

## Square Planar vs Tetrahedral Geometry in Four Coordinate Iron(II) Complexes

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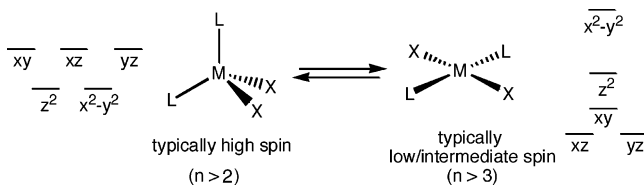
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The geometric preferences of a family of four coordinate, iron(II)  $d^6$  complexes of the general form  $L_2FeX_2$  have been systematically evaluated. Treatment of  $Fe_2(Mes)_4$  ( $Mes = 2,4,6-Me_3C_6H_2$ ) with monodentate phosphine and phosphite ligands furnished square planar *trans*- $P_2Fe(Mes)_2$  derivatives. Identification of the geometry has been accomplished by a combination of solution and solid-state magnetometry and, in two cases ( $P = PMe_3, PEt_2Ph$ ), X-ray diffraction. In contrast, both tetrahedral and square planar coordination has been observed upon complexation of chelating phosphine ligands. A combination of crystallographic and magnetic susceptibility data for (depe)Fe( $Mes$ )<sub>2</sub> (depe = 1,2-bis(diethylphosphino)ethane) established a tetrahedral molecular geometry whereas SQUID magnetometry and Mössbauer spectroscopy on samples of (dppe)Fe( $Mes$ )<sub>2</sub> (dppe = 1,2-bis(diphenylphosphino)ethane) indicated a planar molecule. When dissolved in chlorinated solvents, the latter compound promotes chlorine atom abstraction, forming tetrahedral (dppe)Fe( $Mes$ )Cl and (dppe)FeCl<sub>2</sub>. Ligand substitution reactions have been studied for both structural types and are rapid on the NMR time scale at ambient temperature.

### Introduction

The geometry and electronic structure of a transition metal complex are interrelated properties and dictate both the physical characteristics and chemical reactivity of a given molecule. Four coordinate compounds of the first transition series are particularly intriguing, given the choice between a low-/intermediate-spin square planar ground state and a high-spin tetrahedral configuration (Scheme 1).<sup>1,2</sup> The tetrahedral arrangement is sterically preferred and typically observed with large ligands and small metal ions.<sup>3</sup> For high-spin complexes with  $d^n$  electronic configurations with  $n > 2$ , occupation of antibonding molecular orbitals is unavoidable,

Scheme 1



able, providing little ligand field stabilization energy (LFSE). In contrast, square planar coordination, while sterically disfavored, offers substantial electronic stabilization that is a natural consequence of a high-lying, empty, antibonding  $d(x^2-y^2)$  orbital (Scheme 1).

For  $d^8$  metal ions, the factors that govern the choice between square planar and tetrahedral geometry are fairly well understood.<sup>3</sup> For larger second and third row metals such as Pd(II), Pt(II), and Au(III), the LFSE dominates and square planar geometries are almost exclusively observed.<sup>3</sup> The lighter Ni(II) congener offers both limiting structural types. When weak field ligands such as halides or arylated phosphines are present, as is the case with  $NiCl_4^{2-}$  or  $(Ph_3P)_2NiCl_2$ , tetrahedral coordination is observed<sup>4,5</sup> whereas compounds with strong field ligands or alkylated phosphines such

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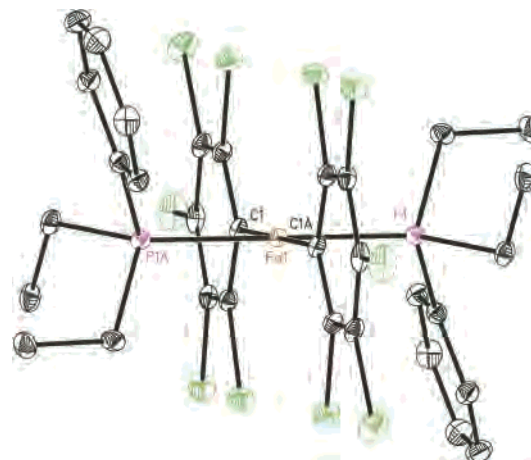
(2) The d-orbital splitting diagrams shown in Scheme 1 are for idealized, high-symmetry cases.

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as  $\text{Ni}(\text{CN})_4^{2-}$  and  $(\text{Cy}_3\text{P})_2\text{NiCl}_2$  are square planar.<sup>6</sup> Interestingly, complexes supported by mixed alkyl/aryl phosphines such as  $[(\text{PhCH}_2)\text{Ph}_2\text{P}]_2\text{NiBr}_2$  contain both tetrahedral and square planar geometries in the same crystal lattice.<sup>7</sup>

Unlike the  $d^8$  cases, the geometric preferences of lower  $d^n$  configurations have not been as thoroughly studied. Our laboratory has been exploring the chemistry of organometallic iron complexes as potential surrogates for precious metals in catalytic bond forming reactions such as olefin hydrogenation and hydrosilation.<sup>8</sup> As part of these investigations, we have prepared and characterized a family of four coordinate, in some cases enantiomerically pure, iron(II) dialkyl complexes.<sup>9</sup> While formally 14 electron species, these compounds are unreactive toward olefins, possibly a consequence of their tetrahedral geometry and high-spin,  $S = 2$  ground state, which provides no vacant low-lying molecular orbitals for substrate coordination. On the basis of this hypothesis, we became interested in exploring alternative geometries and spin states with the goal of generating catalytically active iron complexes.

Square planar coordination for iron(II)  $\text{L}_2\text{FeX}_2$  compounds, while amply preceded, is generally limited to complexes containing porphyrin, salicylaldimato, and phthalocyanine ligands, where the macrocyclic chelate confines the geometric preference of the metal center.<sup>10,11</sup> Iron(II) complexes containing only mono- or bidentate ligands where the molecule can adopt either geometry have not been systematically investigated. While both structural types have been reported, only tetrahedral  $\text{L}_2\text{FeX}_2$  complexes have been crystallographically characterized.<sup>12–15</sup> The geometry of the square planar complexes, such as  $(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$ ,<sup>16</sup> has



**Figure 1.** Molecular structure of  $\text{trans}-(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$  at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for  $\text{trans}-(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$  and **6**

$\text{trans}-(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$		<b>6</b>	
Fe(1)–C(1)	1.999(3)	Fe(1)–C(1)	2.031(2)
Fe(1)–P(1)	2.2990(8)	Fe(1)–P(1)	2.2597(6)
C(1)–Fe(1)–C(1A)	180.0	C(1)–Fe(1)–C(1A)	180.0
C(1)–Fe(1)–P(1)	88.31(9)	C(1)–Fe(1)–P(1)	89.72(7)
C(1A)–Fe(1)–P(1)	91.69(9)	C(1A)–Fe(1)–P(1)	90.29(7)
C(1A)–Fe(1)–P(1A)	88.31(9)	C(1A)–Fe(1)–P(1A)	90.28(7)

been inferred on the basis of magnetic susceptibility data, where compounds with  $S = 1$  ground states are consistent with intermediate-spin,  $d^6$  planar molecules.<sup>17</sup> Here we describe the synthesis and characterization of a family of  $\text{P}_2\text{Fe}(\text{Mes})_2$  ( $\text{P}$  = phosphine, phosphite;  $\text{Mes}$  = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ) complexes and explore the factors that govern their geometric preferences. In addition, crystallographic characterization of  $(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$  and two square planar  $\text{P}_2\text{Fe}(\text{Mes})_2$  compounds is also presented.

