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Synthesis, Reactivity, and Solid State Structures of Four-Coordinate Iron(II) and Manganese(II) Alkyl Complexes

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Synthesis and characterization of new, four-coordinate, high-spin iron(II) and manganese(II) complexes of the general form L_2MR_2 (L_2 = neutral chelating ligand, R = alkyl) are described. Alkylation of the α-diimine complex, [ArN═C(Me)−C(Me)═NAr]$FeCl_2$ (Ar = 2,6-diisopropylphenyl), as well as the enantiopure iron dichloride compounds, (−)-(sparteine)-$FeCl_2$ and (*S*)-(^{t}BuBox)$FeCl_2$ ((*S*)-(^{t}BuBox) = 2,2-bis[2-[4(*S*)-(R′)-1,3-oxazolinyl]propane), with $LiCH_2SiMe_3$ afforded the corresponding dialkyl derivatives. Solution magnetic susceptibility measurements and X-ray diffraction studies reveal each of the new iron(II) bis-trimethylsilylmethyl complexes to be high-spin, *S* = 2, tetrahedral molecules. In addition (−)-(sparteine)$Fe(CH_2CMe_3)_2$, (−)-(sparteine)$Fe(CH_2C_6H_5)_2$, and (*S*)-(^{t}BuBox)$Fe(CH_2C_6H_5)_2$ were also prepared and characterized by NMR spectroscopy and elemental analysis. An enantiopure, high-spin, tetrahedral manganese(II) dialkyl complex, (−)-(sparteine)$Mn(CH_2SiMe_3)_2$, has also been synthesized. The catalytic activity of the new iron complexes in carbon−carbon bond forming processes has been evaluated, and stoichiometric reactions of the dialkyls with olefins, carbon monoxide, and the Lewis acid $B(C_6F_5)_3$ have been examined.

Introduction

Transition metal alkyl complexes are of practical importance due to their role in numerous catalytic transformations such as olefin hydrogenation, hydroformylation, and polymerization.[1] Alkyl complexes of iron(II) are traditionally coordinatively saturated, 18-electron species supported by cyclopentadienyl and carbonyl ligands.[2] More recently, considerable attention has been devoted to preparing low-coordinate, unsaturated Fe(II) derivatives supported by tris(pyrazolyl)-borate,[3] β-diiminate,[4,5] and phosphine-amide[6] ligands.

One class of iron alkyl, L_2FeR_2 (L = neutral ligand, R = alkyl, aryl, hydride), is particularly attractive, since these molecules are formally 14-electron species and are relatively rare examples of open-shell organometallic molecules that bridge classical Werner-type coordination compounds with more modern organometallic complexes.[7] Chatt and Shaw provided the first example of an L_2FeR_2 complex with the preparation of $(PhEt_2P)_2$-$Fe(C_6Cl_5)_2$, which on the basis of magnetic data has been described as a low-spin, square-planar molecule.[8] Since this initial report, a few other examples of L_2FeR_2 species have been described and a range of magnetic properties measured. Seidel has described a series of $(R_3P)_2Fe(Mes)_2$ (PR_3 = tertiary phosphine or phosphite, Mes = mesityl) compounds that range from high to low spin, depending on the phosphine or phosphite donor.[9] In addition, (dme)$Fe(Mes)_2$ (dme = 1,2-dimethoxyethane) has also been synthesized, and X-ray diffraction revealed the molecule to be tetrahedral in the solid state.[10] Sen has also observed the intermediacy of (tmeda)$Fe(CH_2C_6H_5)_2$ during the iron-promoted coupling of benzyl halides.[11] More recently, Hermes and Girolami[12] have reported the synthesis of a family of (dippe)FeR_2 (dippe = 1,2-bis(diisopropylphosphinoethane) compounds, all of which are tetrahedral and high spin.

The recent independent reports by Brookhart[13] and Gibson[14] using five-coordinate Fe(II) dihalide complexes as precatalysts for the polymerization of ethylene and α-olefins suggested to us that iron(II), when in the

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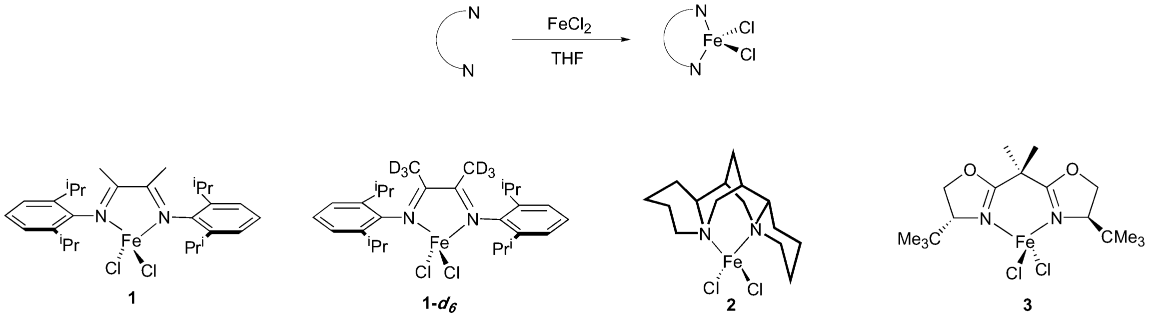
10.1021/om034188h CCC: $27.50

Scheme 1

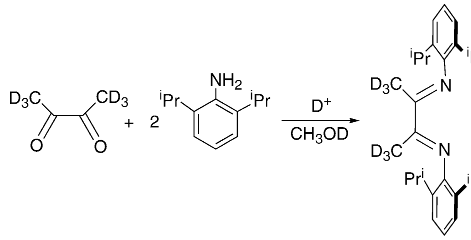


appropriate coordination environment and spin state, may be an active catalyst for C−C and C−H bond forming reactions for small organic molecules. Iron is an attractive metal for this purpose given its low cost and relatively low toxicity. In this report, we describe our initial efforts in this area with the synthesis and characterization of (N−N)FeR_2 (N−N = α-diimine, diamine) complexes and determination of their reactivity toward olefins, carbon monoxide, and the Lewis acid $B(C_6F_5)_3$.

Results and Discussion

Synthesis of Iron(II) and Manganese(II) Dihalide Complexes. Our studies commenced with the preparation of α-diimine Fe(II) complexes. This class of ligand was chosen due to its ease of synthesis, excellent steric and electronic tunability, and precedent for stabilizing four-coordinate Fe(II). A series of α-diimine Fe(II) dichloride complexes of the general form (RN=CR′−CR′=NR)$FeCl_2$, first prepared by tom Dieck and Dietrich, were found to be active catalysts for the dimerization of butadiene to 4-vinyl-1-cyclohexene.[15] More recently, Gibson has explored this class of molecule as catalysts for atom transfer radical polymerization.[16]

Another attractive feature of α-diimine ligands is the ease with which deuterium can be incorporated into the ligand backbone, providing a diagnostic handle for characterization by ^{2}H NMR spectroscopy. For paramagnetic molecules, ^{2}H NMR resonances are sharper than corresponding ^{1}H NMR lines, and as a result, ^{2}H NMR spectroscopy has proven useful in characterizing a range of paramagnetic transition metal complexes,[17] including iron(II) compounds.[18] Synthesis of the desired deuterated ligand, ArN=C(CD_3)−C(CD_3)=NAr (Ar = 2,6-diisopropylphenyl), was accomplished by initial H/D exchange of 2,3-butadione with D_2O in D_2SO_4 to afford butadione-d_6,[19] followed by condensation with 2,6-diisopropylaniline to provide the deuterated α-diimine in 84% yield and 67% isotopic purity (eq 1). Improved isotopic purity can be achieved by submitting the partially deuterated 2,3-butadione to further H/D exchange cycles;[19] however the material obtained after four iterations was sufficiently pure for subsequent ^{2}H NMR characterization.



(1)

Complexation of the deuterated α-diimine as well as its protio isotopomer to iron(II) was accomplished by addition of ArN=C(CD_3)−C(CD_3)=NAr or ArN=C(CH_3)−C(CH_3)=NAr to a THF slurry of $FeCl_2$. In this manner, both [ArN=C(CD_3)−C(CD_3)=NAr]$FeCl_2$ (**1-*d*₆**) and [ArN=C(CH_3)−C(CH_3)=NAr]$FeCl_2$ (**1**) were isolated as blue crystalline solids in >90% yield (Scheme 1). Although α-diimine iron dihalides have been known for quite some time and have been the subject of numerous studies, ^{1}H NMR spectroscopic data have not been reported. Given the high-spin ($S = 2$) electronic configuration of these molecules, the NMR peaks are expected to be paramagnetically shifted and broadened but observable.[4,6,12] In chloroform-*d*, the ^{1}H NMR spectrum of **1** displays five of the six expected ligand resonances, some of which can be readily assigned on the basis of integration. Diastereotopic isopropyl methyl groups appear at −3.83 and 3.10 ppm, whereas the methyl backbone of the ligand is centered at 60.82 ppm. Confirmation of the latter assignment was obtained from both ^{1}H and ^{2}H NMR spectra of **1-*d*₆**. As expected, the ^{2}H NMR resonance is much sharper ($\Delta\nu_{1/2} = 18.4$ Hz) than the corresponding ^{1}H signal ($\Delta\nu_{1/2} = 120$ Hz).

