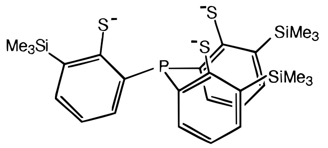
Five-Coordinate Diamagnetic Iron(IV) Complexes With A Trigonal Planar Arrangement of Thiolate Ligand Atoms: Synthesis and Crystal Structure of [FeX(PS_3)] (X = Cl, Br or I; PS_3H_3 = [P(C‴$_6H_3$-3-Me_3Si-2-SH)$_3$])

Jodi D. Niemoth-Anderson, Kerry A. (Fusie) Clark,
T. Adrian George,* and Charles R. Ross, II†

Department of Chemistry, University of Nebraska-Lincoln
Lincoln, Nebraska 68588-0304

Received November 12, 1999

One of the intriguing results to emerge from the structure of the FeMo−protein of nitrogenase from *Azotobacter vinelandii* deduced from X-ray diffraction data is the unprecedented formal three-coordinate geometry for the six μ^3-S-bridged iron atoms in the [$MoFe_7S_9$] cluster.[1] To study the chemistry of a single iron atom with this trigonal near-planar geometry, we chose to synthesize tristhiolate complexes of the type $[Fe(SR)_3]^{n-}$. This strategy has been employed successfully by Koch and by Millar using tetradentate tripodal ligands such as $[P(C_6H_4\text{-}2\text{-}S)_3]^{3-}$ and $[N(CH_2\text{-}o\text{-}C_6H_4S)_3]^{3-}$ to stabilize a series of complexes of iron and nickel in different oxidation states,[2,3] and more recently by Richards et al. using $[N(CH_2CH_2S)]^{3-}$, $(NS_3)^{3-}$.[4] The tristhiolatophosphine ligand system was first employed by de Vries and Davison who showed that $[P(C_6H_4\text{-}2\text{-}S)_3]^{3-}$ coordinates to Tc(III) to form a trigonal bipyramidal complex, $[Tc[P(C_6H_4\text{-}2\text{-}S)_3](CNC_3H_7)]$.[5] Here we report that the reaction of $[P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3]^{3-}$, $(PS_3)^{3-}$ (**1**), with $FeCl_2$ yields a series of products among which (i) a stable, neutral iron(IV) complex, $[FeCl[P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3]]$, $[FeCl(PS_3)]$ (**2-Cl**), and (ii) a stable, neutral binuclear iron(III) complex, $[Fe_2(PS_3)_2]$ (**3**), have been crystallographically characterized. These results led to the synthesis and crystallographic characterization of $[FeBr(PS_3)]$ (**2-Br**) and $[FeI(PS_3)]$ (**2-I**).



1

Addition of acetonitrile to a 1:1:3 molar mixture of $FeCl_2$, PS_3H_3,[6] and Et_3N produced an immediate emerald solution.[7] After the solution stirred for 1 h, the solvent was removed in vacuo. The addition of CH_2Cl_2 to the product-mixture resulted in the color rapidly turning brown. After stirring for 0.3 h, 1 equiv of solid ferrocenium hexafluorophosphate, fc(PF_6), was added. Within 0.3 h, the color had changed from brown to intense purple. The latter color change also occurs, but more slowly, in the presence of adventitious dioxygen. The solution was stirred for 1 h and then extracted twice with water. Water was removed via cannula. The organic phase was dried over $MgSO_4$ and then transferred via cannula to a flask where solvent was removed in vacuo. The resulting solid was dissolved in a minimum volume of benzene and 3 times that volume of pentane was added. The solution was cooled to −18 °C for 12 h. Purple $[FeCl(PS_3)]$ was filtered off, washed with pentane, and dried in vacuo. The yield was ~40%. The remaining black filtrate was worked-up separately (see Supporting Information). Crystals suitable for X-ray diffraction studies were obtained from the benzene solution. The ^1H NMR spectrum of crystals of **2-Cl** shows the presence of C_6H_6 and H_2O in CD_2Cl_2, and C_6H_6, H_2O, and CH_2Cl_2 in C_6D_6. So far no sample of **2-Cl** has been obtained solvent-free.[7] The structure of **2-Cl**[8] is shown in Figure 1. Stable iron(IV) complexes are relatively rare.[9−11] **2-Cl** represents, to the best of our knowledge, the first crystallographically characterized example of (i) a trigonal bipyramidal iron(IV) complex and (ii) a diamagnetic iron(IV) complex. The iron atom is 0.086 Å out of the plane of the three sulfurs toward chlorine. The Fe−S distance is significantly shorter than those reported for other five-coordinate iron(IV) thiolate complexes.[9] The Fe−P distance is short, and the Fe−Cl distance is long compared to other Fe(IV)-P, −Cl distances.[9,10] The only complex similar to **2-Cl** is the purple, diamagnetic, five-coordinate iron(IV) complex $[Fe(CN)[N(CH_2CH_2NSiMe_2Bu^t)_3]]$ that contains a sterically bulky tripodal triamidoamine ligand reported by Cummins and Schrock.[11] The crystal structure of this complex was not reported.

