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Neutral Four-Coordinate (Selenolato)iron(II) Complexes: Syntheses and Structures of Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(PMe$_2$Ph)$_2$ and Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(Et$_2$PCH$_2$CH$_2$PEt$_2$)

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The first neutral four-coordinate selenolato iron(II) complexes, Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(PMe$_2$Ph)$_2$, **1**, and Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(Et$_2$PCH$_2$CH$_2$PEt$_2$), **2**, are prepared by metathesis of chloride ligands of iron(II) chloride with selenolate in the presence of 2 equiv of dimethylphenylphosphine or 1 equiv of 1,2-bis(diethylphosphino)ethane, respectively. The room temperature magnetic moment of both **1** and **2** is about 5 μ_B as determined both in the solid state and in solution. The proton NMR spectra exhibit paramagnetic shifts and broadening associated with the unpaired electron density at the metal center. The spectra were completely assigned using integration and linewidth information. Cyclic voltammetry and electronic spectra of **1** and **2** and the Mössbauer spectrum of **1** are also reported. Single crystal X-ray diffraction studies at 296 K revealed a crystallographically imposed C_2 symmetry for **1**. The coordination geometry about the iron centers is distorted tetrahedral for both complexes. The Se−Fe−Se angle is much larger than tetrahedral with a value of about 130° for both complexes. Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(PMe$_2$Ph)$_2$, **1**, crystallizes in the monoclinic space group *C*2/*c* with $a = 22.330(4)$, $b = 12.485(2)$, $c = 16.667(3)$ Å, $\beta = 118.03(3)°$, $Z = 4$, $V = 4101.6(12)$ Å^3, $d_{calc} = 1.316$ g cm^{-3}, $R = 0.0431$, $R_w = 0.0551$. Fe(Se-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(depe), **2**, crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.418(1)$, $b = 19.484(4)$, $c = 20.631(3)$ Å, $\beta = 93.79(1)°$, $Z = 4$, $V = 3777.5(13)$ Å^3, $d_{calc} = 1.306$ g cm^{-3}, $R = 0.0529$, $R_w = 0.0626$.

Introduction

Four-coordinate iron(II) complexes have elicited much current interest. Some of this interest is spurred by the modeling of the iron center of reduced rubredoxins[1,2] (Rd); a metalloprotein with iron(II) in a coordination environment of four cysteine residues. There are a number of examples of homoleptic four-coordinate thiolato iron(II) complexes.[3,4] A neutral dithiolato iron(II) complex with mixed donor ligands has been prepared by the reaction of iron(II) with the zinc finger peptide CP-1.[5] There is only one report of a structurally-characterized neutral four-coordinate thiolato iron(II) complex, Fe(SC(NMe$_2$)$_2$)$_2$(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$.[6] (Selenolato)iron(II) complexes are even less abundant. There is but one example of a structurally characterized four-coordinate selenolato iron(II) complex, the homoleptic tetrakis(benzeneselenolato)ferrate(II) anion, [Fe(SePh)$_4$]$^{-2}$.[7] We report the synthesis and structure of the first neutral four-coordinate iron(II) complexes with selenolato donor ligands.

There have been relatively few other structurally characterized neutral four-coordinate iron(II) complexes. Girolami has reported the structures of FeCl$_2$(dippe)[8] and Fe(CH$_2$C$_6$H$_4$Me)$_2$(dippe)[9] (dippe = 1,2-bis(diisopropylphosphino)ethane) as well as the proton NMR spectra of FeX$_2$(dippe)[8] (X = Cl, Br, I) and Fe(R)$_2$(dippe)[9] (R = CH$_2$CMe$_3$, CH$_2$SiMe$_3$, CH$_2$Ph). The complex Fe(CH$_2$Ph)$_2$(Me$_2$NCH$_2$CH$_2$NMe$_2$) has recently been reported and characterized by solution proton NMR studies.[10] Earlier work showed that iron(II) halide complexes with phosphine and amine co-ligands could be isolated, though characterization of these complexes was limited to electronic spectroscopy, magnetic susceptibility and elemental analyses. These complexes include FeCl$_2$(PEt$_n$Ph$_{3-n}$)$_2$ ($n = 0-3$),[11] FeX$_2$(OPPh$_3$)$_2$,[12,13] FeX$_2$(OAsPh$_3$)$_2$,[14] FeX$_2$(C$_9$H$_7$N)$_2$ (X = Cl, Br),[14] FeBr$_2$(diamine) (diamine = Me$_2$NCH$_2$CH$_2$NMe$_2$, Me$_2$NCHMeCH$_2$NMe$_2$),[15] FeX$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (X = Cl,[16] I[17]) and FeCl$_2$(Et$_2$PCH$_2$CH$_2$PEt$_2$).[18]

Experimental Section

General Data. Unless otherwise noted all operations were carried out under a dry, oxygen free nitrogen atmosphere using either glovebox or Schlenk techniques. Tetrahydrofuran, diethyl ether and hexanes were distilled from sodium benzophenone under argon and ethanol was distilled from magnesium ethoxide under argon. Deuterated NMR solvents were obtained from Aldrich (benzene−d_6) or MSD Isotopes (chloroform-*d*). Dimethylphenylphosphine was obtained from Digital Specialty Chemicals and anhydrous iron(II) chloride was purchased from Aldrich. 2,6-Diisopropylphenylbromide was prepared by a literature method.[19] Microanalyses of complexes **1** and **2** were performed by Canadian Microanalytical Services (Delta, BC) and the analysis of bis(2,6-diisopropylphenyl) diselenide was performed by

