

Iron Carbonyl Clusters with ECl₂ Units (E = P, As)

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Dedicated to Richard D. Adams on the occasion of his 70th birthday

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Abstract: Reaction of [PPN][HFe(CO)₄] (PPN = bis(triphenylphosphine)iminium) with PCl₃ in a 1:1 ratio produced small amounts of [PPN][P{Fe(CO)₄}₂Cl₂] ([PPN][**Ia**]). Reaction of [Et₄N][HFe(CO)₄] with AsCl₃ in a 1:0.75 ratio in THF at -78 °C produced [Et₄N][As{Fe(CO)₄}₂Cl₂] ([PPN][**Ib**]) as the majority product. The compound [PPN][(CO)₄FePCl₂O] ([PPN][**II**]) was obtained from the reaction of Fe₂(CO)₉ with PCl₃ in THF. In contrast, [Et₄N][HFe(CO)₄] reacted with PCl₃ at -78 °C in a 2:1 ratio to yield [Et₄N][Fe₂(CO)₆{(μ₄-PFe(CO)₄)₂(μ-CO)}{μ-PCl₂}] ([Et₄N][**III**]) as the majority product. The compounds were characterized spectroscopically and by single-crystal X-ray diffraction analyses.

1. Introduction

Significant effort has been directed towards obtaining members of the iron phosphide family (Fe_4P , FeP_2 , FeP , Fe_2P , Fe_3P) as nanomaterials as these materials are important catalysts, energy storage compounds, and magnetic materials.¹⁻¹¹ These properties are phase-dependent; therefore, directing syntheses to obtain phase-pure materials is of key importance. One such route is with single-source precursors whose heavy element stoichiometry can be tailored to target specific phases. In our laboratory, we have shown that the precursor $\text{H}_2\text{Fe}_3(\text{CO})_9\text{P}^t\text{Bu}$ decomposes to Fe_3P as a thin film by simple MOCVD, that $\text{Fe}_4(\text{CO})_{12}(\text{P}^t\text{Bu})_2$ can be converted to nanostructures of Fe_2P , and that $\text{FeMn}(\text{CO})_8(\mu\text{-PH}_2)$ decomposes to nanoparticles of $\text{Fe}_{2-x}\text{Mn}_x\text{P}$.¹²⁻¹⁴ As a further demonstration of the versatility of the method, blends of isolobal organometallic complexes were used as the MOCVD feedstock for ternary $(\text{Fe}_{1-x}\text{Co}_x)_3\text{P}$ and $\text{Fe}_3(\text{P}_{1-x}\text{Te}_x)$ thin films.¹⁵ We have also dedicated effort to the pursuit of naked-main group element mixed metal carbonyl precursors to mixed P/As metal pnictide phases.^{16,17}

The purpose of this work was to develop a low-cost, high yield method to obtain molecular precursors containing iron and phosphorus to target specific iron phosphide phases. Despite many examples of metal carbonyl clusters containing iron, phosphorus, and alkyl groups, there are very few such clusters that contain only iron and phosphorus.^{16,18,19} While alkyl groups may be chosen that are good leaving groups, there is the possibility that their presence could introduce carbon contamination in the materials produced. Moreover, there is a need to prepare neutral iron carbonyl phosphide clusters with Fe:P ratios matching known Fe-P phases in order to avoid complications arising from the presence of counterions and to obtain volatile precursors. Effort has been directed, therefore, at developing routes based on the use of the main group element halides and iron carbonyl ions.

The pnictide trichlorides ECl_3 ($\text{E} = \text{P}, \text{As}$) were chosen as the pnictide source for its commercial scale of production, high intrinsic reactivity, and lack of alkyl groups which could be a source of carbon contamination in the produced phosphide materials were an alkyl group retained in the precursor. PCl_3 is already known to react with $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ to give $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\}(\mu_3\text{-PFe}(\text{CO})_4)]^-$.^{16,20} The corresponding reaction with AsCl_3 yields a mixture of $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\}(\mu_3\text{-AsFe}(\text{CO})_4)]^-$ and $[\{\text{AsFe}_2(\text{CO})_8\}_2(\mu\text{-}(\text{Fe}_2(\text{CO})_6)]^-$.¹⁶ There are, however, no reports of PCl_3 having been reacted with the simple and easily prepared anion $[\text{HFe}(\text{CO})_4]^-$. In this study, reactions between PCl_3 and $[\text{HFe}(\text{CO})_4]^-$ were undertaken to evaluate whether iron-carbonyl clusters with novel Fe:P ratios could be obtained.

2. Results and Discussion

2.1 Structure and Bonding

The reaction of $[\text{PPN}][\text{HFe}(\text{CO})_4]$ with PCl_3 in a 1:1 ratio at room temperature proceeds rapidly to produce a mixture of products. When the solution is taken to dryness, an oil results from which small crystals of $[\text{PPN}][\mathbf{Ia}]$ appeared after standing for three months. Similarly reaction of

AsCl₃ and [Et₄N][HFe(CO)₄] at -78 °C in a 0.75 AsCl₃ to 1.0 [HFe(CO)₄]⁻ ratio, formed [Et₄N][**Ib**] in good yield, but separation of the crystalline materials from an unidentified metal carbonyl impurity made isolation of a pure compound difficult. An FTIR spectrum of crystals mechanically separated from the impurity was, however, collected and found to be the majority constituent in solution.

