ORGANOMETALLICS

Synthesis and Hydrogenation Activity of Iron Dialkyl Complexes with Chiral Bidentate Phosphines

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S Supporting Information

ABSTRACT: The activity of bis(phosphine) iron dialkyl complexes for the asymmetric hydrogenation of alkenes has been evaluated. High-throughput experimentation was used to identify suitable iron-phosphine combinations using the displacement of pyridine from $py_2Fe(CH_2SiMe_3)_2$ for precatalyst formation. Preparative-scale synthesis of a family of bis(phosphine) iron dialkyl complexes was also achieved using both ligand substitution and salt metathesis methods. Each of the isolated organometallic iron complexes was



INTRODUCTION

The asymmetric hydrogenation of prochiral alkenes has emerged as a powerful tool for the synthesis of single enantiomer compounds and relies almost exclusively on enantiopure transition-metal compounds as catalysts.^{1,2} Since the introduction of chiral bidentate phosphines by Kagan³ and later Knowles⁴ in the rhodium-catalyzed asymmetric hydrogenation of dehydroamino acids, this class of ligand has been one of the most widely explored in reactions of this type,⁵⁻¹⁰ has enabled expansion in substrate scope,^{11–13} and has been employed in commercial processes.^{14–17} Despite these tremendous advances, asymmetric hydrogenation with bis-(phosphine)-ligated rhodium and ruthenium catalysts typically relies on the presence of a coordinating functionality to achieve high enantioselectivity.^{2,18,19} For substrates that are minimally functionalized, chiral derivatives of Crabtree's catalyst using phosphine-oxazoline and related ligands have been developed.20-22

Catalysts that employ metals other than rhodium, ruthenium, and iridium offer the opportunity to overcome limitations with existing technology and may also offer cost and environmental advantages.^{23,24} Because of their widespread use, commercial availability, and demonstrated success in industrial processes, we sought to explore the application of enantiopure bidentate bis(phosphines) to asymmetric hydrogenation reactions with base metals such as iron and cobalt. Unlike carbonyl reductions, which are now well demonstrated with a host of base-metal catalysts,^{25,26} asymmetric alkene hydrogenations that operate



High-throughput experimentation, made possible by reproducible, high-yielding reactions between a suitable metal precursor and libraries of ligands, has proven invaluable for the discovery of precious-metal asymmetric alkene hydrogenation catalysts.^{17,33} Our laboratory recently reported that simple cobalt salts such as $CoCl_2$, $Co(OAc)_2$, and $Co(ClO_4)_2$. $6H_2O$ in combination with an appropriate activator are useful precursors for the evaluation of libraries of bidentate, enantiopure phosphines for the hydrogenation of functionalized and minimally functionalized alkenes.³⁴ Using this approach, highly active and enantioselective cobalt precatalysts were identified and rationally synthesized, isolated, and optimized.

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The success with cobalt inspired the study of analogous iron precursors. Iron-catalyzed alkene hydrogenation was first reported using thermally activated or photoactivated iron carbonyl complexes such as $Fe(CO)_5$ and $Fe_2(CO)_9$.^{35,36} Modification of these complexes by replacement of carbonyl ligands with weakly coordinating and labile η^2 -Si-H bonds in 1,2-bis(dimethylsilyl)benzene resulted in iron compounds that are active for the hydrogenation of unactivated terminal and internal olefins.³⁷ Reduced, aryl-substituted bis(imino)pyridine iron complexes have been reported by our laboratory that are highly active for the hydrogenation of unactivated alkenes under mild conditions.³⁸⁻⁴¹ Introduction of electron-donating substituents into the 4-position of the pyridine or replacing the imine donors with N-heterocyclic carbenes produced iron dinitrogen precatalysts that exhibited high activity for the hydrogenation of sterically hindered alkenes.⁴² Thomas has since reported in situ activation of iron dihalide complexes with ⁱPrMgCl for the hydrogenation of a host of alkenes under 50 bar of H₂⁴³ or using borohydride reductants.⁴⁴

To date, no asymmetric, iron-catalyzed alkene hydrogenation that yields alkanes with a synthetically useful enantiomeric excess has been reported. On the basis of our recent findings in cobalt chemistry, we sought to develop iron precursors compatible with high-throughput experimentation for the evaluation of libraries of chiral bidentate phosphines. Girolami and co-workers reported seminal synthetic and structural studies of iron dialkyl complexes bearing the sterically demanding chelating bis(phosphine) ⁱPr₂PCH₂CH₂PⁱPr₂ (dippe) and established formation of high-spin, idealized tetrahedral molecules in each case.^{45,46} Hydrogenolysis in *p*xylene or toluene resulted in formation of iron(0) arene complexes with liberation of alkane, and notably, no catalytic alkene hydrogenation was reported.⁴⁷ Our laboratory subsequently reported iron dialkyl complexes bearing α -diimine, bis(oxazoline), and (-)-sparteine supporting ligands.⁴⁸ In each case, high-spin (S = 2) tetrahedral molecules were isolated and exhibited poor activity for the hydrogenation of simple olefins such as 1-hexene with coordination of the arene solvent identified as a primary catalyst deactivation pathway.⁴⁹ Here we describe iron precursors for the high-throughput evaluation of established libraries of chiral bidentate phosphines in the catalytic asymmetric hydrogenation of alkenes. Examples of iron dialkyl complexes with representative examples of phosphines were prepared and structurally characterized and the isolated compounds also evaluated as precatalysts for olefin hydrogenation.