## Results and Discussion

**Crystallographic and NMR Spectroscopic Characterization of  $\text{trans}-(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$ .** Because no example of a square planar iron(II) compound with monodentate ligands had been structurally characterized, our study commenced with crystallographic verification of the structure of the previously reported  $\text{trans}-(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$ .<sup>9</sup> Yellow plates suitable for X-ray diffraction were obtained by layering a concentrated dichloromethane solution with pentane. The solid-state structure (Figure 1) definitively establishes the square planar geometry of the molecule, in agreement with the previous assignment based on magnetometry.<sup>9</sup> Selected bond distances and angles are presented in Table 1. The crystallography also reveals *trans*-phosphine and pentachlorophenyl ligands that are related by a center of inversion. To avoid steric interactions with the phosphines, the aryl ligands are orthogonal to the square plane, placing the *ortho*-chlorine substituents above and below the iron center. The structural data are consistent with Chatt and Shaw's asser-

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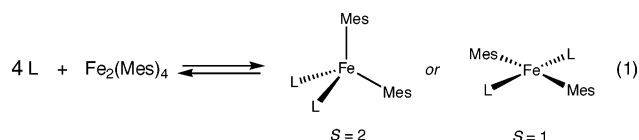
Chart 1



tion<sup>16</sup> that strong field, *ortho*-substituted aryl groups are essential for square planar coordination. In addition, the aryl groups on the phosphine ligands are essentially parallel to the pentachlorophenyl ligands, presumably to avoid steric interactions with the ring substituents.

Analysis of *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> by <sup>1</sup>H NMR spectroscopy in benzene-*d*<sub>6</sub> confirms the presence of only one compound in solution. As expected for an *S* = 1 molecule, the phosphine resonances are shifted dramatically from their diamagnetic reference values. For example, the ethyl substituents on the phosphine ligands appear at -18.6 (CH<sub>3</sub>) and -0.15 (CH<sub>2</sub>) ppm, while three peaks are observed at -7.8, -53.2, and 12.1 (*para*) ppm for the corresponding phenyl protons. Attempts to observe either <sup>31</sup>P or <sup>13</sup>C NMR spectra have been unsuccessful.

**Evaluation of Geometric Preferences of L<sub>2</sub>Fe(Mes)<sub>2</sub> Compounds.** With both NMR spectroscopic and solid-state characterization of a square planar iron(II) complex in hand, the geometric preferences of a family of four coordinate Fe(II), d<sup>6</sup> compounds were systematically evaluated. For rapid screening, a series of neutral donors was added to Fe<sub>2</sub>(Mes)<sub>4</sub> (eq 1). This iron precursor was chosen due to its synthetic availability, versatility as a synthon for a range of iron complexes, and reported ability to provide both square planar and tetrahedral complexes. Using this approach, Floriani and co-workers have prepared (py)<sub>2</sub>Fe(Mes)<sub>2</sub> and (phen)Fe(Mes)<sub>2</sub> (py = pyridine, phen = 9,10 phenanthroline).<sup>14,18</sup> X-ray crystallography has established that both molecules are tetrahedral in the solid state. Likewise, Siedel and co-workers have synthesized and structurally characterized tetrahedral (dme)Fe(Mes)<sub>2</sub> (dme = 1,2-dimethoxyethane).<sup>15</sup>



Nitrogen donors were the first class of ligand explored. Treatment of Fe<sub>2</sub>(Mes)<sub>4</sub> with *N,N*-dimethylaminopyridine (DMAP) furnished a yellow powder identified as (DMAP)<sub>2</sub>Fe(Mes)<sub>2</sub> (**1**) (Chart 1). The solution magnetic moment (benzene-*d*<sub>6</sub>, 22 °C) of **1** was measured by the Evans method<sup>25</sup> and produced a magnetic moment of 5.1 μ<sub>B</sub>,

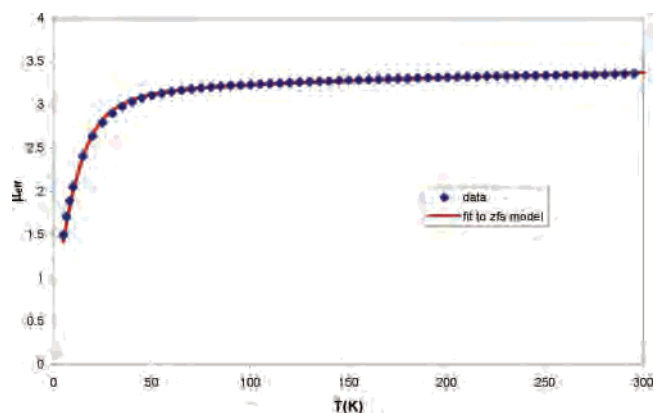


Figure 2. SQUID magnetization data for **3**.

consistent with a high-spin, *S* = 2 tetrahedral molecule. This result is consistent with Floriani's observation of a tetrahedral geometry for (py)<sub>2</sub>Fe(Mes)<sub>2</sub>, which has also been characterized by X-ray diffraction.<sup>14</sup> Addition of a chelating diamine such as *N,N,N',N'*-tetramethylethylenediamine (tmeda) to Fe<sub>2</sub>(Mes)<sub>4</sub> yielded (tmeda)Fe(Mes)<sub>2</sub> (**2**) as a tan solid in modest yield (Chart 1). Measurement of the benzene-*d*<sub>6</sub> solution magnetic moment at 22 °C produced a value of 5.1 μ<sub>B</sub>, consistent with an *S* = 2 tetrahedral molecule. Addition of more hindered amines such as NEt<sub>3</sub> or *N,N,N',N'*-tetraethylethylenediamine to Fe<sub>2</sub>(Mes)<sub>4</sub> produced no reaction.

In addition to nitrogen-based ligands, bis(mesityl)iron(II) complexes supported by phosphines and phosphites were studied. The commercial availability of these ligands along with their diverse steric and electronic properties makes them attractive for a systematic study of the coordination preferences of four coordinate iron(II) complexes.