While both products [PPN][**Ia**] and [Et₄N][**Ib**] were only obtained as a mixture with other substances, the single crystals that were obtained from those mixtures were suitable for single crystal X-ray diffraction (**Figure 1**). Crystallographic data collection and refinement parameters are summarized in **Table 1S** (see Supporting Information). [PPN][**Ia**] crystallizes in the monoclinic C2/c space group, while [Et₄N][**Ib**] crystallizes in the monoclinic space group P2₁/c. The phosphorus atom of [**Ia**]⁻, sits on a two-fold rotation axis such that each iron-phosphorus bond and phosphorus-chlorine bond are identical in length. The arsenic atom in [**Ib**]⁻, however, sits on a general position and possesses no crystallographically-imposed symmetry. The anions are isostructural and electron precise. They can be readily viewed as an ECl₂⁻ unit possessing two lone pairs of electrons that are then donated to neutral Fe(CO)₄ groups.

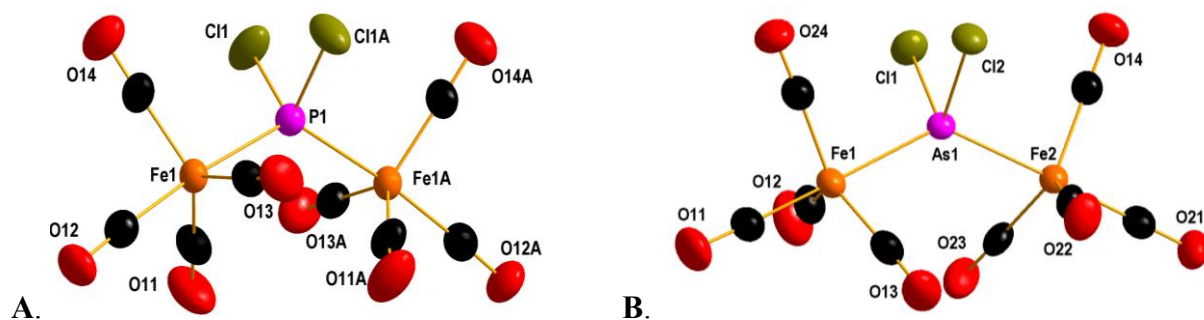


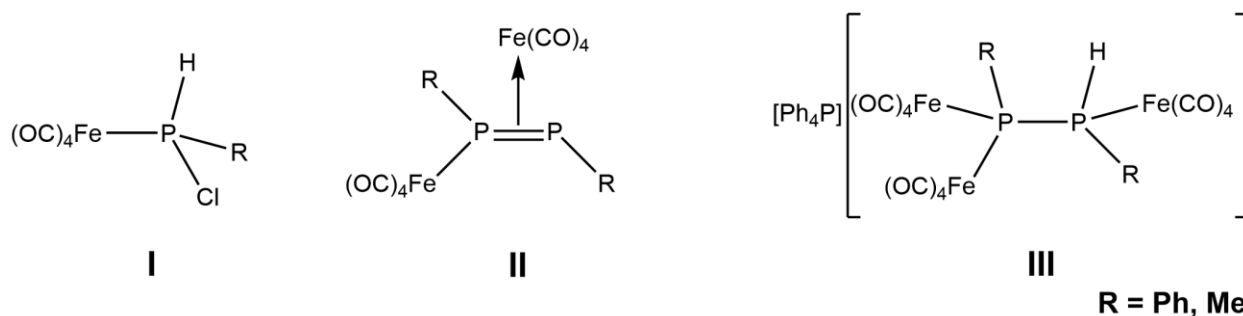
Figure 1. The structures of the anionic portions of (A) [PPN][**Ia**] and (B) [Et₄N][**Ib**].

The iron-phosphorus bond length of 2.2479(10) Å is typical of similar Fe-P covalent bonds and is comparable to the distance from phosphorus to Fe(CO)₄ of 2.2343(18) Å in [{Fe₃(CO)₉(μ-CO)}(μ₃-PFe(CO)₄)]⁻.¹⁶ The corresponding distances in Fe(CO)₄PH₃, Fe(CO)₄PPh₃, and Fe(CO)₄P(^tBu)₃ are similar at 2.219, 2.244(1), and 2.364(1) Å respectively.^{16,21–23}

The P-Cl bond length of 2.1051(17) Å in [**Ib**]⁻ is slightly longer than the 2.082(3) Å length of the respective bonds in the only other bimetallated bridging PCl₂ species that has been structurally characterized, [{CpW(CO)₃}(μ-PCl₂){CpW(CO)₃Cl}].²⁴ That compound is formed by the action of PCl₃ on [{CpW(CO)₃}]⁻.²⁴ The mean P-Cl lengths in Cr(CO)₅PCl₃ and W(CO)₅PCl₃ are 2.025, and 2.028 Å, respectively, which are markedly shorter.²⁵ This can be compared the gas phase value for the P-Cl bond length for free PCl₃ of 2.043 Å.²⁶ For [**Ib**]⁻, the mean As-Cl bond length is 2.210(15) Å, which is significantly shorter than that of [PyH][{Cr(CO)₅}₂(μ-AsCl₂)] at 2.294(15) Å,²⁷ which may occur due to steric crowding by the Cr(CO)₅ unit. By contrast, the As-Cl distance in

AsCl₃ is approximately 2.18 Å, again shorter.^{28–30} The longer E-Cl bonds in [Ia][−] and [Ib][−] may also reflect greater population of the E-Cl σ* orbital.

