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Iron(II)-Catalyzed Asymmetric Hydrosilylation of Acetophenone

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Four new ligands containing a pentasubstituted cyclopentadiene tethered to a stereogenic diamine unit have been prepared and used in the iron-catalyzed enantioselective hydrosilylation of acetophenone. Catalytically active species have been generated in situ starting from various sources of iron. $Fe(acac)_2$ was the catalyst precursor of choice, whereas other simple Fe^{II} or Fe^{III} compounds resulted in significantly lower or no catalytic activity. Quantitative conversions were obtained working with 4 mol-% Fe at room temp. and phenylsilane as the reducing agent. Under these conditions, ligand **4** afforded an enantioselectivity of 37 % *ee*. Attempts to isolate the single-component Fe complexes containing ligands **3**–**6** have failed so far.

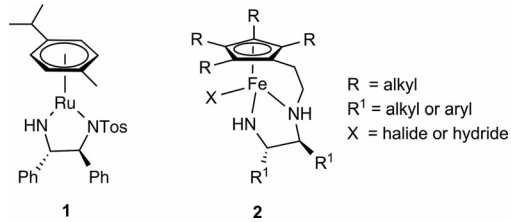
Introduction

Selective, efficient, and sustainable organic synthesis is one of the primary goals of ongoing chemical research.[1] Catalytic approaches have already been applied to a wide variety of synthetic problems. In addition, organometallic catalysts have played a major role in the production of many fine and bulk chemicals. However, many of the highly active catalysts in use today[2] utilize the transition metals palladium, rhodium, iridium, or ruthenium, each of which have significant drawbacks such as limited availability, high cost, and toxicity. Thus, recent industrial and academic research has focused on more economical and environmentally friendly catalytic systems that operate without significant loss of efficiency or selectivity. First row transition metals such as iron, copper, zinc, and manganese may be the solution to the above-mentioned shortcomings. What distinguishes iron[3] from the other first row transition metals is its high availability. As the second most common metal in the lithosphere, iron is cheap, and a wide variety of its salts are available on a technical scale.

Among the uses of newly developed catalytic systems based on iron, the preparation of enantiomerically pure secondary alcohols through an asymmetric reduction has attracted a great deal of attention. Industrial demand for these alcohols is quite high, because of their value as building blocks in the synthesis of pharmaceuticals, agrochemicals, and advanced materials.[4] To obtain enantiopure alcohols, most synthetic routes start with prochiral ketones which are either asymmetrically hydrogenated[5] or reduced in a mild asymmetric hydrogen-transfer reaction or an even milder and synthetically convenient asymmetric hydrosilylation.[6]

Initial work on iron-catalyzed hydrogenation and hydrosilylation of C=C double bonds or C=O double bonds was carried out by Markó et al.[7] in the early 1980s and by Nesmeyanov[8] in the 1960s. More recently, several Fe catalysts have been reported, including systems with chiral ligands affording products in high yields and acceptable enantiomeric excesses.[9]

To develop a new Fe-based catalyst for reduction reactions, we sought inspiration from Noyori's ruthenium transfer hydrogenation catalyst[10] (Figure 1). By virtue of the chiral nitrogen ligands containing an NH group, complex **1** exemplifies the bifunctional catalytic system which led to a significant breakthrough in asymmetric transfer hydrogenation.[10,11] The mechanism involves a concerted hydrogen transfer without prior coordination of the substrate to the metal. Earlier catalysts contained chiral phosphane ligands which were later found to facilitate the racemization of the enantio-enriched alcohols produced during the reaction.[12] However, catalyst **1** suffers much less from this undesired reaction.[10] Thus, even after more than ten years, Noyori's catalyst is still one of the most effective and most selective for asymmetric transfer hydrogenation.



1 2

Figure 1. Noyori's ruthenium catalyst **1** and generalized structure of envisioned iron catalyst **2**.

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Results and Discussion

To reach this goal, a series of cyclopentadienyl-bearing (Cp-) chiral diamine ligands were envisaged (Figure 2). Such a ligand design is necessary because iron is easily oxidized, and the organic environment provided by the ligand should lend stability to the complex without restricting catalytic activity. The tethered ligand systems used by Wills[13] to achieve high rigidity in rhodium, ruthenium, and iridium complexes and the Cp-stabilized piano-stool-type iron complexes reported by Astruc[14] both provide precedence for a ligand system composed of alkylated cyclopentadienyl derivatives bearing chiral diamine moieties for use in a new iron-based catalyst for asymmetric reductions.