RESULTS AND DISCUSSION

Initial High-Throughput Evaluations. On the basis of the success obtained in cobalt chemistry,³⁴ initial high-throughput catalyst evaluation experiments were conducted using $py_2Fe-(CH_2SiMe_3)_2$ in combination with 24 chiral bidentate phosphines for the hydrogenation of *trans-* α -methylstilbene, dimethyl itaconate, and 3-methylindole. In an attempt to maximize identification of successful iron–-phosphine combinations, each experiment was conducted with 10 mol % of each the iron precursor and desired phosphine ligand in a 0.041 M solution of substrate in toluene with 34 atm (500 psi) of H₂. In all cases, no detectable catalytic hydrogenation activity was observed. A complete listing of the phosphines used in these experiments is presented in the Supporting Information.

The lack of activity prompted exploration of alternative iron sources and activators. In cobalt chemistry, the presence of pyridine proved deleterious for coordination of some phosphine ligands.³⁴ As such pyridine-free iron sources, FeCl₂ and Fe(OAc)₂ were selected as iron precursors with LiCH₂SiMe₃ and 4-F-BnZnCl as activators. Combinations that produced >5% conversion for the hydrogenation of *trans-α*-methylstilbene and *α*-isopropylstyrene are reported in Tables 1 and 2, respectively. Depictions of the structures of the

Table 1. Combinations of Iron Precursor, Activator, and Chiral Bidentate Phosphine for the Asymmetric Hydrogenation of *trans-* α -Methylstilbene

phosphine	iron source	activator	$(\%)^a$	ee (%)
SL-W001-1	$Fe(OAc)_2$	LiCH ₂ SiMe ₃	36.1	-0.2
SL-W005-2	$Fe(OAc)_2$	LiCH ₂ SiMe ₃	12.3	0.6
SL-T001-1	$Fe(OAc)_2$	4-F-BnZnCl	5.3	47.8
(+)-Cy-SEGPHOS	$Fe(OAc)_2$	4-F-BnZnCl	5.1	40.8
SL-W001-1	FeCl ₂	4-F-BnZnCl	5.0	32.1
^{<i>a</i>} Conversions determixture.	mined by ga	as chromatograph	y of the	reaction

Table 2. Combinations of Iron Precursor, Activator, and Chiral Bidentate Phosphine for the Asymmetric Hydrogenation of α -Isopropylstyrene

phosphine	iron source	activator	$(\%)^a$	ee (%)
SL-W003-1	$Fe(OAc)_2$	LiCH ₂ SiMe ₃	14.8	3.0
SL-W001-1	$Fe(OAc)_2$	LiCH ₂ SiMe ₃	13.9	4.0
(+)-Cy-SEGPHOS	$Fe(OAc)_2$	LiCH2SiMe3	7.3	6.1
SL-J010-1	$Fe(OAc)_2$	LiCH ₂ SiMe ₃	7.0	5.2
SL-J009-1	FeCl ₂	LiCH ₂ SiMe ₃	6.4	8.5
^a Conversions deter mixture	mined by ga	as chromatograph	y of the	reaction

phosphines and their shorthand designations are presented in Figure 1. In general, both the conversion and the enantioselectivities are poor, with ferrocenyl-based ligands yielding the most promising results. These findings are in contrast with those for cobalt, where bidentate phosphines with two-carbon linkers proved the most effective.

Preparation and Characterization of Iron Dialkyl Compounds with Bidentate Phosphines. The poor catalytic performance observed in the high-throughput evaluation experiments prompted a more detailed study of the organometallic chemistry of phosphine-ligated iron dialkyl complexes. Bis(diphenyl)phosphinoethane (dppe) was selected for initial synthetic efforts due to its commercial availability and structural similarity to dippe, the chelating phosphine at the core of Girolami's seminal reports.⁴⁵ Relevant to the highthroughput experiments, $py_2Fe(CH_2SiMe_3)_2$, originally described by Cámpora and co-workers,⁵⁰ was generated in situ as a purple pentane solution and 1 equiv of dppe was added. A yellow precipitate identified as $(dppe)Fe(CH_2SiMe_3)_2$ was isolated in 77% yield (eq 1). An alternative procedure was





Figure 1. Enantiopure bidentate phosphines that produced modest activity in the asymmetric hydrogenation of *trans-\alpha*-methylstilbene and α -isopropylstyrene.

developed whereby dppe was added to a THF solution of $FeCl_2$ followed by dialkylation with 2 equiv of LiCH₂SiMe₃. This route furnished (dppe)Fe(CH₂SiMe₃)₂ in 91% yield and is the preferred method of preparation.