Addition of the smallest phosphine in the series, PMe<sub>3</sub>, to Fe<sub>2</sub>(Mes)<sub>4</sub> in diethyl ether at -78 °C afforded (Me<sub>3</sub>P)<sub>2</sub>Fe(Mes)<sub>2</sub> (**3**) as a yellow crystalline solid in high yield. The solution magnetic moment of **3** was measured by the Evans method in benzene-*d*<sub>6</sub> and produced a value of 2.9 μ<sub>B</sub>, consistent with the spin-only value for two unpaired electrons. The *S* = 1 ground state suggests an intermediate-spin, d<sup>6</sup> planar molecule. Corroboration of this value was obtained from solid state magnetic susceptibility measurements on a powdered sample of **3** (Figure 2). The  $\chi T$  versus *T* data may be fitted to a zero-field-splitting model for *S* = 1<sup>19</sup> with a temperature-independent paramagnetism term that yields *g* = 2.26 ± 0.01, *D/k* = 51 ± 1 K, and TIP = 5 × 10<sup>-4</sup> (emu K)/mol. The high value of the TIP may reflect a trace ferromagnetic impurity. Deviation of the *g*-value from the free electron value is consistent with incomplete quenching of the orbital angular momentum as has been seen previously for square planar Fe(II).<sup>20</sup>

As with *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>, <sup>1</sup>H NMR spectroscopy has proven useful for the identification of **3**. A representative spectrum recorded at 22 °C in benzene-*d*<sub>6</sub> is presented in Figure 3. A relatively sharp ( $\Delta\nu_{1/2}$  = 36 Hz) peak corresponding to 18 hydrogens is observed at -35.8 ppm and is assigned as the phosphine methyl groups.<sup>21</sup> Distinct resonances for the *ortho* and *para* methyl groups of the mesityl ligands are observed at 20.5 and -4.8 ppm, respectively,

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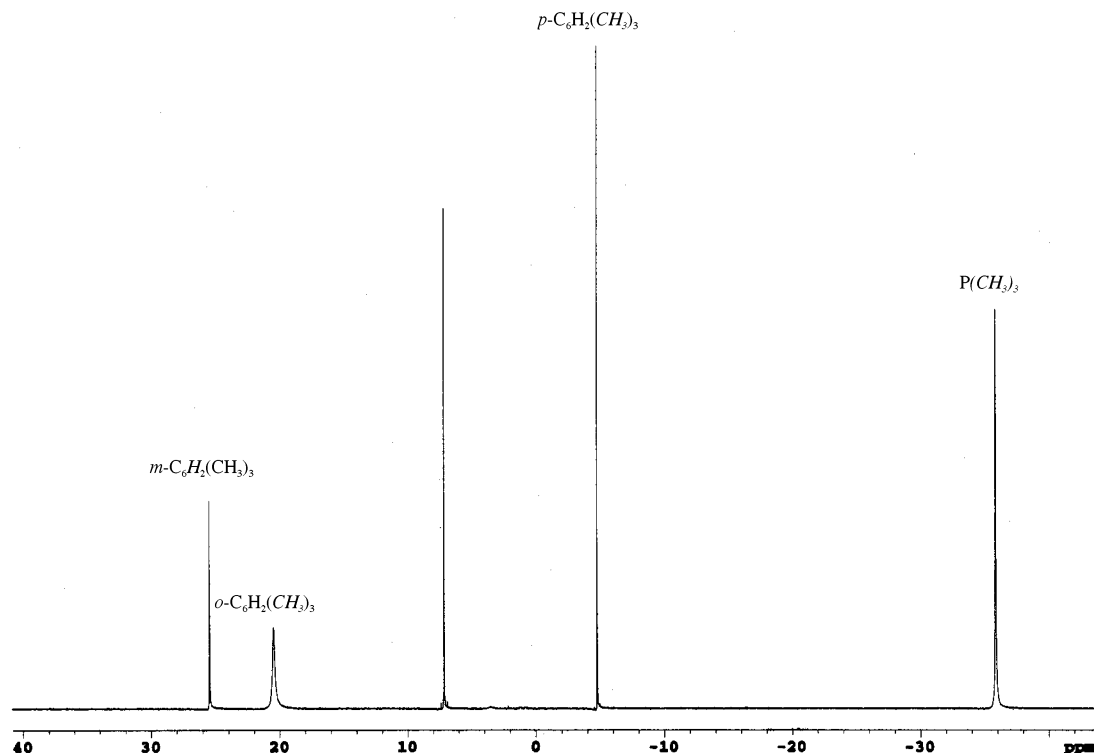


Figure 3.  $^1\text{H}$  NMR spectrum of **3** in benzene- $d_6$ .

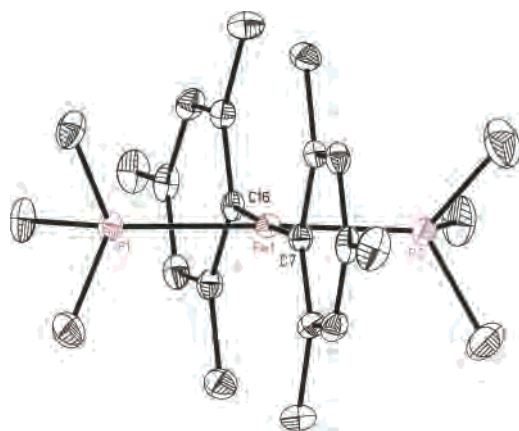


Figure 4. Molecular structure of **3** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**

Fe(1)–C(7)	2.032(3)	Fe(1)–P(1)	2.2552(10)
Fe(1)–C(16)	2.017(3)	Fe(1)–P(2)	2.2475(10)
C(16)–Fe(1)–C(7)	176.61(13)	C(7)–Fe(1)–P(1)	89.62(9)
C(16)–Fe(1)–P(1)	89.31(9)	C(7)–Fe(1)–P(2)	90.91(9)
C(16)–Fe(1)–P(2)	90.91(9)	P(1)–Fe(1)–P(2)	177.74(4)

while a single resonance is observed at 25.5 ppm for the *meta* hydrogen on the aryl rings.

Single crystals suitable for X-ray diffraction were obtained by cooling a concentrated diethyl ether solution of **3** to  $-35$  °C. The molecular structure is shown in Figure 4, and selected bond distances and angles are presented in Table 2. As with the molecular structure of *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>, **3** is square planar with *trans* phosphine and mesityl ligands. The mesityl ligands are oriented perpendicular to the plane

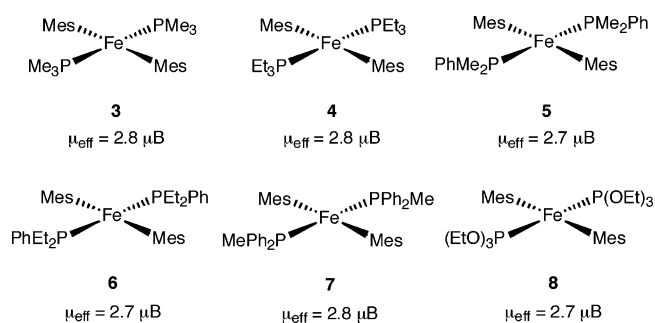
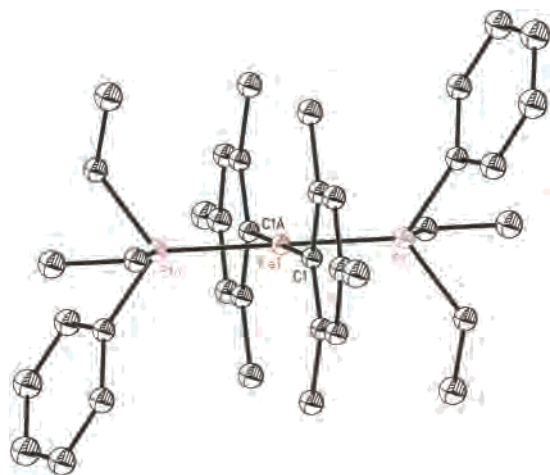


Figure 5. Square planar iron(II) complexes.

of the iron with the *ortho* methyl groups avoiding steric interactions with the phosphine ligands and protecting the axial sites on the iron center, again supporting the Chatt and Shaw hypothesis.<sup>16</sup>

