ORGANOMETALLICS

Synthesis, Electronic Structure, and Alkene Hydrosilylation Activity of Terpyridine and Bis(imino)pyridine Iron Dialkyl Complexes

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Supporting Information

ABSTRACT: Iron dialkyl complexes, $[N_3]Fe(CH_2SiMe_3)_2$, with three different classes of tridentate, nitrogen-based " $[N_3]$ ligands, aryl-substituted bis(imino)pyridines, terpyridine, and pyridine bis(oxazoline), have been synthesized and evaluated in the catalytic hydrosilylation of olefins with tertiary silanes. The 2,2':6',2"-terpyridine (terpy) complex, (terpy)Fe-(CH₂SiMe₃)₂, was prepared either via alkylation of (terpy)-FeCl₂ with LiCH₂SiMe₃ or by pyridine displacement from (pyridine)₂Fe(CH₂SiMe₃)₂ by free terpyridine. The aryl-



substituted bis(imino)pyridine compounds, (^RPDI)Fe(CH₂SiMe₃)₂ (^RPDI = 2,6-(2,6-R₂-C₆H₃N=CMe)₂C₅H₃N), with smaller 2,6-dialkyl substituents (R = Et, Me) or a 2-^{*i*}Pr substituent (^{2-*i*Pr}PDI)Fe(CH₂SiMe₃)₂ (^{2-*i*Pr}PDI = 2,6-(2-^{*i*}Pr-C₆H₄N= CMe)₂C₅H₃N, are effective precursors (0.5 mol %) for the anti-Markovnikov hydrosilylation of 1-octene with (Me₃SiO)₂MeSiH and (EtO)₃SiH over the course of 1 h at 60 °C. No hydrosilylation activity was observed with Et₃SiH. The most hindered member of the series, $({}^{iPr}PDI)Fe(CH_2SiMe_3)_2$, and the pyridine bis(oxazoline) iron compound, $(R,R)-({}^{iPr}Pybox)Fe(CH_2SiMe_3)_2$ (^{iPr}Pybox = 2,6-bis[isopropyl-2-oxazolin-2-yl]pyridine), were inactive for the hydrosilylation of 1-octene with all tertiary silanes studied. By contrast, the terpyridine precursor, (terpy)Fe(CH₂SiMe₃)₂, reached >95% conversion at 60 °C with Et₃SiH and (Me₃SiO)₂MeSiH. In addition, the hydrosilylation of vinylcyclohexene oxide was accomplished in the presence of 1.0 mol % (terpy)Fe(CH₂SiMe₃)₂, demonstrating functional group compatibility unique to this compound that is absent from bis(imino)pyridine iron compounds. The electronic structures of all three classes of iron dialkyl compounds have been evaluated by a combination of X-ray diffraction, magnetochemistry, Mössbauer spectroscopy, and density functional theory calculations. All of the compounds are best described as high-spin iron(III) compounds with antiferromagnetic coupling to chelate radical anions.

INTRODUCTION

Transition-metal-catalyzed alkene hydrosilylation is a key transformation in the commercial synthesis of numerous silicones with applications in personal care, agrochemical, adhesive, and molding products.^{1,2} Most commercial silicones are derived from the anti-Markovnikov addition of a tertiary silane to a terminal alkene, motivating the discovery of catalysts that exhibit exclusive terminal selectivity. For over three decades, platinum compounds, such as Karstedt's and Speier's catalysts, $Pt_2\{[(CH_2=CH)SiMe_2]_2O\}_3$ and $H_2PtCl_6 \cdot 6H_2O/^iPrOH$, respectively, have been the most widely used and studied.^{1,3,4} The success of these catalysts can be traced, in part, to their preference for formation of anti-Markovnikov products, high activity, commercial availability, and stability.