A solution magnetic moment (Evans method) of 4.9 $\mu_{\rm B}$ was measured in benzene- d_6 at 23 °C and established a high-spin, S = 2 compound. The solid-state structure of (dppe)Fe-(CH₂SiMe₃)₂ was determined by X-ray diffraction (Figure 2)



Figure 2. Molecular structure of $(dppe)Fe(CH_2SiMe_3)_2$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

and confirms the tetrahedral geometry about the iron center. Selected bond distances and angles for this and all structurally characterized iron dialkyl complexes in this work are reported in Table 3.

The successful and straightforward synthesis of (dppe)Fe-(CH₂SiMe₃)₂ prompted exploration of iron dialkyls with enantiopure bis(phosphines). The two-carbon-bridged bis-(phosphines) (R,R)-^{Me}DuPhos and (1R,1'R,2S,2'S)-DuanPhos were selected because of the discrepancy between their success in cobalt chemistry³⁴ and poor performance with iron. Yellow, S = 2 ((R,R)-^{Me}DuPhos)Fe(CH₂SiMe₃)₂ was isolated in 86% yield from addition of the free phosphine to FeCl₂ in THF followed by dialkylation with LiCH₂SiMe₃ in diethyl ether. A similar procedure was used for the synthesis of ((1R,1'R,2S,2'S)-DuanPhos)Fe(CH₂SiMe₃)₂, which was isolated as a yellow-brown solid in 80% yield (Scheme 1). Relevant to the high-throughput experimentation, attempts to prepare ((1R,1'R,2S,2'S)-DuanPhos)Fe(CH₂SiMe₃)₂ by substitution of the pyridine ligands in py₂Fe(CH₂SiMe₃)₂ produced no reaction.

The solid-state structures of both iron dialkyl complexes were determined by X-ray diffraction (Scheme 1, Table 1). As expected from the magnetic data and literature precedent, 45,48 idealized tetrahedral molecules were observed in both cases. The Fe–C and Fe–P bonds are elongated in both compounds, also consistent with a high-spin iron(II) oxidation state.

The synthesis of an iron dialkyl complex with a ferrocenylbased bis(phosphine) was also explored, given the relative success of this structural motif in the high-throughput evaluation experiments. The Josiphos derivative SL-J212-1 was selected due to its commercial availability. Addition of the free bis(phosphine) to a THF slurry of FeCl₂ resulted in isolation of an orange powder identified as (SL-J212-1)FeCl₂ in >99% yield. As expected, (SL-J212-1)FeCl₂ is a high-spin, tetrahedral iron(II) complex whose structure was confirmed by X-ray diffraction (Figure 3). The structural confirmation of (SL-J212-1)FeCl₂ establishes that bis(phosphines) with larger chelates form isolable iron complexes. The desired alkyl complex (SL-J212-1)Fe(CH₂SiMe₃)₂ was isolated as an orange powder in 73% yield. The product was characterized by ¹H NMR spectroscopy, combustion analysis, magnetic susceptibility, and Mössbauer spectroscopy (vide infra). Relevant to the high-throughput experimentation, attempts to prepare (SL- J_{212-1} Fe(CH ₂SiMe₃)₂ by substitution of the pyridine ligands in $py_2Fe(CH_2SiMe_3)_2$ produced no reaction.

Mössbauer Spectroscopy and DFT Calculations. Each of the bis(phosphine) iron dialkyl complexes was additionally characterized by zero-field ⁵⁷Fe Mössbauer spectroscopy. One iron dichloride, (SL-J212-1)FeCl₂, was also included. The measured isomer shifts and quadrupole splitting values are reported in Table 4. Also reported in Table 4 are the Mössbauer parameters for related iron dialkyl compounds. Similar values were observed for (dppe)Fe(CH₂SiMe₃)₂, $((R,R)^{-Me}DuPhos)Fe(CH_2SiMe_3)_2$, and $((1R,1'R,2S,2'S)^{-D}DuanPhos)Fe(CH_2SiMe_3)_2$, with the isomer shifts ranging

	(dppe)FeNs ₂	$((R,R)-M^{e}DuPhos)FeNs_{2}$	((1 <i>R</i> ,1′ <i>R</i> ,2 <i>S</i> ,2′ <i>S</i>)-DuanPhos)FeNs ₂
Fe(1)-P(1)	2.5057(6)	2.4340(5)	2.4500(3)
Fe(1)-P(2)	2.4578(7)	2.4333(6)	2.4311(4)
Fe(1)-C(1)	2.058(2)	2.064(2)	2.056(1)
Fe(1)-C(2)	2.043(2)	2.069(2)	2.063(1)
P(1)-Fe(1)-P(2)	81.14(2)	81.33(2)	81.35(1)
P(1)-Fe(1)-C(1)	115.16(6)	109.35(6)	107.75(4)
P(1)-Fe(1)-C(2)	112.33(7)	111.47(6)	119.79(3)
P(2)-Fe(1)-C(1)	105.05(6)	113.25(6)	116.63(4)
P(2)-Fe(1)-C(2)	120.60(7)	108.83(6)	107.24(3)
C(1)-Fe(1)-C(2)	117.38(9)	124.39(8)	118.63(5)

