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Synthesis and Structures of Iron(II) Alkyl and Thiolate Compounds Containing Sterically Hindered N-Functionalized Alkyl Ligands

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Iron(II) dialkyl compounds $[\mathrm{FeR_2}]$ ($\mathrm{R = C(SiMe_3)_2C_5H_4N\text{-}2}$ (**1**), $\mathrm{C(Ph)(SiMe_3)C_5H_4N\text{-}2}$ (**2**), $\mathrm{CH(SiMe_3)C_9H_6N\text{-}8}$ (**4**)) and $[\{\overline{\mathrm{Fe(CHSi^tBuMe_2C_5H_4N}}\mathrm{\text{-}2)_2}\}_2]$ (**3**) have been prepared from the reaction of $\mathrm{FeCl_2}$ with the appropriate N-functionalized alkyllithium reagent in a 1:2 molar ratio. The monoalkylated iron(II) complex $[\overline{\mathrm{Fe\{CPhSiMe_3C_5H_4N}}\mathrm{\text{-}2\}(Cl)(TMEDA)}]$ (**5**) has been prepared by treating $\mathrm{FeCl_2}$ with a stoichiometric amount of the organolithium reagent. X-ray analysis revealed that the alkyl ligands are bonded to the metal centers in a chelating manner in the mononuclear compounds **1** and **5**, whereas in **3** one of the alkyl ligands forms an interligand bridge betwen the two iron centers. Compounds **1**, **2**, **4**, and **5** have magnetic moments in the range 4.24−4.96 μ_B that are characteristic of a high-spin d^6 electronic configuration with four unpaired electrons. The magnetic moment of the binuclear compound **3** is 2.92 μ_B per iron atom, apparently a consequence of antiferromagnetic coupling between the two metal centers. Subsequent reaction of **1** with $\mathrm{Ar^{Me}OH}$ ($\mathrm{Ar^{Me} = 2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2}$) and ArSH ($\mathrm{Ar = 2,4,6\text{-}^tBu_3C_6H_2}$) gave the neutral monomeric iron(II) bis(aryloxide) $[\mathrm{Fe(OAr^{Me})_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}}]$ (**6**) and dithiolate $[\mathrm{Fe(SAr)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}}]$ (**7**), respectively. Both of the latter compounds have a rare coordination number of 3 at the iron(II) center. The magnetic moment of 5.11 μ_B for **7** indicates a high-spin configuration with four unpaired electrons on the iron(II) center. Electrochemical studies on the compoounds are also reported.

Introduction

The vast majority of organoiron(II) complexes that have been isolated so far exist either in the form of $[\mathrm{FeRXL}_n]$ or $[\mathrm{FeR_2L}_n]$, where R may be an alkyl or aryl group, X is generally $\eta^5\text{-}\mathrm{C_5H_5}$, and L is a strong-field ligand such as CO, $\mathrm{PR_3}$, or bipyridine.[1] These complexes are diamagnetic and obey the 18-electron rule. In contrast, paramagnetic and coordinatively unsaturated organoiron(II) compounds are less abundant, and studies on the reactivities of these compounds are rare.

Earlier work by Chatt and Shaw showed that iron(II) diaryls of the type $[\mathrm{FeR_2(PEt_2Ph)_2}]$ ($\mathrm{R = C_6Cl_5}$) could be obtained by treating $[\mathrm{FeCl_2(PEt_2Ph)_2}]$ with the appropriate Grignard reagents.[2] Yamamoto *et al.* have reported the synthesis of $[\mathrm{FeEt_2(bpy)_2}]$ by treating $\mathrm{Fe(acac)_3}$ with $\mathrm{Et_2Al(OEt)}$ in the presence of bipyridine.[3] By a similar approach, Kochi *et al.* have also prepared the methyl and *n*-propyl analogues.[4] Recently, the series of iron(II) diaryl complexes $[\mathrm{FeR_2(dippe)}]$ (dippe = 1,2-bis(diisopropylphosphino)ethane) have been reported by Girolami *et al.*[5] These complexes possess a very low electron count of 14, which usually occurs in organotransition-metal complexes. The complex $[\mathrm{Fe(CH_2Ph)_2(TMEDA)}]$ ($\mathrm{TMEDA = Me_2NCH_2CH_2NMe_2}$) was recently reported and characterized by NMR studies.[6] To date, only a few examples of simple homoleptic iron dialkyl or diaryl compounds have been synthesized. The well-characterized homoleptic diaryl complexes have the formula $[\{\mathrm{FeR_2}\}_2]$ ($\mathrm{R = 2,4,6\text{-}Me_3C_6H_2}$ or $\mathrm{2,4,6\text{-}^iPr_3C_6H_2}$),[7−9] and their dimeric nature was established by X-ray structural analysis recently.[8] A monomeric form of the iron dimesityl compound $[\mathrm{FeMes_2(py)_2}]$ can be obtained from the reaction of $[\{\mathrm{FeMes_2}\}_2]$ with pyridine in toluene.[9] To date, the only known monomeric homoleptic diaryl complex with a two-coordinate iron(II) center is $[\mathrm{FeAr_2}]$ ($\mathrm{Ar = 2,4,6\text{-}^tBu_3C_6H_2}$).[10]

In a recent communication, we reported the preparation and structural characterization of the iron(II)