The high cost of platinum and the volatility of the precious metals market have motivated the search for more affordable alternatives.⁵ Accordingly, there has been a renewed interest in discovering catalysts based on iron and other earth-abundant transition metals.^{6,7} Early studies into iron-catalyzed alkene hydrosilylation centered on homoleptic iron carbonyl complexes, such as $Fe(CO)_5$ and $Fe_2(CO)_9$, which required hightemperature thermolysis or photolysis conditions for catalyst activation.⁸ In addition to Si-H addition, undesired products from dehydrogenative silvlation of the alkene were also observed depending on the specific reaction conditions.⁵ Most recently, Nakazawa and co-workers reported a unique and selective dehydrogenative silvlation-hydrogenation reac-

Received: May 23, 2012 Published: June 27, 2012 tion with 1,3-divinyldisiloxane in the presence of catalytic amounts of $(\eta^5-C_5H_5)Fe(CO)_2Me$.¹⁰ Ritter and co-workers have also reported imine-pyridine-supported iron precatalysts for the 1,4-addition of silanes, such as $(EtO)_3SiH$ to dienes.¹¹

In 2004, our laboratory reported the synthesis of the bis(imino)pyridine iron dinitrogen compound, $({}^{iPr}PDI)Fe(N_2)_n$ $({}^{iPr}PDI = 2,6-(2,6-{}^{i}Pr_2-C_6H_3N=CMe)_2C_5H_3N; n = 1, 2), and$ established its utility for the hydrosilylation of terminal alkenes with primary and secondary silanes.¹² This compound is also active for the more commercially relevant anti-Markovnikov addition of the tertiary silanes (EtO)₃SiH and (Me₂SiO)₂MeSiH (MD'M) to 1-octene and allvl polvethers.¹³ Reducing the size of the 2,6-aryl substituents, as in the cases of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2-N_2)$ and $[(^{Et}PDI)Fe(N_2)]_2(\mu_2-N_2)$, resulted in significantly higher hydrosilylation activity, a trend first observed in alkene hydrogenation catalysis.¹⁴ Notably, in all of these cases, no side products arising from olefin hydrogenation, isomerization, or dehydrogenative silylation were observed, establishing important advantages in the selectivity of the base metal catalysts relative to established platinum compounds.

The limited number of synthetically accessible bis(imino)pyridine iron bis(dinitrogen) complexes¹⁵ and their air and moisture sensitivity have inspired the search for alternative iron precatalysts. Iron dialkyl complexes, (^RPDI)Fe(CH₂SiMe₃)₂, are attractive as potential precatalysts given the number of derivatives that can be synthesized by straightforward pyridine displacement from (pyridine)₂Fe(CH₂SiMe₃)₂ by addition of the free bis(imino)pyridine.^{16–19} Here, we describe evaluation of terpyridine, bis(imino)pyridine, and pyridine bis(oxazoline) iron dialkyl complexes for the hydrosilylation of alkenes. In addition, the electronic structure of each class of compounds has been elucidated by a combination of magnetochemistry, structural, spectroscopic, and computational studies.

RESULTS AND DISCUSSION

Synthesis and Characterization of $(terpy)Fe-(CH_2SiMe_3)_2$. Iron complexes of 2,2':6',2"-terpyridine (terpy) were of interest due to the conceptual relationship to established bis(imino)pyridine compounds.^{13,14,20} During the course of these investigations, Nakazawa and co-workers have reported the hydrosilylation of 1-hexene with PhSiH₃, Ph₂SiH₂, and Me(Ph)SiH₂ upon treatment of a catalytic amount of various substituted (terpy)FeX₂ (X = Cl, Br) derivatives with NaBEt₃H, demonstrating the catalytic competency of this class of iron compounds.²¹ High activity for mono- and disilylation of the terminal alkene was observed upon heating to 100 °C. These mixtures were reported to be inactive for the hydrosilylation of 1-hexene or 1-octene with tertiary silanes and for the hydrosilylation of internal olefins.

Attempts to prepare a terpyridine iron dinitrogen complex by reduction of (terpy) FeX_2 (X = Cl_2^{22} Br) with excess 0.5% sodium amalgam or 2 equiv of NaBEt₃H produced an intractable mixture of products. To avoid the complications of reductive methods, the synthesis of iron dialkyl complexes was pursued. Previous studies from our group have established that such compounds are effective precatalysts for aldehyde and ketone hydrosilylation, and the synthesis of these compounds is general among tridentate [N₃] ligands.¹⁹ The desired iron dialkyl complex, (terpy)Fe(CH₂SiMe₃)₂, was synthesized either by straightforward addition of the free ligand to (pyridine)₂Fe-(CH₂SiMe₃)₂ in pentane solution or by direct alkylation of (terpy)FeCl₂ with LiCH₂SiMe₃ (Scheme 1). The latter route is

Scheme 1. Synthetic Routes to (terpy)Fe(CH₂SiMe₃)₂



preferred as yields between 85% and 90% were reproducibly obtained. This specific alkyl group was chosen due to the commercial availability of the requisite lithio salt, stability to β -H elimination, and established precedent in bis(imino)pyridine iron chemistry.^{16,17}

