Synthesis and Structure of the New Fe complex, [Fe^{II}Cl$_3$(PEt$_3$)]$^-$

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Reduced simple Fe salt has played an important role in the synthesis of high nuclearity transition metal clusters.[1] Especially trialkylphosphine ligand-containing Fe compounds, such as FeCl$_2$(PEt$_3$)$_2$, have been valuable starting materials in the synthesis of model compounds of nitrogenase cofactor (MoFe$_7$S$_9$X).[2,3] The dissociation of trialkylphosphine opens up vacant coordination sites around the Fe atom to build high nuclearity clusters. At the same time, the dissociated trialkylphosphine can act as an additional ligand for the product and as a weak reducing reagent in the reaction.[4] On the line of this logic, a new phosphine-containing mono-metallic Fe reagent, (Et$_4$N)[FeCl$_3$(PEt$_3$)] was synthesized.

$$FeCl_2 + PEt_3 + Et_4NCl \xrightarrow{\ THF/MeCN\ } \left[\ \right]^- \quad [Et_4N]^+$$
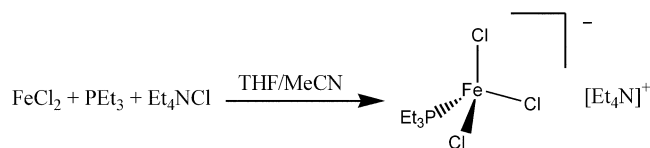
Although its isolation has been noted previously as a reaction by-product,[3(c)] its synthetic method has never been reported. Here, we report a new simple Fe complex that may have a great potential in synthetic inorganic chemistry.

Experimental Section

All experiments and reactions were carried out under a dinitrogen atmosphere using standard Schlenk line techniques or in an inert atmosphere glove box. All solvents were distilled under dinitrogen and nitrogen gas was bubbled through before each use in the glove box. PEt$_3$ was purchased from Aldrich and used without further purification. Fe(PEt$_3$)$_2$Cl$_2$ was prepared according to the published methods.[3(c)]

^{1}H-NMR spectra were recorded on a 400 MHz using a Bruker 400 MHz NMR spectrometer. FT-IR spectra were collected on a Nicolet DX V. 4.56 FT-IR spectrometer in KBr pellets and the spectra were corrected for background. Elemental analyses were performed in the Microanalytical Laboratory at the University of Michigan. The data were corrected using acetanilide as a standard. Mössbauer spectrum for the compound was obtained with the high-sensitivity Mössbauer spectrometer by Dr. Namdoo Moon in the Biophysics department at the University of Michigan.[5] Mössbauer measurement was carried out at 125 K in zero

applied magnetic field using a crystalline sample. The source was ^{57}Co in a Rh matrix and the isomer shift was reported versus Fe metal at room temperature. The Magnetic susceptibility measurement was carried out on a MPMS SQUID magnetometer, and the data were corrected for diamagnetic contributions.[6] FAB$^-$ mass spectra were obtained with a 3-nitrobenzoyl alcohol matrix. UV-Vis spectrum was recorded on a Hewlett Packard 8453 spectrophotometer equipped with a circulating water bath.

(Et$_4$N)[FeCl$_3$(PEt$_3$)]. FeCl$_2$·4H$_2$O (1.0 g, 5.0 mmol) and PEt$_3$ (740 ul, 5.0 mmol) were added into the solution of THF/MeCN (1 : 1, 40 mL) and stirred for 30 min. After Et$_4$NCl (840 mg, 5.0 mmol) was added, the reaction mixture was stirred for additional 1 hour to dissolve FeCl$_2$·4H$_2$O completely. The pale green solution was filtered through the sintered glass filter and copious amount of ether was layered over the solution to induce incipient crystallization. Rhombic-shaped clear crystals were isolated (*ca.* 1.5 g, 3.65 mmol, 73% yield). ^{1}H-NMR (CD$_3$CN): δ – 1.27 (br. s. NCH$_2$CH$_3$), 2.59 (br. s. PCH$_2$CH$_3$), 3.17 (br. d. NCH$_2$), 96 (br. s. PCH$_2$). FT-IR (KBr) v (C-H of PEt$_3$); 2968 (s), 2938 (s), 2901 (w), 2879 (m), v (C-H of Et$_4$N); 3014 (m), 1458 (s). Far-IR (KBr) v(Fe-Cl). 469 (s). FAB$^-$-MS (NBA, m/z) 278.1 ([FeCl$_3$(PEt$_3$)]$^-$), 160.8 ([FeCl$_3$]$^-$). Analysis. Calculated for C$_{14}$H$_{35}$Cl$_3$FeNP. (I. MW. 410.61): C, 40.95; H, 8.59; N, 3.41. Found: C, 40.76; H, 8.78; N, 3.45. UV-Vis (in MeCN): λ_{max} (ε) $-$ 291 nm (250 M^{-1}cm^{-1}).