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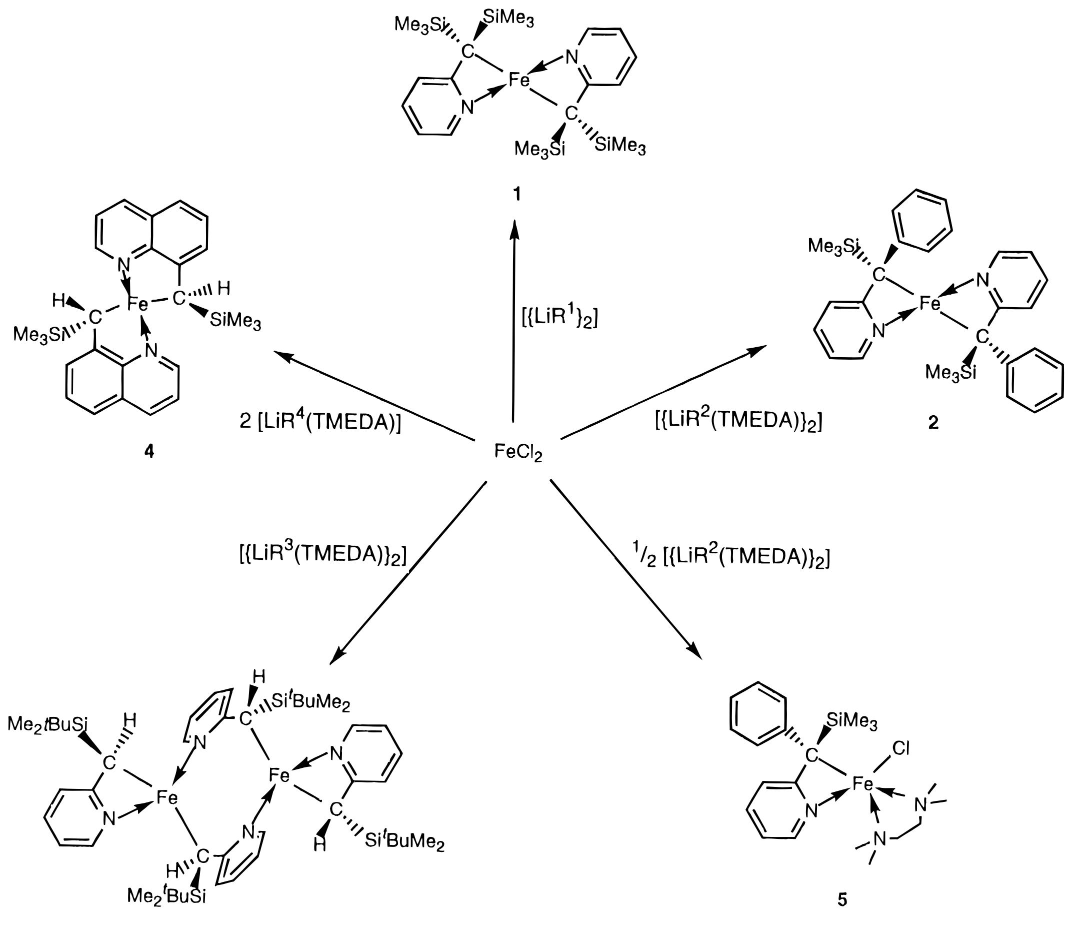
Scheme 1



dialkyl [Fe(R^1)$_2$][11] and cobalt(II) dialkyl [Co(R^1)$_2$],[12] in which R^1 is the sterically hindered N-functionalized alkyl ligand [C(SiMe$_3$)$_2$C$_5$H$_4$N-2]$^-$. Early work involving R^1 has shown that it stabilizes several novel main-group metal alkyl complexes which exhibit unusual coordination behavior.[13] We have focused our attention on the use of similar alkyl ligands in the preparation of kinetically labile homoleptic transition-metal alkyl complexes with a low electron count (≤14). Accordingly, the series of N-functionalized alkyl ligands [(CPhSiMe$_3$)-C$_5$H$_4$N-2]$^-$ (R^2),[14] [CH(Si^{t}BuMe$_2$)C$_5$H$_4$N-2]$^-$ (R^3),[14] and [CH(SiMe$_3$)$_2$C$_9$H$_6$N-8]$^-$ (R^4) have been developed.[14] We now report the synthesis and structural characterization of a series of iron(II) dialkyl complexes of stoichiometry [Fe(R^i)$_2$] where R^i is a bulky pyridine- or quinoline-functionalized alkyl ligand. In addition, the reactivity of the coordinatively unsaturated organoiron compound **1** toward the bulky phenol 2,6-^{t}Bu$_2$-4-MeC$_2$H$_2$OH and thiophenol 2,4,6-^{t}Bu$_3$C$_6$H$_2$SH has also been investigated.

Results

Synthesis of Iron(II) Dialkyl Complexes. Treatment of 2 molar equiv of organolithium reagents with ferrous chloride in ether leads to the formation of the corresponding lipophilic homoleptic iron(II) dialkyl complexes **1**−**4** (Scheme 1). The physical properties of the compounds prepared are listed in Table 1. Compounds **1**, **2**, and **4** were isolated as extremely air-sensitive yellow, brown, and dark brown crystals, respectively, while **3** was obtained as a dark red powder. These compounds are thermally stable with melting points ranging from 110 to 159 °C. Compound **1** can be sublimed at 116 °C under high vacuum (10^{-2} mmHg).[11] The thermal stability contrasts remarkably with the

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[10] The compound was prepared and structurally characterized by two independent groups: Müller, H.; Seidel, W.; Görls, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 325. Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264.

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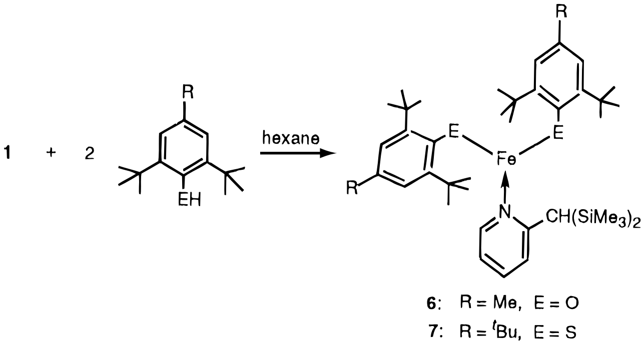
Table 1. Physical Properties of Compounds 1−7

compd	yield (%)	color	mp (°C)	μ_{eff} (μ_B)[a]
$[\mathrm{Fe\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2}]$ (**1**)	80	yellow	110−112[b]	4.24
$[\mathrm{Fe\{(CPhSiMe_3)C_5H_4N\text{-}2\}_2}]$ (**2**)	52	red	118−120 dec	4.92
$[\{\mathrm{Fe(CH(Si^tBuMe_2)C_5H_4N\text{-}2)_2}\}_2]$ (**3**)	58	brown	155−159	2.92[c]
$[\mathrm{Fe\{(CHSiMe_3)C_9H_6N\text{-}8\}_2}]$ (**4**)	65	dark brown	161−163 dec	4.96
$[\mathrm{Fe\{(CPhSiMe_3)C_5H_4N\text{-}2\}(Cl)(TMEDA)}]$ (**5**)	71	red	124−126 dec	4.45
$[\mathrm{Fe(OC_6H_3\text{-}4\text{-}Me\text{-}2,6\text{-}^tBu_2)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}}]$ (**6**)	41	colorless	129−131	
$[\mathrm{Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}}]$ (**7**)	65	yellow	182−185 dec	5.11

[a] Evans NMR method in C_6D_6 solution at 298 K. [b] Sublimed at 116 °C/10^{-2} mmHg. [c] *Per* iron atom.

Scheme 2



case for the iron(II) dialkyls, which readily decompose to coupled products at ambient temperature.