Enantiopure iron(II) dihalide complexes were also of interest. The naturally occurring alkaloid (−)-sparteine has been shown to be an excellent ligand for a variety of transition metals and has enjoyed success in catalytic asymmetric transformations.[20] Synthesis of (−)-(sparteine)$FeCl_2$ (**2**) was first reported by Long[21] and more recently crystallographically characterized by Lorber.[22] Although the synthesis of **2** has been described previously, we have found that simply stirring stoichio-

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metric quantities of commercially available (−)-spartiene with $FeCl_2$ in THF at ambient temperature afforded the desired iron dihalide complex in near quantitative yield (Scheme 1). Furthermore, high-spin **2** may also be easily characterized by ^1H NMR spectroscopy. Both the free ligand and diamagnetic transition metal complexes containing (−)-sparteine display complicated ^1H NMR spectra that cannot be readily interpreted due to the presence of 26 inequivalent hydrogens with a relatively narrow chemical shift dispersion. In contrast, the ^1H NMR spectrum of **2** in chloroform-*d* displays 26 distinct resonances over a 500 ppm range, facilitating characterization of **2**. Unfortunately, attempts to obtain ^{13}C NMR data have been unsuccessful.

Despite its relatively low cost and commercial availability, (−)-sparteine is not an easily manipulated ligand. Access to the other antipode, (+)-sparteine, or derivatization of (−)-sparteine requires sophisticated synthesis,[23] potentially limiting their utility in asymmetric transformations. However, C_2-symmetric bis-oxazoline ligands are easily synthesized, are readily tuned, and in some cases are commercially available as both antipodes. This class of ligand has enjoyed considerable success in coordination chemistry[24] and asymmetric catalysis.[25] With respect to iron, both Corey[26] and Takacs[27] have implicated iron(III) halide complexes with 2,2-bis[2-[4(*S*)-(R′)-1,3-oxazolinyl]propane ($R' = C_6H_5$, CH_2Ph) as chiral Lewis acids in the Diels−Alder reaction and in the carbocyclizations of trienes, respectively. Provided these reports, we explored the preparation and characterization of well-defined iron(II) dialkyl compounds supported by bis-oxazoline ligands.

Reaction of 2,2-bis[2-[4(*S*)-(CMe_3)-1,3-oxazolinyl]propane ((*S*)-(^{t}BuBox)) with $FeCl_2$ in THF at ambient temperature afforded (*S*)-(^{t}BuBox)$FeCl_2$ (**3**) as a white crystalline solid in 72% yield. As with **1** and **2**, **3** was readily identified by ^1H NMR spectroscopy. Chloroform-*d* solutions of **3** display five resonances, consistent with a C_2-symmetric Fe(II) complex. Equivalent *tert*-butyl groups are observed at 20.01 ppm, whereas the methyl groups on the methylene bridge are observed at 17.71 ppm. The solution magnetic moment was found to be 4.26 μB (Evans method) in chloroform-*d* and is consistent with a tetrahedral, high-spin Fe(II) complex.

The solid state structure of **3** was determined by X-ray diffraction and confirms the chirality and distorted tetrahedral geometry of the iron center (Figure 1). An acute N(1)−Fe(1)−N(2) angle of 86.6(2)° is observed due to the chelating bis-oxazoline, which is compensated by a more open Cl(1)−Fe(1)−Cl(2) angle of 117.12(9)°. The core of the ligand is slightly puckered, with a dihedral angle of 46.7° arising from the planes formed by N(1)−Fe(1)−N(2) and C(3)−C(4)−C(5). The Fe−Cl distances of 2.2416(9) and 2.266(2) Å are in accord with other crystallographically characterized four-coordinate Fe(II) dihalide complexes,[16b,22,28] and the C=N bond distances of 1.282(8) and 1.292(9) Å are in the range typically observed in other structurally characterized transition metal bis-oxazoline complexes.[29]

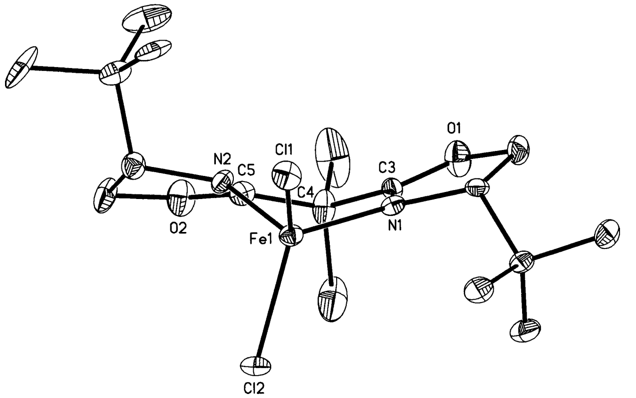
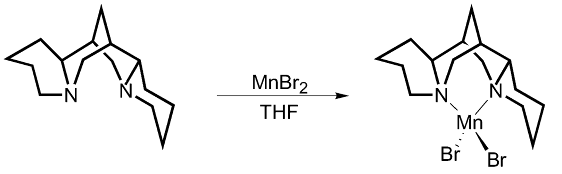


Figure 1. Molecular structure of (*S*)-(^{t}BuBox)$FeCl_2$ (**3**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

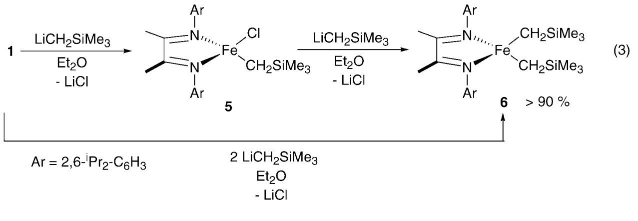
Synthesis of an enantiopure, manganese(II) dihalide complex has also been achieved. Stirring stoichiometric quantities of (−)-sparteine and $MnBr_2$ in THF at ambient temperature for 16 h followed by filtration afforded (−)-(sparteine)$MnBr_2$ (**4**) in 93% yield (eq 2). Unlike the Fe(II) dihalide complexes, **4** is NMR silent. The solution magnetic moment of **4** was measured as 5.96 μB in chloroform-*d* and is consistent with the spin-only value expected for five unpaired electrons.



(**4**)

(2)

Preparation of Fe(II) and Mn(II) Dialkyl Derivatives. Addition of 1 equiv of $LiCH_2SiMe_3$ to a diethyl ether slurry of **1** at −78 °C followed by filtration and recrystallization from pentane afforded [$ArN=C(CH_3)-C(CH_3)=NAr$]$Fe(CH_2SiMe_3)Cl$ (**5**) as green needles in 84% yield (eq 3). The solution magnetic moment was determined in benzene-d_6, and the value of 4.88 μB is consistent with the spin-only value for an $S = 2$ iron complex. In benzene-d_6, **5** displays five broad resonances in the ^1H NMR spectrum, whereas the ^2H NMR spectrum of **5-d_6** contains a single peak centered at −77.71 ppm, assigned to the methyl groups on the backbone of the α-diimine ligand.