X-ray crystallography. A Siemens SMART system was used for the collection of all diffraction data at 158(2) K. A SHELX-97 package WinGx version was used for structure refinement.[7] Direct methods were used for the structure solutions. The structures were refined by a Full-matrix least-squares method on F^2. Crystal data and structure refinement for the compounds are shown at Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-230921). The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystalline (Et$_4$N)[FeCl$_3$(PEt$_3$)] was synthesized from

Notes

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Table 1. Crystal data and structure refinement for the (Et₄N)-[FeCl₃(PEt₃)]

Empirical formula	C14 H35 Cl3 Fe N P
Formula weight	410.60
Temperature	158(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.003(4) Å = 93.290(5)°.
	b = 13.851(5) Å = 90.321(6)°.
	c = 12.646(4) Å = 90.466(6)°.
Volume	2099.0(12) Å³
Z	4
Density (calculated)	1.299 Mg/m³
Absorption coefficient	1.169 mm⁻¹
F(000)	872
Crystal size	0.24 × 0.20 × 0.20 mm³
Theta range for data collection	1.47 to 26.63°.
Index ranges	-14 ≤ h ≤ 15, -17 ≤ k ≤ 17, -15 ≤ l ≤ 15
Reflections collected	20064
Independent reflections	8521 [R(int) = 0.0665]
Completeness to theta = 26.63°	96.8%
Refinement method	Full-matrix least-squares on F²
Data / restraints / parameters	8521 / 0 / 363
Goodness-of-fit on F²	0.996
Final R indices [I>2sigma(I)]	R1 = 0.1456, wR2 = 0.3902
R indices (all data)	R1 = 0.1753, wR2 = 0.3988

Table 2. Selected bond lengths (Å) and angles (°) for the (Et₄N)-[FeCl₃(PEt₃)]

Fe(1)-Cl(3)	2.264(4)	Fe(2)-Cl(4)	2.281(5)
Fe(1)-Cl(2)	2.285(4)	Fe(2)-Cl(5)	2.290(4)
Fe(1)-Cl(1)	2.288(4)	Fe(2)-Cl(6)	2.289(5)
Fe(1)-P(1)	2.437(4)	Fe(2)-P(2)	2.438(4)
P(1)-C(1)	1.796(17)	P(2)-C(9)	1.796(17)
P(1)-C(5)	1.827(15)	P(2)-C(11)	1.809(18)
P(1)-C(3)	1.834(18)	P(2)-C(7)	1.828(16)
Cl(3)-Fe(1)-Cl(2)	113.64(18)	Cl(4)-Fe(2)-Cl(5)	113.35(17)
Cl(3)-Fe(1)-Cl(1)	113.67(17)	Cl(4)-Fe(2)-Cl(6)	111.15(18)
Cl(2)-Fe(1)-Cl(1)	109.94(17)	Cl(5)-Fe(2)-Cl(6)	111.86(18)
Cl(3)-Fe(1)-P(1)	106.28(16)	Cl(4)-Fe(2)-P(2)	104.62(16)
Cl(2)-Fe(1)-P(1)	108.53(16)	Cl(5)-Fe(2)-P(2)	105.72(15)
Cl(1)-Fe(1)-P(1)	104.17(15)	Cl(6)-Fe(2)-P(2)	109.70(17)
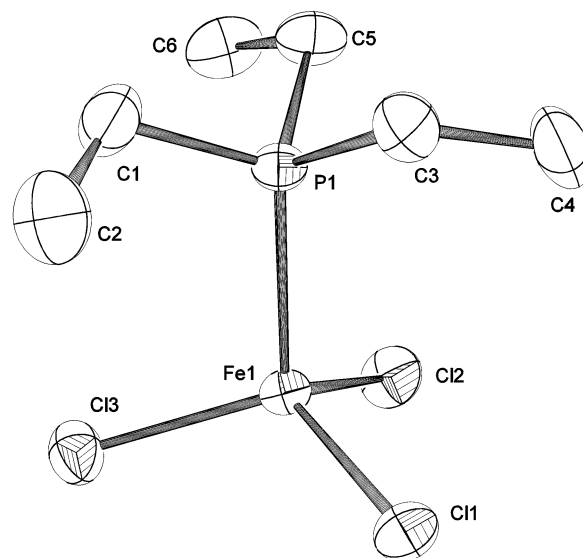
Figure 1. Single-crystal X-ray structure of the [FeCl₃(PEt₃)] anion. The hydrogen atoms were omitted for clarity.