Crystals of $(terpy)Fe(CH_2SiMe_3)_2$ suitable for X-ray diffraction were obtained from a concentrated diethyl ether solution stored at -35 °C. A representation of the molecule is presented in Figure 1, and selected metrical parameters are



Figure 1. Solid-state molecular structure of (terpy)Fe(CH₂SiMe₃)₂ at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

reported in Table 1. In the solid-state structure of (terpy)Fe-(CH₂SiMe₃)₂, the geometry about the iron is best described as distorted trigonal-bipyramidal with the N(2), C(12), and C(12I) defining the equatorial plane. The large SiMe₃ groups are directed over the plane of the terpyridine chelate, likely to avoid steric interactions.

It is now well established that perturbations in ligand bond distances are diagnostic of redox activity, including terpyridine ligands.²³ To probe the role of the terpyridine ligand in the electronic structure of $(terpy)Fe(CH_2SiMe_3)_2$, the bond distances of the tridentate chelate were compared to those of free terpyridine²⁴ as well as a coordination complex, (terpy)-ZnCl₂,²⁵ where the ligand is undoubtedly in its neutral form (Table 1). Also contained in Table 1 are the bond distances for [$(terpy)_2Cr]PF_{6'}$ a coordination compound with an established

Table	1. S	elected	Bond	Distances	(A	.) and	l Ang	les (a	deg)	for	(terpy)Fe(CH ₂ S	iMe ₃)	2
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	$(terpy)Fe(CH_2SiMe_3)_2$	terpyridine	(terpy)ZnCl ₂	$[(terpy^{1-})_2Cr]PF_6$		
M(1)-N(1)	2.150(2)		2.196(3)	2.047(3)		
M(1)-N(2)	2.014(2)		2.112(1)	1.928(2)		
M(1)-C(12)	2.073(2)					
N(1)-C(5)	1.353(2)	1.343(2)	1.340(5)	1.369(6)		
N(2)-C(6)	1.375(2)	1.342(3)	1.342(4)	1.381(5)		
C(5) - C(6)	1.457(2)	1.496(3)	1.487(6)	1.448(5)		
C(6) - C(7)	1.390(2)	1.397(3)	1.385(6)	1.388(6)		
C(7) - C(8)	1.386(2)	1.381(3)	1.393(5)	1.391(7)		
C(12)-Fe(1)-C(12I)	118.12(8)					
N(1)-Fe(1)-N(2)	75.48(3)		74.54(9)	78.68(15)		
N(1)-Fe(1)-N(1I)	150.96(7)		149.09(9)	157.35(15)		
^a Distances for free terpyridine, ²³ (terpy)ZnCl ₂ , ²¹ and $[(terpy^{1-})_2Cr]PF_6^{22}$ are included for comparison.						

Scheme 2. Aryl-Substituted Bis(imino)pyridine Iron Dialkyl Compounds Evaluated for Catalytic Hydrosilyation of 1-Octene Using Tertiary Silanes



terpyridine radical anion.²² The bond distances of the chelate in $(terpy)Fe(CH_2SiMe_3)_2$ are most consistent with a monoreduced, anionic radical ligand with the most pronounced distortions in the central pyridine ring.

The catalytic performance of $(terpy)Fe(CH_2SiMe_3)_2$ was assayed in the hydrosilylation of 1-octene with tertiary silanes. Interest in the resulting alkyl silanes derives from their application as agricultural adjuvants, and as a sensory and performance enhancer in cosmetic formulations. Examples of bis(imino)pyridine iron dialkyls and the pyridine bis(oxazoline) compound, (R,R)-(^{iPr}Pybox)Fe(CH_2SiMe_3)₂, were also included in this study for comparison. Depictions of these compounds and their shorthand designations are presented in Scheme 2. Two examples, $rac/meso-(^{2\cdotiPr}PDI)Fe(CH_2SiMe_3)_2$ and (^{iPr}Pybox)Fe(CH_2SiMe_3)₂, do not have synthetically accessible iron dinitrogen compounds, and thus the iron dialkyls represent a convenient entry point to assay the catalytic performance of these specific iron—chelate combinations.