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Guelph Chemical Laboratories (Guelph, Ontario). All NMR spectra were recorded at room temperature in the indicated solvent. Proton NMR spectra were obtained on Varian Gemini-200 (at 200 MHz), Gemini-300 (at 300 MHz), or Unity 500 (at 500 MHz) spectrometers, and are referenced internally to the residual solvent peak ($CHCl_3$) for the diamagnetic compound or externally to tetramethylsilane in benzene-d_6 for the paramagnetic complexes. The ^{13}C NMR spectrum was performed on a Varian Gemini-200 spectrometer (at 50.3 MHz) and referenced internally to the solvent peak. The ^{77}Se spectrum was obtained on a Varian Gemini-300 spectrometer (at 57.2 MHz) and referenced externally to dimethyl selenide in benzene-d_6. Electronic spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer at room temperature in an anaerobic cell under nitrogen in tetrahydrofuran solvent. Magnetic moment measurements were obtained in solution by an NMR technique[20] and in the solid state with a Johnson Matthey magnetic susceptibility balance. A Bioanalytical Systems CV-1B electrochemical controller was used for cyclic voltammetry studies in the inert atmosphere glovebox. The electrochemical cell contained Pt working and counter electrodes and Ag wire reference electrode; THF solutions were 0.2 M in n-Bu_4NPF_6. Reported potentials are referenced to the ferrocenium/ferrocene couple.

(Se-2,6-i-$Pr_2C_6H_3)_2$. The preparation of bis(2,6-diisopropylphenyl)diselenide is performed in an analogous manner to the preparation of diphenyl disulfide.[21] 2,6-Diisopropylphenylbromide (10.0 g, 41.5 mmol) is refluxed with magnesium metal (1.11 g, 45.6 mmol) in dry diethyl ether (150 mL) for 4 h. The reaction mixture is cooled to room temperature, selenium metal (3.60 g, 45.6 mmol) added and the mixture stirred at room temperature overnight. In an efficient fumehood air is bubbled through the filtered solution until a deep orange color has developed and the odor is greatly diminished. Concentrating and cooling the solution (0 °C) results in the formation of an orange powder which is collected on a medium frit and washed three times with cold ethanol. Yield: 7.8 g (78%). Anal. Calcd for $C_{24}H_{34}Se_2$: C, 60.00; H, 7.13. Found: C, 60.21; H, 7.23. ^1H NMR ($CDCl_3$): δ 1.06 (d, $CH(CH_3)_2$, $J = 6.8$ Hz), 3.59 (septet, $CHMe_2$, $J = 6.9$ Hz), 7.08−7.32 (m, meta and para). ^{13}C NMR ($CDCl_3$): δ 24.0 (quartet of virt. quintets, $CH(CH_3)_2$, $^1J_{CH} = 126$ Hz, $^2J_{CH} \approx {}^3J_{CH} = 5$), 34.1 (doublet of septets, $CHMe_2$, $^1J_{CH} = 130$, $^2J_{CH} = 5$), 123.2 (ddd, meta, $^1J_{CH} = 157$, $^2J_{CH} = 5$, $^3J_{CH} = 8$), 130.0 (dt, para, $^1J_{CH} = 159$, $^2J_{CH} = 5$), 130.7 (m, ortho), 153.7 (m, ipso). ^{77}Se NMR ($CDCl_3$): δ 365 (s). UV−vis: λ 248 nm ($\epsilon = 4000\ M^{-1}\ cm^{-1}$), 296 (4250), 378 (690). EI-MS (*m/e*) Calcd for $C_{24}H_{34}Se_2$ 480.45: Found; 480 $[M]^+$, 240 $[ArSe]^+$, 162 $[Ar]^+$. The pattern of the mass peaks was successfully modeled with the natural abundance isotope ratios. Cyclic voltammetry (vs Fc^+/Fc, 50 mV/s, CH_3CN) irreversible oxidation at −0.23 V, irreversible reduction at −1.14 V; (THF, see Figure 1) irreversible oxidation at −0.7 V, irreversible reduction at −2.15 V.

$Fe(Se$-2,6-i-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, 1. Sodium borohydride is added to a solution of bis(2,6-diisopropylphenyl) diselenide (266 mg, 0.55 mmol) in tetrahydrofuran-ethanol (1:1; 10 mL) until the solution is colorless. This solution is filtered to remove any excess $NaBH_4$ and added to a mixture of dimethylphenylphosphine (153 mg, 1.1 mmol) and iron(II) chloride (70 mg, 0.55 mmol) in tetrahydrofuran (10 mL). After stirring for 2 h at room temperature the volatile compounds are removed *in vacuo* and the resulting oil is extracted with hexanes (250 mL). The solution is filtered and the solvent removed *in vacuo*. The resulting orange powder was dissolved in a minimum amount of diethyl ether (8 mL) and complex **1** is isolated as very oxygen sensitive, bright red prisms on standing overnight at −30 °C. Yield: 312 mg (0.38 mmol, 70%). Anal. Calcd for $C_{40}H_{56}FeP_2Se_2$: C, 59.12; H, 6.95%. Found: C, 59.03; H, 6.94%. ^1H NMR (C_6D_6) δ 85.4 ($w_{1/2} = 270 \pm 30$ Hz) $P(CH_3)_2$; 37.4 (31 ± 4) *meta* H of SeAr; 20.6 (very broad) $CH(CH_3)_2$; 16.2 (40 ± 2) *meta* H of PPh; 13.1 (65 ± 8) $CH(CH_3)_2$; −3.5 (150 ± 30) *ortho* H of PPh; −6.0 (37 ± 3) *para* H of PPh; −18.7 (28 ± 1) *para* H of SeAr. UV−vis (THF): λ 388 nm ($\epsilon = 10\,000\ M^{-1}\ cm^{-1}$), 474 (2700), 642 (800). Electrochemistry (vs Fc^+/Fc, 50 mV/s, THF) multiple irreversible oxidations (see Figure 1), irreversible reduction at −2.2 V. Magnetic moment 5.0 μ_B (solution and solid state).