Dropwise addition of RPCl₂ (R = Ph, Me,) and [HFe(CO)₄][−] yields Fe(CO)₄P(Cl)RH (**I**),³¹ so we had anticipated that addition of PCl₃ with the iron hydride could produce Fe(CO)₄PCl₂H. This species may be formed initially, but it is likely to be unstable due to its ability to evolve HCl intramolecularly, to react further with [HFe(CO)₄][−], or to add PCl₃ with the formation of a P-P bond and elimination of HCl. When the authors of the original report of **I** conducted the addition by adding the RPCl₂ to the [HFe(CO)₄][−] solution and vice versa, they obtained different higher nuclearity clusters.³² When solutions of RPCl₂ (Ph, Me) and [Ph₄P][HFe(CO)₄] are added drop-by-drop in tandem, RP(H)ClFe(CO)₄ is formed quantitatively as determined by ³¹P and ¹H-NMR spectroscopies. If the [HFe(CO)₄][−] in solution is added to a solution of the PhPCl₂, **II** is formed. This species reacts with an additional equivalent of [HFe(CO)₄][−] to give **III**. The formation of the latter two species is accounted for by addition of PCl₃ to **I** with loss of HCl, addition of a further equivalent of [HFe(CO)₄][−], and loss of a further HCl to yield edge-on product **I** this species can then accept an additional molecule of [HFe(CO)₄][−] to yield anion **III**.

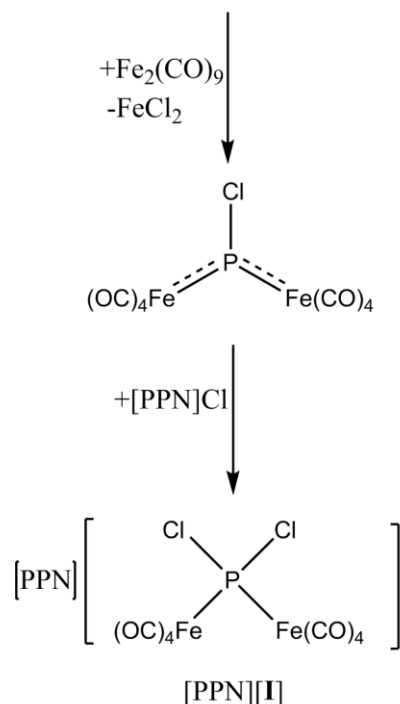
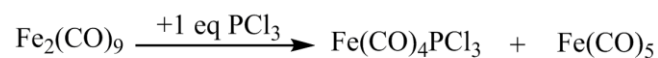


2.2 Attempted Synthesis of [$\{Fe(CO)_4\}_2P_2Cl_2\}^-$ from $Fe_2(CO)_9$ and PCl_3

von Seyerl *et al.* obtained the related compound [Et₄N][{Cr(CO)₅}₂(μ-AsCl₂)] by treatment of Cr(CO)₅(THF) with AsCl₃.²⁷ Those authors proposed the intermediate production of the indenone complex {Cr(CO)₅}₂(μ-AsCl) which subsequently added a chloride ion to give the final [$\{Cr(CO)_5\}_2(\mu-AsCl_2)\}^-$ ion. Given this hypothesis, we reasoned that the reaction here could proceed via reaction of Fe(CO)_x fragments with ECl₃ and decided to examine the reaction of PCl₃ and Fe₂(CO)₉ in the presence of [PPN]Cl in THF, a solvent in which the cluster is known to undergo fragmentation.³³ Fe₂(CO)₉ has been shown to react with PCl₃ in two different ways previously; when Fe₂(CO)₉ is stirred with eight times molar excess of PCl₃ at 50°C for two hours, Fe(CO)₄PCl₃, which can be fractionally distilled at 40°C, is produced along with Fe(CO)₅.³⁴ Oxidation was not observed although unaccounted for decomposition products were noted. Huttner *et al.* showed Fe₂(CO)₉ reacts in a ~2.2:1 ratio with PCl₃ at 40°C in toluene to form [$\{Fe_2(CO)_8\}(\mu_4-P)\{Fe_2(CO)_6(\mu-Cl)\}$] implying some degree of P-Cl bond reduction took

place.³⁵ It can be speculated that $\text{Fe}(\text{CO})_4\text{PCl}_3$ itself is stable but can react with $\text{Fe}_2(\text{CO})_9$ (or fragments thereof) to form higher nuclearity cluster species.

For this study, a suspension of $\text{Fe}_2(\text{CO})_9$ in THF was reacted with one equivalent of PCl_3 in THF in the presence of one equivalent of $[\text{PPN}]\text{Cl}$ in parallel with the work reported by von Seyerl *et al.* (**Scheme 1**). After one hour, the suspension had darkened to deep black-brown and the FTIR-spectrum showed stretches matching those determined for $[\mathbf{Ia}]^-$ along with the characteristic pattern of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{PCl}_3$. The solution was allowed to stir for another two hours, filtered through celite, and then the solvent and $\text{Fe}(\text{CO})_5$ were pumped away. Diethyl ether was added and the solids allowed to stand under an inert atmosphere overnight. Even though the presence of the $[\mathbf{Ia}]^-$ was obvious by FTIR after three hours of reaction, after filtration and evaporation of the solvent *in vacuo*, only crystals of the what proved to be the novel $[\text{Et}_4\text{N}][\text{Fe}(\text{CO})_4\text{PCl}_2\text{O}]$ ($[\text{Et}_4\text{N}][\mathbf{II}]$) were obtained. The IR spectrum was no longer consistent with $[\mathbf{Ia}]^-$, and no $[\mathbf{Ia}]^-$ was observed by ESI-MS of the crude product. The structure of the anion is shown in **Figure 2** and crystallographic data collection and refinement parameters are summarized in **Table 1S**.



Scheme 1. Possible inidene route to $[\mathbf{Ia}]^-$.