Synthesis of the Monoalkyliron(II) Complex [Fe(R^2)Cl(TMEDA)]. Monoalkyliron(II) species may be considered as intermediates during the course of reaction to form the corresponding dialkyl complex. Their preparation normally requires a strict and proper control of stoichiometry. Alkylation of ferrous chloride with 1 molar equiv of the organolithium reagent [R^{2}Li(TMEDA)] in ether gave the monoalkyliron(II) complex **4**, which was isolated as reddish brown crystals. The coordinated TMEDA is presumably a requirement for coordination saturation which contributes to the stability and solubility of the adduct formed.

Reactivities of [Fe(R^1)$_2$] (1). Reactivities of dialkyl complex **1** toward protic reagents such as the phenol Ar$^{\mathrm{Me}}$OH (Ar$^{\mathrm{Me}}$ = $2,6\text{-}^t\mathrm{Bu_2}\text{-}4\text{-}\mathrm{MeC_6H_2OH}$) and thiophenol ArSH (Ar = $2,4,6\text{-}^t\mathrm{Bu_3C_6H_2SH}$), which bear bulky *ortho* substituents, have been investigated. Reaction of **1** with 2 equiv of Ar$^{\mathrm{Me}}$OH or ArSH in hexane yielded, respectively, the monomeric iron(II) bis(aryloxide) or dithiolate complexes with a coordination number of 3 for the metal and an electron count of only 12 (Scheme 2).

Attempted reaction of **1** with benzonitrile was unsuccessful, and only the dialkyl **1** was recovered. The inertness of compound **1** toward benzonitrile *via* an insertion reaction may be ascribed to steric hindrance from the two bulky alkyl ligands.

X-ray Structural Studies. [Fe(R^1)$_2$] (1). The molecular structure of **1** along with the atom-numbering scheme is shown in Figure 1. The selected bond distances and angles are shown in Table 2. The iron(II) center has a highly distorted tetrahedral coordination environment with each of the two alkyl ligands acting in a C,N-chelating manner. Coordination from the pyridyl nitrogens is believed to impose a stabilizing effect on the metal complex. The observed Fe−C$_\alpha$ bond distances are 2.129(7) and 2.154(8) Å, and the Fe−N distances are 2.11(8) and 2.135(5) Å. The bite angles C−Fe−N are 66.8(2) and 67.2(3)°, and the interligand angle C(1)−Fe−C(13) is large, *viz.* 160.4(3)°.

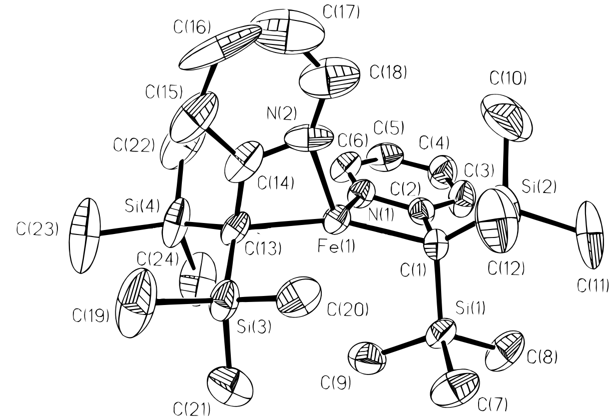


Figure 1. Molecular structure of $[\mathrm{Fe\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2}]$ (**1**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

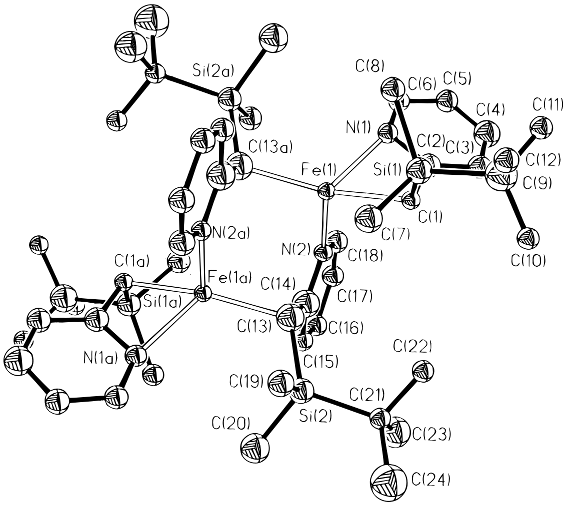


Figure 2. Molecular structure of $[\mathrm{Fe\{CH(Si^tMe_2)C_5H_4N\text{-}2\}_2}]_2$ (**3**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

[{Fe(R^3)$_2$}$_2$] (3). The dimeric molecular structure of **3** is depicted in Figure 2, and selected bond distances and angles are shown in Table 2. The long Fe···Fe distance of 3.828 Å excludes any possibility of an iron−iron bond. The Fe−C$_\alpha$ distance of 2.163(2) Å, involving the bridging C(13) ligand, is only 0.03 Å longer than that of the terminal C(1) ligand. However, the Fe−N(2) distance of 2.189(2) Å is substantially longer than the Fe−N(1) distance of 2.097(2) Å. A weak interaction