$Fe(Se$-2,6-i-$Pr_2C_6H_3)_2$(depe), 2. The preparation of **2** is carried out as for **1** with the exception of the use of 1 equiv of 1,2-bis(diethylphosphino)ethane for 2 equiv of PMe_2Ph. Bis(2,6-diisopropylphenyl) diselenide (830 mg, 1.73 mmol), in THF-EtOH (1:1, 30 mL) is reduced with $NaBH_4$ until the solution is colorless. This solution is filtered to remove any excess $NaBH_4$ and added to a suspension of $FeCl_2$ (220 mg; 1.74 mmol) and depe (370 mg, 1.8 mmol) in THF (30 mL). The mixture is stirred for 1 h and the volatile compounds removed under vacuum and the resulting oil is extracted with hexanes (100 mL) and filtered. Removal of hexanes *in vacuo* produced an orange powder which was recrystallized from ether. Complex **2** is isolated as very oxygen sensitive, bright red cubes on standing overnight at −30 °C. Yield: 899 mg (1.21 mmol, 70%). Anal. Calcd for $C_{34}H_{58}FeP_2Se_2$; C, 55.00; H, 7.87%. Found: C, 54.86; H, 7.89%. ^1H NMR (C_6D_6) δ 117.1 ($w_{1/2} = 348 \pm 5$) $P(CH_aH_bCH_3)_2$; 60.6 (334 ± 4) PCH_2CH_2P; 44.3 (403 ± 6) $P(CH_aH_bCH_3)_2$; 37.0 (50 ± 5) *meta* H of SeAr; 19.2 (400 ± 50) $CH(CH_3)_2$; 14.5 (124 ± 7) $CH(CH_3)_2$; 6.5 (160 ± 10) $P(CH_2CH_3)_2$; −16.3 (36 ± 4) *para* H of SeAr. UV−vis (THF): λ 296 nm ($\epsilon = 9000\ M^{-1}\ cm^{-1}$), 400 (6000), 456 (4000). Cyclic voltammetry (vs Fc^+/Fc, 50 mV/s, CH_2Cl_2) irreversible oxidations at +0.10 and +0.50 V, irreversible reduction at −2.6 V; (THF) irreversible oxidations at −1.47 and +0.07 V, irreversible reduction at −2.23 V. Magnetic moment: 5.2 μ_B (solid state); 5.0 (solution).

X-ray Crystallographic Studies. Crystals of **1** and **2** were obtained from concentrated solutions of the corresponding complex in diethyl ether at −30 °C. In both cases the data collection was carried out on a single crystal which was coated with epoxy resin in a glovebox to exclude oxygen and mounted on a glass fiber.

Intensity data for both complexes were collected on an Enraf-Nonius CAD-4 diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell dimensions were determined and refined using the positions of 19 high angle reflections ($19.5° < 2\theta < 41.5°$). Intensity data were collected in four shells using $\omega-2\theta$ scan technique, employing variable scan speeds with a maximum time per datum of 60 s. In each case the intensities of three standard reflections measured every 2 h showed no decay. Data for the compounds were corrected for Lorentz and polarization effects and for absorption.

In the case of complex **1**, the systematic absences, *hkl* for $h + k$ odd and *h0l* for l odd, are consistent with either *Cc* or *C*2/*c* as possible space groups. The intensity data provided strong evidence for a centric space group. The structure was successfully solved and refined in space group *C*2/*c*. For both structures the Fe and Se atoms position were solved by the Patterson method and other non-hydrogen atoms were located by successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically by full matrix least-squares to minimize $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F) + g(F)^2]$. Hydrogen atoms were positioned on geometric grounds (C−H 0.96 Å , U_{iso} = 0.105 (4) Å ^{2} for **1** and 0.115 (5) Å ^{2} for **2**). Crystal data, data collection, and least squares refinement parameters are listed in Table 1. All calculations were performed and diagrams created using SHELXTL-PC[22] on a 486-33 personal computer.

The structures of **1** and **2**, including the crystallographic labeling schemes are shown in Figures 2 and 3, respectively. Selected positional parameters, bond distances and angles are listed in Tables 2 to 4.

Results and Discussion

Preparation of the Complexes 1 and 2. The complexes $Fe(Se$-2,6-i-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**, and $Fe(Se$-2,6-i-$Pr_2C_6H_3)_2$(depe), **2**, were prepared by metathesis of the two chloride ligands of iron(II) chloride with 2,6-diisopropylbenzeneselenolate in the presence of two equivalents of dimethylphenylphosphine or 1 equiv of 1,2-bis(diethylphosphino)ethane, respectively (Scheme 1). We have found that areneselenolate anions can be readily generated *in situ* by reduction of the diaryl diselenide with sodium borohydride. This method greatly reduces the odor

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Table 1. Summary of Crystal Data, Details of Intensity Collection and Least-Squares Refinement Parameters