(3)

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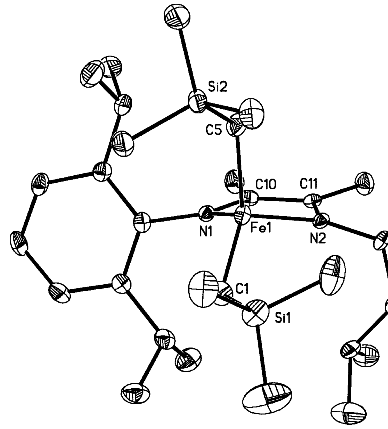


Figure 2. Molecular structure of [ArN=C(CH$_3$)−C(CH$_3$)=NAr]Fe(CH$_2$SiMe$_3$)$_2$ (**6**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

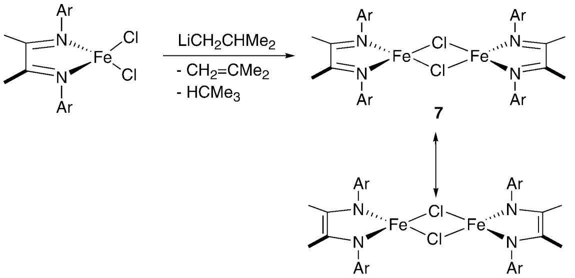
Table 1. Selected Bond Distances (Å) and Angles (deg) for 6

bond distances		bond angles	
Fe(1)−C(1)	2.042(3)	N(2)−Fe(1)−N(1)	79.59(9)
Fe(1)−C(5)	2.072(3)	N(2)−Fe(1)−C(1)	114.88(15)
Fe(1)−N(1)	2.025(2)	N(1)−Fe(1)−C(1)	113.70(12)
Fe(1)−N(2)	2.013(2)	N(2)−Fe(1)−C(5)	107.41(11)
N(1)−C(10)	1.329(3)	N(1)−Fe(1)−C(5)	106.49(13)
N(2)−C(11)	1.320(3)	C(1)−Fe(1)−C(5)	125.31(16)
C(10)−C(11)	1.507(3)	fold angle[a]	20.3

[a] Angle between N(1)−C(10)−C(11)−N(2) and N(1)−Fe(1)−N(2) planes.

Synthesis of the dialkyl complex [ArN=C(Me)−(Me)C=NAr]Fe(CH$_2$SiMe$_3$)$_2$ (**6**) was accomplished by addition of 1 equiv of LiCH$_2$SiMe$_3$ to **5** or by direct alkylation of **1** with 2 equiv of LiCH$_2$SiMe$_3$ (eq 3). Purple, benzene-d_6 solutions of **6** have a magnetic moment of 4.71 μB and display six of the eight expected ^{1}H NMR signals. Curiously, no ^{2}H NMR signal could be detected for the methyl backbone of **6-*d*$_6$**. However, the identity of the molecule was confirmed by single-crystal X-ray diffraction. The solid state structure of **6** is shown in Figure 2 and reveals the expected pseudotetrahedral geometry about iron. The aryl rings are rotated such that the isopropyl substituents flank the plane that defines the ligand core. Selected bond distances and angles are reported in Table 1. The iron carbon distances of 2.042(3) and 2.072(2) Å are similar to those reported by Holland[4b] for three-coordinate iron(II) alkyls and are slightly shorter than the value of 2.120(6) reported by Girolami[12] for (dippe)Fe(CH$_2$C$_6$H$_5$)$_2$.

Attempts to prepare other dialkyl complexes from **1** have met with limited success. Reaction of **1** with MeLi, MeMgBr, EtMgBr, and KCH$_2$Ph resulted in deposition of Fe(0) and dissociation of the α-diimine ligand. Interestingly, addition of 1 equiv of LiCH$_2$CHMe$_2$ to **1** resulted in reduction, rather than alkylation, forming the formally iron(I)−iron(I) dimer, [ArN=C(Me)−(Me)C=NAr)Fe]$_2$(μ−Cl)$_2$ (**7**), as green crystals in low yield (eq 4). Monitoring the reaction by ^{1}H NMR spectroscopy also revealed formation of isobutene and isobutane. Similar results are obtained from the attempted arylation of **1** with PhLi.[30]



(4)

The chloride dimer, **7**, has been characterized by ^{1}H NMR spectroscopy, elemental analysis, and X-ray diffraction. The ^{1}H NMR spectrum displays two diastereotopic isopropyl methyl groups at −21.19 and −18.06 ppm as well as other resonances arising from the methine and aryl protons at −9.50, −0.01, and 5.42 ppm. As with the dialkyl complex, **6**, no resonance for the methyl backbone of the ligand was observed. Similarly, no peak was observed in the ^{2}H NMR spectrum of **7-*d*$_6$**. A solution magnetic moment of 3.86 μB was measured at ambient temperature in benzene-d_6 and is indicative of antiferromagnetic coupling through the bridging chloride ligands.[31]

The solid state structure of **7** is shown in Figure 3 and displays idealized D_{2h} symmetry with two tetrahedral iron centers. The Fe−Fe distance of 2.9764(6) Å is considerably longer than that of iron metal (2.48 Å) and is longer than the sum of the covalent radii (2.50 Å), making it outside of the range typically ascribed to iron−iron bonds.[32] The carbon−carbon bond length of the ligand backbone, C(1)−C(1A), is 1.420(3) Å and is slightly shorter than the corresponding C(10)−C(11) bond length of 1.507(3) Å in **6**, suggesting that the enediamide form of the ligand is an important contributor to the resonance hybrid. In such a limit, one can consider the iron centers in the (+3) ferric form rather than the uncommon monovalent oxidation state.

Enantiopure dialkyl derivatives, **8**−**12**, were also prepared by reaction of the corresponding iron(II) dichloride complex with 2 equiv of the appropriate alkylating reagent in diethyl ether (Scheme 2). (−)-Sparteine iron(II) bis-trimethylsilylmethyl, neopentyl, and benzyl complexes were prepared in approximately 65% yield, whereas bis-oxazoline iron(II) trimethylsilylmethyl and benzyl derivatives were prepared in 88% and 57% yields, respectively. Solution magnetic data obtained in benzene-d_6 are consistent with an $S = 2$ ground state for each dialkyl complex. As with **5** and **6**, the enantiopure iron(II) dialkyl complexes are readily characterized by ^{1}H NMR spectroscopy, the details of which can be found in the Experimental Section.

Alkylation of the manganese(II) dibromide complex, **4**, with 2 equiv of LiCH$_2$SiMe$_3$ resulted in clean conversion to (−)-(sparteine)Mn(CH$_2$SiMe$_3$)$_2$ (**13**) in 79% yield. Clear, colorless **13** has been characterized by elemental analysis, magnetic susceptibility, and X-ray diffraction. The solution magnetic moment in benzene-d_6 was found to be 5.77 μB, consistent with the spin-only value for five unpaired electrons.

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(30) Reaction of **1** with PhLi also produces a significant quantity of the iron(0) arene complex, ArN=C(Me)−(Me)C=NAr(η^6-biphenyl). Hawrelak, E. J.; Chirik, P. J. Manuscript in preparation.

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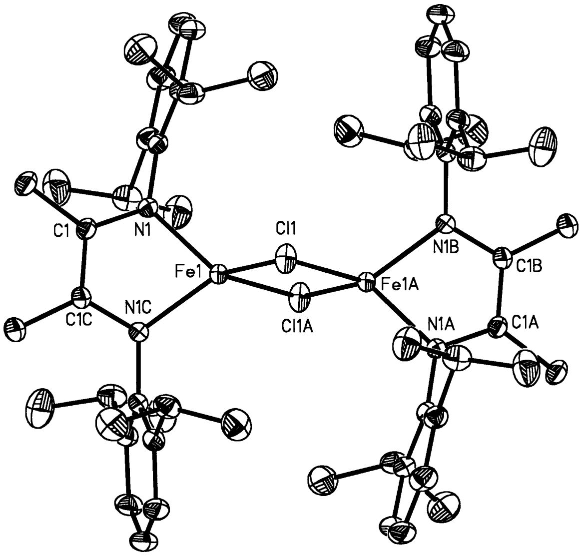
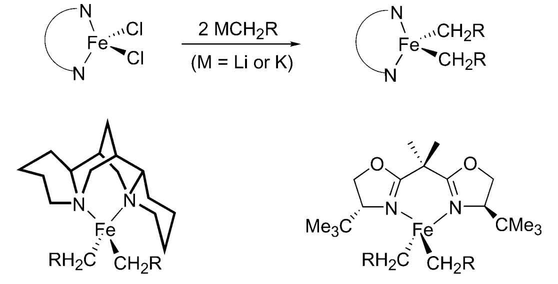


Figure 3. Molecular structure of [ArN=C(CH$_3$)−C(CH$_3$)=NArFe]$_2$(μ_2-Cl)$_2$ (**7**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Scheme 2



8: R = SiMe$_3$ (66 %); μ_{eff} = 4.83 μ_B
9: R = CMe$_3$ (67 %); μ_{eff} = 4.68 μ_B
10: R = C$_6$H$_5$ (93 %); μ_{eff} = 4.59 μ_B

11: R = SiMe$_3$ (88 %); μ_{eff} = 4.83 μ_B
12: R = C$_6$H$_5$ (57 %); μ_{eff} = 4.60 μ_B

The dialkyl complexes, **8**, **13**, and **11** were characterized by X-ray diffraction, and their solid state structures are shown in Figures 4−6. Selected bond distances and angles are provided in Table 2. The (−)-(sparteine) iron(II) and manganese(II) dialkyls, **8** and **13**, are nearly isostructural, with **13** having slightly longer metal−carbon and metal−nitrogen bonds arising from the larger Mn(II) center. The iron complex **8** is a distorted tetrahedron with an acute N(1)−Fe(1)−N(2) angle of 80.20(4)° arising from the bite angle of the diamine ligand. To compensate, the C(16)−Fe(1)−C(20) angle opens to 129.46(6)°. The trimethylsilyl groups are oriented in an "up−down" fashion as to avoid unfavorable steric interactions. The iron−carbon bond lengths of 2.0856(16) and 2.0963(13) Å are similar to those observed in the α-diimine iron(II) dialkyl complex **6**.