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

	$[Fe\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$ (**1**)		
Fe(1)−C(1)	2.154(8)	C(1)−Fe−C(13)	160.4(3)
Fe(1)C(13)	2.139(7)	N(1)−Fe−N(2)	116.3(2)
Fe(1)−N(1)	2.135(5)	C(1)−Fe−N(2)	124.1(3)
Fe(1)−N(2)	2.111(8)	N(1)−Fe−C(13)	125.4(3)
C(1)−C(2)	1.489(9)	C(1)−Fe−N(1)	66.8(2)
C(2)−N(1)	1.347(10)	C(13)−Fe−N(2)	67.2(3)
C(2)−C(3)	1.391(10)	Fe(1)−C(1)−Si(1)	109.4(3)
C(3)−C(4)	1.348(12)	Fe(1)−C(1)−C(2)	87.7(5)
C(4)−C(5)	1.362(14)	Fe(1)−N(1)−C(2)	92.3(4)
C(5)−C(6)	1.389(11)	Fe(1)−C(13)−C(14)	87.2(5)
C(13)−C(14)	1.469(12)	Fe(1)−N(2)−C(14)	91.7(6)
C(6)−N(1)	1.321(9)	Fe(1)−C(13)−Si(3)	111.3(4)
C(1)−Si(1)	1.861(8)	Fe(1)−N(2)−C(18)	144.5(9)
	$[Fe\{CH(Si^tBuMe_2)C_5H_4N\text{-}2\}_2]_2$ (**3**)		
Fe(1)−C(1)	2.133(2)	N(1)−Fe(1)−C(1)	66.1(1)
Fe(1)−C(13a)	2.163(2)	C(1)−Fe(1)−N(2)	103.6(1)
Fe(1)−N(1)	2.189(2)	C(1)−Fe(1)−C(13a)	148.0(1)
Fe(1)−N(2)	2.097(2)	N(1)−Fe(1)−N(2)	103.2(1)
N(1)−C(6)	1.347(4)	N(1)−Fe(1)−C(13a)	121.0(1)
C(1)−C(2)	1.473(4)	N(2)−Fe(1)−C(13a)	104.4(1)
C(2)−C(3)	1.395(4)	Fe(1)−N(1)−C(2)	87.6(1)
C(3)−C(4)	1.368(5)	Fe(1)−C(1)−C(2)	86.9(1)
C(4)−C(5)	1.363(5)	Fe(1)−N(2)−C(14)	119.2(2)
C(5)−C(6)	1.362(5)	Si(2)−C(13)−Fe(1a)	108.4(1)
N(1)−C(2)	1.352(3)	Fe(1)−N(1)−C(6)	145.9(2)
		C(14)−C(13)−Fe(1a)	107.6(1)
	$[Fe(CPhSiMe_3C_5H_4N\text{-}2)(Cl)(TMEDA)]$ (**5**)		
Fe(1)−Cl(1)	2.310(2)	Cl(1)−Fe(1)−N(1)	98.0(2)
Fe(1)−N(2)	2.284(6)	N(1)−Fe(1)−N(2)	167.6(2)
Fe(1)−C(6)	2.212(6)	N(1)−Fe(1)−N(3)	92.6(2)
Fe(1)−N(1)	2.218(6)	Cl(1)−Fe(1)−C(6)	128.8(2)
Fe(1)−N(3)	2.206(6)	N(2)−Fe(1)−C(6)	111.8(2)
N(1)−C(1)	1.333(10)	Cl(1)−Fe(1)−N(2)	93.5(2)
N(1)−C(5)	1.345(8)	Cl(1)−Fe(1)−N(3)	106.0(2)
C(1)−C(2)	1.367(11)	N(2)−Fe(1)−N(3)	79.8(2)
C(2)−C(3)	1.371(12)	N(1)−Fe(1)−C(6)	63.8(2)
C(3)−C(4)	1.369(11)	N(3)−Fe(1)−C(6)	121.3(2)
C(4)−C(5)	1.384(9)	Fe(1)−N(1)−C(5)	92.6(4)
C(5)−C(6)	1.471(10)	Fe(1)−C(6)−C(5)	89.5(4)
C(6)−C(7)	1.492(10)	Fe(1)−C(6)−C(7)	121.1(4)
C(6)−Si(1)	1.880(8)	C(5)−C(6)−C(7)	121.1(4)
	$[Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_2\{CH(SiMe_3)_2C_5H_4N\text{-}2\}]$ (**7**)		
Fe(1)−S(1)	2.259(4)	S(1)−Fe(1)−S(2)	117.8(1)
Fe(1)−S(2)	2.261(3)	S(1)−Fe(1)−N(1)	118.7(2)
S(2)−C(31)	1.80(1)	S(2)−Fe(1)−N(1)	123.4(2)
Fe(1)−N(1)	2.086(9)	Fe(1)−S(1)−C(13)	113.1(4)
S(1)−C(13)	1.80(1)	Fe(1)−S(2)−C(31)	101.0(3)

between Fe(1) and C(2) (2.525 Å) is consistent with a slight distortion from planarity for the pyridyl ring on the terminal ligand.

$[Fe(R^2)(Cl)(TMEDA)]$ (5). Figure 3 shows the molecular structure of **5**. The structural data are shown in Table 2. The five-coordinate iron atom is surrounded by a C,N-chelating R^2 ligand, a chloride ligand, and two *N*-donors from TMEDA. The Fe−C$_\alpha$ distance is 2.212 Å, and the Fe−N(pyridine) distance is 2.218(6) Å. Coordination of the TMEDA molecule is unsymmetrical and the two unexceptional Fe−N distances differ by about 0.08 Å.

$[Fe(SAr)_2(HR^1)]$ (7). The molecular structure of **7** is shown in Figure 4, with selected bond distances and angles listed in Table 2. The dithiolate complex possesses a trigonal-planar coordination geometry around the central Fe(II) atom (sum of bond angles 359.9°). Owing to their bulkiness, the three ligands are oriented in such a way that the complex adopts a propeller-like structure. The Fe−S bond distances are 2.259(4) and 2.261(3) Å, and the Fe−N distance in **7** is 2.086(9) Å. The three interligand angles around the iron center are different, namely 117.8(1), 118.7(2), and 123.4(2)°.

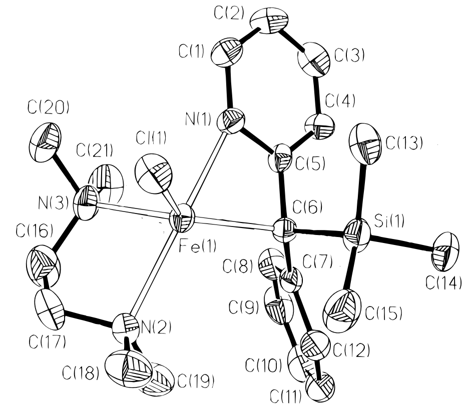


Figure 3. Molecular structure of $[Fe\{CH(Si^tMe_2)C_5H_4N\text{-}2\}(Cl)(TMEDA)]$ (**5**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

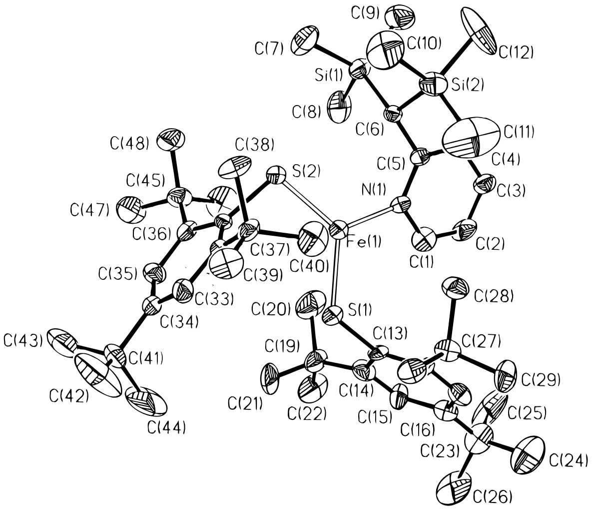


Figure 4. Molecular structure of $[Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_2\text{-}\{CH(SiMe_3)_2C_5H_4N\text{-}2\}]$ (**7**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