$[FeCl(PS_3)]$ is not a strong oxidant. In the cyclic voltammogram,[12] **2-Cl** undergoes a reversible one-electron reduction at −0.27 V due to the Fe(IV)/Fe(III) couple followed by a quasi-reversible reduction at −1.39 V (vs fc^+/fc couple = 0.00 V). Irreversible oxidation occurs at ~+1.9 V. Although **2-Cl** is stable

---

[†] Current address: Department of Structural Biology, St. Jude Children's Research Hospital, Memphis, TN 38105-2794.

(1) (a) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677. (b) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 553. (c) Kim, J.; Woo, D.; Rees, D. C. *Biochemistry* **1993**, *32*, 7104. (d) Kim, J.; Rees, D. C. *Biochemistry* **1994**, *33*, 389. (e) Rees, D. C.; Chan, M. K.; Kim, J. *Adv. Inorg. Chem.* **1993**, *40*, 89.

(2) (a) Franolic, J. D.; Millar, M.; Koch, S. A. *Inorg. Chem.* **1995**, *34*, 1981. (b) Govindaswamy, N.; Quarless, D. A.; Koch, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 8468. (c) Hsu, H.-F.; Koch, S. A.; Popescu, C. V.; Münck, E. *J. Am. Chem. Soc.* **1997**, *119*, 8371.

(3) (a) Franolic, J. D.; Wang, W. Y.; Millar, M. *J. Am. Chem. Soc.* **1992**, *114*, 6587. (b) Nguyen, D. H.; Hsu, H.-F.; Millar, M.; Koch, S. A.; Achim, C.; Bominaar, E. L.; Münck, E. *J. Am. Chem. Soc.* **1996**, *118*, 8963.

(4) Davies, S. C.; Hughes, D. L.; Richards, R. L.; Sanders, J. R. *Chem. Commun.* **1998**, 2699.

(5) (a) de Vries, N.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1989**, *165*, 9. (b) de Vries, N.; Cook, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1991**, *30*, 2662.

(6) Synthesis of PS_3H_3; Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327.

(7) In a typical reaction, CH_3CN (20 mL) was added to a mixture of $FeCl_2$ (0.0114 g, 0.0899 mmol) or $FeCl_2{\cdot}4H_2O$, H_3PS_3 (0.0502 g, 0.0873 mmol), and Et_3N (0.0317 g, 0.313 mmol). CH_3CN was removed and replaced by CH_2Cl_2 (20 mL). After excess fc[PF_6] was added, the solution was extracted with H_2O (2 × 20 mL). The resulting purple solid was dissolved in benzene (5 mL), and pentane (15 mL) was added. The yield of **2-Cl** (dec pt 201−205 °C) was 0.0128 g (0.0193 mmol, 39%). Anal. Calcd (i) for $C_{27}H_{36}ClFePS_3Si_3{\cdot}1H_2O{\cdot}1CH_2Cl_2{\cdot}0.25C_6H_6$ (after pumping in vacuo for 1 day): C, 45.09.; H, 5.32. Found: C, 45.25; H, 5.32. (ii) for $C_{27}H_{36}ClFePS_3Si_3{\cdot}0.17H_2O{\cdot}0.33CH_2Cl_2{\cdot}0.25C_6H_6$ (after pumping in vacuo for 3 days): C, 48.49.; H, 5.43. Found: C, 48.38; H, 5.41. ^1H NMR (δ CD_2Cl_2) of **2**: 0.35 (s, 27H, $SiMe_3$), 1.55 (s, H_2O), 7.35 (s, 6H, cocrystallized C_6H_6), 7.39 (t, 3H, J_{HH} = 7.5 Hz, C_6H_3-5$\underline{H}$), 7.71 (dd, 3H, J_{HH} = 7.3, J_{HH} = 0.98 Hz, C_6H_3-4$\underline{H}$), and 7.98 (d, 3H, J_{HH} = 7.7 Hz, C_6H_3-6$\underline{H}$). $^{31}P\{^1H\}$ NMR (δ CD_2Cl_2) 130.6 (broad). $^{13}C\{^1H\}$ NMR (δ CD_2Cl_2) −0.22 (s, $SiMe_3$), 128.9 (s, C_6H_3-5$\underline{C}$), 129.9 (s, C_6H_3-6$\underline{C}$), 130.3 (br, C_6H_3-1$\underline{C}$), 140.9 (s, C_6H_3-4$\underline{C}$), 143.4 (s, C_6H_3-3$\underline{C}$), and 164.3 (s, C_6H_3-2$\underline{C}$). UV−vis (CH_2Cl_2) λ_{max} nm (ϵ, M^{-1} cm^{-1}) 378 (5658), 523 (4532), 733 (4113), 904 (2258). FAB-MS (*m/z*): 627 (M^+ − Cl).