Scheme 1. Preparation and Molecular Structures of ((R,R)-^{Me}DuPhos)Fe(CH₂SiMe₃)₂ (Left) and ((1R,1'R,2S,2'S)-DuanPhos)Fe(CH₂SiMe₃)₂ (Right)^{*a*}



^aStructures are shown with 30% probability ellipsoids, and hydrogen atoms are omitted for clarity.

from 0.33 to 0.41 mm/s and the quadrupole splitting (ΔE_{0}) ranging from 1.07 to 1.30 mm/s. The observed isomer shifts are lower than those expected for typical high-spin Fe(II) compounds but are consistent with a previously characterized example of a bis(phosphine) iron diaryl, (depe)Fe(Mes)₂ (depe = bis(diethyl)phosphinoethane).⁵¹ As with the compounds prepared in this work, $(depe)Fe(Mes)_2$ is tetrahedral with S =2. Substitution of the depe chelate with dppe resulted in isolation of (dppe)Fe(Mes)₂, a distorted planar compound with an S = 1 ground state. The isomer shift observed for this compound is similar to that for the tetrahedral compounds, but the quadrupole splitting is much larger (4.53 mm/s), as is expected for iron in a planar geometry.⁵¹ In the examples containing the SL-J212-1 "Josiphos"-type ligand, the Mössbauer spectrum exhibits a second quadrupole doublet arising from the ferrocenyl ligand framework, which is readily accounted for and fit. For $(SL-J212-1)Fe(CH_2SiMe_3)_2$ the isomer shift and quadrupole splitting of the non-ferrocenyl iron center is consistent with those of other isolated bis(phosphine) iron dialkyls, despite its unique phosphine linker.

The electronic structures of the bis(phosphine) iron dialkyls were examined by full-molecule DFT calculations using the ORCA program with the B3LYP functional.⁵² The crystal structures were used as the starting point for the geometry optimization,s except in the case of (SL-J212-1)Fe- $(CH_2SiMe_3)_2$, where structural data are not available. The optimized structure exhibited Fe-P and Fe-C bond distances consistent with the crystallographically characterized iron dialkyl compounds. Unrestricted Kohn-Sham (UKS) calculations were performed as a result of the S = 2 ground states and each calculation converged, as expected, to a high-spin Fe(II) compound. The computed bond distances and angles, along with the Mössbauer parameters, are in good agreement with the observed values (Table 4), further validating the computational outputs. A truncated qualitative molecular orbital diagram for (dppe)Fe(CH₂SiMe₃)₂ and associated spin density plot are reported in Figure 4. Those for the other computed iron compounds are reported in the Supporting Information.

Evaluation of Catalytic Activity: Isolated Iron Dialkyl Complexes. With isolated bis(phosphine) iron dialkyl



Figure 3. Molecular structure of $(SL-J212-1)FeCl_2$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Zero-Field ⁵⁷ Fe Mössbauer Parameters	for
Bis(phosphine) Iron Dialkyl Complexes ^a	

compd	$\delta~({ m mm/s})$	$\Delta E_{\rm Q} ({\rm mm/s})$
(dppe)Fe(CH ₂ SiMe ₃) ₂	0.41	1.23
	0.33	0.97
$(DuanPhos)Fe(CH_2SiMe_3)_2$	0.33	1.30
	0.30	1.01
$((D, D))$ MeD $(D_{1}, D_{2}) = (C \cup C \cup C \cup C)$	0.25	1.07
$((R,R)$ - DuPhos)Fe $(CH_2SIMe_3)_2$	0.35	1.07
	0.31	1.07
(SL-J212-1)FeCl ₂	0.73	2.76
	0.45	2.40
$(SL-J212-1)Fe(CH_2SiMe_3)_2$	0.42	1.35
	0.35	1.13
	0.49	2.35
	0.59	3.41
$(depe)Fe(Mes)_2$	0.39	1.71
(dppe)Fe(Mes) ₂ ⁵¹	0.33	4.53
Calculated values are presented i	n italics below the	observed values

complexes in hand, their catalytic hydrogenation performance was evaluated (Table 5). Because of the low conversions obtained from the high-throughput screening experiments, simpler substrates and higher catalyst loadings were initially used to differentiate the activities of these compounds. Each catalytic reaction was carried out in a J. Young NMR tube with 4 atm of H₂. During the course of the hydrogenation, the tubes were mechanically rotated to ensure efficient mixing. With 1-butene, complete conversion was observed after 24 h with all of the iron precatalysts. With more sterically hindered 3,3-dimethylbutene as the substrate reduced activity was observed with each precursor, with the exception of (SL-J212-1)Fe-(CH₂SiMe₃)₂. Geminal and internal alkenes proved problematic, as no conversion was observed in all cases, again with the

a



Figure 4. DFT computed (ORCA, B3LYP functional) qualitative molecular orbital diagram (top) and spin density plot (bottom) for (dppe)Fe(CH₂SiMe₃)₂.