Discussion

Although a large number of organoiron(II) compounds which contain stabilizing ligands (e.g., CO, C_5H_5, PR_3, bipyridines) have been reported, examples of simple homoleptic iron dialkyl or diaryl species of the type $[FeR_2]$ are rare.[1] Recently, a few homoleptic iron(II) diaryl complexes, which contain bulky hydrocarbon substituents, have been prepared and structurally characterized.[7−10] In contrast, homoleptic dialkyl complexes of iron(II) remain virtually unknown. Indeed, an interesting exception of a homoleptic organoiron compound which contains Fe−C(sp^3) bonds is probably Fe(1-norbornyl)$_4$,[15] which decomposes slowly at room temperature with a half-life of *ca.* 30 h.[15]

Compounds **1**−**4** were prepared by the reaction of the appropriate organolithium reagents with ferrous chloride, while the monoalkyl species **5** was prepared with proper control of the stoichiometries of starting materials.

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Table 3. Selected X-ray Data Collection and Structure Analysis Parameters for Compounds 1, 3, 5, and 7

	1	3	5	7
mol formula	$C_{24}H_{44}N_2Si_4Fe$	$C_{48}H_{80}N_4Si_4Fe_2$	$C_{21}H_{34}N_3ClSiFe$	$C_{48}H_{81}NSi_2S_2Fe$
mol wt	528.8	937.2	447.9	848.29
color and habit	dark brown plates	brown prism	red needle	yellow prism
cryst size, mm	0.36 × 0.40 × 0.60	0.24 × 0.28 × 0.38	0.30 × 0.16 × 0.44	0.30 × 0.30 × 1.00
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	23.882(5)	10.850(2)	10.598(2)	14.585(5)
b, Å	16.820(6)	11.254(2)	14.205(6)	19.894(6)
c, Å	16.406(4)	11.580(2)	16.334(4)	19.266(5)
β, deg	107.32(1)	84.32(2)	96.290(0)	111.16(1)
V, Å^3	6291(3)	1350.6(4)	2444(1)	5213(3)
Z	8	1	4	4
density, g cm^{-3}	1.117	1.152	1.217	1.081
abs coeff, mm^{-1}	0.645	0.66	0.79	0.44
transmissn factor	0.691−0.819	0.686−0.872	0.664−0.912	0.921−0.965
scan type	ω-scan	ω-scan	ω-scan	$\omega-2\theta$ scan
scan rate, deg min^{-1}	3.08−29.3	3−29.3	3−29.3	4.19−29.3
$2\theta_{max}$, deg	50	50	45	45
no. of unique data measd	10957	4762	4281	6826
no. of obsd rflns	4418	4049	2137	3656
no. of variable	559	451	407	487
R	0.041	0.035	0.060	0.085
R_w	0.062	0.046	0.060	0.125

Protonolysis of **1** by $Ar^{Me}OH$ and ArSH yielded the iron(II) bis(aryloxide) **6** and dithiolate **7**, respectively. The three bulky ligands, namely the two thiolato groups and a free ligand molecule of R^1H, are believed to play a vital role in preventing association of the neighboring $[Fe(EAr)_2]$ (E = O, S) moieties, thus leading to the formation of the neutral, mononuclear, three-coordinate iron(II) bis(aryloxide) and dithiolate complexes.

Transition-metal aryloxides and thiolates tend to form aggregates that show very poor solubility in hydrocarbon solvents.[16−19] This makes structural characterization of these compounds difficult to carry out. With the introduction of aryloxy and thiolato ligands which bear bulky hydrocarbyl substituents, the degree of association of these compounds can be greatly reduced. Furthermore, the structural geometry of these compounds also depends on the steric requirements of the substituents. Recently it has been reported that reaction of the iron(II) amide $[Fe\{N(SiMe_3)_2\}_2]$ with phenols and thiophenols bearing bulky *ortho* substituents provides a convenient route to the corresponding metal aryloxide and thiolate complexes with two- or three-coordinate metal centers.[20,21] Known examples of these include $[Fe(SAr^1)_2]$ (**8**),[21b] $[Fe(SAr^1)\{N(SiMe_3)_2\}]$ (**9**),[21b] $[\{Fe(EAr)_2\}_2]$ (E = O,[20b] S (**10**)[21a]), $[\{Fe(OAr)\{N(SiMe_2)_2\}\}_2]$,[20b] and $[\{Fe(SAr^2)_2\}_2]$ (**11**;[21c] Ar^1 = 2,6-$Mes_2C_6H_3$, Ar^2 = 2,4,6-$Ph_3C_6H_2$). Among these complexes, only **8** and **9** are mononuclear species with a two-coordinate iron(II) center and the rest are binuclear species with a three-coordinate iron(II) center. The Lewis acid centers of these complexes are free from base coordination in spite of the presence of the byproduct $NH(SiMe_3)_2$. Reaction of **1** with $Ar^{Me}OH$ and ArSH, giving **6** and **7**, provides an alternative route for the preparation of monomeric metal aryloxide and thiolate compounds *via* metal alkyls in which a free R^1H molecule remains coordinated to the Fe(II) center through N-coordination. To our knowledge, apart from the mononuclear two-coordinate species **8**,[21b] a structurally characterized neutral mononuclear iron(II) dithiolate with a coordination number of 3 around the Fe(II) center has not been reported.

Structural Comparison. X-ray diffraction studies of complexes **1** and **3** have revealed different structural features, with **1** being mononuclear and **3** being dinuclear. Nevertheless, the iron centers are four-coordinate in both compounds. In **3**, the anionic ligand bridges the two metallacycle units through C(13) and N, forming an eight-membered $Fe_2(CN)_2$ core which adopts a stairlike conformation. Hence, two different bonding modes are observed for the ligand R^3 in each molecule of **3**, namely C,N-bridging and terminal C,N-chelating. Steplike eight-membered-ring structures have been reported for dimeric lithium,[13a] copper,[13a] silver,[13d] and gold[13i] complexes which contain analogous pyridine-functionalized alkyl ligands,[13] although the iron centers in **3** have additional terminal C,N-chelating ligands. Despite the increased steric bulk of the R^1 ligand in **1**, shorter Fe−C_α distances are observed than in **3**. The Fe−C(terminal) and Fe−C(bridging) distances in **3** are 2.160(2)−2.163(2) Å, while the Fe−C_α distances in **1** are 2.129(7)−2.154(8) Å. This may be attributted to an electronic effect in which the two trimethylsilyl substituents greatly stabilize the negative charge on C_α of the alkyl ligand R^1 through polarization. The Fe−C_α bond lengths in **1** and **3** are longer than those observed in $[FeEt_2(bpy)_2]$ (2.065 Å)[3,4] and $[Fe(CH_2C_6H_4\text{-}Me)_2(dippe)]$ (2.120(6) Å).[5] They are also longer than the Fe−C(terminal) distances in the dinuclear aryl complex $[\{FeMes_2\}_2]$ (2.024 Å) and $[\{FeAr^{ip}{}_2\}_2]$ (2.083(9)−2.104(9) Å).[8,9] However, they are similar to those of 2.141(5) and 2.156(5) Å in the monomeric dimesityl complex $[FeMes_2(py)_2]$.[9b] The relatively long Fe−C(sp^2) σ bonds in the latter complex may be due to the steric hindrance of the mesityl groups, which contain *ortho*-