The results of the catalytic hydrosilylation assays of 1-octene are summarized in Table 2. Each reaction was conducted neat at 60 °C using 0.5 mol % of the iron complex. For the 1-octene hydrosilylations with (terpy)Fe(CH₂SiMe₃)₂ and the tertiary silanes Et₃SiH and MD'M, >95% conversion to the corresponding anti-Markovnikov alkyl silane was observed after 1 h at 60 °C. Small (<5%), yet detectable, amounts of 1-silyl-1-octene, arising from dehydrogenative silylation, were also observed by gas chromatography and NMR spectroscopy. No catalytic turnover was observed with (EtO)₃SiH due to competing redistribution of the silane to (EtO)₄Si (and likely SiH₄) under catalytic conditions.^{26,27} No catalytic activity was observed with the pyridine bis(oxazoline) iron dialkyl complex, (*R*,*R*)-(^{*i*Pr}Pybox)Fe(CH₂SiMe₃)₂.

The catalytic performance of the bis(imino)pyridine iron dialkyl compounds was dependent on both the size of the aryl

 Table 2. Catalytic Hydrosilylation of 1-Octene with Tertiary

 Silanes in the Presence of Various Iron Dialkyl Complexes

C_6H_{13} + R ₃ Si-H $\frac{0.5 \text{ mol }\%}{60 \text{ °C}}$ 1 hour	[Fe] [5]	C ₆ H ₁₃
compound	R ₃ Si-H	percent conversion
(terpy)Fe(CH ₂ SiMe ₃) ₂	Et ₃ SiH	>95
	MD'M	>95
	(EtO) ₃ SiH	NR ^a
(^{<i>i</i>Pr} PDI)Fe(CH ₂ SiMe ₃) ₂	Et ₃ SiH	NR
	MD'M	NR
	(EtO) ₃ SiH	NR
(^{Et} PDI)Fe(CH ₂ SiMe ₃) ₂	Et ₃ SiH	NR
	MD'M	>95
	(EtO) ₃ SiH	>95
(MePDI)Fe(CH ₂ SiMe ₃) ₂	Et ₃ SiH	NR
	MD'M	>95
	(EtO) ₃ SiH	>95
<i>rac/meso-</i> (^{2-<i>i</i>Pr} PDI)Fe(CH ₂ SiMe ₃) ₂	Et ₃ SiH	NR
	MD'M	>95
	(EtO) ₃ SiH	>95
(R,R) - $(^{iPr}Pybox)$ Fe $(CH_2SiMe_3)_2$	Et ₃ SiH	NR
	MD'M	NR
	(EtO) ₃ SiH	NR
NR = no reaction defined as <5%	conversion at	1 h.

substituents and the identity of the tertiary silane. As was observed with related bis(imino)pyridine iron dinitrogen compounds,¹³ Et₃SiH is the least reactive silane with no turnover being observed after prolonged periods at 60 °C. The most substituted compound in the series, (^{*i*Pr}PDI)Fe-(CH₂SiMe₃)₂, also exhibited no catalytic hydrosilylation activity. For the less sterically protected compounds, selective

anti-Markovnikov hydrosilylation of 1-octene was observed with the alkoxy silanes, MD'M and $(EtO)_3SiH$, after 1 h at 60 °C. For $(^{Et}PDI)Fe(CH_2SiMe_3)_2$ and $(^{Me}PDI)Fe(CH_2SiMe_3)_2$, the higher temperatures required for catalytic activity are a consequence of initiation of the iron compounds, likely through iron–carbon bond homolysis to generate the active species.

The utility of the iron dialkyl complexes for the catalytic hydrosilylation of 1-octene prompted exploration of the scope of these compounds with other substrates of commercial importance. Vinylcyclohexene oxide (VCHO, used as a mixture of cis and trans isomers) was selected due to the utility of the silvlated product for UV-release coating applications, textile finishes, and for preparing silicone-modified organic polymers.²⁸ Attempted hydrosilylation with the iron dinitrogen compounds, $[(^{R}PDI)Fe(N_{2})]_{2}(\mu_{2}-N_{2})$ (R = Me, Et) or the corresponding iron dialkyl complexes, (^RPDI)Fe(CH₂SiMe₃)₂, and MD'M resulted in decomposition of the iron compounds, likely due to incompatibility with the epoxide functional group.²⁹ Similar results have been observed with Karstedt's catalyst where up to 50% decomposition of the platinum compound has been reported.³ Introduction of N-heterocyclic carbene ligands to the platinum-catalyzed reactions suppresses this competing decomposition pathway.³ By contrast, complete conversion to hydrosilylated product was achieved using 1 mol % (terpy)Fe(CH₂SiMe₃)₂ at 60 °C at 1 h. Exclusive conversion to the anti-Markovnikov product was observed and demonstrates the unique function of the terpyridine iron dialkyl precatalysts in this process as compared to their bis(imino)pyridine iron and precious metal counterparts (eq 1).