Table 5. Evaluation of Catalytic Hydrogenation of Activity of Bis(phosphine) Iron Dialkyl Complexes for Unactivated Alkenes^a



^{*a*}Each reaction was carried out for 24 h at 23 °C with 20 mol % of the iron dialkyl precursor. Conversions were determined by ¹H NMR spectroscopy. ^{*b*}15% isomerization to *trans* isomer. ^{*c*}60% isomerization to *trans* isomer.

>95

>95

>95

>95

(SL-J212-1)Fe(CH₂SiMe₃)₂

exception of $(SL-J212-1)Fe(CH_2SiMe_3)_2$, which reached complete conversion after 24 h. These results obtained with the preformed catalysts are consistent with those of the high-

Table 6. Evaluation of the Catalytic Hydrogenation Activity of (SL-J212-1)Fe(CH₂SiMe₃)₂ for Alkenes^a



^aReactions were conducted at 0.15 M concentration of the substrate. Conversions were determined by GC analysis of the reaction mixture except in the case of 1-butene, 3,3-dimethylbutene, and 2,3,3-trimethylbutene, which were determined by ¹H NMR spectroscopy.

throughput screens, which identified predominantly ferrocenyl based bidentate phosphines as the most reactive in combination with an appropriate iron precursor and activating agent. Surprisingly, the SL-J212-1 ligand did not produce any observed hydrogenation activity in the high-throughput evaluations, likely a result of problematic precatalyst formation under those conditions. Similar effects were observed in the analogous cobalt chemistry.³⁴

Because of its superior performance, only (SL-J212-1)Fe- $(CH_2SiMe_3)_2$ was further evaluated for the hydrogenation of other more challenging alkene substrates. These reactions were also performed in J. Young tubes with mechanical rotation and 5 mol % of the iron dialkyl precursor. The results of these studies are reported in Table 6. The hydrogenation of both 1butene and 3,3-dimethylbutene reached complete conversion in 24 h with the reduced catalyst loading. Two 1,2-disubstituted olefins, cyclohexene and stilbene, yielded the alkane with quantitative conversion. The geminal alkenes (+)-limonene, 2,3,3-trimethylbutene, and α -isopropylstyrene also reached complete conversion after 24 h. Notably, no enantiomeric excess was observed with α -isopropylstyrene. With more substituted and hence more difficult to reduce geminal olefins, such as β -pinene, only 78% conversion of starting material was observed. This value also includes 24% of the isomerized product, α -pinene. The trisubstituted alkene trans- α -methylstilbene reached 67% conversion in 24 h, which improved to 84% conversion after 48 h. Again, no enantiomeric excess was observed. The functionalized alkenes 2-acetamidoacrylate and dimethyl 2-methylenesuccinate, as well as 1,1-dicyclohexylethene, produced no alkane under these conditions.

The catalytic hydrogenation of *trans-\alpha*-methylstilbene and methyl 2-acetamidoacrylate was also conducted with higher hydrogen pressures with the goal of improving the activity or selectivity of the iron catalyst. Each high-pressure experiment was conducted at 34 atm (500 psi) of H_2 with each of the four isolated iron dialkyl precursors. No conversion was observed in all four cases with methyl 2-acetamidoacrylate. Somewhat surprisingly, the hydrogenation of *trans-\alpha*-methylstilbene with $(SL-J212-1)Fe(CH_2SiMe_3)_2$ reached only 9% conversion as compared to the 67% value observed with 4 atm of H₂. The observed decrease in catalyst performance may be a result of more adventitious water in the high-pressure experiments (as a consequence of more H₂ gas or the steel reactor) or from the more dilute reaction conditions used to perform these procedures on a preparative scale. We do note that carrying out the reaction under more dilute conditions with 4 atm of H_2 produced no conversion.

Understanding Activation of the Bis(phosphine)Iron Dialkyl Complexes: Role of Heterogeneous Iron. Given the success of the bis(phosphine)cobalt dialkyl complexes in asymmetric alkene hydrogenation,³⁴ the origin of the relatively poor performance of the analogous iron compounds was of interest. Previous studies have established formation of iron arene complexes upon hydrogenolysis of the corresponding dialkyl complexes in arene solvents. These compounds tend to be robust and not be active precursors for catalysis.^{47,49} However, relatively high activity was observed with (SL-J2121)Fe(CH₂SiMe₃)₂ in benzene- d_6 (Table 6), arguing against this possibility. To further explore this hypothesis, the hydrogenation of *trans-* α -methylstilbene was conducted in cyclohexane and THF with 5 mol % of (SL-J212-1)Fe(CH₂SiMe₃)₂ and 73 and 53% conversions were observed, respectively.