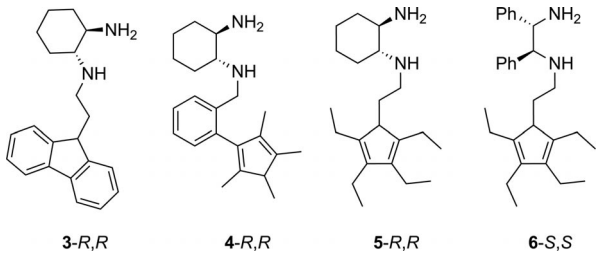
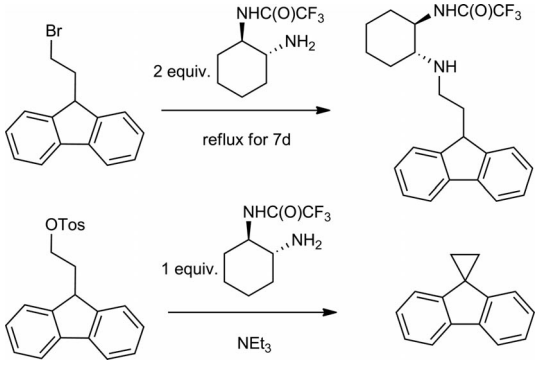


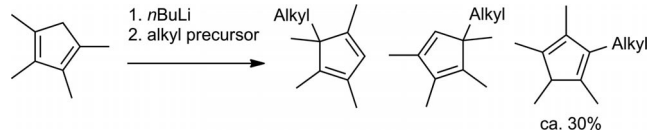
Figure 2. The four new ligands synthesized in this study, each containing a chiral diamine moiety and a cyclopentadiene.

The general synthetic strategy was to start with an alkylated Cp core and then add the chiral amine moiety. Along these lines, ligand **4** was readily synthesized by modified literature procedures,[15] and the critical step of the straightforward synthesis of ligand **3** is shown in Scheme 1. Unfortunately, the reaction time for the synthesis of **3** was long, and the reaction required 2 equiv. of the chiral amine. However, it did result in a 67% yield of the desired chiral Cp-amine ligand. Attempts were made to utilize inorganic bases such as K_2CO_3, K_3PO_4, or Cs_2CO_3 to trap the acid and consume only 1 equiv. of the chiral amine, but these were unsuccessful. Lastly, changing the leaving group from a bromide to a tosylate failed to increase the rate of the substitution reaction. Adding triethylamine under these conditions led to an intramolecular reaction, yielding a spiro compound rather than the desired substitution product (Scheme 1).

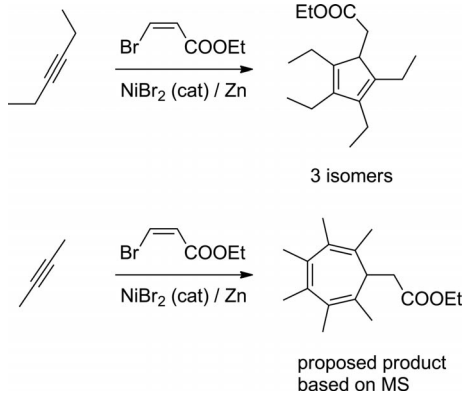


Scheme 1. Time-consuming substitution reaction to yield 67% of **3**-C(O)CF_3.

The syntheses of the tetramethylcyclopentadienyl analogs of ligands **5** and **6** by lithiation of 2,3,4,5-tetramethylcyclopentadiene followed by alkylation were unsuccessful. This finding is in line with the quantum-chemical calculations performed by Krut'ko,[16] predicting the formation of comparable amounts of three isomeric products for the alkylation of 2,3,4,5-tetramethylcyclopentadiene, including *gem*-dialkyl-substituted cyclopentadienes and 1,2,3,4-tetramethyl-5-alkylcyclopentadiene in an approximately 1:1:1 ratio (Scheme 2). Since separation of the isomeric mixture proved unfeasible, another synthetic route was explored. The 2,3,4,5-tetraethylcyclopentadienyl moiety was formed by Ni-catalyzed coupling of 3-hexyne with (*Z*)-3-bromopropenoate[17] (Scheme 3). Applying the same reaction conditions to 2-butyne and (*Z*)-3-bromopropenoate failed to yield the targeted pentasubstituted cyclopentadiene and led instead to the formation of ethyl (2,3,4,5,6,7-hexamethylcycloheptatrien-1-yl)acetate (identified by its molecular weight of 262.2 g/mol). Therefore, the substituted 2,3,4,5-tetraethylcyclopentadienyl derivative was used as the Cp core for the syntheses of the desired ligands.



Scheme 2. Product mixture derived from the alkylation of 1,2,3,4-tetramethylcyclopentadiene.