	1	2
empirical formula	$C_{40}H_{56}FeP_2Se_2$	$C_{34}H_{58}FeP_2Se_2$
cryst color, shape	red, plate	red, block
approx cryst dimens, mm	0.40 × 0.40 × 0.20	0.35 × 0.20 × 0.30
M_r	812.6	742.5
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
a, Å	22.330(4)	9.418(1)
b, Å	12.485(2)	19.484(4)
c, Å	16.667(3)	20.631(3)
β, deg	118.03(3)	93.79(1)
V, Å^3	4101.6(12)	3777.5(13)
Z	4	4
d_{calc}, g cm^{-3}	1.316	1.306
μ(MoKα) mm^{-1}	2.245	2.431
F(000)	1680	1544
ω scan width, deg	0.55 + 0.76 tan θ	1.06 + 0.74 tan θ
range 2θ collected, deg	5.1 − 50.0 ($\pm h,k,l$)	5.1 − 52.5 ($\pm h,k,l$)
temp, K	296	296
abs corr	semi/empirical	semi/empirical
min, max transm	0.4311, 0.7084	0.2210, 0.2650
no. of data; no. of stds collcd	3969; 45	8417; 84
no. unique reflcns	3449	7606
R_{int}	0.0792	0.0168
no. obsd data [$F > 4\sigma(F)$]	2250	3683
R^a	0.0431	0.0529
$R_w{}^b$	0.0551	0.0626
g in weighting scheme	0.0015	0.0020
goodness of fit	1.11	1.03
largest, mean Δ/σ	0.01, 0.00	0.00, 0.00
params refined	205	353
max^c density in ΔF map e/Å^3	0.47	1.06
min density in ΔF map e/Å^3	−0.72	−0.43

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. ^{c} Largest peaks were within 1.0 Å from Fe atom.

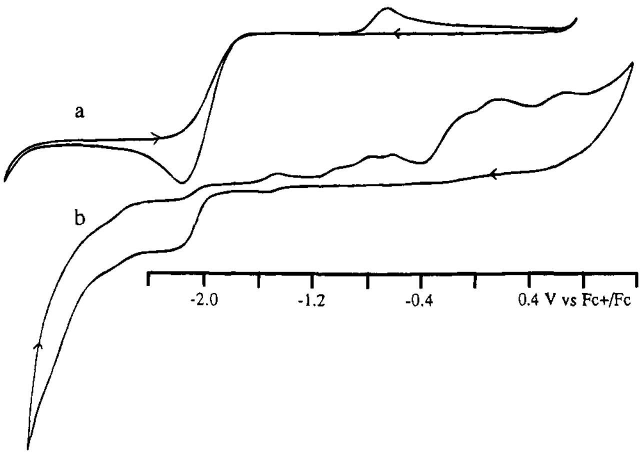

Figure 1. (a) Cyclic voltammogram of 2,6-*i*-$Pr_2C_6H_3SeSeC_6H_3$-2,6-*i*-Pr_2 in THF under N_2. (b) Cyclic voltammogram of **1** in THF under N_2. Scan rate: 50 mV s^{-1}.

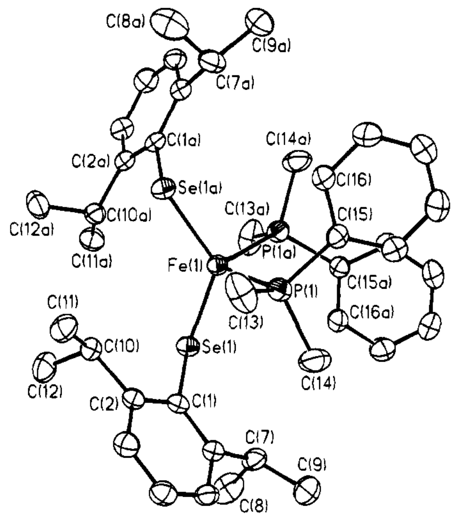

Figure 2. The structure and labeling of Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**. Thermal ellipsoids represent the 50% probability surfaces.

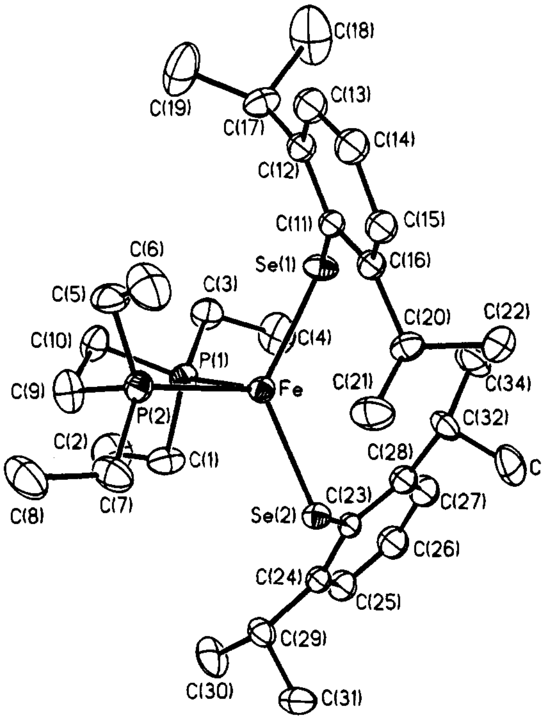

Figure 3. The structure and labeling of Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2$(depe), **2**. Thermal ellipsoids represent the 50% probability surfaces.

associated with the handling of selenol compounds. The reduction of diselenide complexes with sodium borohydride likely produces a boroselenolato complex in solution which has better solubility properties than the non-complexed selenolato compounds. For example reduction of diphenyl diselenide with sodium in tetrahydrofuran produces an insoluble product.[23,24]

Characterization of Complexes 1 and 2. Compounds **1** and **2** are formally fourteen-electron, coordinatively unsaturated complexes. A variety of methods have been used to characterize these compounds, including elemental analysis, magnetic measurements, Mössbauer spectroscopy, cyclic voltammetry, proton NMR, UV−vis spectroscopy, and X-ray crystallography.