Electronic Structure of Bis(imino)pyridine and Terpyridine Iron Dialkyl Complexes. The electronic structures of the three classes of iron dialkyl complexes used in this study, bis(imino)pyridine, terpyridine, and pyridine bis(oxazoline), were investigated using a combination of metrical parameters from X-ray diffraction, magnetic measurements, Mössbauer spectroscopy, and DFT calculations. The redox activity of the bis(imino)pyridines^{30,31} and terpyridines^{22,32–34} is now wellestablished, although this possibility has not been as thoroughly investigated for the corresponding pyridine bis(oxazolines). Electrochemical studies from our laboratory have established that this last class of chelate is the most challenging to reduce in the series.^{19a,22}

Three specific compounds were selected for this study: (^{Et}PDI)Fe(CH₂SiMe₃)₂, (terpy)Fe(CH₂SiMe₃)₂, and (*R*,*R*)-(^{iPr}Pybox)Fe(CH₂SiMe₃)₂. Our laboratory has previously reported that the bis(imino)pyridine and pyridine bis-(oxazoline) iron dialkyls exhibit magnetic moments at 23 °C, consistent with four unpaired electrons, and are *S* = 2 compounds.^{19a} Solid-state measurements at 23 °C on (terpy)-Fe(CH₂SiMe₃)₂ produced an effective magnetic moment of 4.6 μ B, also diagnostic of an *S* = 2 ground state and a high spin state for the iron center.

Zero-field, ⁵⁷Fe Mössbauer spectroscopic measurements were also performed (80 K) on all three classes of iron dialkyl complexes. The experimentally determined isomer shifts (δ) and quadrupole splittings (ΔE_Q) are reported in Table 3. Also

Table 3. Experimental and Computationally Determined Zero-Field, ⁵⁷Fe Mössbauer Parameters^a

compound	$\delta~({ m mm\cdot s^{-1}})$	$\Delta E_{\rm Q} ({\rm mm} \cdot {\rm s}^{-1})$
$(terpy)Fe(CH_2SiMe_3)_2$	0.29	2.37
	0.22	+2.62
(^{Et} PDI)Fe(CH ₂ SiMe ₃) ₂	0.26	2.66
	0.25	+2.80
$(R,R)-(^{iPr}Pybox)Fe(CH_2SiMe_3)_2$	0.26	3.15
	0.25	+3.49

^{*a*}The experimental values were measured at 80 K. Computed values are presented in italics. All experimental quadrupole splittings are absolute values.

reported in Table 3 are DFT-computed (vide infra) parameters for all three compounds. The isomer shifts for all three iron dialkyl complexes are nearly identical, indicating the same electronic structure.³⁵ It is also noteworthy that the isomer shifts are lower than the range typically accepted for high-spin iron(II) compounds, suggesting that the traditional electronic structure description of a ferrous compound with a redoxneutral chelate is not an accurate representation of the true ground states of the molecules.

Full molecule density functional theory (DFT) calculations were carried out on all three compounds to gain additional insight into the electronic structures of the iron dialkyl complexes and evaluate the possibility of redox-active chelates. The accuracy of the calculations was assayed by comparison of experimental and computed metrical parameters for each compound (see the Supporting Information) as well as by comparison of computed and experimental ⁵⁷Fe Mössbauer parameters (Table 3). On the basis of the magnetic data, two possible electronic structure models were explored: a high-spin ferrous center ($S_{\text{Fe}} = 2$) with a redox-innocent chelate ($S_{\text{L}} = 0$) and a high-spin ferric center $(S_{\text{Fe}} = 5/2)$ antiferromagnetically coupled to a chelate radical anion $(S_L = 1/2)$. These configurations correspond to a spin-unrestricted quintet and a broken symmetry (BS) 5,1 approach, respectively. At the B3LYP level of density functional theory, both (EtPDI)Fe- $(CH_2SiMe_3)_2$ and $(R,R)-({}^{iPr}Pybox)Fe(CH_2SiMe_3)_2$ spontaneously broke symmetry and converged to the redox-active, BS(5,1) solution. For $(terpy)Fe(CH_2SiMe_3)_2$, both redoxinnocent and redox-active solutions were found. Comparison of the total energies revealed that the broken-symmetry solution was 1.9 kcal/mol lower in energy than the spin-unrestricted solution. For all of the broken symmetry solutions, excellent agreement between the experimental and the computed data was observed. While the metrical parameters of (terpy)Fe-(CH₂SiMe₃)₂ were acceptably reproduced by the redoxinnocent, spin-unrestricted quintet model, an isomer shift of 0.45 mm \cdot s⁻¹ and quadrupole splitting of +2.92 mm \cdot s⁻¹ were computed, which is outside the generally accepted range.³⁶