Scheme 3. Synthesis of substituted cyclopentadienes by nickel-catalyzed coupling reactions of alkynes.[17]

The most significant difficulty encountered with using the 2,3,4,5-tetraethylcyclopentadienyl-1-methyl derivative as the Cp core was avoiding isomerization to the corresponding thermodynamically favored, fully conjugated, *exo*-double-bond derivative (Scheme 4). In all steps during and following the coupling reaction toward ligands **5** and **6**, reaction time and temperature needed to be carefully controlled to obtain the desired product and avoid unnecessary loss of material, as no procedure is known to isomerize the thermodynamically favored product back to the desired isomer.

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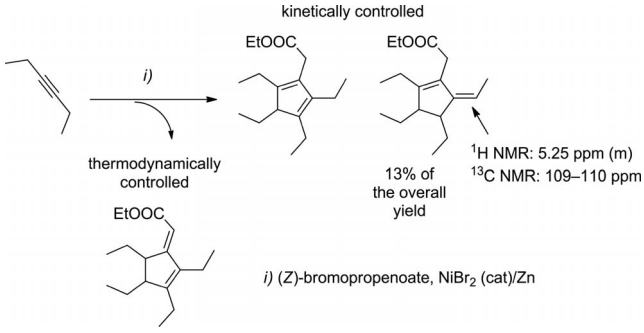
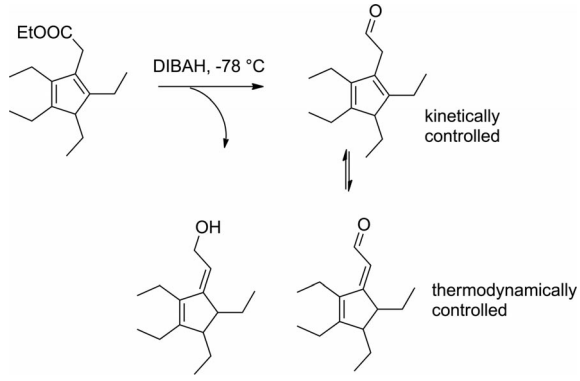


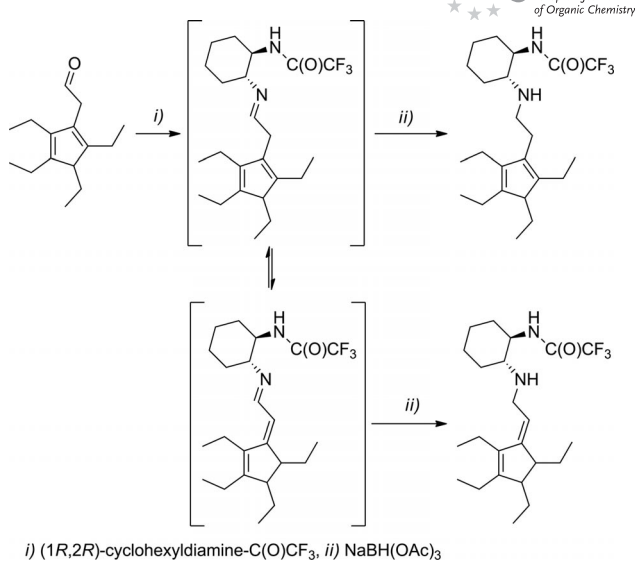
Scheme 4. Formation of isomeric tetraethylcyclopentadienyl derivatives under kinetic/thermodynamic control.

Despite careful temperature control during the coupling reaction, the formation of a second unexpected and undesired *exo*-double-bond derivative was identified, based on a multiplet in the ^{1}H NMR spectrum at δ = 5.25 ppm and the corresponding signal in the ^{13}C NMR spectrum at δ = 109–110 ppm. At a maximum of 13% of the overall yield, this product could not be separated from the three desired isomers (Scheme 4) which were directly reduced to the corresponding aldehydes in a single step (Scheme 5). During the reaction, the temperature was maintained below –70 °C to avoid further reduction to the corresponding alcohols. After workup, the mixture of aldehydes could be stored for several weeks in the refrigerator without isomerization to the thermodynamically favored *exo*-double-bond derivative.



Scheme 5. Synthesis of a cyclopentadienyl aldehyde.

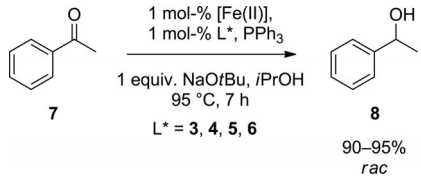
The final step involved the introduction of the chiral amine moiety by reductive amination. The imine formed prior to reduction was, once again, prone to isomerize. To avoid any further isomerization, the reducing agent $NaBH(OAc)_3$ needed to be present at the beginning of the reaction to drive the reduction step forward following formation of the imine (Scheme 6). Finally, removal of the trifluoroacetyl protecting group was achieved by treating the amine with $NaBH_4$ in ethanol, followed by chromatographic purification.