The compounds are very oxygen sensitive both in the solid state and in solution. The organic products of the air oxidation of a benzene solution of **1** have been characterized by gas chromatography as dimethylphenylphosphine oxide and bis(2,6-diisopropylphenyl) diselenide. The formation of iron(II) bound diphenyl disulfide has been observed in the oxidation studies of complexes, $[CpFe(L)(L')SPh]^+$.[25,26] No study of the metal containing oxidation products in the present system has been conducted. In a related system, Fe(S-2,6-*i*-$Pr_2C_6H_3)_2$(depe), preliminary results indicate that an intermediate in this reaction, a coordinated phosphine oxide, can be isolated.[27] Although iron

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Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients (10^3 × Å^2) for the Non-Hydrogen Atoms of Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
Fe(1)	0.0	838.1(7)	2500	48.5(4)
Se(1)	714.8(2)	23.8(4)	1938.7(3)	56(1)
P(1)	641(1)	2042(1)	3759(1)	61(1)
C(1)	1564(2)	−167(3)	3054(3)	49(2)
C(2)	1600(2)	−903(4)	3712(3)	51(2)
C(3)	2217(3)	−1002(4)	4503(3)	66(2)
C(4)	2776(3)	−423(5)	4645(4)	70(2)
C(5)	2730(2)	285(5)	3982(3)	64(2)
C(6)	2132(2)	422(4)	3180(3)	55(2)
C(7)	2131(3)	1143(5)	2453(4)	75(3)
C(8)	2328(4)	481(7)	1839(4)	109(4)
C(9)	2594(3)	2123(6)	2805(5)	107(4)
C(10)	1010(2)	−1610(4)	3583(3)	59(2)
C(11)	970(3)	−1884(5)	4443(4)	82(3)
C(12)	1035(3)	−2636(5)	3087(4)	87(3)
C(13)	904(4)	1410(6)	4852(4)	108(4)
C(14)	1433(3)	2562(6)	3867(5)	115(4)
C(15)	171(2)	3208(4)	3785(3)	54(2)
C(16)	−412(3)	3062(5)	3865(4)	79(3)
C(17)	−800(3)	3923(6)	3854(5)	96(4)
C(18)	−615(4)	4926(5)	3765(5)	96(4)
C(19)	−50(4)	5084(5)	3690(5)	101(4)
C(20)	343(3)	4230(5)	3694(4)	80(3)

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (10^3 × Å^2) for the Non-Hydrogen Atoms of Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2$(depe), **2**

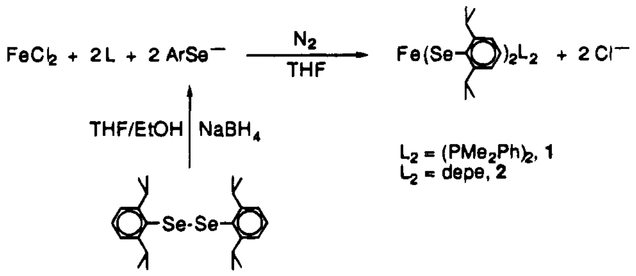
	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
Se(1)	980.6(9)	4284.3(4)	1562.6(4)	54.8(3)
Se(2)	3335.6(8)	2493.1(4)	911.1(3)	44.9(2)
Fe	1563.5(11)	3082.1(5)	1501.6(5)	44.0(4)
P(1)	−766(2)	2640(1)	1183(1)	51(1)
P(2)	1196(2)	2493(1)	2525(1)	55(1)
C(1)	−820(8)	1862(4)	691(4)	70(3)
C(2)	−2224(11)	1507(5)	578(5)	123(6)
C(3)	−2085(8)	3207(4)	790(4)	72(4)
C(4)	−1666(11)	3445(6)	135(5)	113(5)
C(5)	879(12)	2993(5)	3253(4)	88(4)
C(6)	2155(13)	3312(6)	3585(5)	120(6)
C(7)	2483(10)	1834(4)	2797(4)	79(4)
C(8)	2112(13)	1393(5)	3344(5)	112(5)
C(9)	−445(9)	2002(5)	2379(4)	83(4)
C(10)	−1545(9)	2409(5)	1949(4)	72(3)
C(11)	2021(7)	4658(3)	2324(3)	40(2)
C(12)	1245(8)	5022(4)	2772(3)	49(3)
C(13)	1986(9)	5309(4)	3313(4)	61(3)
C(14)	3444(9)	5253(4)	3404(4)	67(3)
C(15)	4181(8)	4897(4)	2969(4)	57(3)
C(16)	3498(8)	4600(4)	2410(3)	48(3)
C(17)	−354(8)	5119(4)	2693(4)	59(3)
C(18)	−741(11)	5816(7)	2513(6)	164(8)
C(19)	−1099(11)	4901(7)	3624(6)	147(7)
C(20)	4397(8)	4236(4)	1939(3)	53(3)
C(21)	5243(10)	3648(4)	2247(4)	85(4)
C(22)	5363(12)	4707(5)	1617(5)	116(5)
C(23)	2589(7)	2519(4)	10(3)	38(2)
C(24)	2238(7)	1898(4)	−311(3)	48(3)
C(25)	1727(9)	1916(5)	−954(4)	69(3)
C(26)	1536(10)	2519(5)	−1281(4)	81(4)
C(27)	1897(9)	3130(4)	−976(4)	73(4)
C(28)	2408(8)	3145(4)	−326(3)	50(3)
C(29)	2485(8)	1213(4)	21(3)	55(3)
C(30)	1474(11)	638(4)	−241(4)	95(4)
C(31)	4030(10)	994(4)	−14(4)	83(4)
C(32)	2884(10)	3821(4)	−22(4)	60(3)
C(33)	4434(10)	3923(5)	−116(5)	97(5)
C(34)	2018(11)	4443(4)	−286(5)	95(4)

complexes in sulfur coordination environments are thought to activate dihydrogen in biological systems,[28] complexes **1** or **2** do not react with 1 atm of pure dihydrogen at 20 °C.