(8) Crystal data for **2-Cl**$\cdot C_6H_6$ ($FeClPS_3Si_3C_{27}H_{36}{\cdot}C_6H_6$) (293 K): cubic, $I\bar{4}3m$, $a = 20.471(1)$ Å, $V = 8579(1)$ Å^3, $Z = 8$. Final least-squares refinement on F^2 using 888 unique reflections, 92 parameters, and 19 restrictions on the geometry of the included disordered benzene solvent molecules yielded $wR_2 = 0.092$ ($R_1 = 0.034$ on 811 reflections with $F > 4s(F)$) and GOF = 1.09.

(9) (a) Epstein, E. F.; Bernal, I. *Inorg. Chim. Acta* **1977**, *25*, 145. (b) Miyamae, H.; Sato, S.; Saito, Y.; Sakai, K.; Fukuyama, M. *Acta Crystallogr. B* **1977**, *33*, 3942. (c) Sellmann, D.; Geck, M.; Knoch, F.; Ritter, G.; Dengler, J. *J. Am. Chem. Soc.* **1991**, *113*, 3819. (d) Knof, U.; Weyhermüller, T.; Wolter, T.; Wieghardt, K.; Bill, E.; Butzlaff, C.; Trautwein, A. X. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1635.

(10) (a) Collins, T. J. *Acc. Chem. Res.* **1994**, *27*, 279. (b) Russo, U.; Long, G. J. In *Mössbauer Spectroscopy Applied to Inorganic Chemistry*; Long, G. J., Grandjean, F., Eds.; Plenum: New York, 1989; Vol. 3, p 295. (c) Harbron, S. K.; Higgins, S. J.; Levason, W.; Feiters, M. C.; Steel, A. T. *Inorg. Chem.* **1986**, *25*, 1789.

(11) Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.

(12) Electrochemical studies: Solutions were 0.001 M in CH_2Cl_2 with 0.1 M supporting electrolyte $[NBu^n{}_4][PF_6]$; scan rate was 50 mV/s, referenced to a silver wire electrode (potentials quoted vs ferrocinium/ferrocene couple = 0.00 V.; 0.535 V vs SCE in CH_2Cl_2). Complex **2-Cl** (Pt glass electrode) showed a reversible one-electron reduction $(E_{pc} + E_{pa})/2 = E_{1/2}$ (DE_p, i_{pa}/i_{pc}) at −0.27 V (54 mV, 1.04) and a quasi-reversible one-electron reduction at −1.39 V (104 mV, 0.69). Data were recorded and analyzed using a Cypress Systems model CS-1090 electroanalytical instrument and software.

10.1021/ja993988+ CCC: $19.00

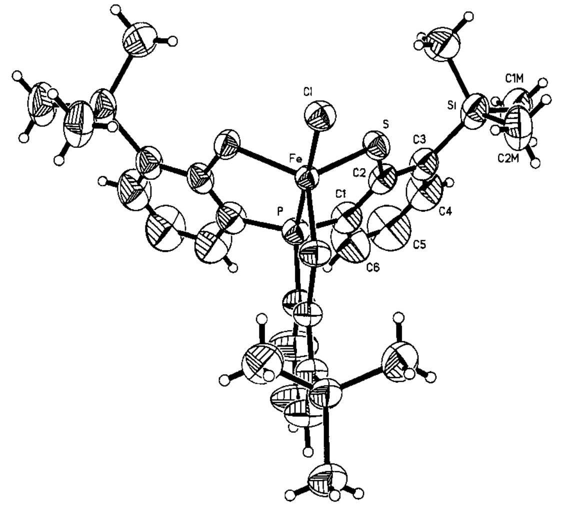


Figure 1. Thermal ellipsoid diagram of [FeCl(PS_3)] (**2-Cl**). Selected bond distances (Å) and angles (deg): Fe−S = 2.108(1); Fe−P = 2.157(3); Fe−Cl = 2.281(2); P−Fe−S = 87.65(5); Cl−Fe−S = 92.35(5); Cl−Fe−P = 180.0(2).