Using the synthetic approach outlined in eq 1, several other bis(phosphine)iron(II) bis(mesityl) complexes were prepared in moderate to good yield (Figure 5). Each complex was characterized by a combination of  $^1\text{H}$  NMR spectroscopy, elemental analysis, and solution magnetometry. For all of the complexes containing monodentate phosphine ligands, the magnetic susceptibility data are consistent with intermediate-spin,  $S = 1$  ground states, indicative of a square planar geometry. The geometry of **6** was corroborated by X-ray diffraction, and the solid-state structure is presented in Figure 6, while selected bond distances and angles are reported in Table 1. **6** is structurally similar to both *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> and **3** with a square planar iron center and *trans*-phosphine ligands. The orientation of both the phosphines and the aryl ligands is similar to that observed in *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>. The iron–carbon bonds in **6** are elongated by 0.03 Å as compared to those of *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>-



**Figure 6.** Molecular structure of **6** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

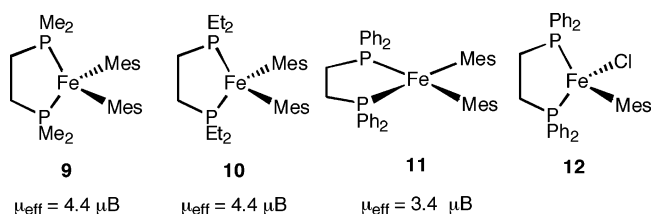
$\text{Fe}(\text{C}_6\text{Cl}_5)_2$ , while the iron–phosphorus bonds are contracted by approximately the same distance.

Treatment of  $\text{Fe}_2(\text{Mes})_4$  with the trialkyl phosphite,  $\text{P}(\text{OEt})_3$ , furnished *trans*- $[(\text{EtO})_3\text{P}]_2\text{Fe}(\text{Mes})_2$  (**8**), which has a solution magnetic moment (benzene- $d_6$ , 22 °C) of  $2.7 \mu_{\text{B}}$ , consistent with a planar, intermediate-spin  $S = 1$  molecule. Attempts to prepare similar bis(phosphite) complexes by addition of more hindered and electron-poor precursors such as  $\text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OSiMe}_3)_3$ , or  $\text{P}(\text{O}-2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3)_3$  produced no reaction.

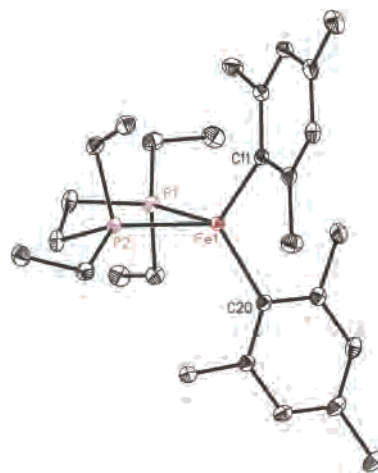
The effect of chelating phosphines on the geometric preference of bis(phosphine)iron(II) bis(mesityl) complexes was also explored. Stirring either *dppf* (*dppf* = 1,2-bis(diphenylphosphino)ferrocene) or ( $\pm$ )-*BINAP* (*BINAP* = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) with  $\text{Fe}_2(\text{Mes})_4$  in diethyl ether produced no reaction even after extended reaction times or gentle heating. However, addition of *dmpe* (1,2-bis(dimethylphosphino)ethane) to an ethereal solution of  $\text{Fe}_2(\text{Mes})_4$  furnished a bright yellow powder identified as (*dmpe*) $\text{Fe}(\text{Mes})_2$  (**9**) on the basis of magnetic data and elemental analysis.

Further characterization of **9** by solution  $^1\text{H}$  NMR spectroscopy was hampered by the low solubility of the compound in common organic solvents such as toluene, benzene, THF, diethyl ether, acetone, acetonitrile, and dimethyl sulfoxide. Dissolution of **9** in chlorinated solvents such as dichloromethane- $d_2$  resulted in decomposition (*vide infra*). Despite these limitations, a magnetic moment of  $4.2 \mu_{\text{B}}$  was measured in the solid state using the Gouy method. While low, this value is most consistent with tetrahedral coordination. The origin of the low moment is not understood at this time and may be a consequence of an impurity or population of a low-spin, planar isomer. It should be noted, however, that the magnetic measurements were conducted on analytically pure material.

To circumvent the solubility problems associated with **9**, a chelating phosphine with more lipophilic alkyl substituents was explored. Addition of *depe* (1,2-bis(diethylphosphino)ethane) to  $\text{Fe}_2(\text{Mes})_4$  furnished an orange powder identified as (*depe*) $\text{Fe}(\text{Mes})_2$  (**10**) in 79% yield (Figure 7). Solution



**Figure 7.** Iron(II) bis(mesityl) complexes with chelating phosphine ligands.



**Figure 8.** Molecular structure of **10** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

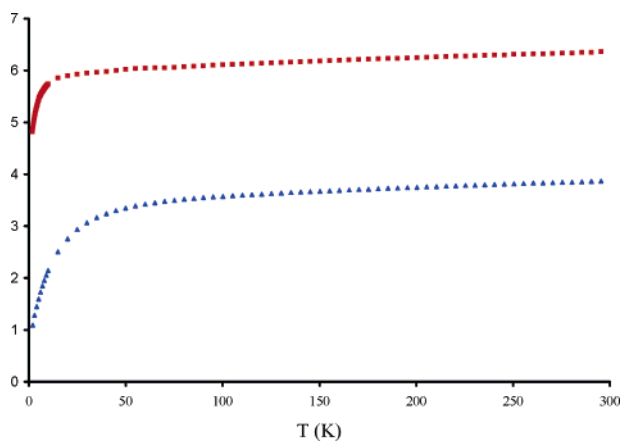
**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **10**

Fe(1)–C(11)	2.0702(14)	Fe(1)–P(1)	2.4692(4)
Fe(1)–C(20)	2.0745(3)	Fe(1)–P(2)	2.4859(4)
C(11)–Fe(1)–C(20)	120.41(5)	C(20)–Fe(1)–P(1)	100.90(4)
C(11)–Fe(1)–P(1)	126.18(4)	C(20)–Fe(1)–P(2)	123.20(4)
C(11)–Fe(1)–P(2)	100.97(4)	P(1)–Fe(1)–P(2)	80.35(1)

magnetometry in benzene- $d_6$  at 22 °C provided a magnetic moment of  $4.4 \mu_{\text{B}}$ , slightly lower than the spin-only value expected for four unpaired electrons but well within the range of high-spin tetrahedral ferrous complexes.<sup>9</sup>

The tetrahedral geometry of **10** was corroborated by X-ray diffraction. The solid-state structure is presented in Figure 8, and selected bond distances and angles are provided in Table 3. As expected for a tetrahedral iron center, the mesityl ligands are oriented above and below the iron–phosphine chelate plane and are slightly twisted to avoid steric interactions between the *ortho* methyl groups. The ethyl substituents on the phosphorus atoms are directed in a “front–back” arrangement where the two carbon chain directed toward the iron is parallel to the plane of the adjacent aryl ring. Comparison of the iron–phosphorus bond distances in **10** to those found in *trans*- $(\text{PhEt}_2\text{P})_2\text{Fe}(\text{C}_6\text{Cl}_5)_2$ , **3**, and **6** establishes a lengthening by approximately 0.2 Å from square planar to tetrahedral coordination, consistent with population of antibonding molecular orbitals in the tetrahedral case. In contrast, little change is observed in the iron–carbon bond lengths in the two limiting geometries.