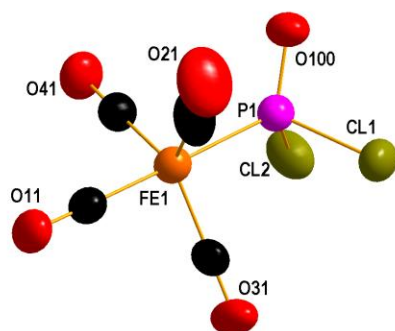
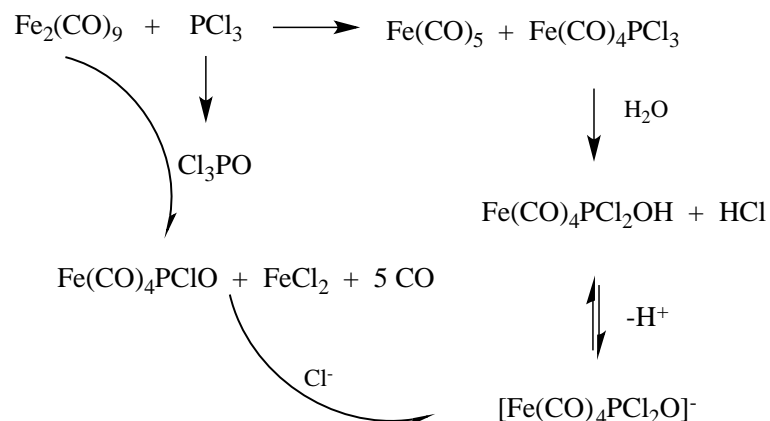


Figure 2. The structure of the anion in [PPN][**II**].

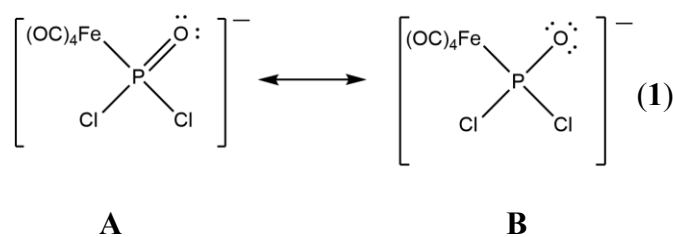
The anion [**II**]⁻ consists of an Fe(CO)₄ group coordinated by a [PCl₂O]⁻ anion and is electron precise. The Fe-P bond is 2.1942(6) Å, shorter than the corresponding distance of 2.2479(10) Å in [**Ia**]⁻, and short for an Fe-P bond in general,^{16,21–23} probably due to the ionic character of the P-O bond. The P-Cl bonds 2.090(13) Å (ave) are of similar distance to those in [**Ia**]⁻ and longer than 2.056(7) Å found in *trans*-[Ir(CO)Cl₂(PEt₃)₂{PCl₂O}], which is the only other known example of a [PCl₂O]⁻ unit bound to a metal. That compound was reported to form very slowly by direct action of O₂ on *trans*-[Ir(CO)Cl₂(PEt₃)₂{PCl₃}]³⁶ and steric crowding at the [PCl₂O]⁻ moiety should be less severe given the larger size of Ir as compared to Fe. The P=O double bond distance of length 1.466(4) Å is similar to that of PCl₃O (1.45 Å) and shorter than the corresponding distance in *trans*-[Ir(CO)Cl₂(PEt₃)₂{PCl₂O}] of 1.50 Å.

In considering the structure, a question arises about the route by which this compound is formed and the nature of the phosphorus atom's final oxidation state. There are two extremes in the way the PCl₂O⁻ ligand can be viewed: (1) [Cl₂P-O]⁻ with P in a 3+ oxidation state arising from simple hydrolysis of Fe-bound PCl₃ to give Fe(CO)₄PCl₂OH, which would then undergo deprotonation, or (2) a P(V) derivative created by oxidation of PCl₃ to Cl₃P=O followed by reaction with Fe₂(CO)₉ to produce an inidene-like Fe(CO)₄=PClO that could back-add a halide ion (**Scheme 2**). This suggests that there are two likely Lewis structures for the [**II**]⁻ as shown as structure **A** and **B** in **Equation 1**. Although PCl₃ is known to rapidly give HCl on contact with water, the intermediate production of PCl₂OH followed by elimination to give PClO + HCl under ambient conditions is not known. Direct formation of PClO is quite difficult. Literature reports give the synthesis as either the high temperature reaction of PCl₃O with silver wire or of water vapor with PCl₃ heated to 900 K,^{37,38} but the process could be promoted by binding to the transition metal center. In order to examine which Lewis picture of [**II**]⁻ is more reasonable, simple density functional theory (DFT) calculations were performed (See Experimental). The Wiberg bond indices calculated for the Fe and P atoms in a series of relevant molecules are given in **Table 1**. From this data, it can be seen that both the Fe and P of [**II**]⁻ have bond indices similar to those of

the other $\text{Fe}(\text{CO})_4\text{PX}_3$ species with somewhat higher Wiberg bond indices at P than the simple PX_3 molecules examined and a lower Wiberg bond index at P than in PCl_3O . The similarity of the bond indices of $[\text{II}]^-$ to both $\text{Fe}(\text{CO})_4\text{PH}_3$ and $\text{Fe}(\text{CO})_4\text{PCl}_3$ is consistent with the phosphorus remaining in a primarily 3+ oxidation state.



Scheme 2. Possible routes for the formation of the $[\text{Fe}(\text{CO})_4\text{PCl}_2\text{O}]^-$ ion.