Table 4. Selected Bond Distances and Angles for Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**, and Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2$(depe), **2**

Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**			
Bond Distances (Å)			
Fe−Se(1)	2.421(1)	P(1)−C(13)	1.812(6)
Se(1)−C(1)	1.97(4)	P(1)−C(14)	1.811(7)
Fe−P(1)	2.426(1)	P(1)−C(15)	1.808(5)
Bond Angles (deg)			
Se(1)−Fe−Se(1A)	130.3(1)	Fe−Se(1)−C(1)	101.9(2)
P(1)−Fe−P(1A)	103.5(1)	Fe−P(1)−C(13)	112.4(2)
P(1)−Fe−Se(1)	111.5(1)	Fe−P(1)−C(14)	117.4(3)
P(1A)−Fe−Se(1)	98.9(1)	Fe−P(1)−C(15)	114.0(1)
Fe(Se-2,6-*i*-$Pr_2C_6H_3)_2$(depe), **2**			
Bond Distances (Å)			
Fe−Se(1)	2.411(1)	Fe−Se(2)	2.420(1)
Se(1)−C(11)	1.938(6)	Se(2)−C(23)	1.944(6)
Fe−P(1)	2.408(2)	Fe−P(2)	2.447(2)
P(1)−C(1)	1.823(9)	P(2)−C(5)	1.831(9)
P(1)−C(3)	1.812(8)	P(2)−C(7)	1.828(9)
P(1)−C(10)	1.843(9)	P(2)−C(9)	1.827(9)
Bond Angles (deg)			
Se(1)−Fe−Se(2)	130.8(1)	P(1)−Fe−P(2)	83.7(1)
Se(1)−Fe−P(1)	98.9(1)	Se(2)−Fe−P(1)	109.8(1)
Se(1)−Fe−P(2)	111.4(1)	Se(2)−Fe−P(2)	110.7(1)
Fe−Se(1)−C(11)	107.6(2)	Fe−Se(2)−C(23)	104.6(2)
Fe−P(1)−C(1)	116.2(3)	Fe−P(2)−C(5)	119.9(3)
Fe−P(1)−C(3)	119.3(3)	Fe−P(2)−C(7)	117.8(3)
Fe−P(1)−C(10)	105.1(3)	Fe−P(2)−C(9)	105.6(3)

Scheme 1



NMR Spectroscopy and Magnetic Susceptibility. The room temperature magnetic moment of **1** and **2** in solution (Evans method[20]) was determined to be 5.0 μ_B, while the solid state measurements yielded magnetic moments of 5.0 μ_B for **1** and 5.2 μ_B for **2** (no corrections for diamagnetism of the ligands were made). These values are close to the spin only value of 4.9 μ_B, which suggests that the iron centers are formally high spin with four unpaired electrons.

As expected for paramagnetic compounds the proton NMR spectra of complexes **1** and **2** (Figures 4 and 5) exhibit paramagnetic shifts and large linewidths associated with the presence of unpaired electron density at the metal centers. The spectrum of **1** spans a range of about 104 ppm (+85.4 to −18.7 ppm) and that of **2** about 133 ppm (+117.1 to −16.3 ppm). Proton NMR spectra of the complexes were measured at different concentrations and the chemical shifts reported in the experimental section were calculated by extrapolation to infinite dilution. In this manner the paramagnetic shift due to the paramagnetism of the solution was eliminated. The chemical shifts reported therefore represent the intramolecular paramagnetism due to the unpaired electron density on the metal center. The linewidths of the resonances were treated in the same manner.

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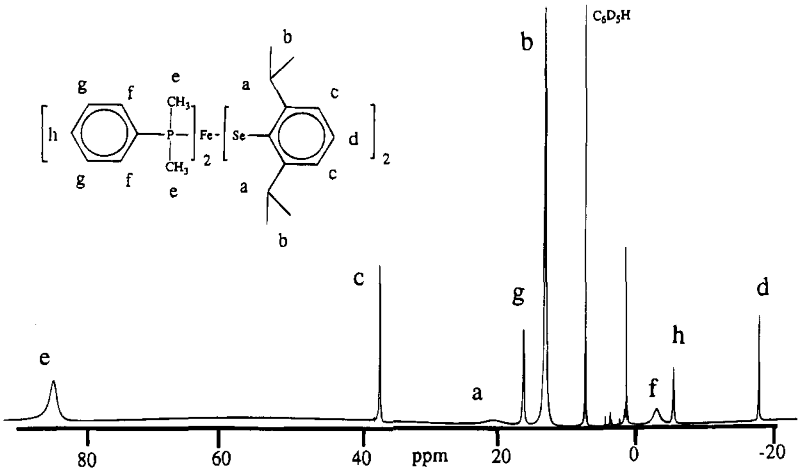

Figure 4. The 500 MHz ^1H NMR spectrum of **1** in C_6D_6 at 295 K.

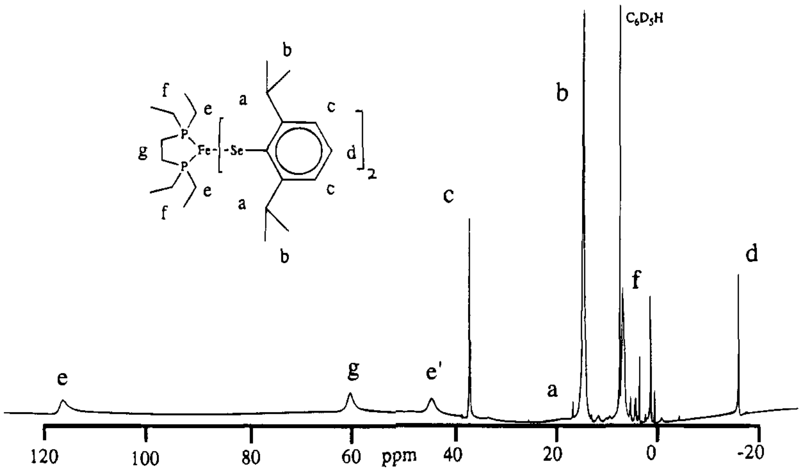

Figure 5. The 300 MHz ^1H NMR spectrum of **2** in C_6D_6 at 295 K.