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substituted methyl groups. The Fe−C$_\alpha$ distances in **1** and **3** are also longer than the corresponding distance of 2.051(5) Å in the two-coordinate iron diaryl complex [FeAr$_2$].[10] The Fe−N distances of 2.111(8) and 2.135(5) Å in **1** are significantly longer than those of 1.937(2) and 1.943(2) Å in [FeEt$_2$(bpy)$_2$].[3,4] However, they are only slightly shorter than those of 2.169(8) and 2.179(7) Å in the dimesityl complex [FeMes$_2$(py)$_2$].[9b] The Fe−C and Fe−N(aromatic) bond lengths in the monoalkyl species **5** are longer than the corresponding bond lengths in **1** and **3**, probably related to the increased coordination number of the metal in **5**.

The C−Fe−N bite angles in the three complexes **1**, **3**, and **5** are similar and fall in the range 63.8(2)−66.8(2)°.

The dithiolate **7** exhibits a trigonal-planar geometry in which the three ligands are bound to the iron center in a propeller-like manner. The Fe−S distances in **7** are similar to the terminal Fe−S distances of 2.256(3) Å observed in the binuclear complexes **10**; these distances are shorter than the bridging Fe−S distances of 2.365(3) and 2.366(3) Å in **10**. They are similar to the range of Fe−S distances of 2.267(1)−2.285(1) Å in [Fe(SAr)$_3$]$^-$, where the Fe(II) atom in the latter complex exhibits a slightly distorted trigonal planar geometry.[22] With reference to the monomeric thiolate complexes **8** and **9**,[21b] the Fe−S distances in **7** are comparable to those of 2.277(2) and 2.275(2) Å in **8** but are shorter than those of 2.308(2) and 2.314(2) Å in **9**. However, Fe−S(thiolate) bonds are observed to increase in the order 2.259(4)−2.261(3) Å for **7**,[21a] 2.315(1) Å for [Fe(SAr^{ip})$_2$(SC(NMe$_2$)$_2$)$_2$],[23] and 2.338(2) Å for [Fe(SPh)$_4$]$^{2-}$,[24] although the steric bulk of the thiolato ligands increases in the reverse order −SPh > −SAr^{ip} > −SAr. Obviously, this effect is not related to the steric bulk of the hydrocarbon substituents on the thiolato ligands but may be attributed both to the increased coordination number around the central metal, which renders a closer approach of thiolato ligands to the metal centers difficult, and to the presence of electronic repulsion in the anionic tetrathiolate complex.

The trigonal-planar arrangement of the three ligands in **7** around the central metal is actually unsymmetrical. The S−Fe−S angle in **7** is less than the corresponding angles in the neutral dithiolate complexes **8** (121.8°) and [Fe(SAr^{ip})$_2$(SC(NMe$_2$)$_2$)$_2$] (125.7(1)°).[23] The large N(1)−Fe−S(2) angle of 123.4(2)° in **7** over the remaining two angles, *viz.* 118.7(2) and 117.8(1)° in the FeS$_2$N plane, may be attributed to the steric bulk of the C(SiMe$_3$)$_2$ group at the *ortho* position of the pyridine ring.

It has been reported that there is a weak agostic interaction in **10**, as indicated by a small M···H distance of *ca.* 1.8 Å.[21a] A relatively close M···C distance of *ca.* 2.5 Å involving adajcent phenyl groups has also been observed in the two-coordinate compounds **8** and **9** and the dimeric three-coordinate compound **11**.[21b,c] In this work, no such agostic interaction is detected in compound **7**.

Magnetic Properties and Electrochemistry. The magnetic moments of the dialkyl compounds **1**, **2**, and **4** at room temperature in benzene solution are in the range of 4.24−4.96 μ_B, which are close to the spin-only value of 4.90 μ_B for four unpaired electrons. This suggests a high-spin d^6 electronic configuration with four unpaired electrons for the iron(II) center in these complexes. Since X-ray analysis has established that compound **1** has a highly distorted tetrahedral geometry, and the small crystal field splitting resulting from tetrahedral geometry favors a high-spin electronic configuration, it is conceivable that, at least from the standpoint of their effective magnetic moments, the iron(II) centers in **2** exist in a tetrahedral environment. Nevertheless, attempts to obtain single crystals of **2** and **4** suitable for X-ray diffraction studies have not been successful.

Table 4. Electrochemical Data for Compounds 1, 2, 4, 5 and 7[a]

compd		E_p^a (V)	E_p^c (V)	$E_{1/2}$ (V)	ΔE_p (mV)[b]
[Fe(R^1)$_2$] (**1**)	W$_1$	0.85			
	W$_2$	−2.11	−2.32	−2.21	110
	W$_3$	−2.54	−2.73	−2.72	190
[Fe(R^2)$_2$] (**2**)	W$_1$	0.64			
	W$_2$	−1.82	−2.03	−1.93	210
	W$_3$		−2.31		
[Fe(R^4)$_2$] (**4**)	W$_1$	0.61			
	W$_2$		−2.23		
	W$_3$	−2.52	−2.72	−2.62	200
[FeR^2(Cl)(TMEDA)] (**5**)	W$_1$	0.71			
	W$_2$		−2.90		
[Fe(SAr)$_2$(R^{1}H)] (**7**)	W$_1$	0.15			
	W$_2$	0.58			
	W$_3$		−2.00		

[a] Conditions: solvent, THF; supporting electrolyte, 0.4 M Bu$_4$NBF$_4$ solution; room temperature. [b] $\Delta E_p = E_p^c - E_p^a$.

Likewise, the magnetic moment of 4.45 μ_B of the pentacoordinated monoalkyl compound **5** implies a high-spin d^6 configuration with four unpaired electrons for the iron(II) center.