The bis-oxazoline iron(II) dialkyl complex **11** displays similar structural features. Similar to the dichloride complex **3**, a puckered ligand core is observed with a dihedral angle of 25.0° between the planes formed by N(1)−Fe(1)−N(2) and C(17)−C(16)−C(15). The trimethysilyl groups of the alkyl ligands are canted away from the *tert*-butyl groups of the bis-oxazoline ligand to avoid unfavorable steric interactions. The acute N(1)−Fe(1)−N(2) bond angle of 85.17(15)° and iron−carbon bond distances of 2.074(5) and 2.087(4) Å are in accord with those observed in **6** and **8**.

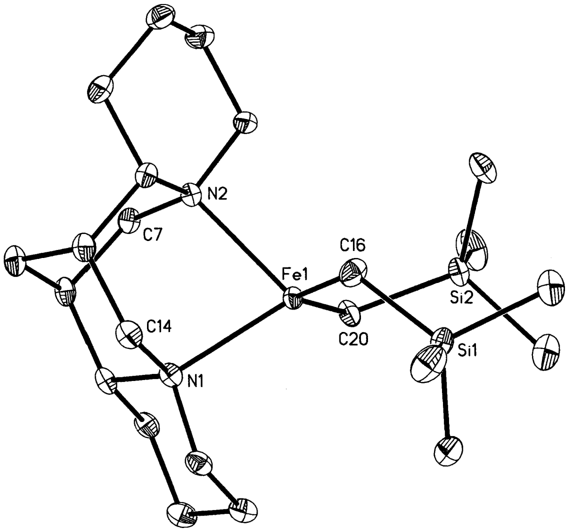


Figure 4. Molecular structure of (−)-(spartiene)Fe(CH$_2$SiMe$_3$)$_2$ (**8**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

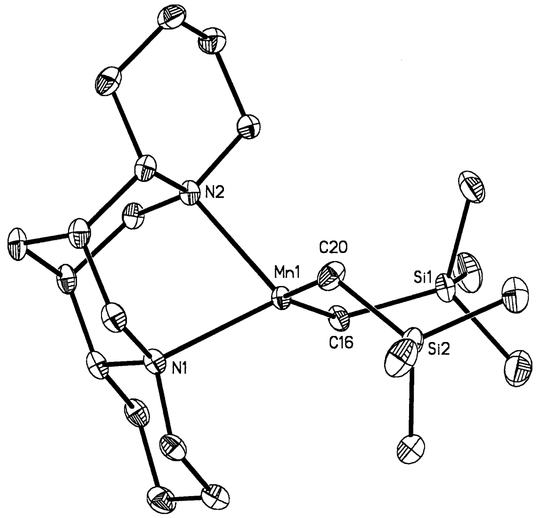


Figure 5. Molecular structure of (−)-(spartiene)Mn(CH$_2$SiMe$_3$)$_2$ (**13**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Reactivity of Iron(II) Dialkyl Complexes. The competency of the iron complexes to promote catalytic C−C bond formation was initially assayed by polymerization of ethylene. Although the goal of our work is not to develop new catalysts for polyolefin synthesis, ethylene polymerization was chosen as a test reaction due to its simplicity and the rate with which precatalysts can be screened for activity. The four-coordinate iron(II) dichloride complexes **1**−**3** when activated with methylalumoxane (MAO) are active for the solution phase polymerization of ethylene.[22] Although each catalyst did produce several hundred milligrams of polyethylene, the activity of the four-coordinate iron precatalysts was significantly diminished in comparison to the Brookhart−Gibson, five-coordinate Fe(II) dichloride complexes, which produced multigram quantities of polymer under identical conditions. Stephan has recently reported diminished ethylene polymerization activity with four-coordinate pyridine- and imidazole-phosphinimine-based iron(II) dihalide catalyst precursors.[33] The origin of this effect is most likely electronic rather than steric in origin. Although the structure of

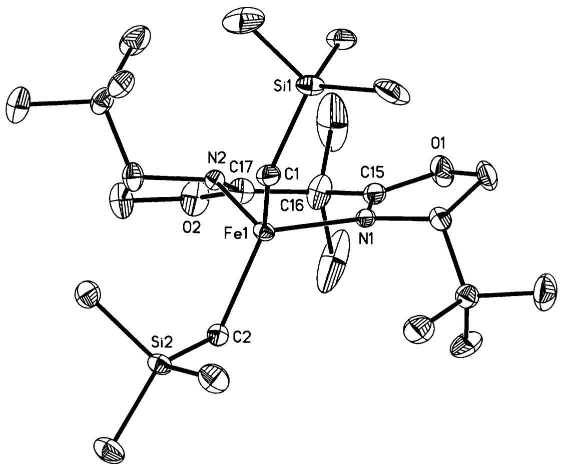


Figure 6. Molecular structure of (*S*)-(^{t}BuBox)Fe(CH$_2$SiMe$_3$)$_2$ (**11**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

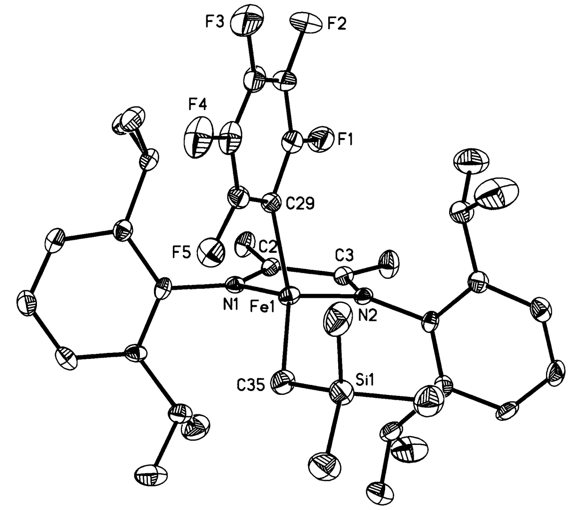


Figure 7. Molecular structure of ArN=C(CH$_3$)−C(CH$_3$)=NArFe(CH$_2$SiMe$_3$)(C$_6$F$_5$) (**15**) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 8, 11, and 13

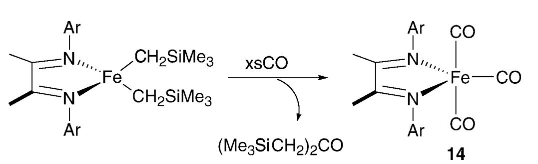
	8	**11**	**13**
M^a−C	2.0856(14)	2.074(5)	2.1582(18)
	2.0963(13)	2.087(4)	2.165(17)
M−N(1)	2.2662(11)	2.140(4)	2.2967(14)
M−N(2)	2.2475(12)	2.173(4)	2.3288(13)
N(2)−M−N(1)	80.20(4)	85.17(15)	78.12(5)
N(2)−M−C(1)^b	106.77(5)	120.14(18)	102.92(6)
N(1)−M−C(1)	106.27(6)	109.36(18)	117.68(6)
N(2)−M−C(2)	103.96(5)	98.10(17)	106.89(6)
N(1)−M−C(2)	117.85(4)	113.80(17)	103.76(7)
C(1)−M−C(2)	129.46(6)	123.74(18)	132.84(7)

[a] M = Fe (**8**, **11**) or Mn (**13**). [b] For **8** and **11**, C(1) refers to C(16), and C(2) refers to C(20) in Figures 4 and 5.

the active polymerization catalyst is open to speculation, the $S = 2$ electronic configuration of the precatalyst has no low lying empty molecular orbitals available for olefin binding.

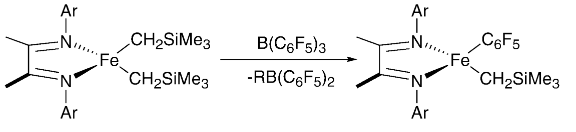
To address this issue, experiments with the more well-defined four-coordinate iron(II) dialkyl complexes were examined. In general, the dialkyl complexes display good thermal stability, eventually undergoing slow decomposition after heating to 85 °C for several days. Addition of 1 atm of dihydrogen to **6**, **8**, or **11** resulted in alkane formation along with decomposition to free ligand and metallic iron. Each of the dialkyl complexes was also unreactive toward excess ethylene and not active for the hydrogenation of olefins such as 1-hexene and styrene.