Scheme 6. Reductive amination.

Because ligands **4**–**6** were obtained as a mixture of isomers, all with very similar NMR spectroscopic data, unambiguous assignments of the corresponding signals were impossible. Thus, for characterization we relied on the absence of signals attributed to unwanted products as well as on mass spectrometric data.

Investigations were carried out on the catalytic potential of ligands **3**–**6** in combination with an iron(II) precursor, forming the catalyst in situ, followed by the asymmetric transfer hydrogenation protocol reported by Beller[18] using acetophenone (**7**) as a substrate (Scheme 7). In contrast to previously published findings, we obtained high conversions of **7** to 1-phenylethanol (**8**), albeit with no enantiomeric excess with or without the presence of iron salts in the reaction mixture. We also found that triphenylphosphane, previously claimed to be an important additive for Fe-catalyzed transfer hydrogenation, was unnecessary to obtain high yields.



Scheme 7. Conditions for catalytic hydrogen transfer from literature.[18] Neither Fe^{II}, L*, or triphenylphosphane are necessary to obtain the conversions reported.

These findings have recently been verified independently by Ouali and Taillefer.[19] Although the mechanism of the iron-free transformation is not completely clear, it may be a variation of the well-known Meerwein–Ponndorf–Verley reduction.[20]

Application of transfer hydrogenations protocols using only catalytic amounts of base or changing the hydrogen source from 2-propanol to formic acid or triethyl ammonium formate (TEAF)[21] failed to yield a functioning cata-

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lytic system. Under the above-mentioned conditions, the protic environment necessary for transfer hydrogenation may inhibit the in situ formation of the desired catalyst. Instead, under the basic conditions used in all of these protocols, $Fe(OH)_2$ was likely to form. This hypothesis was further supported by successful asymmetric hydrosilylation experiments, not requiring a protic environment. In addition, hydrosilylation required only stoichiometric amounts of the reducing agent, as opposed to the large excesses of hydrogen donor necessary for transfer hydrogenation. After completion of the reaction under aprotic conditions, the silylether could easily be transformed to the desired secondary alcohol by aqueous workup.

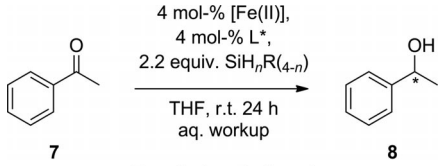
Using acetophenone (**7**) as a standard substrate and phenylsilane as the reducing agent, a simple screening of various iron compounds as catalyst precursors was carried out with ligands **3** and **6**. The results of these experiments showed that using $Fe(acac)_2$ as the iron source led to the highest conversion of **7** to **8** (Table 1, Entries 11–17). Iron(II) acetate was also an effective iron source, but required elevated reaction temperatures which resulted in reduced chiral induction (Table 1, Entries 8 and 9). Iron(II) tetrafluoroborate showed moderate activity, although reproduction of the results proved difficult (Table 1, Entries 5 and 6).

Ligands **3**–**6** gave similar results yielding low enantiomeric excesses between 24 and 37% (Table 1, Entries 11–15). The bulkier chiral amine moiety of ligand **6** increased the *ee* value significantly compared to ligand **5**. The effect of the alkyl moiety on the secondary amine was less clear. Ligand **4** yielded the product with the highest enantiomeric excess, whereas the less bulky ligand **5** showed the lowest performance with regard to chiral induction. Ligand **3** led to a somewhat lower overall conversion of **7** to **8**, as compared to **4**–**6**, probably due to its bulky and rigid fluorene moiety.

Initially, 2 equiv. of ligand relative to the catalyst precursor were used with the aim of ensuring complete complex formation. Subsequently, it was found that the reaction time was prolonged by adding 2 equiv. of ligand. If the ratio of ligand to $Fe(acac)_2$ was 1:1, 24 h were required for complete conversion, whereas with a ratio of 2:1, 40 h were necessary. Although this is the case, the enantiomeric excess and conversion remained unaffected. (Table 1, Entries 14 and 15).