simple starting ferrous chloride with equal molar amounts of PEt₃ and Et₄NCl. Upon addition of triethylphosphine, the initial clean solution was turned into green. Filtration of the reaction product gave pale purple solution similar to [Fe₂Cl₃(etriphos)₂]⁻, a dimeric Fe compound synthesized using a similar method.[8,9] The same compound can be also prepared from the reaction between [FeCl₂(PEt₃)₂] and Et₄NCl. Both reactions are achieved through ligand substitution. Compared to [Fe₂Cl₃(etriphos)₂]⁺, it is very sensitive to air and turns into red upon exposure to air. Even crystals were decomposed immediately into hydrated ferric compounds generating triethylphosphine. ¹H-NMR characterization of the (Et₄N)[FeCl₃(PEt₃)] in CD₃CN shows the signals corresponding to four sets of protons. The signals of ethyl protons of tetraethylammonium ion and methyl protons of triethylphosphine are found in a diamagnetic region. The signal of methylene groups of triethylphosphine is found approximately at 96 ppm, which implies the high-spin state of the Fe complex. FT-IR measurement of the (Et₄N)[FeCl₃(PEt₃)] proved the existence of triethylphosphine and tetraethylammonium cation in the product. The Fe-Cl stretching at 469 cm⁻¹ was characteristic for this compound.[10] The crystalline compound is readily soluble in MeCN resulting in a transparent solution resulted and has a weak absorption at 291 nm. Although it does not react with elemental sulfur, it shows reactivity with alkylthiolates.

The crystal data and structure refinement table is shown at Table 1. Selected bond lengths (Å) and angles (°) for the

(Et₄N)[FeCl₃(PEt₃)] are shown at Table 2. The Fe complex has a pseudo-C3 rotation symmetry around the Fe1-P1 axis and triethyl group and three chloride atoms are skewed about 17° along the Fe1-P1 axis as shown at Figure 1. The average Fe-Cl distance of 2.283(2) Å is a little shorter than that of 2.292(2) Å in (Me₄N)₂[FeCl₄] (Table 2).[11] Trialkylphosphine is known to stabilize reduced Fe centers in the transition metal/chalcogenide clusters as a π-acceptor and it is evident here by the shorten Fe-Cl bonds.[1] When the chloride ligands are bridged to the other Feᴵᴵ atom, the Fe-Cl distance of the [Fe₂Cl₃(etriphos)₂]⁺ is found at the range of 2.358(3) Å-2.400(3) Å.[9] This is probably due to the formation of Fe-Fe bonding in the complex which weakens Fe-Cl bonding. Similar compound has been reported as a non-coordinating anion of the organometallic compound, and the Fe-Cl bond distances of the [FeCl₃(PMe₃)]⁻ are found in the range of 2.275(1) Å-2.287(2) Å.[12]

Mössbauer spectrum of the (Et₄N)[FeCl₃(PEt₃)] is shown at Figure 2. The isomer shift (δ), indicative of oxidation state