Stoichiometric experiments were also conducted. Exposure of a benzene- d_6 solution of (SL-J212-1)Fe(CH₂SiMe₃)₂ to 4 atm of H₂ resulted in a color change from yellow-brown to brown-black upon shaking the tube. A broad, featureless ¹H NMR spectrum was obtained which was not useful for characterization. Vacuum transfer of the volatiles and analysis by ¹H NMR spectroscopy confirmed formation of SiMe₄, consistent with rapid hydrogenation of the iron alkyl groups. This experiment was repeated in the presence of 20 equiv of 1-butene with the goal of stabilizing the iron species formed after hydrogenolysis of the alkyl groups. A similarly broad and featureless ¹H NMR spectrum was observed along with black precipitate.

The lack of a measurable enantioselectivity in combination with the observation of a black precipitate upon the addition of dihydrogen suggested that heterogeneous iron may be responsible for the observed catalytic activity.53-57 To further explore this possibility, a filtration experiment was performed. The iron dialkyl complex (SL-J212-1)Fe(CH₂SiMe₃)₂ was exposed to 4 atm of H₂ for 1 h, forming the black precipitate. The solution was filtered under an inert atmosphere followed by addition of 20 equiv of *trans-\alpha*-methylstilbene and exposure to a fresh dihydrogen atmosphere. In a separate tube, a control experiment was prepared whereby the same procedure was followed except for the filtration step. Notably, the filtered solution produced only 1% conversion, while the control furnished 30% conversion to the alkane over the same time period, lower than the 67% conversion observed under standard conditions. These results suggest that a well-defined homogeneous iron catalyst is not likely responsible for the observed hydrogenation performance and heterogeneous iron, resulting from phosphine dissociation following hydrogenolysis of the iron alkyl ligands, is responsible for the observed modest turnover. This finding is also consistent with the unique catalytic activity observed with SL-J212-1-supported iron compounds. The presence of a six- rather than a five-membered chelate may result in reduced affinity of the phosphine for the metal center, facilitating dissociation. TEM analysis of the suspension resulting from hydrogen addition to (SL-J212-1)Fe(CH₂SiMe₃)₂ was performed in order to better understand the nature of the active iron species. The images are consistent with the formation of a zerovalent amorphous iron species and are presented in the Supporting Information. Iron nanoparticles were not observed.

Concluding Remarks. A series of bis(phosphine)iron dialkyls have been prepared, their electronic structures have been determined, and their catalytic hydrogenation activity has been evaluated. X-ray diffraction studies, Mössbauer spectroscopy, magnetic measurements, and full-molecule DFT calculations all support tetrahedral, high-spin iron(II) compounds. Evaluation of the isolated precatalysts established (SLJ212-1)Fe(CH₂SiMe₃)₂ as the most active for catalytic hydrogenation, but no enantioselectivity was observed with prochiral substrates. Filtration experiments were consistent with formation of heterogeneous iron rather than well-defined homogeneous iron compounds as the active species, likely a result of phosphine dissociation following hydrogenolysis of the iron alkyl ligands.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.⁵⁸ Hydrogen was 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, dried over Na, and stored over 4 Å molecular sieves. All reagents were purchased from Sigma Alrich, Alfa Aesar, or Acros Organics and used directly without further purification. Bidentate chiral phosphines were obtained from commercial sources, including Aldrich, Strem, Solvias, Takasago, and Chiral Quest.

¹H NMR spectra were recorded on Bruker AVANCE 300, Varian Inova 400, and Bruker AVANCE 500 spectrometers operating at 300.13, 399.78, and 500.62 MHz, respectively. ¹³C NMR spectra were recorded on a Bruker AVANCE 500 instrument operating at 125.89 MHz. All ¹H chemical shifts are reported relative to SiMe₄ using the ¹H (residual) chemical shifts of the solvent as a secondary standard. Solution magnetic moments were determined by the method of Evans⁵⁹ using a ferrocene standard and are the average of two or three independent measurements. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance and were collected at 22 °C. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a Restek 15 m \times 0.25 mm RTX-5 5% diphenyl/95% dimethyl polysiloxane column with a film thickness of 0.25 μ m. The following temperature program was used: 60 °C, 1 min; 15 °C/min to 250 °C; hold 1 min. Chiral gas chromatography for the alkane products was performed on a Shimadzu GC-2010 gas chromatogram using a Supelco 30 m × 0.25 mm BETA DEX 120 capillary column. Supercritical fluid chromatography (SFC) was performed on a Berger Minigram equipped with a diode array UV detector (λ 214–300 nm) using a chiral column (25 cm) and guard column (5 cm). The alkane products were identified by comparison to literature values.34 Micrographs were obtained at an accelerating energy of 200 kV using a Phillips CM-200 FEG-TEM instrument . Samples were drop cast under an inert atmosphere onto a Formvar film supported on a copper mesh grid, supplied by Electron Microscopy Sciences. Exposure to the atmosphere during introduction to the analysis chamber was on the order of 30 s.