Qualitative molecular orbital diagrams and spin density plots derived from the BS(5,1) solutions are presented in Figures 2 and 3, respectively. The molecular orbital diagrams illustrate the high-spin ferric centers engaged in antiferromagnetic coupling with each of the chelate radical anions. Thus, the combined computational and experimental data clearly establish that all



Figure 2. Qualitative molecular orbital diagrams of $(^{Et}PDI)Fe(CH_2SiMe_3)_2$ (left), $(terpy)Fe(CH_2SiMe_3)_2$ (middle), and $(R,R)-(^{iPr}Pybox)Fe-(CH_2SiMe_3)_2$ (right).



Figure 3. Spin density plots obtained from a Mulliken population analysis of the BS(5,1) solutions for $(^{Et}PDI)Fe(CH_2SiMe_3)_2$ (left), (terpy)Fe(CH_2SiMe_3)_2 (middle), and (*R*,*R*)- $(^{Pt}Pybox)Fe(CH_2SiMe_3)_2$ (right).

three ligand classes are redox-active in iron dialkyl chemistry. The overlap (S) values are high for each example, ranging between 0.73 and 0.76, and indicate a high degree of covalency between the metal (principally d_{xz}) and ligand radical (principally b_2) orbitals. It is also noteworthy that the spin density plots (Figure 3) establish that the central pyridine ring in both the terpyridine and the pyridine bis(oxazoline) iron dialkyl complexes contains most of the radical character, consistent with the metrical parameters determined by X-ray diffraction. Wieghardt and co-workers have also observed a more reduced central pyridine ring in hexacoordinate chromium(III) coordination compounds with terpyridine radical anions.²²

CONCLUDING REMARKS

Iron dialkyl complexes with three different types of meridionally coordinating $[N_3]$ -based chelates have been synthesized and their electronic structures established as high-spin ferric compounds with redox-active chelate radical

monoanions. The terpyridine iron dialkyl, $(terpy)Fe-(CH_2SiMe_3)_2$, is an active precatalyst for the hydrosilylation of 1-octene and VCHO with tertiary silanes. Successful hydrosilylation of the latter type of substrate represents a unique function of the terpyridine compounds. Aryl-substituted bis(imino)pyridine iron dialkyl complexes were also found to be effective precursors of 1-octene hydrosilylation using alkoxy-substituted tertiary silanes. These compounds are a more synthetically accessible class of iron precatalyst than the previously reported dinitrogen compounds, although higher temperatures are required to observe catalytic turnover.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were carried out using a standard high-vacuum line, Schlenk or cannula techniques, or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were

dried and deoxygenated using literature procedures.³⁷ Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The iron compounds, $({}^{iPr}PDI)Fe(CH_2SiMe_3)_2$, $({}^{Et}PDI)Fe(CH_2SiMe_3)_2$, $({$

¹H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to SiMe₄ using ¹H (residual) chemical shifts of the solvent as a secondary standard. ¹³C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. ¹³C chemical shifts are reported relative to SiMe₄ using chemical shifts of the solvent as a secondary standard where applicable. For paramagnetic molecules, the ¹H NMR data are reported with the chemical shift, followed by the peak width at half-height in hertz or multiplicity, followed by integration value and, where possible, peak assignment. Solution magnetic moments were determined by the method of Evans at 22 °C using a ferrocene standard unless otherwise noted. Magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with HgCo(SCN)₄. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NI.