Addition of strong field ligands to the dialkyl complexes **6** and **8** has also been examined. Carbonylation of the α-diimine iron(II) dialkyl, **6**, with 1 atm of CO at ambient temperature produced an immediate reaction, affording the ketone Me$_3$SiCH$_2$C(O)CH$_2$SiMe$_3$ and [ArN=C(Me)−(Me)C=NAr]Fe(CO)$_3$ (**14**) (eq 5). In addition, small (~10%) amounts of free α-diimine ligand and Fe(CO)$_5$ are also observed. The identity of the ketone was established by NMR spectroscopy, mass spectrometry, and infrared spectroscopy.[34] Similar observations have been reported by Girolami for the carbonylation of (dippe)FeR$_2$ with 3 atm of carbon monoxide.[35] However, in the phosphine system no competing reaction producing free ligand and Fe(CO)$_5$ was reported. Red, diamagnetic **14** is related to α-diimine iron tricarbonyl complexes reported by tom Dieck prepared by reaction of the free ligand with either Fe(CO)$_5$ under photochemical conditions or by thermal reaction with Fe$_2$(CO)$_9$.[36] The corresponding reaction with the enantiopure dialkyl complex **8** resulted in clean formation of ketone along with free (−)-sparteine and Fe(CO)$_5$, suggesting (−)-sparteine is not a good ligand for Fe(0).



14 (5)

To generate more reactive iron(II) organometallic complexes, alkyl abstraction with B(C$_6$F$_5$)$_3$ was attempted. Reaction of **6** with 1 equiv of B(C$_6$F$_5$)$_3$ produced green crystals upon recrystallization from pentane at −35 °C. A combination of NMR spectroscopy, elemental analysis, and X-ray diffraction revealed the product of the reaction to be [(ArN=C(Me)−(Me)C=NAr)Fe(CH$_2$SiMe$_3$)]C$_6$F$_5$ (**15**) arising from aryl group transfer rather than the expected contact ion-pair, [(ArN=C(Me)−(Me)C=NAr)] Fe(CH$_2$SiMe$_3$)][Me$_3$SiCH$_2$B(C$_6$F$_5$)$_3$] (eq 6). The borane byproduct Me$_3$SiCH$_2$B(C$_6$F$_5$)$_3$ was also detected by both ^{1}H and ^{19}F NMR spectroscopy.[37] Attempts to generate the desired contact ion-pair by conducting the alkyl abstraction reaction at low temperature consistently yielded **15**. No ^{1}H NMR reso-



6 **15** (6)

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Scheme 3

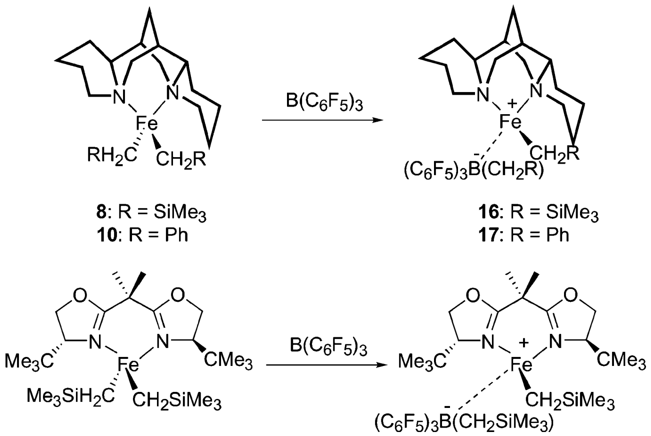

Table 3. ^{19}F and ^{11}B NMR Chemical Shifts for Fe(II) Ion-Pairs

compound	δ ^{19}F NMR (ppm)	δ ^{11}B NMR (ppm)
[(−)-(sparteine)Fe(CH$_2$SiMe$_3$)]-[B(C$_6$F$_5$)$_3$CH$_2$SiMe$_3$] (**16**)	−161.49	−14.52
	−158.59	
	−124.45	
(−)-(sparteine)Fe(CH$_2$C$_6$H$_5$)-(B(C$_6$F$_5$)$_3$CH$_2$C$_6$H$_5$) (**17**)	−164.72	−14.75
	−163.00	
	−126.41	
[(*S*)-(^{t}BuBox)Fe(CH$_2$SiMe$_3$)]-[B(C$_6$F$_5$)$_3$CH$_2$SiMe$_3$] (**18**)	−162.61	−14.48
	−160.53	
	−128.18	
[(*S*)-(^{t}BuBox)Fe(CH$_2$C$_6$H$_5$)]-[B(C$_6$F$_5$)$_3$CH$_2$C$_6$H$_5$] (**19**)	−162.93	−13.12
	−161.82	
	−129.24	

nances were observed for **15**, although a single peak centered at 28.20 ppm ($\Delta\nu_{1/2} = 12.02$ Hz) was detected in the corresponding ^{2}H NMR spectrum of **15-d_6**. In addition, three broad ^{19}F resonances were observed at −139.06, −154.04, and −162.32 ppm. The magnetic susceptibility of **15** was determined by SQuID magnetometry and yielded a value of 5.38 μB, indicative of a high-spin, $S = 2$ molecule. Variable-temperature magnetic data collected between −80 and 40 °C yielded a Curie constant of 3.60 mol·K/emu, consistent with the expected value ($\Theta > 0$) for a paramagnetic molecule.

Unlike the α-diimine complex, reaction of the enantiopure iron(II) dialkyl complexes with B(C$_6$F$_5$)$_3$ did produce the desired ion-pair complexes. Thus, addition of 1 equiv of B(C$_6$F$_5$)$_3$ to a pentane solution of **8** resulted in immediate formation of a thick yellow clatharate identified as [(−)-(sparteine)Fe(CH$_2$SiMe$_3$)][(C$_6$F$_5$)$_3$B(CH$_2$SiMe$_3$)] (**16**) (Scheme 3). Although a ^{1}H NMR spectrum was not observed, three distinct resonances were observed in the ^{19}F NMR spectrum. Similar results were obtained from reaction of **10** and **11** (Scheme 3). The ^{19}F and ^{11}B NMR data for each ion-pair complex are compiled in Table 3 and are consistent with values typically observed for four-coordinate borate anions.[38] Although the structures of **16**−**18** have not been definitively established by X-ray diffraction, NMR spectroscopic data, elemental analysis, and their solubility properties are suggestive of alkyl group abstraction. Although the dialkyl complexes are inert toward excess ethylene, the contact ion-pair **16** is modestly active for polymerization. Stirring a toluene solution of **16** with 90 psi of ethylene yielded 0.104 g of monodisperse polyethylene (PDI = 2.74, M_n = 333 000 versus polyethylene) with a melting temperature of 132 °C.

Concluding Remarks

Synthesis of a series of tetrahedral, high-spin iron(II) dialkyl complexes of the general form L$_2$FeR$_2$ has been described. This straightforward methodology has been expanded to include the preparation of enantiopure dialkyl derivatives from readily available and inexpensive ligands and metal sources. Despite their relatively low formal electron count, the 14-electron iron(II) dialkyl derivatives are unreactive due to electronic factors arising from their $S = 2$ ground states rather than steric considerations. However, addition of strong field ligands such as carbon monoxide is sufficient to induce spin crossover and, in the case of the α-diimine-ligated iron(II) dialkyl, produce ketone and the iron(0) tricarbonyl complex. Reaction of the dialkyl complexes with the now ubiquitous Lewis acid B(C$_6$F$_5$)$_3$ produced results that were dependent on the ancillary ligation. In the case of the α-diimine ligand, aryl group transfer was observed, whereas in the case of the (−)-sparteine and (*S*)-(^{t}BuBox) ligands, contact ion-pair complexes were obtained. In the latter case, the contact ion-pairs were found to be active for catalytic carbon−carbon bond formation as judged by the polymerization of ethylene.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.[39] The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Argon and hydrogen gas were purchased from Airgas Incorporated 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 or sodium metal. Bromobenzene-d_5 and chloroform-*d* were purchased from Cambridge Isotope Labs and distilled from CaH$_2$. Iron(II) chloride, (−)-sparteine, carbon monoxide, and LiCH$_2$SiMe$_3$ were purchased from Aldrich. The FeCl$_2$ was used as received, whereas (−)-sparteine was distilled from CaH$_2$ and the LiCH$_2$SiMe$_3$ was recrystallized from pentane and used as a solid. Carbon monoxide was passed through a liquid nitrogen-cooled trap immediately before use. B(C$_6$F$_5$)$_3$ was purchased from Strem Chemicals and was used as received. LiCH$_2$CMe$_3$,[40] (*S*)-(^{t}BuBox),[41] and ArN=C(Me)−(Me)C=NAr[42] were prepared according to literature procedures.

