

In order to probe which compounds/isomers were present in the reaction, ESI mass spectra were collected for isolated crystalline $[\text{Et}_4\text{N}][\text{III}]$ redissolved in MeCN which showed only two compounds present: As_2P and AsP_2 (SI). While not a quantitative compositional assessment, the As_2P species was predominant. 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 41% of the As_2P isomer and 59% of the AsP_2 isomer could be estimated.

This ratio is supported by the ^{31}P -NMR data. As one molecule of the AsP_2 isomer has two P atoms, its shift should have twice the signal as a molecule of the As_2P isomer; the crystal and MS data predict two signals integrating to a ratio of 1:0.35. Experimentally, ^{31}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 close agreement with the X-ray data. The composition of the crystals as a mixture of the As_2P and AsP_2 isomers is further supported by the analytical data; the 1 As_2P to 1.42 AsP_2 ratio predicts C/H/N percentages of 29.35%, 2.22 %, and 1.56%, respectively. Elemental analysis gave 29.35% C, 2.31 %H, and 1.66% N.

The ESI/MS of the crude product from the reaction of $[\text{Et}_4\text{N}]_2[\text{I}]$ and PCl_3 (**1b**, Supporting Information) dissolved in acetonitrile contains the As_2P compound, AsP_2 compound, $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-AsFe}(\text{CO})_4\}_2]$, another *nido*-octahedral cluster, as well as the previously unknown mixed pnictogen $[\text{Et}_4\text{N}]_2[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-PFe}(\text{CO})_4\}\{\mu_3\text{-AsFe}(\text{CO})_4\}]$.¹²

The As₃ compound was not detected. Given that the products have a similar square-pyramidal core, it stands to reason that they are all formed by a fragmentation event whose fragments recombine in the square-pyramidal configuration.

Since the M₃E₂ compounds are present in the reaction mixture (**1a**, Supporting Information), we also considered the possibility that the M₃E₂ compound [Et₄N]₂[Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂] forms as a result of initial oxidation by PCl₃ and then undergoes vertex substitution of Fe(CO)₃⁻ by PCl₃. [Et₄N]₂[Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂] was reacted with PCl₃ (**1c**, Supporting Information) which led to the formation of small amounts of the AsP₂ variant, but also the P₃ variant, unseen in the original reaction of [Et₄N]₂[**I**] with PCl₃ (**1b**, Supporting Information) after 48 hours of reaction time. This would suggest vertex substitution is possible, but the low yield indicates it is not the prevailing mechanism for the formation of the AsP₂ and As₂P variants.

[Et₄N][**III**] is not susceptible to protonation. Treatment with the super acid HSO₃CF₃ was insufficient to protonate the bridging pnictogen atom. Efforts to alkylate and metallate the bridge pnictogen with ethyl bromide and Mn(CO)₅Br were also unsuccessful.

³¹P 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 may be attributed to phosphorus at the bridging position. 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.^{41,43} And, free white phosphorus (P₄) shows one signal at ~-525 ppm.⁴⁸ Theoretical calculations (see below) support a

~327-364 ppm location for the flanking phosphorus atoms and a ~185-285 ppm location for the bridging phosphorus atoms (see SI).

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 SI). In the case of the As₂P and AsP₂ 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 P₃ 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)₄ 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.

Conclusions

The tendency of [Et₄N]₂[HAs{Fe(CO)₄}], [Et₄N][**I**], to react with PCl₃ to form the mixed P/As [Et₄N][**III**] is similar to the manner in which [Et₄N][**I**] behaves upon oxidation wherein [Et₄N]₂[Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂] is the majority product after treatment with one equivalent of a one-electron oxidant. Both products share square-pyramidal cores, with the former bearing an

M₂E₃ core and the latter an M₃E₂ core. This would suggest PCl₃ interacts in an oxidative manner with [Et₄N][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 M₂E₃ core formation, the clusters in which they are incorporated are unstable and subject to electrophilic attack.