GC analyses were performed using a Shimadzu GC-2010 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Shimadzu SHRXI-5MS capillary column (15 m \times 250 μ m). The instrument was set to an injection volume of 1 μ L, an inlet split ratio of 100:1, and inlet and detector temperatures of 120 and 250 °C, respectively. UHP-grade helium was used as carrier gas with a flow rate of 1.12 mL/min. The temperature program used for all the analyses is as follows: 80 °C, 1 min; 20 °C/min to 240 °C; 4 min. Quantification was assessed externally using calibration curves of peak area versus concentration covering the relevant concentration regime, to correct for sample-dependent detector response, using pure samples of the alkenes, silanes, and the hydrosilylation products. An aliquot of the reaction mixture was removed periodically, quenched by exposure to air and then diluted to a concentration covered within the calibration curves and analyzed by GC-FID. All reactions were performed under neat conditions, and an internal standard was not used to avoid dilution of the samples.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop, and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer 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.

Quantum-Chemical Calculations. All DFT calculations were performed with the ORCA program package.³⁸ The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level^{39–41} of DFT. This hybrid functional often gives better results for transitionmetal compounds than pure gradient-corrected functionals, especially with regard to metal–ligand covalency.⁴² The all-electron Gaussian basis sets were those developed by the Ahlrichs group.^{43–45} Triple- ζ quality basis sets def2-TZVP with one set of polarization functions on the metals and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used, that were of double- ζ quality in the valence region and contained a polarizing set of d-functions on the non-hydrogen atoms. Auxiliary basis sets were chosen to match the orbital basis.^{46–48} The RIJCOSX^{49–51} approximation was used to accelerate the calculations. Throughout this paper, we describe our computational results by using the broken-symmetry (BS) approach by Ginsberg⁵² and Noodleman.⁵³ Because several broken-symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation $BS(m,n)^{54}$ has been adopted, where m(n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. Canonical and corresponding⁵⁵ orbitals, as well as spin density plots, were generated with the program Molekel.⁵⁶

Nonrelativistic single-point calculations on the optimized geometry were carried out to predict Mössbauer spectral parameters (isomer shifts and quadrupole splittings). These calculations employed the CP(PPP) basis set for iron.⁵⁷ The Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{58,59}

Preparation of (terpy)Fe(CH₂SiMe₃)₂. A round-bottom flask was charged with 0.360 g (1.0 mmol) of (terpy)FeCl₂ and approximately 10 mL of diethyl ether. The flask was chilled to -35 °C, and a solution containing 0.188 g (2.0 mmol) of LiCH₂SiMe₃ and approximately 10 mL of diethyl ether was added. A color change was observed immediately upon addition of the solution, and the resulting slurry was stirred and warmed to ambient temperature. After 1 h, the reaction mixture was filtered through Celite and the volatiles were removed in vacuo. The resulting purple solid was washed with approximately 5 mL of cold pentane, yielding 0.400 g (87%) of (terpy)Fe(CH₂SiMe₃)₂. Analysis for C₂₃H₃₃FeN₃Si₂ Calcd: C, 59.59; H, 7.18; N, 9.06. Found: C, 59.19; H, 6.81; N, 9.10. Magnetic susceptibility (MSB, 23 °C): μ_{eff} = 4.6 μ_B.¹H NMR (benzene-*d*₆, 20 °C): δ = 319.80 (bs, 1H), 194.68 (bs, 2H), 154.65 (bs, 2H), 115.20 (bs, 2H), 59.36 (bs, 2H), 38.56 (bs, 2H), 8.73 (bs, 18H).