The tetrahedral geometry of **10** is somewhat surprising in light of the observation of square planar complexes for the monodentate phosphines and phosphite in **3–8**. At first glance, it may appear that the tetrahedral geometry is favored

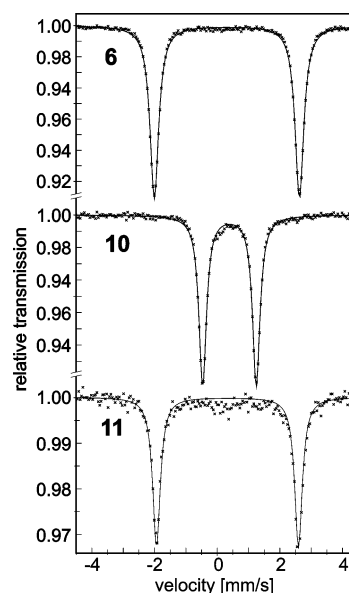


**Figure 9.** SQUID magnetization data for **10** (red) and **11** (blue).

due to the inability of the chelate to adopt a trans disposition of the phosphines and mesityl ligands. However, Siedel and Lattermann<sup>17</sup> have reported (dppe)Fe(Mes)<sub>2</sub> (**11**) (dppe = 1,2-bis(diphenylphosphino)ethane) as a planar molecule on the basis of magnetic susceptibility data. Observation of a square planar complex with *arylated* chelating phosphines and tetrahedral molecules with *alkylated* phosphines also contrasts the coordination preferences observed in classic Ni(II) complexes.<sup>3–6</sup>

On the basis of these puzzling observations, **11** was prepared and studied in more detail. As was reported previously,<sup>17</sup> addition of dppe to an ethereal solution of Fe<sub>2</sub>(Mes)<sub>4</sub> afforded an orange powder, identified as **11**, that is sparingly soluble in ethereal and hydrocarbon solvents. The low solubility of the compound in common NMR solvents precluded measurement of the solution magnetic moment. Solid-state magnetic data were collected from 2 to 300 K using SQUID magnetometry (Figure 9). For comparison, similar data was recorded on powdered samples of **10**, a crystallographically verified tetrahedral molecule. For **11**, the magnetic moment from 50 to 300 K ranges from 3.3 to 3.9 μ<sub>B</sub> and is slightly higher than the values measured over the same temperature range for **3**. Importantly, the values of the magnetic susceptibility for **11** are substantially lower than those for **10**, supporting Siedel's original conclusion of a planar molecule with an intermediate-spin, *S* = 1 ground state.

Mössbauer spectroscopy was also used to investigate the geometry of **11**. For comparison, spectra were recorded on the known tetrahedral compounds, **10** and (–)-(sparteine)-FeCl<sub>2</sub><sup>22</sup> as well as square planar **6**. Selected spectra are presented in Figure 10, and the experimentally determined isomer shifts and quadrupole splittings are reported in Table 4. As expected for a series of iron(II) compounds, the isomer shifts are essentially invariant for the four compounds. In contrast, **6** and **11** have large quadrupole splitting parameters consistent with planar, *S* = 1 molecules in which covalency contributions to the electric field gradient are significant. The unique appearance of the zero-field spectra showing unusually large quadrupole splittings of more than 4 mm/s and small isomer shifts of 0.3–0.5 mm/s is fully characteristic of ferrous ions in the intermediate *S* = 1 spin state. Thus,



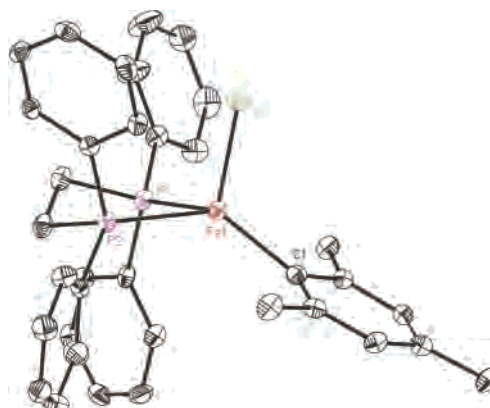
**Figure 10.** Zero-field Mössbauer spectra for **6**, **10**, and **11** recorded at 80 K.

**Table 4.** Mössbauer Parameters for a Series of Four Coordinate Iron(II) Compounds

compound	$\delta$ (mm/s)	quad splitting (mm/s)
<b>6</b>	0.31	4.63
<b>10</b>	0.39	1.71
<b>11</b>	0.33	4.53
(–)-(sparteine)FeCl <sub>2</sub>	0.91	2.43

both magnetic susceptibility studies and Mössbauer spectroscopy are consistent with a square planar geometry for **11**.

Attempts to verify the geometry of **11** by X-ray diffraction have been frustrated by the inability to obtain single crystals. The complex is essentially insoluble in both hydrocarbon and ethereal solvents but dissolves freely in dichloromethane. Recrystallization of the complex from a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of **11** layered with diethyl ether at –35 °C afforded large yellow blocks suitable for X-ray diffraction. The solid-state structure, shown in Figure 11, is not the desired complex but rather (dppe)Fe(Mes)Cl (**12**). Monitoring the reaction between **11** and dichloromethane-*d*<sub>2</sub> by <sup>1</sup>H NMR spectroscopy established clean conversion to **12** over the course of minutes at ambient temperature. Concomitant with

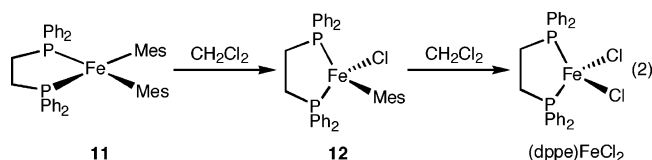


**Figure 11.** Molecular structure of **12** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for **12**

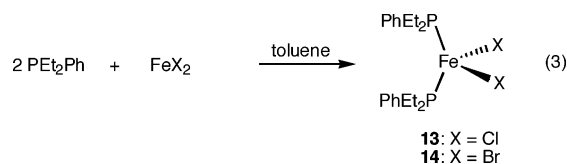
Fe(1)–C(1)	2.044(5)	Fe(1)–P(1)	2.4598(15)
Fe(1)–Cl(1)	2.2486(14)	Fe(1)–P(2)	2.5169(15)
C(1)–Fe(1)–Cl(1)	117.17(14)	Cl(1)–Fe(1)–P(1)	98.60(6)
C(1)–Fe(1)–P(1)	123.21(14)	Cl(1)–Fe(1)–P(2)	127.06(16)
C(1)–Fe(1)–P(2)	127.06(16)	P(1)–Fe(1)–P(2)	82.01(5)

this process is a second chlorine atom abstraction by **12** to form (dppe)FeCl<sub>2</sub> (eq 2). This competing atom transfer process makes isolation of pure **12**, free of **11** or (dppe)FeCl<sub>2</sub>, challenging. In both chlorine atom abstraction reactions, the fate of the mesityl ligand is unknown.