Molecule	Wiberg bond indices at Fe	Wiberg bond indices at P
PCl_3	—	2.8769
PCl_2OH	—	2.5267
$[\text{PCl}_2\text{O}]^-$	—	2.6161
PCl_3O	—	4.0415
$\text{Fe}(\text{CO})_4\text{PCl}_3$	4.5616	3.7026
$\text{Fe}(\text{CO})_4\text{PH}_3$	4.5538	3.6584
$[\text{II}]^-$	4.6412	3.5497

Reexamination of the reaction in the absence of $[\text{PPN}]\text{Cl}$ was undertaken; in this case, $\text{Fe}(\text{CO})_4\text{PCl}_3$ and $\text{Fe}(\text{CO})_5$ appeared to be the majority species in the THF reaction medium as

found previously,³⁴ after removal of the Fe(CO)₅ and Fe(CO)₄PCl₃ at 40 °C under vacuum, a toluene extract of the solids contained Huttner's [$\{\text{Fe}_2(\text{CO})_8\}(\mu_4\text{-P})\{\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})\}$] and residual Fe(CO)₄PCl₃. Thus, it is possible that the phosphinidene complex which gives rise to [Ia]⁻ can convert to [$\{\text{Fe}_2(\text{CO})_8\}(\mu_4\text{-P})\{\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})\}$] if it is not trapped as [PPN][Ia]. In any case, [PPN][Ia] appears to be inherently unstable.

2.3 Low Temperature Reaction of PCl₃ with [Et₄N][HFe(CO)₄]

When [Et₄N][HFe(CO)₄] was treated with PCl₃ in a 4:3 ratio of reactants-at -78 °C, [Et₄N][III] formed as the majority product. At -78 °C, the solution acquired a light yellow-orange coloration which deepened over three hours. The solution then warmed to room temperature and the solvent removed in vacuo. Certain side reactions necessitate the use of low temperature conditions. Among these, the reaction of HCl and [HFe(CO)₄]⁻ which produces H₂Fe(CO)₄ is problematic. H₂Fe(CO)₄ can undergo substitution reactions at low temperature to yield Fe(CO)₄L species and H₂. At temperatures above -20 °C, decomposition to "Fe(CO)₄" appears to occur.³⁹ The presence of either Fe(CO)₄ or Fe(CO)₄L could complicate the formation of [Et₄N][III].

The ³¹P-NMR spectrum of crystalline [Et₄N][III] shows two sets of phosphorus environments: a doublet of $J=99.79$ Hz at 69.65 ppm and a triplet of $J=99.95$ Hz at 197.43 ppm integrating to a 2.01:1 ratio, consistent with the P2/P3 and P1 environments respectively. Further confirmation of the composition of [Et₄N][III] is its ESI/MS mass spectrum where a peak series beginning with principal peak of $m/z = 806.5$ and its subsequent CO loss peaks is observed, consistent with the [Fe₄P₃Cl₂C₁₅O₁₅]⁻ formulation of the anion. Isolation of crystalline [Et₄N][III] in sufficient quantities for elemental analysis was not undertaken.

The structure of the anion of [Et₄N][III] is shown in **Figure 3**. Selected bond distances and angles are found in **Table 2**. It consists of an Fe₂P₃ core with non Fe-Fe bond. Other molecules are known with bridging carbonyl groups between phosphorus atoms: Fe₂(CO)₆{(P^tBu)₂(μ-CO)} (**IV**) and Fe₂(CO)₆{(PNR₂)₂(μ-CO)} (R = ⁱPr (**Va**), NMe₂ (**Vb**), NCy₂ (**Vc**)) formed by the action of RPCl₂ on Na₂Fe(CO)₄ in Et₂O.⁴⁰ These molecules possess an Fe-Fe bond. The CO-bridged P-P distance in [III]⁻ is much longer. While not true bonds, the P-P distances in [(ⁱPr₂NP)₂{Fe₂(CO)₆(μ-CO)}] and [(^tBuP)₂{Fe₂(CO)₆(μ-CO)}] are notably shorter at and 2.539(3) Å 2.524(5) Å, respectively.^{41,42} The corresponding distance in [III]⁻ is 2.6425(7) Å, likely due to the effect of the μ-PCl₂ in [III]⁻ and the lack of an Fe-Fe bond. Additionally, the longer P-P distances leads to a shorter P-μ-CO distances: 1.884(5) Å and 1.877(4) Å in [(ⁱPr₂NP)₂{Fe₂(CO)₆(μ-CO)}] and [(^tBuP)₂{Fe₂(CO)₆(μ-CO)}], respectively, versus 1.855(14) Å in [III]⁻. The bonds to the central iron atoms from the μ₃-P atoms are also shorter in **IV** and **Va** at mean distances of 2.230(3) Å and 2.226(4) Å, respectively, than those in [III]⁻ which average 2.379(6) Å.

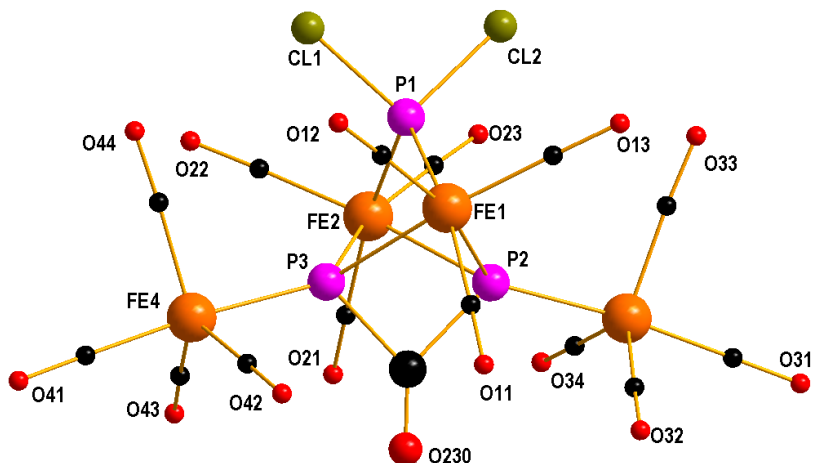


Figure 3. The anion of [Et₄N][III].