In the case of [Et₄N][I] reacting with AsCl₃, [Et₄N][{Fe₃(CO)₁₀}As{Fe(CO)₄}] is the majority product with a small amount of [Et₄N][II] formed. The appearance of the latter suggests that the reactivity of [Et₄N][I] towards AsCl₃ mirrors at least in part its reactivity with PCl₃ although another pathway, perhaps the same observed for the formation of [Et₄N][{Fe₃(CO)₁₀}As{Fe(CO)₄}] from the reaction of [Et₄N][I] with hydride abstraction agent [CPh₃][BF₄] may be involved.⁴⁹

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 M₂E₃ clusters. A reexamination of some of the known M₃E₂ clusters might yield insights into other instances in which PCl₃ and a suitable starting material might yield an M₂E₃-type cluster with metals in addition to iron and main-group elements in addition to 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. [Et₄N]₂[HAs{Fe(CO)₄}₃] was prepared according to literature methods.¹² PCl₃ was obtained from Sigma Aldrich, distilled, and stored under argon.

Triethylamine was obtained from Sigma Aldrich, dried over KOH, and distilled under argon. AgPF₆ was obtained from Strem Chemicals and used without further purification. IR measurements were obtained using a Perkin Elmer Spectrum Two FTIR spectrometer. ¹H and ³¹P NMR data were recorded on a 500 MHz Bruker spectrometer (202 MHz for ³¹P). H₃PO₄ (85%) was used as the reference standard for the ³¹P NMR spectra. ESI mass spectra were obtained on a Bruker Daltonics MicroTOF analyzer equipped with an Agilent 1200 HPLC system.

1a) Synthesis of [Et₄N][Fe₂(CO)₆E₃{Fe(CO)₄}₂], E = P/As [Et₄N][**II**]: 1.4 g of (Et₄N)₂{H-As(Fe(CO)₄)₃} (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 PCl₃ (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 Et₂O 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 [Et₄N][**II**] grew along the walls of the flask above and below the solution level. Yield 225 mg, 26% (Based on As). IR, ν_{CO} (DCM) 2064 (vw), 2032 (vs), 2019, (s), 1983 (w), 1960 (w), and 1935 (m) cm⁻¹. ³¹P-NMR (500 MHz, d⁶-acetone):δ 323.54 (1P, s), 307.13 (0.32P, s) ppm. (C/H/N= 29.49%/2.31%/1.66%). ESI-MS (m/z, (relative %)) 752.5 ([Fe₂(CO)₆AsP₂{Fe(CO)₄}₂]⁻ calcd for Fe₄AsP₂C₁₄O₁₄ 752.39 (35.5)), 796.5 ([Fe₂(CO)₆As₂P{Fe(CO)₄}₂]⁻ calcd for Fe₄As₂PC₁₄O₁₄ calcd for Fe₄As₂PC₁₄O₁₄ 796.34 (64.5)).

1b) Synthesis of [Et₄N][Fe₂(CO)₆As₃{Fe(CO)₄}₂]: 1.380 g of (Et₄N)₂{H-As(Fe(CO)₄)₃} (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 AsCl₃ (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 Et₂O 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. Brownish rhombs of product were obtained as a mixture with crystals of [Et₄N][Fe₃(CO)₉(μ-CO){μ₃-AsFe(CO)₄}]. Yield Trace, not isolated. ν_{CO} (DCM) 2062 (vw), 2030 (vs), 2014, (s), 2001 (m), 1980 (w), 1960 (w), and 1936 (w) cm⁻¹. ESI-MS (m/z, (relative %)) 840.4 (4) [Fe₂(CO)₆As₃{Fe(CO)₄}₂]⁻ calcd for Fe₄As₃C₁₄O₁₄ 840.29..

1c) Preparation and Reaction of [Et₄N]₂[Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂] with PCl₃ and Et₃N: Preparation of [Et₄N]₂[Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂]: 1.4 g of [Et₄N]₂[HAs{Fe(CO)₄}₃] (1.6 mmol) was dissolved in 20 mL of THF. To this was added dropwise a solution of 0.4 g AgPF₆ (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 [Fe₃(CO)₉{μ₃-AsFe(CO)₄}₂]²⁻. To this solution was then added a solution of 0.14 mL PCl₃ (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

Supporting Information

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

AUTHOR INFORMATION

Corresponding Author

*Email for K.H.W.: whitmir@rice.edu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally. (match statement to author names with a symbol)

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1450681 and the National Science Foundation under Grant No. CHE-1411495.