in CH_2Cl_2, $CHCl_3$, and 1,2-$C_6H_4Cl_2$ for extended periods of time, very rapid decomposition occurs in polar solvents such as CH_3CN, CH_3OH, and thf at room temperature. The reaction of a CH_2Cl_2 solution of **2-Cl** with solid AgS_2CNEt_2 at 0 °C resulted in a slow change in color and the isolation of an orange-brown solid. The FAB$^+$MS of this product diplays a peak corresponding to the parent ion of [Fe(S_2CNEt_2)(PS_3)], and the broadening of the peaks in the ^{1}H NMR spectrum suggests it is paramagnetic and therefore a six-coordinate iron(IV) complex.

The formation of [FeCl(PS_3)], as described above, requires (i) coordination of the ligand, (ii) creation of an Fe−Cl bond, and (iii) oxidation of iron(II) to iron(IV). The first step in the reaction includes coordination of the ligand to form an oxygen-sensitive emerald iron(II) complex mixed with other products.[13] The emerald complex could be four-coordinate [Fe(PS_3)]$^-$, or [Fe(CH_3CN)(PS_3)]$^-$ or [FeCl(PS_3)]$^{2-}$. The latter complex can be eliminated at this stage in the reaction because the identical emerald product is formed when $Fe(ClO_4)_2 \cdot 6H_2O$ is used instead of $FeCl_2$. When the reaction using $Fe(ClO_4)_2 \cdot 6H_2O$ or $FeCl_2$ is done in thf, a distinctly different green color is formed. Thus, although the emerald complex has not been isolated analytically pure, qualitative data suggest it is the anion [Fe(CH_3CN)(PS_3)]$^-$ (eq 1; X = Cl, ClO_4). This anion is analogous to the crystallographically characterized iron(II) complexes [Fe(CO)[P(C_6H_3-3-Ph-2-S)$_3$]]$^-$ [3b] and [Fe(CO)(NS_3)]$^-$.[4]

$$FeX_2 + PS_3H_3 + 3Et_3N \xrightarrow{CH_3CN} [Fe^{II}(CH_3CN)(PS_3)]^- + 3Et_3NH^+ + 2X^- \quad (1)$$

The formation of the Fe−Cl bond was studied by repeating the earlier experiments starting with $Fe(ClO_4)_2 \cdot 6H_2O$. First, the reaction of $Fe(ClO_4)_2 \cdot 6H_2O$ with PS_3H_3/Et_3N/CH_3CN was carried out, followed by removal of solvent in vacuo and addition of CH_2Cl_2. After the emerald solution turned brown (0.3 h), solid fc(PF_6) (1 equiv) was added. Immediately, the solution turned purple. Following workup, **2-Cl** was isolated in ∼50% yield. Second, the reaction of $Fe(ClO_4)_2 \cdot 6H_2O$ with PS_3H_3/Et_3N/CH_3CN was carried out, followed by removal of solvent in vacuo and addition of benzene. (*n*-Bu_4N)Cl (2 equiv) was added to the suspension with stirring. After the emerald colored suspension turned brown (3 h), fc(PF_6) (2 equiv) was added. A purple color appeared (3−4 h). Following workup, **2-Cl** was isolated in ∼20% yield. These results suggest that [Fe(CH_3CN)(PS_3)]$^-$ or [Fe(PS_3)]$^-$ is able to (i) abstract a chlorine atom from CH_2Cl_2 to form an iron(III) anion (eq 2)[14] or (ii) undergo substitution with Cl$^-$ to form an iron(II) dianion (eq 3). An ES MS of the brown solid obtained by adding CH_2Cl_2 to a green solution prepared from the mixture $FeCl_2$/PS_3H_3/Et_3N/CH_3CN showed two peaks with the correct masses and isotope ratios for [FeCl(PS_3)]$^-$.[15] Electrochemical studies of **2-Cl**[12] provide direct evidence for the existence of [Fe^{III}Cl(PS_3)]$^-$ and indirect evidence for [Fe^{II}Cl(PS_3)]$^{2-}$. These putative chloroiron(III) and chloroiron(II) complexes are similar to crystallographically characterized [FeCl(NS_3)]$^-$ [4] and [Fe(CN)[P(C_6H_4-2-S)$_3$]]$^-$.[2c]

$$[Fe^{II}(CH_3CN)(PS_3)]^- + CH_2Cl_2 \rightarrow [Fe^{III}Cl(PS_3)]^- + CH_3CN + \{\bullet CH_2Cl\} \quad (2)$$

$$[Fe^{II}(CH_3CN)(PS_3)]^- + Cl^- \rightarrow [Fe^{II}Cl(PS_3)]^{2-} + CH_3CN \quad (3)$$