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^{1}H NMR spectra were recorded on 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 $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{2}H NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.851 MHz, and the spectra were referenced using an external benzene-d_6, toluene-d_8, or chloroform-d standard. ^{19}F NMR spectra were recorded on Varian Inova 400 and 500 spectrometers operating at 376.127 and 470.997 MHz, respectively, and were referenced to C_6F_6 in benzene-d_6. ^{11}B NMR spectra were recorded on a Bruker ARX-300 spectrometer operating at 96.2936 MHz, and spectra are referenced to $BF_3{\cdot}Et_2O$ in benzene-d_6. For paramagnetic compounds, ^{1}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, magnetic moments were measured at 22 °C by the method originally described by Evans[43] 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 running Magnetic Property Measurement System Revision 2 software. Data were recorded at 300 oersteads (Oe), and the sample was prepared by sealing an NMR tube that was sewn into a plastic straw with a needle and thread to prevent sample migration. The ends of the straw were covered in Kapton tape. The sample used was recrystallized several times and purity determined by elemental analysis. The loaded sample was centered within the magnetometer using the DC centering scan at 20 K and 100 Oe. Data were acquired at 190−310 K with one data point every 10 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 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.

The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polyethylene were measured by a Waters Alliance GPCV 2000 size exclusion chromatograph (SEC). The SEC column set (four Waters HT 6E and one Waters HT 2) was equilibrated at 140 °C and eluted with 1,2,4-trichlorobenzene (1.0 mL/min) containing 0.01 wt % di-*tert*-butylhydroxytoluene (BHT). The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured relative to a polyethylene calibration curve. The melting point of the polyethylene sample was measured by a TA Instruments DSC Q100. The sample run was performed from 0 to 220 °C with a heating rate of 10 °C/min.

Preparation of ArN=C(CD_3)−(CD_3)C=NAr. A 100 mL round-bottomed flask was charged with 0.49 g (5.7 mmol) of 2,3-butanedione-d_6, 2.11 g (11.9 mmol) of diisopropylaniline, and 5 mL of CH_3OD and stirred. To the reaction mixture was added 0.50 mL (13.2 mmol) of formic acid-d_1 and resulted in the formation of a yellow precipitate within 10 min. The reaction mixture was stirred for 19 h, and the resulting yellow solid was collected by filtration. The solid was washed with 20 mL of methanol and dried under vacuum to afford 1.96 g (4.8 mmol, 84%) of a yellow solid. Integration of the ^{1}H NMR spectrum revealed approximately 67% D incorporation. ^{1}H NMR (chloroform-d): δ 1.05 (d, 4.7 Hz, 12H, CHMe_2), 1.08 (d, 4.9 Hz, 12H, CHMe_2) 2.07 (s, <2H, CD_2H), 2.72 (sept, 6.9 Hz, 4H, CHMe_2), 7.19 (m, 2H, Ar), 7.17 (s, 4H, Ar). ^{2}H NMR (benzene): δ 2.07 ppm.

Preparation of [ArN=C(Me)−(Me)C=NAr]$FeCl_2$ (1). A 1.0 L round-bottomed flask was charged with 20.7 g (51 mmol) of ArN=C(CH_3)−(CH_3)C=NAr and approximately 600 mL of THF. With stirring, 5.0 g (39 mmol) of $FeCl_2$ was added at 25 °C. The deep blue suspension was stirred for 18 h and filtered through Celite, and the resulting solid was extracted with an additional 1.0 L of THF. The solvent was removed in vacuo, and the resulting residue was washed with toluene to remove any soluble impurities. Removal of the toluene afforded 25.3 g (47.6 mmol, 93%) of blue solid identified as **1** based on comparison to literature data. ^{1}H NMR (chloroform-d): δ −18.31 (26.19, 2H, p-C_6H_3), −3.83 (131.62, 12H, CHMe_2), 3.10 (52.54, 12H, CHMe_2), 6.05 (42.95, 4H), 60.82 (120.41, 6H, C(Me)), one not located. ^{2}H NMR (CH_2Cl_2) for **1-d_6**: δ 60.82 ppm (18.37, CD_3).

Preparation of (−)-(Sparteine)$FeCl_2$ (2). A 20 mL scintillation vial was charged with 1.60 g (12.6 mmol) of $FeCl_2$ and slurried in approximately 5 mL of THF. A THF solution containing 2.95 g (12.6 mmol) of (−)-sparteine was added to the reaction mixture and stirred. Over time, a white solid formed. After 18 h, THF was removed in vacuo and the resulting solid was washed with diethyl ether and collected by filtration. The white solid was washed with several portions of diethyl ether to yield 4.37 g (96% yield) of **2**. Magnetic susceptibility (chloroform-d): $\mu_{eff} = 4.86\ \mu_B$. ^{1}H NMR (chloroform-d): δ −153.02 (893.84, 1H), −91.57 (751.88, 1H), −51.14 (182.43 Hz, 1H), −41.44 (178.22 Hz, 2H), −35.12 (673.38 Hz, 1H), −27.66 (418.29 Hz, 1H), −24.69 (103.04, 1H), −17.32 (79.59 Hz, 1H), −15.46 (104.58, 1H), −8.59 (139.52, 2H), 9.40 (47.82, 1H), 14.47 (94.46, 1H), 28.56 (158.56 Hz, 1H), 30.62 (169.75, 1H), 39.17 (116.59, 1H), 49.75 (184.57, 1H), 51.25 (191.47 Hz, 1H), 123.05 (929.15, 1H), 145.91 (737.87, 1H), 148.92 (820.82, 1H), 207.93 (551.37, 1H), 310.52 (747.33, 1H), 349.94 (153.88, 1H), 388.03 (124.13, 1H).

Preparation of (S)-(^{t}BuBox)$FeCl_2$ (3). A 20 mL scintillation vial was charged with 0.471 g (3.74 mmol) of $FeCl_2$ and approximately 5 mL of THF. A THF solution containing 1.10 g (3.74 mmol) of 2,2-bis[2-[4(S)-(CMe_3)-1,3-oxazolinyl]propane was added and the resulting clear, off-white reaction mixture stirred for 18 h. The THF was removed in vacuo, the remaining off-white solid was dissolved in CH_2Cl_2, and the remaining $FeCl_2$ was removed by filtration. The dichloromethane was removed in vacuo to yield 1.13 g (72% yield) of **3**. Anal. Calcd for $C_{17}H_{38}Cl_2N_2O_2Fe$: C, 48.48; H, 7.18; N, 6.65. Found: C, 48.20; H, 6.71; N, 6.42. Magnetic susceptibility (chloroform-d) $\mu_{eff} = 4.26\ \mu_B$. ^{1}H NMR (chloroform-d): δ −20.01 (288.60 Hz, 18H, CMe_3), −15.47 (484.61, 2H), 12.16 (98.20, 2H), 12.63 (73.44, 2H), 17.71 (109.08, 6H, Me).

Preparation of (−)-(Sparteine)$MnBr_2$ (4). A procedure similar to that for **2** was used with 0.916 g (4.27 mmol) of $MnBr_2$ and 1.09 g (4.27 mmol) of (−)-sparteine, yielding 1.78 g (93%) of **4**. Anal. Calcd for $C_{15}H_{26}Br_2N_2Mn$: C, 40.11; H, 5.84; N, 6.24. Found: C, 39.88; H, 5.69; N, 6.19.

Preparation of [ArN=C(Me)−(Me)C=NAr]Fe(CH_2SiMe_3)Cl (5). A 100 mL round-bottomed flask was charged with 2.00 g (3.80 mmol) of **1** and 0.354 g (3.80 mmol) of $LiCH_2SiMe_3$ and attached to a 180° needle valve. On the vacuum line, approximately 60 mL of diethyl ether was added by vacuum transfer at −78 °C. The reaction mixture was maintained at this temperature for 1 h, and the diethyl ether was removed in vacuo. The blue-green residue was transferred into the drybox, extracted with pentane, and filtered through Celite to afford 1.85 g (84%) of a blue-green solid identified as **5**. Anal. Calcd for $C_{32}H_{51}ClN_2FeSi_2$: C, 65.91; H, 8.82; N, 4.80. Found: C, 65.62; H, 8.51; N, 5.24. Magnetic susceptibility (benzene-d_6): $\mu_{eff} = 4.88\ \mu$B. ^{1}H NMR (benzene-d_6): δ −74.36 (283.29, 6H, C(Me)), −22.29 (51.52, 2H), 2.86 (224.18, 24H, CHMe_2), 15.57 (85.41, 2H), 21.10 (428.30, 9H, CH_2SiMe_3), one not located. ^{2}H NMR (toluene) for **5-d_6**: δ −77.71 (45.76, CD_3).