The assignments of the resonances in the proton NMR spectra were made by finding the common resonances due to the selenolate ligands of complexes **1** and **2** and then by considering the relative integrations and linewidths of the remaining peaks. The methyl protons of the isopropyl groups of **1** are assigned by their integration to the resonance (b) at 13.1 ppm (the corresponding signal for **2** is at 14.5). The resonance (a) at 20.6 ppm for **1** is assigned to the methine protons based on the large linewidth and on the relative integration (for **2** the chemical shift is 19.2). Both spectra have two other common resonances (c) and (d) (at 37.4 and −18.7 ppm for **1** and at 7.0 and −16.3 for **2**) which are assigned to the meta and para protons, respectively, on the basis of the relative integrations.

For complex **1**, the lowest field peak (e in Figure 4) is readily determined on the basis of its intensity to be the methyl protons of the phosphine ligands. The phenyl protons of the phosphine ligand produce three resonances at +16.2 (g), −3.5 (f) and −18.7 (d) ppm. The peak at −18.7 ppm integrates to two protons and is thus assigned to the *para* hydrogens. The two remaining peaks have the same relative integration. The resonance (f) at −3.5 ppm is significantly broader than the peak (g) at 16.2 ppm: linewidths at half-height are 150 and 40 Hz, respectively. Resonance (f) is assigned to the *ortho* protons which are closer to the paramagnetic center (broadening diminishes with separation as a function of r^{-6}).[29] These assignments are in agreement with the observed trend that resonances due to nuclei that are an odd number of bonds away from a paramagnetic center are shifted downfield while those that are an even number of bonds away are shifted upfield.[30] The ortho and para protons are an even number of bonds from the paramagnetic iron center and are shifted upfield.

The hydrogen atoms of the phosphine ligand of complex **2** yield signals at 117.1, 60.6, 44.3 and 6.5 ppm. The resonance (f) at 6.5 ppm integrates for 12 protons and is thus assigned to the methyl protons, $P(CH_2CH_3)_2$. The other three resonances have relative integrations of 1:1:1. The resonance (g) at 60.6 ppm is assigned to the ethylene protons, PCH_2CH_2P, on the basis of the assignment of the ethylene resonance at 55 ppm in the ^1H NMR spectrum of $FeCl_2$dippe, **3**, (dippe = 1,2-bis(diisopropylphosphino)ethane).[8] The methine protons of **3** produce a signal at about +126 ppm, the assignment of which is based on a deuterium labeling study. In complex **2** the methylene protons, $P(CH_2CH_3)_2$, are diastereotopic and produce separate resonances (e and e′) at 44.3 and at 117.1 ppm.

As expected for paramagnetic complexes, no signal could be detected in either ^{31}P or ^{77}Se NMR spectra due to the proximity of these nuclei to the metal center.

Ultraviolet−Visible Spectroscopy. There are three main features in the electronic spectra of complexes **1** and **2**. There is a charge transfer band at 388 nm for **1** and 296 nm for **2**. These appear to involve both the iron and the selenolate since the absorptions due to uncoordinated diselenide are much less intense. There are two other less intense absorptions that are

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Table 5. Mössbauer Data on Four-Coordinate Iron(II) Complexes[a]

complex	δ, mm/s	Q, mm/s	T, K	ref
$Fe(SeC_6H_3\text{-}i\text{-}Pr_2)_2(PMe_2Ph)_2$, **1**	0.39	2.04	293	this work
$[Fe(S_2\text{-}o\text{-}xylyl)_2]^{2-}$	0.61	3.28	77	33
$[Fe(SPh)_4]^{2-}$, **6**	0.54	3.21	293	34
	0.64	3.24	77	34
Rd_{red}	0.65	3.16	77	35
$FeI_2(dppe)$	0.67	3.14	77	36
$FeCl_2(dippe)$	0.72	2.98	77	36
$Fe(SCH_2CH_2OH)_4]^{2-}$	0.73	3.48	4	37
$FeI_2(dippe)$	0.67	3.14	77	36
$FeCl_2(dppe)$	0.74	2.54	77	36
$FeI_2(dippe)$	0.87	3.09	77	36

[a] Abbreviations used: dippe = 1,2-bis(diisopropylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane; Rd_{red} = reduced form of rubredoxin.

assigned to d−d transitions at 474 and 642 nm for **1** and 340 and 456 nm for **2**. All of the absorptions of **2** are blue shifted relative to those of **1**.

Mössbauer Spectroscopy. The Mössbauer spectrum of **1** collected at 293 K revealed an isomer shift of 0.39 mm/s and a quadrupole splitting of 2.04 mm/s. Data that have been reported for other four-coordinate iron(II) complexes are collected in Table 5 for comparison. The isomer shift and quadrupole splitting of **1** are noticeably smaller than those of other $S = 2$ iron(II) complexes.

Cyclic Voltammetry. The voltammogram of the uncoordinated diselenide in THF (Figure 1a) consists of an irreversible reduction to the selenolate at −2.15 V and an irreversible oxidation back to the diselenide at −0.7 V. The redox behavior of both **1** and **2** is complex and both ligand and solvent dependent. The only distinct reduction wave for complex **1** in THF at −2.2 V (Figure 1b) probably corresponds to free diselenide released in the oxidative decomposition of **1**.