Table 2. Bond lengths [Å] and angles [°] for [Et₄N][III]

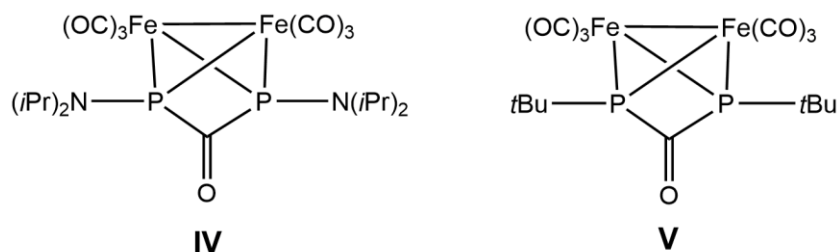
bond distances

Fe(1)-P(1)	2.2029(7)	Cl(1)-P(1)	2.0536(7)
Fe(2)-P(1)	2.1960(7)	Cl(2)-P(1)	2.0631(9)
Fe(1)-P(2)	2.3792(9)	P(3)-P(2)	2.6425(7)
Fe(1)-P(3)	2.3699(7)	P(3)-C(230)	1.8540(14)
Fe(2)-P(2)	2.3800(9)	P(2)-C(230)	1.8564(15)
Fe(2)-P(3)	2.3851(9)	C(230)-O(230)	1.2048(17)
Fe(3)-P(2)	2.2422(6)		
Fe(4)-P(3)	2.2389(7)		

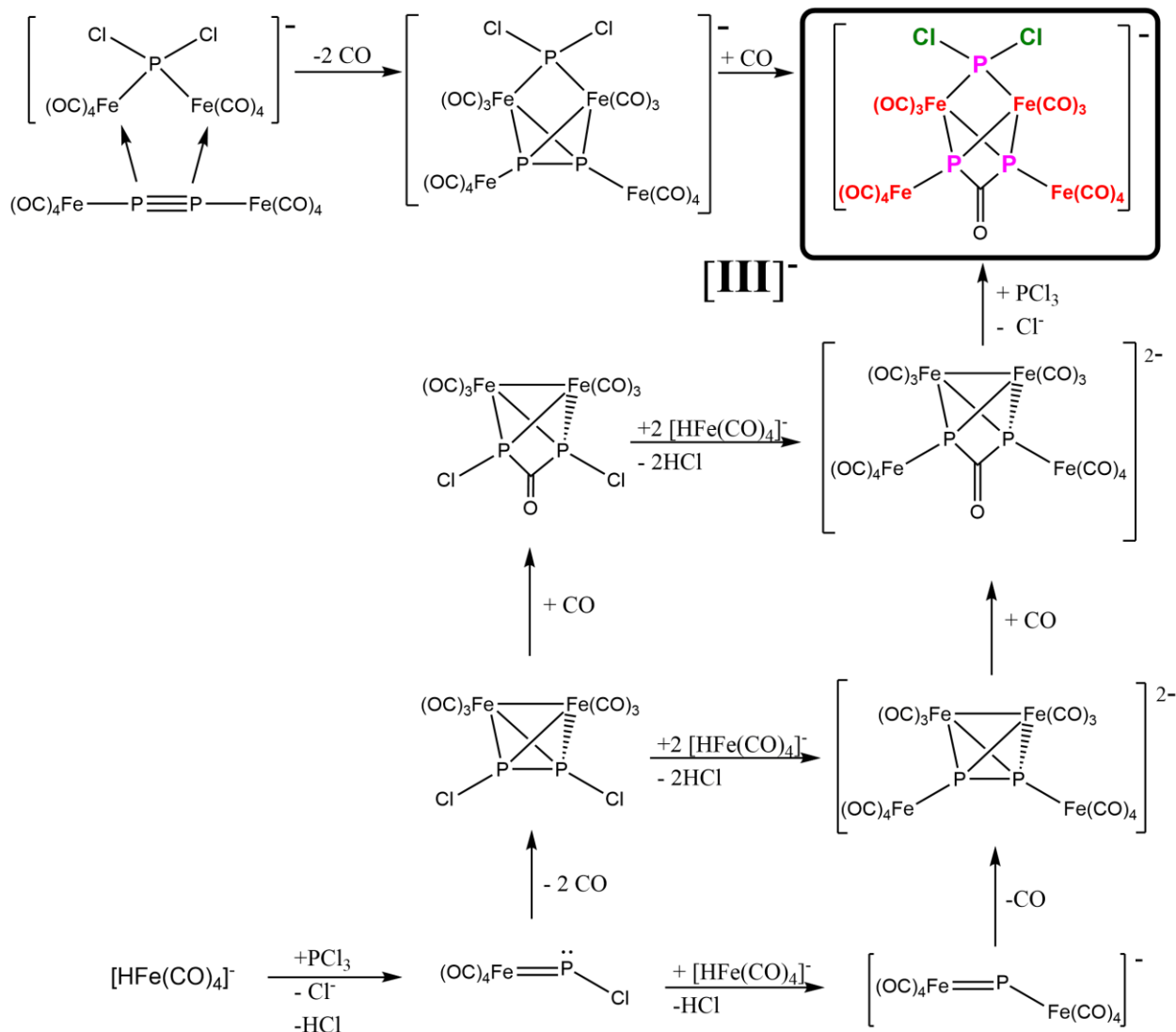
The anion in [III]⁻ can also be compared to [Ia]⁻ as both contain similar [$\{Fe(CO)_x\}_2(\mu-PCl_2)$] fragments. The average Fe-P(Cl) distance in the [III]⁻ unit is 2.199(5) Å, somewhat shorter than the of the corresponding distance in [Ia]⁻ (2.2479(10) Å). In spite of the shorter distance and more expected crowding, the P-Cl bonds in [III]⁻ are shorter with a mean distance of 2.058(7) Å compared to either [Ia]⁻ or [Ib]⁻ (2.1051(17) Å and 2.090(13) Å, respectively). [Et₄N][III] is far more stable than salts of either [Ia]⁻ or [Ib]⁻; crystals were stable for months in their crystallization solutions. It could be speculated that the less accessible, short P-Cl bonds are much less reactive than the longer P-Cl bonds of [I]; additionally, there is no easy route for the central iron atoms in [III]⁻ to form a bond between themselves, whereas [Ia]⁻ can close with concomitant CO loss.