THF was the best solvent with regards to conversion as well as enantiomeric excess (Table 2, Entries 1 and 2). It seemed that not only the coordinating ability of the solvent was important, but also the activation temperature for the catalyst formation. Using weakly coordinating solvents, such as toluene and dichloromethane, a large drop in enantiomeric excess was observed, however only in the case of

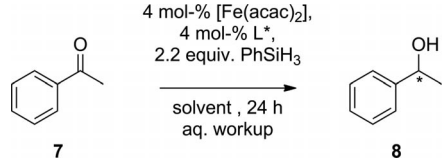
Table 1. Influence of different iron and ligand sources on the iron-catalyzed asymmetric hydrosilylation of **7**.[a]



Entry	Iron source	Ligand	Conv. [%][b]	*ee* [%][c]
0[d,e]			0[f]	
1[d]		**3**	0	
2[g,h]	$FeBr_2$		0[f]	
3[g,h,i]	$FeBr_2$	**6**	0.4[f]	*rac*[j]
4	$FeCl_2$	**6**	0	
5[d,e]	$Fe(BF_4)_2{\cdot}6H_2O$		22.5 (±7)[f]	*rac*[j]
6[d,e,i]	$Fe(BF_4)_2{\cdot}6H_2O$	**3**	52.8 (±7) [f]	5 (*S*)[j]
7[e,g]	$Fe(OAc)_2$		7[f]	*rac*[j]
8[g,i]	$Fe(OAc)_2$	**6**	98[f]	*rac*[j]
9	$Fe(OAc)_2$	**3**	42.8 (±41)	12 (±10)
10	$Fe(acac)_2$		36.6	*rac*
11[d]	$Fe(acac)_2$	**3**	70.5	27 (*S*)
12	$Fe(acac)_2$	**4**	quant.	37 (*S*)
13	$Fe(acac)_2$	**5**	quant.	24 (*S*)
14	$Fe(acac)_2$	**6**	quant.	32 (*R*)
15[d,i]	$Fe(acac)_2$	**6**	quant.	37 (*R*)[j]
16	$Fe(acac)_2$	**9**[k]	quant.	11.4 (*S*)
17	$Fe(acac)_2$	**10**[l]	quant.	18 (*S*)

[a] Reagents and conditions: in situ catalyst (0.02 mmol), L* (0.02 mmol), tetrahydrofuran = THF (1.5 mL), **7** (0.5 mmol) for 10 min at 60 °C, then addition of phenylsilane (1.1 mmol), 24 h at room temp. [b] Conversion was determined by NMR spectroscopy with benzaldehyde as internal standard (conversion is equivalent to yield). [c] Enantiomeric excess was determined by chiral HPLC. [d] Reaction time 40 h. [e] Diethoxymethylsilane (0.55 mmol). [f] Conversion was determined by chiral GC. [g] Reaction temperature was 65 °C, reaction time was 13.5 h. [h] Diethoxymethylsilane (1.1 mmol). [i] L* (0.04 mmol). [j] Enantiomeric excess was determined by chiral GC. [k] **9** = (1*R*,2*R*)-cyclohexyldiamine. [l] **10** = (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine.

Table 2. Influence of different solvents and temperature in the Fe-catalyzed asymmetric hydrosilylation of **7**.[a]



Entry	Ligand	Solvent	Reaction temp. [°C]	Conv. [%][b]	*ee* [%][c]
1	**4**	THF	room temp.	quant.	37 (*S*)
2[d,e]	**6**	THF	room temp.	quant.[f]	36 (*R*)[g]
3[d,h]	**6**	THF	65	quant.[f]	33 (*R*)[g]
4[e]	**3**	THF	room temp.	70.5	27 (*S*)
5[h]	**3**	THF	58	73.5	24 (*S*)
6[i]	**3**	THF	63	80	25 (*S*)
7[j]	**4**	CH_2Cl_2	room temp.	48	16 (*S*)
8[k]	**4**	toluene	room temp.	95	19 (*S*)
9[l]	**4**	Et_2O	room temp.	70	26 (*S*)

[a] Reagents and conditions: $Fe(acac)_2$ (0.02 mmol), L* (0.02 mmol), solvent (1.5 mL), **7** (0.5 mmol) for 10 min at 60 °C, then addition of phenylsilane (1.1 mmol), 24 h at reaction temperature. [b] Conversion was determined by NMR spectroscopy with benzaldehyde as internal standard (conversion is equivalent to yield). [c] Enantiomeric excess was determined by chiral HPLC. [d] L* (0.04 mmol). [e] Reaction time 40 h. [f] Conversion was determined by chiral GC. [g] Enantiomeric excess was determined by chiral GC. [h] Reaction time 14 h. [i] Reaction time 23 h. [j] Formation of in situ catalyst at 35 °C. [k] Formation of in situ catalyst at 60 °C. [l] Formation of in situ catalyst at room temp.