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Preparation of [ArN=C(Me)−(Me)C=NAr]Fe(CH$_2$SiMe$_3$)$_2$ (6). A 100 mL round-bottomed flask was charged with 4.10 g (7.7 mmol) of **1** and 1.50 g (15.5 mmol) of LiCH$_2$SiMe$_3$. A 180° needle valve was attached, and approximately 60 mL of diethyl ether was added by vacuum transfer at −78 °C. The reaction mixture was maintained at this temperature for 1 h, and the diethyl ether was removed in vacuo. The purple residue was transferred into the drybox and extracted with pentane to afford 4.46 g (91%) of a purple solid identified as **6**. Anal. Calcd for C$_{36}$H$_{62}$N$_2$FeSi$_2$: C, 68.10; H, 9.84; N, 4.41. Found: C, 67.86; H, 9.57; N, 4.41. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.71\ \mu$B. ^{1}H NMR (benzene-$d_6$): δ −27.10 (111.41, 2H, p-C$_6$$H_3$), −0.69 (526.91, 12H, CHMe_2), 1.17 (15.77, 4H), 2.72 (185.23, 12H, CHMe_2), 14.17 (527.7, 18 H, CH$_2$SiMe_3), two peaks not located.

Preparation of [[ArN=C(Me)−(Me)C=NAr]Fe(μ-Cl)]$_2$ (7). A 50 mL round-bottomed flask was charged with 0.500 g (0.940 mmol) of **1** and approximately 35 mL of diethyl ether. The resulting slurry was chilled to −35 °C in the glovebox freezer for approximately 15 min. Likewise, a scintillation vial was charged with 0.060 g (0.94 mmol) of LiCH$_2$CH(CH$_3$)$_2$ and approximately 2 mL of diethyl ether and chilled to −35 °C. With stirring, the LiCH$_2$Si(CH$_3$)$_2$ solution was added to the ethereal suspension of **1**. The reaction was allowed to warm to 25 °C and stirred for 45 min. The solution was filtered through Celite and the solvent removed in vacuo to yield 0.180 g (19%) of a green solid identified as **7**. Anal. Calcd for C$_{56}$H$_{80}$N$_4$Cl$_2$Fe$_2$: C, 67.81; H, 8.13; N, 5.65. Found: C, 67.58; H, 8.13; N, 5.18. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 3.86\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −21.19 (41.46, 12H, CHMe_2), −18.06 (34.14, 2H p-C$_6$H$_3$), −9.50 (25.59, 4H), −0.01 (227.57, 4H), 5.42 (22.71, 12H, CHMe_2), one not located (CH_3).

Preparation of (−)-(Sparteine)Fe(CH$_2$SiMe$_3$)$_2$ (8). A 20 mL scintillation vial was charged with 0.200 g (0.554 mmol) of **2** and approximately 5 mL of diethyl ether. A 10 mL diethyl ether solution containing 0.104 g (1.11 mmol) of LiCH$_2$SiMe$_3$ was added, and the reaction mixture was stirred for 6 h, forming a brown solution and white precipitate. The mixture was filtered through a pad of Celite and the diethyl ether removed in vacuo, yielding a brown oil. Recrystallization from pentane afforded 0.170 g (66%) of white crystals identified as **8**. Anal. Calcd for C$_{23}$H$_{48}$N$_2$FeSi$_2$: C, 59.45; H, 10.41; N, 6.03. Found: C, 59.36; H, 10.03; N, 6.00. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.83\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −33.03 (310.62, 1H), −19.23 (129.88, 1H), −18.32 (103.50, 1H), −10.30 (79.62, 1H), −5.83 (71.18, 1H), −1.82 (1.81, 1H), 8.80 (82.76, 1H), 10.14 (156.05, 9H, CH$_2$SiMe_3), 12.67 (59.52, 1H), 13.62 (80.16, 1H), 15.71 (151.02, 9H, CH$_2$SiMe_3), 24.95 (53.17, 1H), 25.66 (64.50, 1H), 27.42 (63.30, 1H), 78.10 (606.23, 1H), 121.60 (245.85, 1H), 130.33 (296.31, 1H), 214.38 (137.82, 1H), 276.06 (235.70, 1H), 279.57 (330.70, 1H).

Preparation of (−)-(Sparteine)Fe(CH$_2$CMe$_3$)$_2$ (9). This molecule was prepared in a manner identical to that for **8** with 0.105 g (0.290 mmol) of **2** and 0.045 g (0.582 mmol) of LiCH$_2$CMe$_3$ to yield 0.084 g (67%) of white crystals identified as **8**. Anal. Calcd for C$_{25}$H$_{48}$N$_2$Fe: C, 69.42; H, 11.19; N, 6.48. Found: C, 69.08; H, 10.51; N, 6.45. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.68\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −50.03 (3406.62, 1H), −46.55 (3762.96, 1H), −38.14 (252.55, 1H), −22.02 (130.08, 1H), −19.77 (112.80, 1H), −11.35 (60.2, 1H), −10.60 (57.7, 1H), −1.47 (102.50, 1H), 0.091 (41.26, 1H), 3.27 (18.11, 1H), 4.15 (78.50, 1H), 10.26 (67.65, 1H), 17.51 (86.58, 1H), 19.41 (96.41, 1H), 22.25 (242.54, 9H, CMe_3), 27.77 (72.95, 1H), 28.44 (72.82, 1H), 30.15 (70.81, 1H), 33.33 (290.80, 9H, CMe_3), 66.50 (334.70, 1H), 117.64 (3024.48, 1H), 129.80 (1124.15, 1H), 205.30 (271.45, 1H), 260.82 (381.55, 1H), 275.94 (377.38, 1H).

Preparation of (−)-(Sparteine)Fe(CH$_2$Ph)$_2$ (10). This molecule was prepared in a manner identical to that for **8** with 0.203 g (0.562 mmol) of **2** and 0.146 g (1.12 mmol) of KCH$_2$C$_6$H$_5$, yielding 0.242 g (93%) of a yellow solid identified as **10**. Anal. Calcd for C$_{29}$H$_{40}$N$_2$Fe: C, 73.72; H, 8.53; N, 5.93. Found: C, 73.62; H, 8.07; N, 5.85. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.59\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −147.96 (1019.38, 1H), −85.51 (559.09, 1H), −75.96 (583.40, 1H), −73.66 (27.52, 1H), −57.68 (25.60, 1H), −49.61 (389.25, 1H), −41.28 (212.29, 1H), −33.23 (95.66, 1H), −22.25 (73.69, 1H), −21.27 (238.03, 1H), −14.81 (40.22, 1H), −12.20 (46.75, 1H), −4.62 (36.11, 1H), 5.37 (19.53, 1H), 6.02 (25.46, 1H), 14.99 (14.23, 1H), 23.95 (19.25, 2H), 25.36 (92.17, 1H), 26.22 (77.78, 1H), 30.60 (22.06, 2H), 31.41 (29.11, 1H), 41.12 (56.27, 2H), 116.226 (129.843, 1H), 131.79 (841.68, 1H), 137.43 (701.40, 1H), 149.27 (625.18, 1H), 218.68 (130.49, 1H).

Preparation of (S)-(^{t}BuBox)Fe(CH$_2$SiMe$_3$)$_2$ (11). A procedure similar to that for **8** was used employing 0.200 g (0.476 mmol) of **3** and 0.090 g (0.957 mmol) of LiCH$_2$SiMe$_3$, yielding 0.221 g (88%) of yellow crystals identified as **11**. Anal. Calcd for C$_{25}$H$_{52}$N$_2$O$_2$Si$_2$Fe: C, 57.23; H, 9.99; N, 5.34. Found: C, 56.95; H, 9.28; N, 5.45. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.83\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −20.64 (475.30, 18H), −12.17 (193.93), −6.92 (41.15), −4.81 (75.82), −1.17 (40.06), 1.24 (17.88), 1.73 (22.48), 12.22 (70.57), 13.71 (115.37, 4H), 15.35 (150.24, 18H), 23.51 (194.26, 2H).

Preparation of (S)-(^{t}BuBox)Fe(CH$_2$Ph)$_2$ (12). This molecule was prepared in a manner identical to that for **8** with 0.208 g (0.495 mmol) of **3** and 0.128 g (0.990 mmol) of KCH$_2$C$_6$H$_5$, yielding 0.095 g (57%) of a yellow solid identified as **12** following recrystallization from diethyl ether. Anal. Calcd for C$_{31}$H$_{44}$N$_2$O$_2$Fe: C, 69.92; H, 8.33; N, 5.26. Found: C, 70.02; H, 8.54; N, 5.63. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 4.60\ \mu_{\mathrm{B}}$. ^{1}H NMR (benzene-$d_6$): δ −65.40 (29.12), −44.09 (222.68), −24.28 (293.29), −17.14 (230.16), −6.00 (64.02), 5.68 (105.38), 10.76 (56.56), 17.41 (55.88), 21.39 (73.35), 29.88 (27.2).