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 DUO diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. 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.

Zero-field ⁵⁷Fe Mössbauer spectra were recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant acceleration mode. ⁵⁷Co/Rh was used as the radiation source. WMOSS software was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzain peaks). The minimum experimental line widths were 0.23 mm/s. The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N2 cryostat within an accuracy of \pm 0.3 K. Isomer shifts were determined relative to α -iron at 298 K.

Quantum Chemical Calculations. All DFT calculations were performed with the ORCA program package.⁶⁰ The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of

DFT.⁶¹⁻⁶³ This hybrid functional often gives better results for transition-metal compounds than pure gradient-corrected functionals, especially with regard to metal-ligand covalency.⁶⁴ The all-electron Gaussian basis sets were those developed by Ahlrichs.⁶⁵⁻⁶⁷ 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, which 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. $^{68-70}$ The RIJCOSX $^{71-73}$ approximation was used to accelerate the calculations. Throughout this paper we describe our computational results by using the broken-symmetry (BS) approach by Ginsberg⁷⁴ and Noodleman et al.⁷⁵ Because several broken-symmetry solutions to the spin-unrestricted Kohn-Sham equations may be obtained, the general notation $BS(m,n)^{76}$ has been adopted, where (m,n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. 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.⁷⁷ The Mössbauer isomer shifts were calculated from the computed electron densities at the iron centers as previously described.^{78,7}

Preparation of (dppe)Fe(CH₂SiMe₃)₂. A 20 mL scintillation vial was charged with 0.300 g (0.753 mmol) of bis(diphenyl)phosphinoethane (dppe) and approximately 10 mL of THF. A second 20 mL scintillation vial was charged with 0.095 g (0.753 mmol) of FeCl₂, and the contents of the first vial were transferred by pipet into the second. The reaction mixture was stirred overnight before the volatiles were removed, leaving a white powder. Approximately 10 mL of toluene was added to the white powder, and the resulting slurry was cooled to -35 °C. A toluene solution containing 0.145 g (1.544 mmol) of LiCH2SiMe3 was added dropwise, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through Celite, and the volatiles were removed from the filtrate to yield 0.473 g (91%) of (dppe)FeNs₂ as an analytically pure yellow-orange powder. Single crystals were grown from a pentane solution of the compound cooled to -35 °C. ¹H NMR (benzene- d_6): δ -4.66, -0.53, 11.57, 18.23 (broad resonances). Anal. Calcd for C₃₄H₄₆FeP₂Si₂: C, 64.95; H, 7.37. Found: C, 64.84; H, 7.19. Magnetic susceptibility (Evans): μ_{eff} = 4.9 $\mu_{\rm B}$ (benzene- d_6 , 23 °C).

Alternative Procedure for the Preparation of (dppe)Fe-(CH₂SiMe₃)₂. A 20 mL scintillation vial was charged with 0.283 g (0.638 mmol) of py_4FeCl_2 and approximately 10 mL of pentane. The solution was cooled to -35 °C, and a pentane solution of LiCH₂SiMe₃ (0.120 g, 1.275 mmol) was added dropwise. A color change from yellow to dark purple was observed upon warming. The reaction mixture was then stirred for 2 h at room temperature. The solution was filtered through Celite into a vial containing 0.254 g (0.638 mmol) of dppe. The resulting mixture was stirred for 2 h before the resulting yellow precipitate was isolated by filtration. The precipitate was washed with 2 × 1 mL portions of pentane to yield 0.306 g (77%) of (dppe)Fe(CH₂SiMe₃)₂ as a yellow-orange powder.

Preparation of ((R,R)-^{Me}DuPhos)Fe(CH₂SiMe₃)₂. A 20 mL scintillation vial was charged with 0.098 g (0.319 mmol) of (+)-1,2bis[(2S,5S)-2,5-dimethylphospholano]benzene (MeDuPhos) and approximately 10 mL of THF. A second 20 mL scintillation vial was charged with 0.040 g (0.319 mmol) of FeCl₂, and the contents of the first vial were transferred by pipet into the second. The reaction mixture was stirred overnight before the volatiles were removed to afford a white powder. Approximately 10 mL of diethyl ether was added to the white powder, and the resulting slurry was cooled to -35°C. A diethyl ether solution (~2 mL) containing 0.063 g (0.669 mmol) of LiCH₂SiMe₃ was added dropwise, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through Celite, and the volatiles from the filtrate were removed to yield 0.147 g (86%) of $((R,R)^{-Me}DuPhos)Fe(CH_2SiMe_3)_2$ as an analytically pure yellow powder. Single crystals were grown from a diethyl ether solution of the compound cooled to -35 °C. ¹H NMR (benzene- d_6):

δ -6.16, -5.36, -0.27, 10.19, 11.75, 45.51, 73.66, 132.39 (broad resonances). Anal. Calcd for C₂₆H₅₀FeP₂Si₂: C, 58.19; H, 9.39. Found: C, 58.19; H, 9.69. Magnetic susceptibility (Evans): $\mu_{\rm eff}$ = 4.6 $\mu_{\rm B}$ (benzene- d_{6r} 23 °C).