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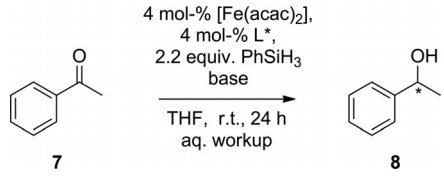
dichloromethane did the yield decrease markedly (Table 2, Entries 7 and 8). In the case of ethyl ether, the drop in the enantiomeric excess was less severe than in the case of toluene, though conversion was significantly lower (Table 2, Entries 8 and 9). Heating the reaction mixture also increased the reproducibility of the catalytic results, as in the case of ligand **3**. A shorter reaction time was required, however the enantiomeric excess did decrease slightly (Table 2, Entries 4 and 6).

Isolation and characterization of iron complexes containing any of the ligands depicted in Figure 2 have been unsuccessful so far. Given that Ru and Rh catalysts containing multidentate ligands comprised of a Cp unit usually afford products with a much higher *ee*,[13] we assume that ligands **3**–**6** are coordinating to iron through the amine groups only. Using chiral 1,2-cyclohexyldiamine and 1,2-diphenylethane-1,2-diamine as the ligands (Table 1, Entries 16 and 17) gave significant lower *ee* values than the ones achieved with ligands **3**–**6**. This corroborates with the assumption that the cyclopentadienyl moiety is uncoordinated, and thus fulfilling merely a steric function. Additionally, it seems unlikely that the Cp moiety is coordinated to iron, as the only base in the system is the acetylacetonate ligand from the catalyst precursor. Acetylacetonate is not sufficiently basic to shift the deprotonation equilibrium of the HCp moiety to any significant extent to the right [cf. the pK_a values of 13.3,[22] 26.1,[23] and 22.6[24] for acetylacetone, 1,2,3,4,5-pentamethylcyclopentadiene, and 9-methylfluorene, respectively, all measured in dimethyl sulfoxide (DMSO)]. Therefore, deprotonation of the HCp moiety was attempted with additional base. Addition of sodium hydride with 15-crown-5 did not interfere with the conversion, but led to a strong decrease in enantiomeric excess (Table 3, Entry 2). Addition of cesium carbonate resulted in an even poorer enantiomeric excess value, giving nearly racemic **8** (Table 3, Entry 5). Lastly, using DABCO (1,4-diazabicyclo[2.2.2]octane) as a base decreased the conversion to trace amounts of product (Table 3, Entry 7).

Interestingly, significant differences in catalytic activity were observed depending on the source of iron(II) acetylacetonate. This suggests that the composition of the starting material may be the reason for such discrepancies. As several Fe-catalyzed reactions, reported in the literature, have been found to be catalyzed by copper, a common impurity in iron salts,[25] hydrosilylation of **7** to **8** with copper(II) chloride or copper(II) acetate was attempted. However, neither copper salt showed any relevant catalytic activity (Table 4, Entries 5 and 6). In addition, a check of the different sources of $Fe(acac)_2$ by LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) showed an elevated percentage of silver in the material used to obtain the best catalytic results. Therefore, a test reaction was run with additional silver oxide. As a result, the conversion dropped dramatically as did the observed enantiomeric excess. (Table 4, Entry 2).

As neither impurities in copper or silver explain the dependent nature of the iron source on the catalytic activity of the system, the oxidation state of the iron in the iron

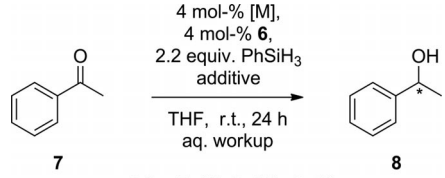
Table 3. Influence of additional bases on the Fe-catalyzed asymmetric hydrosilylation of **7**.[a]



Entry	Ligand	Base	Conv. [%][b]	*ee* [%][c]
1	**6**		quant.	32 (*R*)
2	**6**	NaH in THF/15-crown-5	quant.	24 (*R*)
3	**6**	DBU[d]	43	21 (*R*)
4	**4**		quant.	37 (*S*)
5	**4**	Cs_2CO_3	quant.	5 (*S*)
6[e]	**3**		70.5	27 (*S*)
7	**3**	DABCO	4	n.d.[f]

[a] Reagents and conditions: $Fe(acac)_2$ (0.02 mmol), L* (0.02 mmol), THF (1.5 mL), base (0.02 mmol), **7** (0.5 mmol) for 10 min at 60 °C, then addition of phenylsilane (1.1 mmol), 24 h at room temp. [b] Conversion was determined by NMR spectroscopy with benzaldehyde as internal standard, (conversion is equivalent to yield). [c] Enantiomeric excess was determined by chiral HPLC. [d] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [e] Reaction time: 40 h. [f] n.d.: not determined.