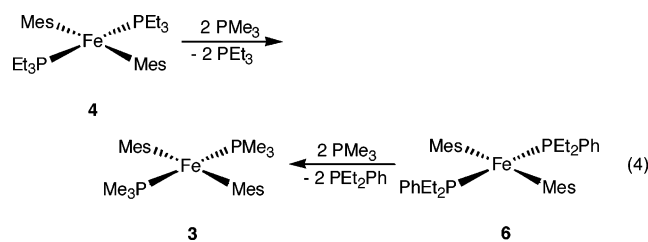
The solid-state structure (Figure 11) and metrical parameters (Table 5) clearly establish a tetrahedral geometry for **12**. The remaining mesityl group is oriented essentially perpendicular to the iron–chlorine bond vector while the phenyl substituents on the phosphorus atoms are arranged in a propeller-like fashion and are related by an idealized C<sub>2</sub> axis of symmetry. Importantly, the iron–phosphorus bond lengths of 2.4598(15) and 2.5169(15) Å found in **12** are elongated from the distances of ~2.3 Å present in the corresponding square planar complexes. In comparison, the iron–carbon bond is barely elongated in **12** as compared to the square planar complexes.

Because substitution of one mesityl ligand by a chloride induces a geometric change from square planar to tetrahedral, the coordination preferences of iron(II) bis(halide) complexes were examined. Heating 2 equiv of PEt<sub>2</sub>Ph, a phosphine known to support square planar complexes, with either anhydrous FeCl<sub>2</sub> or FeBr<sub>2</sub> furnished (PhEt<sub>2</sub>P)<sub>2</sub>FeX<sub>2</sub> (X = Cl (**13**), Br (**14**)) (eq 3). Measurement of the solution magnetic moments (Evans method) yielded μ<sub>eff</sub> values of 4.8 (**13**) and 5.0 μ<sub>B</sub> (**14**), consistent with a S = 2 ground states and a tetrahedral geometries. Observation of tetrahedral complexes with **12–14** highlights the importance of *ortho*-substituted aryl groups for isolation of square planar complexes.

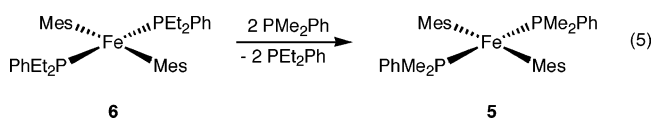


Several other bis(phosphine)ferrous complexes were targeted to further test this hypothesis. Attempts to isolate Fe<sub>2</sub>-Ph<sub>4</sub> or trap the compound in situ in the presence of both monodentate and chelating phosphines resulted in decomposition. Likewise, attempts to alkylate (dppe)FeCl<sub>2</sub> or **13** with MeLi or KCH<sub>2</sub>Ph did not produce a tractable product. It should be noted that Hermes and Girolami have synthesized and in many cases crystallographically characterized (dippe)FeR<sub>2</sub> (dippe = bis(diisopropylphosphino)ethane) complexes, all of which are tetrahedral.<sup>12</sup>

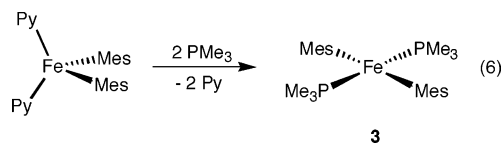
**Ligand Exchange Reactions.** The isolation and crystallographic characterization of a family of square planar iron(II) complexes offered the opportunity to study ligand exchange processes at an intermediate-spin, S = 1 metal center and potentially compare the outcome of these processes to more familiar, S = 0, d<sup>8</sup> complexes. Addition of 2 equiv of PMe<sub>3</sub> to **4** resulted in rapid formation of **3** with liberation of 2 equiv of free PEt<sub>3</sub>. A similarly rapid reaction was observed for the addition of PMe<sub>3</sub> to **6** (eq 4). Addition of PEt<sub>3</sub> or PEt<sub>2</sub>Ph to **3** produced no reaction, indicating that coordination of PMe<sub>3</sub> is in fact thermodynamically favored. Attempts to measure rate constants for the exchange reactions have not been successful due to the rapid rate at which these reactions reach equilibrium.



Exchange reactions were also carried out with **5** and **6**. Addition of PMe<sub>2</sub>Ph to **6** rapidly furnished **5** and free PEt<sub>2</sub>Ph whereas, in the converse experiment, addition of PEt<sub>2</sub>Ph to **5** produced no ligand exchange (eq 5). Given the electronic similarity of these two ligands in combination with the results of the PMe<sub>3</sub> exchange studies, the thermodynamic preference for phosphine coordination appears to be dominated by steric effects, where smaller ligands bind more tightly to the [Fe(Mes)<sub>2</sub>] fragment than their more hindered counterparts.



Exchange reactions between square planar and tetrahedral complexes were also investigated. Addition of 2 equiv of PMe<sub>3</sub> to (py)<sub>2</sub>Fe(Mes)<sub>2</sub> resulted in immediate and quantitative ligand exchange at 22 °C in benzene-*d*<sub>6</sub>. Addition of a slight excess of pyridine to **3** produced no reaction. These experiments clearly demonstrate the thermodynamic preference for phosphine over amine coordination. As with the square planar complexes, substitution of pyridine in (py)<sub>2</sub>Fe(Mes)<sub>2</sub> with PMe<sub>3</sub> or pyridine-*d*<sub>5</sub> is too fast at ambient temperature to be measured by conventional NMR techniques.



## Concluding Remarks

The coordination preferences of a family of four coordinate, d<sup>6</sup> L<sub>2</sub>FeX<sub>2</sub> complexes have been systematically studied as a function of both neutral and anionic ligands. For iron(II) bis(mesityl) compounds, high-spin, S = 2 tetrahedral

complexes are observed exclusively when supported by monodentate or chelating amine ligands. These results, in conjunction with those previously reported for oxygen chelates,<sup>15</sup> suggest that, for first row donors, steric factors overcome competing electronic stabilization offered by the square planar alternative. For monodentate phosphines and phosphites, the opposite situation is observed, where planar, intermediate-spin,  $S = 1$  complexes are favored. Ligand exchange studies establish a preference for phosphine over amine coordination and hence a square planar over a tetrahedral geometry. Thus, stronger phosphine ligands overcome the dominant steric effect observed with the nitrogen and oxygen donors, providing greater ligand field stabilization energy and square planar complexes. Within the series of phosphines, preferential coordination of smaller phosphines was observed.

For chelating phosphines, the conclusions are not as straightforward. Alkyl-substituted chelates such as dmpe and depe furnished tetrahedral molecules whereas the arylated phosphine, dppe, afforded a square planar complex, contrasting observations in classic Ni(II),  $d^8$  chemistry. This shift in geometric preference is not immediately obvious and may be a result of subtle steric interactions. Significantly, replacement of the *ortho*-substituted aryl ligands with weaker field halides induces a change in geometric preference, producing tetrahedral molecules regardless of the field strength of the supporting neutral ligand. These observations are in agreement with Chatt and Shaw's assertion<sup>16</sup> that *ortho*-substituted aryl groups are necessary for intermediate-spin,  $S = 1$  molecules.

## Experimental Section

**General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an Mbraun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.<sup>23</sup> The Mbraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Argon and hydrogen gas were purchased from Airgas Inc. and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Benzene- $d_6$  was purchased from Cambridge Isotope Laboratories and distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Chloroform- $d$  and dichloromethane- $d_2$  were purchased from Cambridge Isotope Laboratories and dried over  $\text{CaH}_2$ . Phosphines and phosphites were purchased from Aldrich, Strem, and Acros and were used as received.  $\text{Fe}_2(\text{Mes})_4$ <sup>24</sup> was prepared according to the literature procedure.

<sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.763, 399.780, and 500.62 MHz, respectively. All chemical shifts are reported relative to  $\text{SiMe}_4$  using <sup>1</sup>H (residual) chemical shifts of the solvent as a secondary standard. For paramagnetic compounds, <sup>1</sup>H NMR data are reported with the chemical shift followed by the peak width

at half-height in hertz followed by integration value and, where possible, peak assignment.

Unless stated otherwise, solution magnetic moments were measured at 22 °C by the method originally described by Evans<sup>25</sup> with stock and experimental solutions containing a known amount of a ferrocene standard. Solid-state magnetic moments were recorded using a Quantum Design SQUID magnetometer. Magnetization versus temperature data were recorded in a 5000 G applied field from 5 to 300 K. The sample holder was constructed from an NMR tube as previously described.<sup>26</sup> Diamagnetic contributions were estimated using Pascal's constants. The sample used was recrystallized several times and purity determined by elemental analysis.

Mössbauer data were recorded on an alternating constant-acceleration spectrometer. The minimum experimental line width was 0.24  $\text{mm s}^{-1}$  (full width at half-height). A constant sample temperature was maintained with an Oxford Instruments Variox or an Oxford Instruments Mössbauer-Spectromag 2000 cryostat. Reported isomer shifts ( $\delta$ ) are referenced versus iron metal at 293 K.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD Area detector system equipped with a molybdenum X-ray tube ( $\lambda = 0.71073$  Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT program, and data were corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed by Robertson Microлит Laboratories, Inc., in Madison, NJ.

**Preparation of (DMAP)Fe(Mes)<sub>2</sub> (1).** A scintillation vial was charged with 0.102 g (0.173 mmol) of  $\text{Fe}_2(\text{Mes})_4$  and approximately 5 mL of diethyl ether. With stirring, 0.085 g (0.696 mmol) of DMAP in 3 mL of diethyl ether was added and the resulting reaction mixture stirred for 3 h. The resulting solid was collected by filtration, washed with pentane, and dried in vacuo yielding 0.157 g (84%) of **1** as a yellow powder. Anal. Calcd for  $\text{C}_{30}\text{H}_{42}\text{FeN}_4$ : C, 70.03; H, 8.23; N, 10.89. Found: C, 70.26; H, 8.14; N, 10.58. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ . <sup>1</sup>H NMR (benzene- $d_6$ ):  $\delta = 4.59$  (59.3), 33.4 (241), 45.2 (814), 92.1 (546), 117 (452).

**Preparation of (TMEDA)Fe(Mes)<sub>2</sub> (2).** This molecule was prepared in a manner similar to that for **1** with 0.200 g (0.340 mmol) of  $\text{Fe}_2(\text{Mes})_4$  and 0.079 g (0.680 mmol) of TMEDA yielding 0.117 g (42%) of tan solid identified as **2**. Anal. Calcd for  $\text{C}_{24}\text{H}_{38}\text{FeN}_2$ : C, 70.24; H, 9.33; N, 6.83. Found: C, 69.84; H, 9.24; N, 6.54. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$ . <sup>1</sup>H NMR (benzene- $d_6$ ):  $\delta = 2.13$  (68.3), 35.24 (1140), 85.17 (84.9), 113 (203).

**Preparation of *trans*-(Me<sub>3</sub>P)<sub>2</sub>Fe(Mes)<sub>2</sub> (3).** A 50 mL round-bottomed flask was charged with 0.200 g (0.340 mmol) of  $\text{Fe}_2(\text{Mes})_4$  and approximately 10 mL of diethyl ether. With stirring, 0.103 g (1.40 mmol) of  $\text{PMe}_3$  was added by a 31.6 mL calibrated gas bulb. The deep red solution was stirred for 2 h forming a yellow solution over time. The solvent was removed in vacuo, and the resulting yellow solid was washed with pentane and dried to afford

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(24) Klose, A.; Solari, E.; Ferguson, R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 2414.

(25) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

(26) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936.



## Four Coordinate Iron(II) Complexes

0.254 g (84%) of **3**. Anal. Calcd for  $C_{24}H_{40}FeP_2$ : C, 64.58; H, 9.03. Found: C, 64.74; H, 9.05. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.9 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -35.8$  (36, 18H,  $P(CH_3)_3$ ),  $-4.8$  (20, 6H,  $CH_3$ - $p$ - $C_6H_5$ ), 20.5 (79, 12H,  $CH_3$ - $o$ - $C_6H_5$ ), 25.5 (25, 4H,  $C_6H_5$ ).

**Preparation of *trans*-(Et<sub>3</sub>P)<sub>2</sub>Fe(Mes)<sub>2</sub> (**4**)**. This molecule was prepared in a manner similar to that for **1** with 0.250 g (0.430 mmol) of  $Fe_2(Mes)_4$  and 0.201 g (1.7 mmol) of  $PEt_3$  yielding 0.318 g (70%) of **4**. Anal. Calcd for  $C_{30}H_{52}FeP_2$ : C, 67.92; H, 9.88. Found: C, 68.82; H, 9.66. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.8 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta$ ,  $-35.2$  (845, 8H,  $CH_3CH_2$ ),  $-19.8$  (727.6, 12H,  $CH_3CH_2$ ),  $-2.2$  (1841, 6H,  $CH_3$ - $p$ - $C_6H_5$ ), 10.4 (936.6, 12H,  $CH_3$ - $o$ - $C_6H_5$ ), 27.6, (979.2, 4H,  $m$ - $C_6H_5$ ).

**Preparation of *trans*-(PhMe<sub>2</sub>P)<sub>2</sub>Fe(Mes)<sub>2</sub> (**5**)**. A scintillation vial was charged with 0.200 g (0.340 mmol) of  $Fe_2(Mes)_4$  and approximately 5 mL of diethyl ether. With stirring, 0.188 g (1.40 mmol) of  $PPhMe_2$  in approximately 3 mL of diethyl ether was added at ambient temperature forming a deep red reaction mixture. An orange precipitate formed over the course of 3 h. The solid was collected by filtration and washed with pentane to afford 0.183 g (78%) of **5**. Anal. Calcd for  $C_{34}H_{44}FeP_2$ : C, 71.58; H, 7.77. Found: C, 71.53; H, 8.04. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.7 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -33.5$  (30.3, 12H,  $PC_6H_5$ - $(CH_3)_2$ ),  $-5.33$  (5.3, 6H,  $CH_3$ - $p$ - $C_6H_5$ ), 0.45 (14.3, 4H), 0.70 (23.4, 4H), 21.3 (74.6, 12H,  $CH_3$ - $o$ - $C_6H_5$ ), 24.7 (11.1, 4H,  $C_6H_5$ ).

**Preparation of *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(Mes)<sub>2</sub> (**6**)**. This molecule was prepared in a manner similar to that for **5** with 0.500 g (0.850 mmol) of  $Fe_2(Mes)_4$  and 0.565 g (3.4 mmol) of  $PEt_2Ph$  in 10 mL of diethyl ether yielding 0.862 g (81%) of an orange powder identified as **6**. Anal. Calcd. for  $C_{38}H_{52}FeP_2$ : C, 72.84; H, 8.36. Found: C, 72.43; H, 7.97. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.7 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -44.0$  (232, 4H),  $-20.53$  (151, 12H,  $CH_3$ - $CH_2$ ),  $-4.0$  (368, 6H,  $C_6H_5$ - $p$ - $CH_3$ ),  $-3.3$  (495, 4H), 0.86 (197, 8H,  $CH_3CH_2$ ), 9.1 (171, 2H,  $p$ - $H$ - $C_6H_5$ ), 14.8 (262, 12H,  $C_6H_5$ - $o$ - $CH_3$ ), 25.4 (185, 4H).