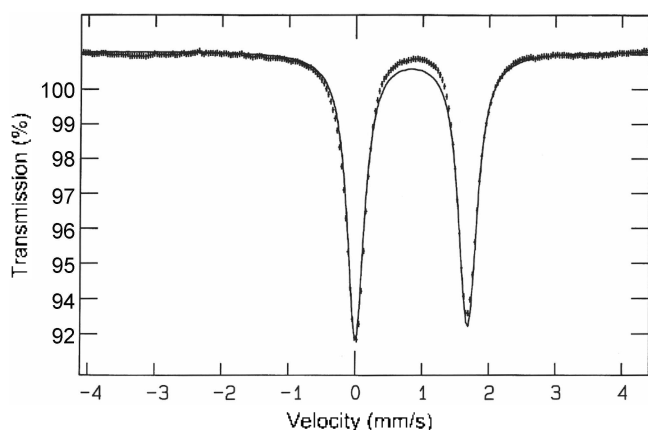**Figure 2.** ^{57}Fe Mössbauer spectrum of the (Et$_4$N)[FeCl$_3$(PEt$_3$)] at 125 K in zero applied magnetic field. The cross marks are for the observed data and the solid line shows the simulated graph fitted with one Fe center with the Mössbauer parameters of δ 0.84 mm/s and ΔE_Q = 1.68 mm/s.

of Fe center, is found at 0.84 mm/s, which implies a ferrous center. The isomer shift value of the (Et$_4$N)[FeCl$_3$(PEt$_3$)] is smaller than that of the (Et$_4$N)$_2$[FeCl$_4$] (δ = 0.90 mm/s), and the quadrupole splitting value of 1.68 mm/s is much larger than that of the (Et$_4$N)$_2$[FeCl$_4$] (δ = 0.76 mm/s).[13] The electronic effect by the triethylphosphine on the Mössbauer spectra of the [FeCl$_n$(PEt$_3$)$_{4-n}$]$^{2-n}$ complexes (n = 2, 3, or 4) has been discussed before.[3(c)] High-spin configuration of the ferrous center has been confirmed by magnetic moment measurement, and μ_{eff} = 5.58 BM and 5.29 BM were found after diamagnetic correction at 300 K and 4 K, respectively.

In summary, we have successfully synthesized the new Fe complex from simple starting material in high yields. This well-characterized high-spin ferrous complex is expected to be useful in synthesizing Fe-containing coordination com-plexes and high nuclearity clusters. Currently, efforts to synthesize high nuclearity clusters as nitrogenase cofactor model compounds using this new inorganic reagent are under way.

References

1. Snyder, B. S.; Reynolds, M. S.; Holm, R. H.; Papaefthymiou, G. C.; Frankel, R. B. *Polyhedron* **1991**, *10*, 203.
2. Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696.
3. (a) Han, J.; Coucouvanis, D. *Inorg. Chem.* **2002**, *41*, 2738. (b) Han, J.; Huang, M.; Coucouvanis, D. *Polyhedron* **2002**, *21*, 2523. (c) Han, J.; Koutmos, M.; Al-Ahmad, S.; Coucouvanis, D. *Inorg. Chem.* **2001**, *40*, 5985.
4. (a) Park, B.-G.; Choi, N.-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1999**, *20*, 314. (b) Jung, J.-H.; Lee, S. W. *Bull. Korean Chem. Soc.* **1993**, *14*, 1.
5. Moon, N.; Coffin, C. T.; Steinke, D. C.; Sands, R. H.; Dunham, W. R. *Nucl. Inst. Meth. Phys. Res. B* **1996**, *119*, 555.
6. *Theory and Applications of Molecular Diamagnetism*; Mulay, L. N.; Boudreaux, E. A., Eds.; Wiley-Interscience: New York, 1976.
7. Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.
8. etriphos = 1,1,1-tris((diethylphosphino)methyl)ethane.
9. Bianchini, C.; Dapporto, P.; Mealli, C.; Meli, A. *Inorg. Chem.* **1982**, *21*, 612.
10. Clausen, C. A. III.; Good, M. L. *Inorg. Chem.* **1970**, *9*, 220.
11. Lauher, J. W.; Ibers, J. A. *Inorg. Chem.* **1975**, *2*, 348.
12. Blecke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 486.
13. Burbridge, C. D.; Goodgame, D. M. L. *J. Chem. Soc. (A)* **1968**, 1074.