Alternatively, anion [III]⁻ can be viewed as an arachno pentagonal bipyramid with the Fe(CO)₃ groups in the axial positions and the three phosphorus atoms occupying three of the five equatorial positions. This would predict a skeletal electron pair count of 8 as observed (one pair from each Fe(CO)₃ group, three electrons from each PFe(CO)₄ unit, one pair from the bridging CO and two pair from the PCl₂⁻ moiety). This analysis, however, would presuppose some bonding between P2 and P3, which seems unlikely given the long distance (2.6425(7) Å). Alternatively, one could use an electron precise model in which each Fe(CO)₃ group receives two electrons from P1 and one electron each from P2 and P3 to achieve an 18-electron metal center. P2 and P3 each receive one electron from each Fe and one from the bridging CO to complete their octets.

It is conceptually interesting to consider that the cluster can be further divided into two units: an [$\{\text{Fe}(\text{CO})_3\}_2(\mu\text{-PCl}_2)\text{]}^-$ unit, derived from [Ia]⁻ by removal of a CO from each iron, attached to an (OC)₄FeP≡PFe(CO)₄ unit, a dimetalladiphosphaalkyne (**Scheme 3**). This is consistent with the formation of [Ia]⁻ followed by subsequent addition across the multiple bond. The addition of CO across a P-P bond in Fe₂(CO)₆(PR)₂ clusters also has precedent.⁴¹ On the other hand, compounds IV and V have been proposed to arise from dimerization of unstable [Fe(CO)₄=PR] upon warming -70°C to -30 °C.⁴⁰



Such intermediates could also be possible here (**Scheme 3**).^{40,43} Treating [HFe(CO)₄]⁻ as a source of [Fe(CO)₄]²⁻, one can envision the first product to form in the reaction of [HFe(CO)₄]⁻ with PCl₃ as Fe(CO)₄=PCl (**Scheme 3**) with loss of [Et₄N]Cl and HCl. This could then follow the route Fe(CO)₄=PR forms to form an [(CIP)₂{Fe₂(CO)₆(μ-CO)}] unit which could react with a further two units of [HFe(CO)₄]⁻ to give [$\{\text{Fe}(\text{CO})_4\text{P}\}_2\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\}$] with the remaining step being nucleophilic displacement of the chloride of an additional molecule of PCl₃, opening the Fe-Fe bond and leaving the cluster a monoanion. The Fe(CO)₄=PCl unit could also react with [HFe(CO)₄]⁻ to give [Fe(CO)₄=PFe(CO)₄]⁻ which could react with itself or Fe(CO)₄=PCl to form the core. In the end, consumption of all of the P-Cl bonds in the growing core structure is achieved.



Scheme 3. Possible routes for the formation of $[III]^-$.

3. Experimental

3.1 General Considerations

All reactions were performed under dry, oxygen-free argon according to standard Schlenk techniques. Tetrahydrofuran, diethyl ether, dichloromethane, and toluene were dried using a Pure Process Technology solvent purification system and degassed prior to use. The compounds $[PPN]Cl$, $[PPN][HFe(CO)_4]$, and $[Et_4N][HFe(CO)_4]$ were prepared according to literature methods.^{44,45} $Fe_2(CO)_9$ was purchased from Strem Chemicals and used as received. PCl_3 and $AsCl_3$ were purchased from Sigma Aldrich. The PCl_3 was distilled prior to use; the $AsCl_3$ was used without further purification. ^{31}P NMR data were recorded on a 500 MHz Bruker spectrometer (202 MHz for ^{31}P). ESI-MS data were collected on a Bruker Daltonics microTOF ESI/MS coupled with an Agilent 1200 HPLC instrument.

3.2 Synthesis of Compounds

[PPN][P{Fe(CO)₄}₂Cl₂] ([PPN][Ia]). To a flask containing 0.8 g of [PPN][HFe(CO)₄] (1.2 mmol) was added 30 mL of Et₂O. To the resulting mixture was added 0.1 mL of PCl₃ (1.2 mmol). The reaction was stirred for six hours, filtered, and the solvent removed *in vacuo* leaving a brown, oily film on the walls of flask. Argon was reintroduced, and the flask was closed and placed in the dark at room temperature. After three months, small orange crystals of [PPN][I] suitable for diffraction were found growing in the brown film.