Crystallographic Results. The structures of **1** and **2** are comprised of discrete molecules in the unit cell. Both complexes have a distorted tetrahedral coordination geometry about the iron center (Figures 2 and 3). The Se−Fe−Se angle of 130.3 (1)° in **1** and 130.8 (1) in **2** is much greater than the tetrahedral angle of 109.5° . Also of note is the dihedral angle between the Se−Fe−Se and P−Fe−P planes. In an ideal tetrahedron this angle is 90° , whereas this angle is 81.5° in **1** and 84.7° in **2**.

Complex **1** has an exact C_2 symmetry, with a crystallographic 2-fold axis passing through the iron atom and bisecting the Se−Fe−Se angle. The iron atom is located at a special position (Wyckoff e, site symmetry 2, multiplicity 0.5). The conformation adopted by the ligands in **2** also reveals an approximate C_2 symmetry and the pseudo-C_2 axis is nearly coincident (to within 10°) with the bisector of the Se−Fe−Se angle.

Complexes **1** and **2** have similar structural features to the neutral dithiolate, $Fe(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(SC(NMe_2)_2)_2$, **4**.[6] The angle between the two thiolato sulfurs and the iron in complex **4** is also wide with a value of 125.7 (1)°, which approaches the value observed in **1** and **2**. This distortion from tetrahedral geometry might be accounted for by the minimization of the steric interactions of the isopropyl groups of the chalcogenolate ligands or by the minimization of the electronic repulsions of the anionic ligands. For comparison the tetrakis(benzeneselenolato)ferrate(II) anion, $[Fe(SePh)_4]^{-2}$, **5**, has Se−Fe−Se angles in the range of 103.6(1)−114.9 (1)°.[7] A similar situation is observed for the tetrakis(benzenethiolato)ferrate(II) anion, $[Fe(SPh)_4]^{-2}$, **6**. The range of S−Fe−S angle in complex **6** is 97.89(9)−115.2(1)°.[31] In both **1** and **2** the methine protons of the isopropyl groups are directed toward the iron center. The closest contact of the iron atom and the methine protons is 2.89 Å in **1** and 2.80 and 2.89 Å in **2**. This separation is outside of the sum of the van der Waals radii (estimated at 2.8 Å).

Despite the increased steric bulk of the 2,6-diisopropylbenzeneselenolato ligand in **1** and **2**, shorter Fe−Se bonds are observed than in complex **5**. The Fe−Se bond lengths in complex **5** are 2.445(2)−2.472(2) Å,[7] while the Fe−Se bond length with the bulkier ligand is 2.421(1) Å in **1** and 2.411(1) and 2.420(1) Å in **2**. This trend is also apparent in the comparison of the Fe−S bond lengths in complexes **4** and **6**. There is actually a longer Fe−S bond length in the less bulky benzenethiolato case (the Fe−S bond length in **6** is 2.338(2) Å,[31] while the $Fe-S_{thiolate}$ bond length in **4** is 2.315(1) Å).[6] This effect can be attributed to the electronic repulsions present in the anionic complexes or by π-donation from the chalcogen to the metal. One might expect the π-donation to be reflected by a M−E−C angle approaching 120° . However this feature is a poor indicator of π-donation as evidenced by the small Mo−S−C angle of 107.6(2)° in the complex $Mo(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4$ which has a short Mo−S distance presumably because of π-bonding interactions.[32] In the present case the Fe−Se−C angles are 101.9(2)° in **1**, while in **2** the angles are 107.6(2) and 104.6(2)° and in complex **4** the $Fe-S_{thiolate}-C$ angle is 108.7 (2)°.[6] The chalcogen−carbon bond lengths within this group of complexes appear to have the reverse trend. The longer iron−chalcogen bond distances correspond to shorter chalcogen−carbon bond lengths. However the uncertainties in the chalcogen−carbon bond distances make these differences barely statistically significant.

The iron−phosphorus separations in **1** and **2** are shorter than those measured for $Fe(CH_2C_6H_4Me)_2(dippe)$, **7**.[9] In **7** the Fe−P distances are both 2.462(2) Å while the Fe-P separation in **1** is 2.426(1) Å and in **2**, 2.408(2) and 2.447(2) Å . Iron−phosphine distances are sensitive to the coordination number, oxidation and spin state of the metal center as well as the steric bulk and π-acceptor ability of the phosphine. In these two examples both metals are high spin iron(II) in pseudotetrahedral coordination environments. The phosphine ligands PMe_2Ph and depe are similar to dippe in their donor characteristics. Therefore the alkyl ligands are probably better σ-donors than the selenolate ligands and this causes the longer iron−phosphorus separations observed in **7**.

Conclusion. The first mononuclear four-coordinate selenolato iron(II) complexes, $Fe(Se\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(PMe_2Ph)_2$, **1**, and $Fe(Se\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(depe)$, **2**, are readily prepared by the metathesis of chloride from iron(II) chloride with areneselenolate in the presence of phosphine. The areneselenolate is generated from the reduction of diaryl diselenide with sodium borohydride. This procedure has the benefits of reducing the odor associated with selenol compounds and avoiding insoluble alkali metal selenolates. The complexes are very oxygen sensitive both in the solid state and in solution. Single crystal X-ray diffraction studies reveal that the complexes possess distorted tetrahedral

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coordination geometries with wide Se–Fe–Se angles. Complex **1** has unusually low isomer shift and quadrupole splitting in the Mössbauer spectrum. The ^1H NMR resonances of ligands of both complexes can be observed and are assigned.

We are continuing the synthesis, characterization and reactivity studies of the class of compounds, $Fe(EAr)_2L_2$ (E = S, Se, Te; Ar = Ph, 2,4,6-$Me_3C_6H_2$, 2,6-*i*-$Pr_2C_6H_3$, 2,4,6-*i*-$Pr_3C_6H_2$; L or L_2 = mono- or bidentate amine, phosphine or imidazole ligands.

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Supplementary Material Available: Tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2** (17 pages). Ordering information is given on any current masthead page.