The magnetic moment of 2.92 μ_B per iron atom for the binuclear compound **3**, being much lower than the spin-only value for tetrahedral iron(II) with four unpaired electrons, is apparently a consequence of antiferromagnetic coupling between the two iron(II) centers.

The magnetic moment of the dithiolate compound **7** at room temperature was determined to be 5.11 μ_B. This value indicates that the trigonal-planar iron(II) center most likely adopts a high-spin d^6 configuration with four unpaired electrons.

The redox behavior of compounds **1**−**5** and **7** has been studied by cyclic voltammetry with THF as solvent and tetrabutylammonium tetrafluoroborate as the supporting electrolyte at a scan rate of 100 mV/s. Table 4 summarizes the electrochemical data for these compounds. The dialkyl compounds **1** and **2** display similar CVs consisting of an irreversible oxidation (0.85 V for **1** and 0.64 V for **2**), a quasi-reversible reduction (−2.21 V for **1** and −1.93 V for **2**), and an irreversible reduction (−2.72 V for **1** and −2.31 V for **2**). The dialkyl **4** shows analogous anodic behavior, but its cathodic behavior is slightly different from those of **1** and **2**. Its CV consists of an irreversible oxidation at 0.61 V, an irreversible reduction at −2.23 V, and a quasi-reversible wave at −2.62 V.

The dinuclear compound **3** did not show any redox behavior within the limits of solvent decomposition. The monoalkyl complex **5** shows an irreversible oxidation at

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0.71 V and an irreversible reduction at −2.90 V. The latter peak was superimposed on the fringe of THF reduction.

Dithiolate complex **7** exhibits two irreversible peaks at 0.15 and 0.58 V and an irreversible cathodic peak at −2.00 V.

Summary

Iron(II) dialkyl complexes [$Fe\{C(SiMe_3)_2C_5H_4N$-2$\}_2$] (**1**), [$Fe\{(CPhSiMe_3)C_5H_4N$-2$\}_2$] (**2**), [{$Fe(CHSi^tBuMe_2$-C_5H_4N-2$)_2\}_2$] (**3**), and [$Fe\{CH(SiMe_3)C_9H_6N$-8$\}_2$] (**4**) are readily prepared by the metathesis of chloride from ferrous chloride with 2 molar equiv of the appropriate sterically demanding N-functionalized alkyl ligands. The monoalkyl iron(II) species **5** is obtained by treating iron(II) chloride with the corresponding organolithium reagent with strict and proper control of stoichiometry. Single-crystal X-ray analysis revealed that **1** possesses a highly distorted tetrahedral geometry, **3** is dimeric in nature with the [$Fe(CN)_2$] core adopting an eight-membered chair conformation, and **5** is a five-coordinate species. Magnetic moment measurements indicate that compounds **1**−**5** are high-spin with four unpaired electrons per iron center.

Compound **1** reacts readily with the bulky phenol 2,6-$^tBu_2$-4-MeC_6H_2OH and the bulky thiophenol 2,4,6-$^tBu_3$-C_6H_2SH to give the corresponding bis(aryloxide) **7** and dithiolate **8**, respectively. Both **7** and **8** are neutral, monomeric, three-coordinate species with each bearing an electron count of only 12.

Experimental Section

General Procedures. All manipulations were carried out under an argon or dinitrogen atmosphere using standard Schlenk techniques or in a drybox. Solvents were dried over and distilled from CaH_2 (hexane) and sodium benzophenone (THF, ether, toluene) and degassed twice prior to use. Anhydrous $FeCl_2$ was used as purchased from Fluka. 2,6-$^tBu_2$-4-MeC_6H_2OH was purchased from Aldrich and recrystallized from pentane before use. The organolithium reagents [{$LiR^1\}_2$],[13a] [{$LiR^2(TMEDA)\}_2$],[14] [{$LiR^3(TMEDA)\}_2$],[14] and [$LiR^4(TMEDA)$] were prepared according to literature procedures.[14] 2,4,6-$^tBu_3C_6H_2SH$ was prepared by the published method.[25]

Physical Measurements. Mass spectra (EI, 70 eV) were obtained on a VG7070F mass spectrometer. Melting points were recorded on an Electrothermal melting point apparatus and were uncorrected. Elemental (C, H, N) analyses were performed by MEDAC Ltd., Brunel University, U.K. Magnetic moments were measured in benzene solution by the Evans method using a JEOL 60 MHz NMR spectrometer. Cyclic voltammetric measurements were performed by using a BAS CV-50W voltammetric analyzer. The electrochemical cell consisted of a platinum-wire working electrode, a silver-wire reference electrode, and a tungsten-wire counter electrode. All samples were manipulated under an argon atmosphere. All sample solutions (THF) were prepared to be 0.4 M in $^nBu_4NBF_4$ (supporting electrolyte) and *ca.* 4×10^{-3} M in sample complexes. Chemical potentials were internally referenced to the $FeCp_2^+/FeCp_2$ reference redox system.

Synthesis. [$Fe\{C(SiMe_3)_2C_5H_4N$-2$\}_2$], (1). An ether solution (30 mL) of [{$LiR^1\}_2$] (1.57 g, 3.2 mmol) was added dropwise to a stirred suspension of $FeCl_2$ (0.41 g, 3.2 mmol) in the same solvent (50 mL) at 0 °C. The suspension was further stirred at room temperature for 20 h. The grayish brown precipitate was separated by filtration, and the filtrate was concentrated to *ca.* 20 mL *in vacuo* followed by cooling to −30 °C for 1 day, affording **1** as yellow crystals. Yield: 1.35 g (80%). Mp: 110−112 °C. MS: *m/z* (%) 529 (3%) [M]$^+$, 456 (26%) [M − $SiMe_3$]$^+$, 293 (6%) [M − R^1]$^+$. Anal. Found: C, 55.82; H, 9.05; N, 5.43. Calcd for $C_{24}H_{44}N_2Si_4Fe$: C, 54.51; H, 8.39; N, 5.30.

[$Fe\{(CPhSiMe_3)C_5H_4N$-2$\}_2$], (2). To a suspension of $FeCl_2$ (0.13 g, 1.06 mmol) in ether (20 mL) at room temperature was added a solution of [{$LiR^2(TMEDA)\}_2$] (0.71 g, 0.98 mmol) in ether (30 mL). After the mixture was stirred for 6 h, all volatile materials were removed *in vacuo* and the residue was extracted with pentane (30 mL). After filtration, the resultant red solution was concentrated under reduced pressure to *ca.*10 mL. When the temperature was lowered to −18 °C, dark red crystals of **2** were obtained. Yield: 0.27 g (52%). Mp: 118−120 °C dec. MS: *m/z* 536 [M]$^+$, 480 [$(R^2)_2$]$^+$, 240 [R^2]$^+$, 225 [R^2 − Me]$^+$, 167 [R^2 − $SiMe_3$]$^+$. Anal. Found: C, 65.72; H, 6.69; N, 5.03. Calcd for $C_{30}H_{36}N_2Si_2Fe$: C, 67.14; H, 6.76; N, 5.22.