Oxidation, to form the ultimate product **2-Cl**, must be done after the formation of the Fe−Cl bond. Thus, if the emerald complex is oxidized by O_2 or fc(PF_6) before the brown solution is formed, **2-Cl** is never obtained.

These experimental results have allowed the designed synthesis of [FeBr(PS_3)] (**2-Br**), [FeI(PS_3)] (**2-I**), and a one-step synthesis of **2-Cl**. Both **2-Br** and **2-I** have been crystallographically characterized. **2-Br**[16] is isostructural with **2-Cl**. In the structure of **2-I**,[17] the Fe(PS_3) unit is metrically the same as in **2-Cl** and **2-Br**, but the iodine atom is slightly displaced from the idealized 3-fold axis; P−Fe−I = 177°.

[FeCl(PS_3)] can be prepared in one-step by adding $FeCl_3$ (2 equiv) to a solution of PhSn(PS_3)[18] in CH_2Cl_2. The solution turned purple immediately. $FeCl_3$ is the source of {FeCl} and the oxidizing agent.

Acknowledgment. We thank the National Science Foundation EPSCoR Grant, the Research Corporation, and the University of Nebraska, Center for Materials Research and Analysis for support of this work, Dr. Jody Redepenning, Mike Anderson, and David Kurk for help with the cyclic voltammetry, and Tom Brett for help with the crystal structures.

Supporting Information Available: Details of the synthesis of **2-Br** and **2-I**, procedures for growing crystals (**2-Cl**, **-Br**, **-I**), isolation and identification of products including [$Fe_2(PS_3)_2$] **3** from black filtrate remaining after isolating **2-Cl**, ^{1}H NMR spectrum of [FeCl(PS_3)], structural diagram of **3**, space-filling representation of FeCl(PS_3)], details of X-ray structure determination and labeled figures and atomic coordinates of **2-Cl**, **2-Br**, **2-I**, and **3** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA993988+

---

(13) FAB-MS of emerald solid, 3-NBA matrix (*m/z*): 1255 ([$Fe_2(PS_3)_2$]$^+$), 627 ([Fe(PS_3)]$^+$), 571 ((PS_3)$^+$).

(14) The reaction works equally well with $CHCl_3$ but not with CCl_4 because of solubility problems.

(15) ES MS of the brown solid in the negative ion mode (*m*/*z*): 664.0 [Fe^{37}Cl(PS_3)$^-$], 662.0 [Fe^{35}Cl(PS_3)$^-$].

(16) Crystal data for **2-Br**·1.7C_6H_6 ($FeBrPS_3Si_3C_{27}H_{36} \cdot C_{10.25}H_{10.25}$) (293 K): cubic, $I\bar{4}3m$, $a = 20.623(1)$ Å, $V = 8771$ Å^3, $Z = 8$. Final least-squares refinement on F^2 using 701 unique reflections, 79 parameters, and 19 restrictions on the geometry of the included disordered C_6H_6 solvent molecules yielded $R_1 = 0.0604$ ($wR_2 = 0.1528$) and GOF = 1.115.

(17) Crystal data for **2-I**·3(1,2-$C_6H_4Cl_2$) ($FeIPS_3Si_3C_{27}H_{36} \cdot C_{18}H_{12}Cl_6$) (293 K): monoclinic, $C2/c$, $a = 31.317(6)$ Å, $b = 16.919(3)$ Å, $c = 21.301(4)$ Å, $\beta = 112.21(3)°$, $V = 10449(4)$ Å^3, $Z = 4$. Final least-squares refinement on F^2 using 7085 unique reflections, 442 parameters, and 50 restrictions on the geometry of the included disordered 1,2-$C_6H_4Cl_2$ solvent molecules yielded $R_1 = 0.0709$ ($wR_2 = 0.1899$) and GOF = 1.094.

(18) Details of the synthesis, reactions and X-ray structure determination of a series of PhSn(PS_3) complexes will appear in: Clark, K. A. (Fusie); George, T. A.; Brett, T. J.; Ross, C. R., II; Shoemaker, R. K., *Inorg. Chem.*, accepted for publication.