**Preparation of *trans*-(Ph<sub>2</sub>MeP)<sub>2</sub>Fe(Mes)<sub>2</sub> (**7**)**. This molecule was prepared in a manner similar to that for **5** with 0.100 g (0.170 mmol) of  $Fe_2(Mes)_4$  and 0.136 g (0.680 mmol) of  $PPh_2Me$  yielding 0.183 g (78%) of a red solid identified as **7**. Anal. Calcd for  $C_{44}H_{48}FeP_2$ : C, 76.08; H, 6.96. Found: C, 75.69; H, 6.25. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.8 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -7.0$  (179, 8H), 2.2 (159, 12H,  $CH_3$ - $o$ - $C_6H_5$ ), 10.4 (169, 6H), 17.9 (184, 4H), 21.3 (167, 4H), 23.4 (72.5, 6H).

**Preparation of [(EtO)<sub>3</sub>P]<sub>2</sub>Fe(Mes)<sub>2</sub> (**8**)**. This molecule was prepared in a manner similar to that for **5** with 0.235 g (0.390 mmol) of  $Fe_2(Mes)_4$  and 0.332 g (2.0 mmol) of  $P(OEt)_3$  yielding 0.287 g (57%) of a red solid identified as **8**. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 2.7 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -8.2$  (43.6, 6H,  $CH_3$ - $p$ - $C_6H_5$ ),  $-4.1$  (213.2, 30H,  $P(OCH_2CH_3)$ ), 19.0 (51.0, 4H,  $C_6H_5$ ), 32.4 (137, 12H,  $CH_3$ - $o$ - $C_6H_5$ ).

**Preparation of (dmpe)Fe(Mes)<sub>2</sub> (**9**)**. This molecule was prepared in a manner similar to that for **5** with 0.047 g (0.080 mmol) of  $Fe_2(Mes)_4$  and 0.024 g (0.160 mmol) of dmpe yielding 0.058 g (82%) of yellow solid identified as **9**. Anal. Calcd for  $C_{24}H_{38}FeP_2$ : C, 64.87; H, 8.62. Found: C, 64.89; H, 8.63. Magnetic susceptibility (Guoy balance):  $\mu_{\text{eff}} = 4.2 \mu_B$ .

**Preparation of (depe)Fe(Mes)<sub>2</sub> (**10**)**. This molecule was prepared in a manner similar to that for **5** with 0.250 g (0.425 mmol) of  $Fe_2(Mes)_4$  and 0.175 mg of depe yielding 0.332 g (79%) of an

orange solid identified as **10**. Anal. Calcd for  $C_{28}H_{46}FeP_2$ : C, 67.20; H, 9.26. Found: C, 67.01; H, 8.75. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 4.4 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = 9.1$  (302, 12H,  $C_6H_5$ - $o$ - $CH_3$ ), 18.4 (836, 6H,  $C_6H_5$ - $p$ - $CH_3$ ), 90.3,  $-94.1$  (2060, 20 H,  $CH_2CH_3$ ), 127.9 (520, 4H,  $PCH_2CH_2P$ ).

**Preparation of (dppe)Fe(Mes)<sub>2</sub> (**11**)**. This molecule was prepared in a manner similar to that for **3** with 0.337 g (0.570 mmol) of  $Fe_2(Mes)_4$  and 0.457 g (1.2 mmol) of dppe yielding 0.594 g (75%) of an orange solid identified as **11**. Anal. Calcd for  $C_{44}H_{46}FeP_2$ : C, 76.30; H, 6.69. Found: C, 76.27; H, 6.31. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 3.7 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -3.7$  (120, 6H,  $CH_3$ - $p$ - $C_6H_5$ ), 16.5 (153, 12H,  $CH_3$ - $o$ - $C_6H_5$ ), 92.1 (2904), 97.6 (2880), 103 (163, 8H), 132 (386, 4H).

**Preparation of (PhEt<sub>2</sub>P)<sub>2</sub>FeCl<sub>2</sub> (**13**)**. A 50 mL round-bottomed flask was charged with 0.363 g (2.90 mmol) of  $FeCl_2$ , 1.0 g (6.0 mmol) of  $PhEt_2P$ , and approximately 30 mL of toluene. A reflux condenser and a 180° needle valve were attached, and the reaction mixture was heated to reflux for 2 h. The reaction mixture was transferred into the drybox and filtered through Celite. The toluene was removed in vacuo, and the off-white residue was washed several times with pentane and dried to afford 1.23 g (93%) of **13**. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 4.8 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -2.6$  (57.4, 2H,  $p$ - $C_6H_5$ ), 2.57 (435.5, 4H), 14.1 (61.5, 4H), 77.9 (1543, 20 H,  $C_2H_5$ ).

**Preparation of (PhEt<sub>2</sub>P)<sub>2</sub>FeBr<sub>2</sub> (**14**)**. This molecule was prepared in a manner similar to that for **13** with 0.156 g (0.720 mmol) of  $FeCl_2$ , 0.250 g (1.5 mmol) of  $PhEt_2P$ , and approximately 20 mL of toluene and afforded 0.302 mg (77%) of **14**. Magnetic susceptibility (benzene- $d_6$ ):  $\mu_{\text{eff}} = 5.0 \mu_B$ .  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -3.4$  (52.3, 2H,  $p$ - $C_6H_5$ ), 4.6 (356.2, 4H), 14.0 (52.6, 4H), 77.1 (648.6, 20 H,  $C_2H_5$ ).

**Procedure for a Typical Exchange Reaction**. A J. Young NMR tube was charged with 0.020 g (0.035 mmol) of **5** and approximately 1.0 mL of benzene- $d_6$ . Using a calibrated gas bulb, 2 equiv (0.070 mmol) of  $PMe_3$  was added at 77 K. The solution was thawed and shaken and the  $^1H$  NMR spectrum recorded.

**$^1H$  NMR Characterization of (py)<sub>2</sub>Fe(Mes)<sub>2</sub>**.  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -5.14$  (77.2,  $CH$ , py), 23.40 (10.8,  $CH$ ,  $p$ -py), 23.4 (127.1,  $CH$ , py), 41.6 (752.3,  $CH_3$ ,  $o$ - $C_6H_5$ ), 112.5 (168.2,  $CH_3$ ,  $p$ - $C_6H_5$ ), 138 (270.6,  $CH$ ,  $m$ - $C_6H_5$ ).

**$^1H$  NMR Characterization of (PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>**.  $^1H$  NMR (benzene- $d_6$ ):  $\delta = -53.0$  (29.5, Ph),  $-18.5$  (19.1,  $CH_3$ ),  $-7.9$  (9.2, Ph), 11.8 (16.6,  $p$ -Ph).

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**Supporting Information Available**: Crystallographic data for *trans*-(PhEt<sub>2</sub>P)<sub>2</sub>Fe(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>, **3**, **6**, **9**, and **11** (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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