Preparation of (−)-(Sparteine)Mn(CH$_2$SiMe$_3$)$_2$ (13). A procedure similar to that for **8** was used with 0.120 g (0.267 mmol) of **4** and 0.050 g (0.531 mmol) of LiCH$_2$SiMe$_3$, yielding 0.097 g (79%) of **13** as white crystals. Anal. Calcd for C$_{23}$H$_{48}$N$_2$MnSi$_2$: C, 59.57; H, 10.43; H, N, 6.04. Found: C, 59.23; H, 10.20; N, 6.14. Magnetic susceptibility (benzene-d_6): $\mu_{\mathrm{eff}} = 5.77\ \mu_{\mathrm{B}}$.

Characterization of ArN=C(Me)−(Me)C=NArFe(CO)$_3$ (14). Anal. Calcd for C$_{31}$H$_{40}$N$_2$FeO$_3$: C, 68.38; H, 7.40; N, 5.14. Found: C, 68.28; H, 7.06; N, 5.01. ^{1}H NMR (benzene-d_6): δ 1.04 (d, 6.87 Hz, CHMe_2), 1.41 (d, 6.60 Hz, CHMe_2), 1.51 (s, 6H, Me), 2.99 (sept, 6.87 Hz, 4H), 7.09−7.22 (m, 6H, Ar). ^{13}C NMR (benzene-d_6): δ 17.59 (CHMe_2), 24.72 (CHMe_2), 24.72 (CHMe$_2$), 28.34 (CH$_3$), 124.34 (Ar), 127.53 (Ar), 140.77 (Ar), 151.37 (Ar), 152.27(C=N), 212.94 (CO). IR (pentane): ν 2030, 1959 cm^{-1}.

Preparation of ArN=C(Me)−(Me)C=NArFe(CH$_2$SiMe$_3$)(C$_6$F$_5$) (15). A 20 mL scintillation vial was charged with 0.100 g (0.157 mmol) of **5** and approximately 5 mL of pentane. A 10 mL pentane solution containing 0.080 g (0.157 mmol) of B(C$_6$F$_5$)$_3$ was added to the vial, resulting in a dark green solution. After 30 min, the pentane was removed in vacuo, yielding a green solid. Successive recrystallizations from pentane were required to remove Me$_3$SiCH$_2$B(C$_6$F$_5$)$_3$ and yielding 0.060 g (55%) of pure **15**. Anal. Calcd for C$_{38}$H$_{51}$BF$_5$N$_2$SiFe: C, 63.86; H, 7.19; N, 3.92. Found: C, 63.78; H, 6.84; N, 3.28. ^{2}H NMR (benzene): δ 28.20 ppm (12.02, 6D). ^{19}F NMR (benzene-d_6): δ −162.32 (m, 2F, m−C$_6$F$_5$), −154.04 (s, 1F, C$_6$F$_5$), −139.06 (m, 2F, C$_6$F$_5$).

Preparation of [(−)-(Sparteine)Fe(CH$_2$SiMe$_3$)][B(C$_6$F$_5$)$_3$CH$_2$SiMe$_3$] (16). A 20 mL scintillation vial was charged with 0.020 g (0.0431 mmol) of **8** and 0.022 g (0.0431 mmol) of B(C$_6$F$_5$)$_3$. Approximately 5 mL of pentane was added. The solution turned bright yellow and a viscous oil settled out. The pentane was decanted and the oil dried in vacuo, yielding 0.024 g (57%) of **16**. Anal. Calcd for C$_{41}$H$_{48}$N$_2$Si$_2$F$_{15}$BFe: C, 50.42; H, 4.94; N, 2.87. Found: C, 50.01; H, 4.43; N, 3.03. ^{19}F NMR (bromobenzene-d_5): δ −161.49 (62.05, 3F), −158.69 (96.74, 6F),

−124.45 (88.82, 6F). ^{11}B NMR (bromobenzene-d_5): δ −14.52 ppm ($\Delta\nu_{1/2}$ = 92 Hz).

Preparation of (−)-(Sparteine)Fe($CH_2C_6H_5$)(B(C_6F_5)$_3$-$CH_2C_6H_5$) (17). The same procedure was used as that for **16** using 0.020 g (0.042 mmol) of **10** and 0.022 g (0.042 mmol) of B(C_6F_5)$_3$, yielding 0.025 g (60%) of a thick yellow oil identified as **17**. Anal. Calcd for $C_{47}H_{40}N_2F_{15}BFe$: C, 57.34; H, 4.10; N, 2.85. Found: C, 56.97; H, 3.84; N, 2.96. ^{19}F NMR (bromobenzene-d_5): δ −164.72 (113.11, 6F), −163.00 (112.17, 3F), −126.41 (114.19, 6F). ^{11}B NMR (bromobenzene-d_5): δ −14.75 ppm ($\Delta\nu_{1/2}$ = 113 Hz).

Preparation of [(*S*)-(^{t}BuBox)Fe(CH_2SiMe_3)][B(C_6F_5)$_3$-CH_2SiMe_3] (18). The same procedure was used as that for **16** using 0.020 g (0.0382 mmols) of **11** and 0.020 g (0.0382 mmols) of B(C_6F_5)$_3$ and yielding 0.029 g (72%). Anal. Calcd for $C_{43}H_{52}N_2O_2F_{15}BSi_2Fe$: C, 49.82; H, 5.06; N, 2.70. Found: C, 49.54; H, 5.16; N, 2.67. ^{19}F NMR (bromobenzene-d_5): δ −162.61 (65.29, 3F), −160.53 (126.89, 6F), −128.18 (144.03, 6F). ^{11}B NMR (bromobenzene-d_5): δ −14.48 ppm ($\Delta\nu_{1/2}$ = 181 Hz).

Preparation of [(*S*)-(^{t}BuBox)Fe($CH_2C_6H_5$)][B(C_6F_5)$_3$-$CH_2C_6H_5$] (19). The same procedure was used as that for **16** using 0.020 g (0.038 mmols) of **12** and 0.19 g (0.038 mmols) of B(C_6F_5)$_3$ and yielding 0.026 g (65%) of **19**. Anal. Calcd for $C_{49}H_{44}N_2O_2F_{15}BSi_2Fe$: C, 56.35; H, 4.25; N, 2.86. Found: C, 56.01; H, 4.44; N, 2.81. ^{19}F NMR (bromobenzene-d_5): δ −162.93 (90.90, 3F), −161.82 (76.11, 3F), −129.24 (75.55, 6F). ^{11}B NMR (bromobenzene-d_5): δ −13.12 ppm ($\Delta\nu_{1/2}$ = 108 Hz).

Ethylene Polymerization Procedure. A 100 mL Fischer−Porter bottle was charged with approximately 40 mL of toluene, 400 equiv of solid MAO, and a stirbar and was sealed. A syringe was charged with 0.025 mmol of the appropriate iron catalyst slurried in approximately 3 mL of toluene. The needle of the syringe was capped with a septum to avoid exposure to air and leakage. The Fischer−Porter bottle was then purged through several times with ethylene. At a pressure of 15 psi, the catalyst solution in the syringe was added. The bottle was then sealed and the pressure was increased to 90 psi. The polymerization was run at ambient temperature for approximately 12 min, at which time the reaction mixture was very viscous. The reaction was quenched with a 25% hydrochloric acid/methanol solution. **Warning: Highly exothermic; vigorous bubbling and heat evolution observed.** The solution was transferred to a beaker with 300 mL of the acidic methanol solution. This was allowed to stir for several hours, resulting in the precipitation of polyethylene. The polymer was then collected by filtration and dried in vacuo. The resulting polymer was characterized by its melting temperature as determined by DSC.

General Hydrogenation Procedure. A thick walled glass vessel was charged with 0.028 mmol of catalyst, approximately 1 mL of toluene, and a stirbar. Approximately 0.5 mL of 1-hexene was vacuum transferred into a calibrated tube. This was then vacuum transferred into the thick walled glass vessel followed by the addition of 4 atm of dihydrogen. The reaction was stirred for 22 h at ambient temperature and the reaction periodically analyzed by GC.

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Supporting Information Available: SQuID magnetic data for **15** as well as crystallographic data for **3**, **6**, **8**, **11**, and **15** including full atom-labeling schemes, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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