[PPN][{Fe(CO)₄}PCl₂O] ([PPN][II]): To a flask containing 1.0 g of Fe₂(CO)₉ (2.8 mmol) and 1.6 g of [PPN]Cl (2.8 mmol) was added a solution of 240 μL PCl₃ (2.75 mmol) in 40 mL THF. Of this reaction at 1 h showed the stretches for Fe(CO)₅, Fe(CO)₄PCl₃, and [PPN][Ia]; at 3 h, only Fe(CO)₅ and [PPN][I] were present. The solids were allowed to react for three hours, whereafter the resulting orange-brown solution was filtered through 5 cm of Celite and taken to dryness *in vacuo*. 50 mL of diethyl ether were then added to the solids and allowed to stand without stirring for 15 hours. Crystalline, prismatic blocks of [PPN][II] were observed in abundance along with some orange matter. [PPN][II] was observed to be soluble in DCM, although it was not isolated.

[Et₄N][As{Fe(CO)₄}Cl₂] ([Et₄N][Ib]). 1.6 g of [Et₄N][HFe(CO)₄] (5.4 mmol) was dissolved in 20 mL THF and chilled to -78 °C in a dry ice/acetone bath. Arsenic trichloride (338 μL, 4.0 mmol) was dissolved in 10 mL THF, also chilled to 0 °C, and transferred to the previous solution via cannula. The solution was allowed to warm to room temperature following the addition. After one hour of stirring at room temperature, the THF was removed. 40 mL of diethyl ether was then added, the mixture stirred for two hours, filtered, and stored in the refrigerator at -10 °C. After three days, large square blocks of [Et₄N][Ib] suitable for single crystal X-ray diffraction were found among a light brown polycrystalline precipitate. The IR spectrum was collected for crystals mechanically isolated from the polycrystalline precipitate. ν_{CO} (THF): 2052 (w), 2047 (vwsh), 2031(s), 2024 (msh), 1955 (vs, br) 1940, (ssh, br), 1928 (wsh) cm⁻¹.

[Et₄N][Fe₂(CO)₆{(μ₄-PFe(CO)₄)₂(μ-CO)}{μ-PCl₂}] ([Et₄N][III]): 1.2 g of [Et₄N][HFe(CO)₄] (3.68 mmol) was dissolved in 20 mL dichloromethane chilled to ~-70 °C in a dry ice/acetone bath. 240 μL of PCl₃ (2.8 mmol) in 20 mL of dichloromethane was cooled to -78 °C and transferred to the first flask rapidly. The mixture was then allowed to stir for three hours before warming to room temperature. After one hour at room temperature, the dichloromethane was removed *in vacuo* without the assistance of a warm water bath leaving a dark red solid. Ether was introduced and allowed to stand over the solid. High-quality crystals of [Et₄N][III] appeared after two days of standing. Mechanical separation from a polycrystalline red solid allowed enough material to be isolated for ESI/MS and ³¹P-NMR. ν_{CO} (dichloromethane): 2063 (s), 2035 (vs), 1964 (vw), 1934, (m), 1605 (w) cm⁻¹. ESI/MS of crystalline material: *m/z* (%) 806.5 (46) [III]⁻, 778.5(35) [III]⁻ - CO, 750.5 (4) [III]⁻ - 2 CO, 722.5 (2) [III]⁻ - 3 CO, 694.5 (2) [III]⁻ - 4 CO, 666.5 (1) [III]⁻ - 5 CO, 638.5 (1) [III]⁻ - 6 CO, 610.5 (1) [III]⁻ - 7 CO, 582.5 (tr) [III]⁻ - 8

CO. ^{31}P NMR data(d^3 -acetonitrile, ppm, shifts relative to H_3PO_4 , SR -70.47: 69.65 (d, 2P, $J=99.79$ Hz), 197.43 (t, 1P, $J=99.95$ Hz).

Density Functional Theory Calculations for [II]⁻ and related molecules. Density functional theory calculations were carried out using the GAUSSIAN09 program⁴⁶ to optimize the geometrical parameters for PCl_3 , PCl_2OH , $[\text{PCl}_2\text{O}]^-$, PCl_3O , $\text{Fe}(\text{CO})_4\text{PCl}_3$, $\text{Fe}(\text{CO})_4\text{PH}_3$, and $[\text{II}]^-$ at the B3LYP level of theory with 6-311G** basis sets.⁴⁷⁻⁴⁹ Full natural bond orbital (NBO) analyses⁵⁰⁻⁵⁷ were then performed with the optimized geometries, and the calculations produced Wiberg bond indices for the respective clusters.

4. Conclusions

A series of iron carbonyl clusters containing rare $\mu\text{-ECl}_2$ units were synthesized. The generation of $[\text{Ia}]^-$ suggests to a phosphinidene intermediate that can be captured or stabilized as $[\text{Ia}]^-$. While compound $[\text{Ib}]^-$ results from a different reaction, this As-containing compound is isostructural to $[\text{Ia}]^-$ but is more stable than its phosphorus relative. Attempts to prepare $[\text{Ia}]^-$ by a rational, stoichiometric route led to $[\text{II}]^-$ instead. Exploration of the effect of temperature on the original reaction that produced $[\text{Ia}]^-$ led to the isolation of $[\text{III}]^-$ that also possesses a $\mu\text{-PCl}_2$ group that bridges two iron carbonyl fragments similarly to $[\text{Ia}]^-$.

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6. Supporting Information

Table 1S summarizing the crystallographic data collection and refinement parameters. ^{31}P spectrum and ESI-Mass Spectrum for $[\text{Et}_4\text{N}][\text{III}]$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with the following reference numbers: $[\text{PPN}][\text{Ia}]$, 1522800; $[\text{Et}_4\text{N}][\text{Ib}]$, 1522799; $[\text{Et}_4\text{N}][\text{II}]$, 1522801; $[\text{Et}_4\text{N}][\text{III}]$, 1522797.

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