Preparation of ((1*R***,1'***R***,2***S***,2'***S***)-DuanPhos)Fe(CH₂SiMe₃)₂. This compound was prepared in a fashion similar to that for ((R,R)^{-Me}DuPhos)Fe(CH_2SiMe_3)_2 using 0.117 g (0.306 mmol) of (1R,1'R,2S,2'S)-DuanPhos, 0.039 g (0.306 mmol) of FeCl₂, and 0.061 g (0.643 mmol) of LiCH₂SiMe₃. This procedure yielded 0.151 g (80%) of ((1R,1'R,2S,2'S)-DuanPhos)Fe(CH₂SiMe₃)₂ as an analytically pure yellow-brown solid. Single crystals were grown from a diethyl ether solution of the compound cooled to -35 °C. ¹H NMR (benzene-d₆): δ 116.04, 42.89, 12.09, 10.43, 7.97, -0.89 (broad resonances). Anal. Calcd for C₃₂H₅₆FeP₂Si₂: C, 62.52; H, 9.18. Found: C, 62.29; H, 8.90. Magnetic susceptibility (Evans): \mu_{eff} = 5.0 \ \mu_{B} (benzene-d₆, 23 °C).**

Preparation of (SL-J212-1)FeCl₂. A 20 mL scintillation vial was charged with 0.194 g (0.371 mmol) of (*R*)-1-{(*S*_p)-2-[bis(2-furyl)-phosphino)ferrocenyl]ethyl}di-*tert*-butylphosphine (SL-J212-1) and approximately 10 mL of THF. A second 20 mL scintillation vial was charged with 0.047 g (0.371 mmol) of FeCl₂, and the contents of the first vial were pipetted into the second. The reaction mixture was stirred overnight before the volatiles were removed to afford 0.240 g (>99%) of an analytically pure orange powder identified as (SL-J212-1)FeCl₂. Single crystals were obtained from a THF solution of the compound cooled to -35 °C. ¹H NMR (THF-*d*₈): δ 71.52, 14.44, 13.09, 11.80, 9.47, 5.83, -13.18 (bs). Anal. Calcd for C₃₀H₄₂Cl₂Fe₂O₂P₂: C, 53.05; H, 6.23. Found: C, 52.79; H, 5.98. Magnetic susceptibility (magnetic susceptibility balance, 23 °C): $\mu_{eff} = 4.7$ $\mu_{\rm B}$.

General Procedure for Olefin Hydrogenation. *Thick-Walled Glass Vessel.* In a typical experiment, a thick-walled glass vessel was charged with 0.0164 mmol of the iron catalyst, 0.328 mmol of the substrate, and 8 mL of THF (in the case of MAC) or 8 mL of toluene (in the case of *trans-* α -methylstilbene). The vessel was transferred out of the drybox and attached to a high-vacuum line, and the contents of the vessel were frozen in liquid nitrogen. Following evacuation of the N₂ atmosphere, 1 atm of H₂ was added at approximately 77 K. The solution was then thawed and stirred in a 23 °C water bath. After 16 h, the reaction vessel was opened to air and the reaction mixture was diluted with acetone. The iron decomposition products were removed by filtration through Celite, and the filtrate was analyzed using GC-FID. Conversions were determined by integrating the peak of the olefin substrate versus the alkane product.

Parr Reactor. In a typical experiment a 45 mL glass well was charged with 0.0164 mmol of the iron catalyst, 0.328 mmol of the substrate, and 8 mL of THF (in the case of MAC) or 8 mL of toluene (in the case of *trans-* α -methylstilbene). The glass well was loaded into the Parr reactor, which was then sealed and pressurized to 34 atm of H₂, and the contents were mechanically stirred. After 16 h, the reaction vessel was opened to air and the reaction mixture was diluted with acetone. The iron decomposition products were removed by filtration through Celite, and the filtrate was analyzed using GC-FID. Conversions were determined by integrating the peak of the olefin substrate versus the alkane product.

J. Young NMR Tube. In a typical experiment a J. Young tube was charged with 0.005 mmol of the iron catalyst, 0.100 mmol of substrate, and 0.68 mL of C_6D_6 . The tube was transferred out of the drybox and attached to a high-vacuum line and the contents of the vessel were frozen in liquid nitrogen. Following evacuation of the N₂ atmosphere, the tube was charged with 1 atm of H₂ at 78 K. The solution was then thawed, and the tube was mechanically rotated for 24 h. Conversions were determined by GC or ¹H NMR analysis of the filtered reaction mixture.

ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF and xyz files giving a complete listing of the results of high-throughput evaluation of iron-phosphine combinations for asymmetric hydrogenation as well as TEM images, crystallographic data for all compounds, and calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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