[$Fe\{CH(Si^tBuMe_2)C_5H_4N-2\}_2]_2$, (3). To a suspension of $FeCl_2$ (0.12 g, 0.91 mmol) in ether (10 mL) was added a solution of [{$LiR^3(TMEDA)\}_2$] (0.60 g, 0.91 mmol) in the same solvent (30 mL). After the mixture was stirred for 10 min, the deep brown mixture was filtered immediately and allowed to stand at ambient temperature for a few days to give **3** as brown prismatic crystals. The crystals were washed with hexane and dried *in vacuo*. Yield: 0.25 g (58%). Mp: 155−159 °C. Anal. Found: C, 60.96; H, 8.53; N, 5.76. Calcd for $C_{48}H_{80}N_4Si_4Fe_2$: C, 61.12; H, 8.60; N, 5.94.

[$Fe\{CH(SiMe_3)C_9H_6N$-8$\}_2$], (4). To a stirred suspension of $FeCl_2$ (0.38 g, 3.0 mmol) in ether (20 mL) at 0 °C was added a solution of [$LiR^4(TMEDA)$] (2.02 g, 6.0 mmol) in ether (40 mL). The resulting dark brown suspension was further stirred at room temperature for 8 h. The gray precipitate was filtered off, and the resultant solution was concentrated to *ca.* 20 mL *in vacuo* followed by cooling to −30 °C to give **4** as dark brown needle-shaped crystals. Yield: 0.94 g (65%). Mp: 161−163 °C dec. MS: *m/z* (%) 484 (4.8) [M]$^+$, 214 (25) [R^3]$^+$, 199 (100) [R^3 − CH_3]$^+$. Anal. Found: C, 62.73; H, 6.52; N, 5.59. Calcd for $C_{26}H_{32}N_2Si_2Fe$: C, 64.45; H, 6.66; N, 5.78.

[$Fe(CPhSiMe_3C_5H_4N$-2$)(Cl)(TMEDA)$], (5). A solution of [{$LiR^2(TMEDA)\}_2$] (0.48 g, 0.65 mmol) in ether (20 mL) was added slowly to a suspension of anhydrous $FeCl_2$ (0.17g, 1.30 mmol) in ether (10 mL). The resultant mixture was stirred at room temperature for 10 h, whereupon a reddish brown mixture was obtained. The mixture was filtered through Celite, and the red filtrate was concentrated to *ca.* 10 mL. When the temperature was lowered to −30 °C, red needle-shaped crystals of 5 were obtained, which were washed with cold pentane and dried *in vacuo*. Yield: 0.41 g (71%). Mp: 124−126 °C dec. Anal. Found: C, 55.73; H, 7.47; N, 8.89. Calcd for $C_{21}H_{34}N_3ClSiFe$: C, 56.31; H, 7.65; N, 9.38.

[$Fe(OC_6H_2$-4-Me-2,6-$^tBu_2)_2\{CH(SiMe_3)_2C_5H_4N-2\}$], (6). A solution of 4-Me-2,6-$^tBu_2C_6H_2OH$ (0.46 g, 2.08 mmol) in hexane (30 mL) was added dropwise to a stirred solution of **1** (0.55 g, 1.04 mmol) in hexane (20 mL) at 0 °C. The resultant clear yellowish brown solution was further stirred at ambient temperature for 8 h. The solution was filtered and then concentrated to *ca.* 20 mL *in vacuo*, followed by cooling to −30 °C for 1 day to give **6** as colorless crystals. Yield: 0.32 g (41%). Mp: 129−131 °C. Anal. Found: C, 69.75; H, 9.96; N, 2.81. Calcd for $C_{42}H_{69}NO_2Si_2Fe$: C, 68.91; H, 9.50; N, 1.91.

[$Fe(SC_6H_2{}^tBu_3$-2,4,6$)_2\{CH(SiMe_3)_2C_5H_4N$-2$\}$], (7). A hexane solution (40 mL) of 2,4,6-$^tBu_3C_6H_2SH$ (0.41 g, 1.47 mmol) was added dropwise to a stirred solution of **1** (0.38 g, 0.73 mmol) in the same solvent (20 mL) at 0 °C. After addition had been completed, the resultant pale brown solution was further stirred for 8 h at ambient temperature. It was filtered and the filtrate concentrated to *ca.* 20 mL *in vacuo*. When

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the temperature was lowered to −30 °C for 1 day, yellow crystals of **7** were obtained. Yield: 0.40 g (65%). Mp: 182−185 °C dec. Anal. Found: C, 67.88; H, 9.70; N, 1.60. Calcd for $C_{48}H_{81}NS_2Si_2Fe$: C, 67.96; H, 9.62; N, 1.65.

X-ray Structure Determination of Compounds 1, 3, 5, and 7. Single crystals were sealed in 0.5 mm Lindemann glass capillaries under argon. X-ray data were collected on a Nicolet P4/PC diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.710\ 73$ Å) in the $\omega/2\theta$ scan mode. N unique reflections were measured, and N_0 "observed" reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used in the structure solution and refinement. The weighting scheme $w = [\sigma^2|F_o| + 0.0008|F_o|^2]^{-1}$ was used for **1**, $w = [\sigma^2|F_o| + 0.0002|F_o|^2]^{-1}$ for **3**, $w = [\sigma^2|F_o| + 0.0005|F_o|^2]^{-1}$ for **5**, and $w = [\sigma^2|F_o| + 0.0035|F_o|^2]^{-1}$ for **7**. The structures were solved by direct phase determination using the computer program SHELXTL-PC on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms.[26] Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors.[27] The crystal data and structure analysis parameters are summarized in Table 3. Atomic coordinates of **1**, **3**, **5**, and **7** are given in the Supporting Information.

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Supporting Information Available: Tables giving structure determination summaries, atomic and thermal parameters, and bond distances and angles for **1**, **3**, **5**, and **7**, additional drawings of the structures of **3** and **7**, and figures giving cyclic voltammetry traces for **1**, **2**, **4**, **5**, and **7** (43 pages). Ordering information is given on any current masthead page.

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