REFERENCES

- (1) Wade, K. *Chem. Commun.* **1971**, 792–793.
- (2) Jaeger, T.; Aime, S.; Vahrenkamp, H. *Organometallics* **1986**, 5 (2), 245–252.
- (3) Vahrenkamp, H.; Wolters, D. *Organometallics* **1982**, 1 (6), 874–875.
- (4) Whitmire, K. H.; Albright, T. A.; Kang, S. K.; Churchill, M. R.; Fettingner, J. C. *Inorg. Chem.* **1986**, 25 (16), 2799–2805.
- (5) Caron, L.; Hudl, M.; Högl, V.; Dung, N. H.; Gomez, C. P.; Sahlberg, M.; Brück, E.; Andersson, Y.; Nordblad, P. *Phys. Rev. B* **2013**, 88 (9), 094440.
- (6) Delczeg-Czirjak, E. K.; Gercsi, Z.; Bergqvist, L.; Eriksson, O.; Szunyogh, L.; Nordblad, P.; Johansson, B.; Vitos, L. *Phys. Rev. B* **2012**, 85 (22), 224435.
- (7) Fujii, H.; Hōkabe, T.; Kamigaichi, T.; Okamoto, T. *J. Phys. Soc. Jpn.* **1977**, 43 (1), 41–46.
- (8) Maeda, Y.; Ikeda, T.; Ichikawa, T.; Nakajima, T.; Matsukura, B.; Sadoh, T.; Miyao, M. *Phys. Procedia* **2011**, 11, 200–203.
- (9) Scheerlinck, D.; Legrand, E. *Solid State Commun.* **1978**, 25 (3), 181–184.
- (10) Tegus, O.; Brück, E.; Buschow, K. H. J.; de Boer, F. R. *Nature* **2002**, 415 (6868), 150–152.

- (11) Tobola, J.; Bacmann, M.; Fruchart, D.; Kaprzyk, S.; Koumina, A.; Niziol, S.; Soubeyroux, J.-L.; Wolfers, P.; Zach, R. *J. Magn. Magn. Mater.* **1996**, 157–158, 708–710.
- (12) Bachman, R. E.; Miller, S. K.; Whitmire, K. H. *Organometallics* **1995**, 14 (2), 796–803.
- (13) Schipper, D. E.; Young, B. E.; Whitmire, K. H. *Organometallics* **2016**, *In Press*.
- (14) Pushkarevsky, N. A.; Konchenko, S. N.; Zabel, M.; Bodensteiner, M.; Scheer, M. *Dalton Trans.* **2011**, 40 (9), 2067.
- (15) Süss-Fink, G.; Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1982**, 224 (1), 59–68.
- (16) Gröer, T.; Palm, T.; Scheer, M. *Eur. J. Inorg. Chem.* **2000**, 2000 (12), 2591–2595.
- (17) Konchenko, S. N.; Pushkarevsky, N. A.; Virovets, A. V.; Scheer, M. *Dalton Trans.* **2003**, No. 4, 581–585.
- (18) Mathur, P.; Payra, P.; Ghose, S.; Hossain, M. M.; Satyanarayana, C. V. V.; Chicote, F. O.; Chadha, R. K. *J. Organomet. Chem.* **2000**, 606 (2), 176–182.
- (19) Scheer, M.; Vogel, U.; Becker, U.; Balazs, G.; Scheer, P.; Hönle, W.; Becker, M.; Jansen, M. *Eur. J. Inorg. Chem.* **2005**, 2005 (1), 135–141.
- (20) Kakizawa, T.; Hashimoto, H.; Tobita, H. *J. Organomet. Chem.* **2006**, 691 (4), 726–736.
- (21) Konchenko, S. N.; Pushkarevsky, N. A.; Scheer, M. *J. Organomet. Chem.* **2002**, 658 (1–2), 204–209.
- (22) Borg-Breen, C. C.; Bautista, M. T.; Schauer, C. K.; White, P. S. *J. Am. Chem. Soc.* **2000**, 122 (16), 3952–3962.
- (23) Zhang, J.; Leong, W. K. *J. Chem. Soc. Dalton Trans.* **2000**, No. 8, 1249–1253.
- (24) Sánchez-Nieves, J.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Inorganica Chim. Acta* **2003**, 350, 486–494.
- (25) Bott, S. G.; Shen, H.; Richmond, M. G. *J. Organomet. Chem.* **2004**, 689 (21), 3426–3437.
- (26) Gröer, T.; Scheer, M. *Organometallics* **2000**, 19 (18), 3683–3691.
- (27) Yang, W.; Fu, Q.; Zhao, J.; Cheng, H.-R.; Shi, Y.-C. *Acta Crystallogr. Sect. C Struct. Chem.* **2014**, 70 (6), 528–532.
- (28) Whitmire, K. H. *Adv. Organomet. Chem.* **42**, 1–145.
- (29) Aumann, R. Z. *Für Naturforschung Teil B Anorg. Chem. Org. Chem.* **1983**, 38B (11), 1325–1331.
- (30) Crocq, V.; Daran, J.-C.; Gouygou, M.; Heim, B.; Jeannin, Y.; Speel, R. *J. Clust. Sci.* **1996**, 7 (4), 505–529.
- (31) Gouygou, M.; Daran, J.-C.; Heim, B.; Jeannin, Y. *J. Organomet. Chem.* **1993**, 460 (2), 219–228.
- (32) López, E. M.; Miguel, D.; Pérez, J.; Riera, V.; Bois, C.; Jeannin, Y. *Organometallics* **1999**, 18 (4), 490–494.
- (33) Miguel, D.; Perez-Martinez, J. A.; Riera, V.; Garcia-Granda, S. *Organometallics* **1993**, 12 (8), 2888–2890.
- (34) Miguel, D.; Riera, V.; Miguel, J. A.; Soláns, X.; Font-Altaba, M. *J. Chem. Soc. Chem. Commun.* **1987**, No. 6, 472–474.
- (35) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics* **1990**, 9 (3), 595–601.
- (36) Alvarez, B.; Garcia-Granda, S.; Jeannin, Y.; Miguel, D.; Miguel, J. A.; Riera, V. *Organometallics* **1991**, 10 (9), 3005–3007.
- (37) Alvarez, B.; Li, J.; Miguel, D.; Morales, M. D.; Riera, V.; García-Granda, S. *Chem. Ber.* **1997**, 130 (10), 1507–1511.
- (38) Baudler, M.; Etzbach, T. *Angew. Chem. Int. Ed. Engl.* **1991**, 30 (5), 580–582.