Table 4. Screening of possible impurities in iron(II) acetylacetonate for catalytic activity in the asymmetric hydrosilylation of **7**.[a]



Entry	Catalyst precursor	Additive	Conv. [%][b]	*ee* [%][c]
1	$Fe(acac)_2$		quant.	32 (*R*)
2	$Fe(acac)_2$	Ag_2O	32.8	22 (*R*)
3[d]	$Fe(acac)_2$ oxidized		0.7[e]	n.d.
4	$Fe(acac)_3$		0	
5	$Cu(acac)_2$		0	
6	$CuCl_2$		5	n.d.

[a] Reagents and conditions: in situ catalyst (0.02 mmol), **6** (0.02 mmol), THF (1.5 mL), **7** (0.5 mmol) for 10 min at 60 °C, then addition of phenylsilane (1.1 mmol), 24 h at room temp. [b] Conversion was determined by NMR spectroscopy with benzaldehyde as internal standard, (conversion is equivalent to yield). [c] Enantiomeric excess was determined by chiral HPLC. [d] **6** (0.04 mmol), reaction time 40 h. [e] Conversion was determined by chiral GC.

salts was examined. This study revealed that the iron(III) content of the precursor salts may be responsible for the differences in the observed catalytic activity. For example, sample 1 was synthesized in the laboratory starting from $Fe(CO)_5$, whereas the starting material for sample 2 was $FeCl_2$. Sample 3 was purchased from Aldrich and sublimed before use. The best results (quantitative conversions) were obtained when sample 1 was used as the iron source. Sample 2 resulted in conversions of approximately 50%, and sample 3 only gave a 15% conversion. ESR measurements showed that the conversion was inversely proportional to

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the increasing concentration of iron(III) in the catalyst precursors. An additional test with commercially available iron(III) acetylacetonate and another with active iron(II) acetylacetonate from sample 1 exposed to air confirmed the assumption that iron(III) is not catalytically active in the asymmetric hydrosilylation of **7** to **8** (Table 4, Entries 3 and 4).

Conclusions

Four new chiral C_1 symmetric diamine ligands have been prepared, and an efficient iron(II) system for the asymmetric hydrosilylation of acetophenone with phenylsilane has been developed. Iron(II) acetylacetonate was the best catalyst precursor. Its purity and molar ratio to the ligand were crucial for catalytic activity. However, the exact composition of the active catalyst and how the ligands coordinate is currently still unclear. We are in the process of studying our new system by EPR spectroscopy, and the corresponding findings will be reported in due course.

Experimental Section

General Methods: NMR spectra were recorded in $CDCl_3$ at ambient temperature without spinning with *Bruker* AC-200 (^{19}F: 188.31) DPX –250 (^{1}H: 250.13), DPX-300 (^{1}H: 300.13, ^{19}F: 282.40, ^{13}C: 75.47), DPX-400 (^{1}H: 400.13, ^{13}C: 100.61), or DPX-500 (^{1}H: 500.23, ^{13}C: 125.78) instruments, operating at the denoted spectrometer frequency given in megahertz (MHz) for the specified nucleus. HPLC analyses were performed with an *Agilent Series* 1100 instrument (detector DAD) using an OD-H column (length = 25 cm; inner diameter = 4.6 mm; particle size = 5 μm; flow rate of the eluent = 0.5 mL/min; hexane/*i*PrOH, 9:1; sample injection volume = 5 μL; and sample concentration is approximately 1 mg/mL). Retention times (t_R) for (*R*)- and (*S*)-1-phenylethanol are 12.2 min and 13.5 min, respectively. GC analyses were performed with a *Hewlett Packard* HP 6890 Series GC system equipped with a EPC split splitless injector using H_2 as the carrier gas, a *Macherey & Nagel* Lipodex E column (25 m × 0.32 mm × 0.25 μm), temperature = 1 min at 70 °C then 1 °C/min to 110 °C, and H_2 pressure = 0.5 bar. Retention times (t_R) for (*S*)- and (*R*)-1-phenylethanol are 31.0 min and 31.7 min, respectively. High resolution mass spectra were measured by the *MS-Service des Labors für Organische Chemie*, ETH Zürich. Optical rotations were measured with a *Perkin–Elmer* 341 polarimeter equipped with a 10 cm cell at a concentration of 1 g of substance per 100 mL (c = 1.0) in the given solvent. All reactions were carried out under argon in oven dried glassware with magnetic stirring or in a dry box under a dinitrogen atmosphere unless explicitly indicated otherwise. All solvents were dried with sodium/benzophenone or calcium hydride and distilled under Argon prior to use. Unless explicitly indicated otherwise, reagents were obtained from commercial sources and used as received. 9-(2-Bromoethyl)fluorene,[26] 2-(2,3,4,5-tetramethylcyclopentadienyl)-benzaldehyde,[15] 2-(2,3,4,5-tetraethylcyclopentadienyl)ethyl acetate,[17] and iron(II) acetylacetonate[27] were synthesized by literature procedures. Silica gel 60 (230–400 mesh) was purchased from Fluka. Because ligands **4**–**6** were isolated as inseparable mixtures of isomers (**5** and **6** also have the minor side product with an *exo* double bond), which were very similar NMR spectroscopically, we do not list the corresponding resonances for ^{1}H and ^{13}C NMR. Instead, the measured spectra can be found in the Supporting Information.