Preparation of rac/meso-(^{2-iPr}PDI)Fe(CH₂SiMe₃)₂. A 20 mL scintillation vial was charged with 0.443 g (1.00 mmol) of (py)₄FeCl₂, and approximately 3-5 mL pentane was added. The resulting slurry was cooled to -35 °C for approximately 30 min, after which time a pentane solution containing 0.188 g of LiCH₂SiMe₃ (2.00 mmol) was added dropwise. A color change from yellow to purple was observed upon warming. The reaction mixture was stirred for 1-2 h at ambient temperature. After this time, the reaction mixture was filtered through Celite and the filtrate was transferred to a fresh scintillation vial. A pentane slurry containing 0.397 g of ^{2-iPr}PDI (1.00 mmol) was added dropwise to the stirring solution. The purple solution immediately turned dark violet. This mixture was stirred for 1-2 h at ambient temperature. The mixture was then cooled to -35 °C and filtered to furnish 0.400 g (65%) of a dark purple crystalline solid identified as (^{2-iPr}PDI)Fe(CH₂SiMe₃)₂. Analysis for C₃₅H₅₃N₃FeSi₂ Calcd: C, 62.96; H, 8.51; N, 6.69. Found: C, 62.43; H, 9.26; N, 7.83. Magnetic susceptibility: $\mu_{\text{eff}} = 4.7 \ \mu\text{B}$ (benzene- d_6 , 23 °C). ¹H NMR (benzene d_6): δ = 323.97 (1H, *p*-py), 317.10 (1H, *p*-py), 51.65 (147 Hz, 2H, *m*pyr), 49.73 (147 Hz, 2H, m-py), 17.52 (136 Hz, 1H, m-py), 14.97 (64 Hz, 1H), 13.64 (147 Hz, 2H, m-py), 11.35 (295 Hz), 17.56, -18.77 (100 Hz), -151.50 (737 Hz, 6H, C(CH₃)), -159.46 (737 Hz, 6H, $C(CH_3)).$

General Procedure for the Hydrosilylation of 1-Octene. A scintillation vial was charged with 0.150 g (1.33 mmol) of 1-octene and 1.33 mmol of the silane (0.295 g of MD'M; 0.220 of (EtO)₃SiH; 0.155 g of Et₃SiH). To this stirring solution was added 0.5 mol % (0.007 mmol) of the iron complex (0.003 g of (terpy)Fe(CH₂SiMe₃)₂; 0.005 g of (^{iPr}PDI)Fe(CH₂SiMe₃)₂; 0.004 g of (^{Et}PDI)Fe(CH₂SiMe₃)₂; 0.004 g of (^{Et}PDI)Fe(CH₂SiMe₃)₂; 0.004 g of (^{ct}PDI)Fe(CH₂SiMe₃)₂; 0.004 g of (^{ct}PDI)Fe(CH₂SiMe₃)₂; 0.004 g of (CH₂SiMe₃)₂; 0.004 g of (CH₂SiMe₃)₂). The vial was sealed, and the reaction mixture was stirred in an oil bath at 60 °C for 1 h. The reaction was then quenched by exposure to air, and the resulting mixture was analyzed by NMR spectroscopy and gas chromatography. A resonance upfield at 0.41 ppm in the ¹H NMR spectrum was indicative of formation of the desired, previously characterized products. The retention time of the hydrosilylated products is between 7 and 8 min.

Hydrosilylation of Vinylcyclohexene Oxide (VCHO) with MD'M Using (terpy)Fe(CH₂SiMe₃)₂. A scintillation vial was charged with 0.150 g (1.33 mmol) of VCHO and 0.295 g (1.33 mmol) of MD'M. To this stirring solution was added 0.006 g (1.0 mol %) of

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 $(terpy)Fe(CH_2SiMe_3)_2$. The reaction was sealed and placed at the desired temperature for 1 h. Following this time, the reaction was quenched by opening the vessel to air and analyzed by ¹H NMR spectroscopy. Along with the disappearance of the Si–H and olefinic resonances, an upfield peak observed at 0.37 ppm was indicative of formation of the desired product.

(2-(7-Oxa-bicyclo[4.1.0]heptan-3-yl)ethyl)bis-(trimethylsiloxy)methylsilane (*cis* and *trans*). ¹H NMR (CDCl₃, 22 °C): 3.16-3.05 (m, 4H), 2.14 (t, 2H, 14.3 Hz), 2.07-1.90 (m, 2H), 1.84-1.72 (m, 1H), 1.72-1.60 (m, 1H), 1.59-1.41 (m, 3H), 1.40-1.20 (m, 5H), 1.19-0.94 (m, 6H), 0.45-0.30 (m, 4H), 0.09 (s, 36H), -0.01 (s, 6H).

ASSOCIATED CONTENT

S Supporting Information

Crystallographic details for $(terpy)Fe(CH_2SiMe_3)_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

We thank Momentive Performance Materials for financial support and the U.S. National Science Foundation and Deutsche Forschungsgemeinschaft for a Cooperative Activities in Chemistry between U.S. and German Investigators grant. C.M. acknowledges the Alexander von Humboldt Foundation for a Feodor Lynen postdoctoral fellowship. We also thank Dr. Marco Bouwkamp for initial experimental investigations into the electronic structure of bis(imino)pyridine iron dialkyl complexes.

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