- (39) Scherer, O. J.; Blath, C.; Wolmershäuser, G. *J. Organomet. Chem.* **1990**, 387 (2), C21–C24.
- (40) Rheingold, A. L.; Mark Fountain. *Organometallics* **1984**, 3 (9), 1417–1421.
- (41) Cossairt, B. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, 131 (42), 15501–15511.
- (42) Davies, J. E.; Kerr, L. C.; Mays, M. J.; Raithby, P. R.; Tompkin, P. K.; Woods, A. D. *Angew. Chem.* **1998**, 110 (10), 1473–1475.
- (43) Scherer, O. J.; Hilt, T.; Wolmershäuser, G. *Organometallics* **1998**, 17 (18), 4110–4112.
- (44) Schwarzmaier, C.; Bodensteiner, M.; Timoshkin, A. Y.; Scheer, M. *Angew. Chem. Int. Ed.* **2014**, 53 (1), 290–293.
- (45) Schwarzmaier, C.; Noor, A.; Glatz, G.; Zabel, M.; Timoshkin, A. Y.; Cossairt, B. M.; Cummins, C. C.; Kempe, R.; Scheer, M. *Angew. Chem.* **2011**, 123 (32), 7421–7424.
- (46) Spinney, H. A.; Piro, N. A.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, 131 (44), 16233–16243.
- (47) Umbarkar, S.; Sekar, P.; Scheer, M. *J. Chem. Soc. Dalton Trans.* **2000**, No. 7, 1135–1137.
- (48) Kagiroy, R. M.; Voloshin, A. V.; Kadirov, M. K.; Nizameev, I. R.; Sinyashin, O. G.; Yakhvarov, D. G. *Mendeleev Commun.* **2011**, 21 (4), 201–203.
- (49) Schipper, D. E.; Young, B. E.; Whitmire, K. H. *Organometallics* **2016**, 35 (4), 471–483.

Synopsis: A series of clusters of the form $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_6(\mu_3\text{-As})\{\mu_3\text{-EFe}(\text{CO})_4\}]$ 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 ECl_3 . AsCl_3 gives the As-only compound; 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 As_2P and 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 M_2E_3 core, structurally analogous to clusters with the well-known M_3E_2 core configuration. Analytical data as well as DFT calculations support the formation and geometries of the new molecules.