Monotrifluoroacetyl-Protected Chiral Diamines

***N*-[(1*R*,2*R*)-2-Aminocyclohexyl]-2,2,2-trifluoroacetamide:** To a solution of (1*R*,2*R*)-diaminocyclohexane (5 g, 43.8 mmol) in dry methanol (53 mL) at 0 °C was slowly added ethyl trifluoroacetate (5.73 mL, 48.2 mmol). After stirring for 15 h at 0 °C, the mixture was concentrated in vacuo, and the title compound was purified by flash chromatography on silica (ethyl acetate/methanol, 9:1; 1% triethylamine) to yield a yellowish solid (7.01 g, 76%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.16–1.45 (m, 6 H), 1.75 (m, 2 H), 1.99 (m, 1 H), 2.16 (m, 1 H), 2.50 (m, 1 H), 3.47 (m, 1 H), 6.54 (br. s, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 24.80, 25.04, 31.73, 36.31, 54.92, 57.05, 116.07 (q, J = 287.77 Hz), 157.57 (q, J = 36.7 Hz) ppm. ^{19}F NMR (188.29 MHz, $CDCl_3$): δ = –75.76 ppm. HRMS: calcd. for $C_8H_{13}F_3N_2O$ [M + H]$^+$ 211.1053; found 211.1052 (δ = 0.6 ppm error). $[a]_D^{20}$ = –32.19 (c = 1, CH_2Cl_2).

***N*-[(1*S*,2*S*)-2-Amino-1,2-diphenylethyl]-2,2,2-trifluoroacetamide:** The same procedure as for *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-2,2,2-trifluoroacetamide was followed. Purification by flash chromatography on silica (cyclohexane/ethyl acetate, 1:1; 1% triethylamine) yielded *N*-[(1*S*,2*S*)-2-amino-1,2-diphenylethyl]-2,2,2-trifluoroacetamide as a colorless solid (86.6%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.29 (s, 2 H), 4.36 (d, J = 2.8 Hz, 1 H), 4.95 (m, 1 H), 7.00–7.30 (m, 10 H), 7.75 (br. d, J = 6.4 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 58.93, 59.29, 116.07 (q, J = 288.38 Hz), 126.12, 126.31, 128.14, 128.25, 128.94, 129.14, 138.85, 141.25, 156.85 (q, J = 36.93 Hz) ppm. ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = –75.76 ppm. HRMS: calcd. for $C_{16}H_{15}F_3N_2O$ [M + H]$^+$ 309.1209; found 309.1209 (δ = 0.2 ppm error). $[a]_D^{20}$ = –0.39 (c = 1, MeOH).

Ligand 3: To a solution of 9-(2-bromoethyl)-fluorene (3.26 g, 12 mmol) in dry dioxane (90 mL) in a Young Schlenk was added (1*R*,2*R*)-*N*-(2-aminocyclohexyl)-2,2,2-trifluoroacetamide (5.04 g, 24 mmol). After stirring at 120 °C for 7 d, the mixture was filtered to separate the hydrobromide salt of *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-2,2,2-trifluoroacetamide. The filtrate was washed with HCl (2 M solution) and extracted with dichloromethane. The organic phase was dried with $MgSO_4$, and the solvents were removed. The crude product was purified by flash chromatography on silica (ethyl acetate, 1% triethylamine) to yield *N*-{(1*R*,2*R*)-2-[2-(9*H*-fluoren-9-yl)ethylamino]cyclohexyl}-2,2,2-trifluoroacetamide [**3**-C(O)CF_3] as an off-white solid (3.24 g, 67.1%). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.88–2.6 (m, 15 H), 3.29 (m, 1 H), 4.07 (t, J = 5.25 Hz, 1 H), 6.71 (br. s, 1 H), 7.28–7.40 (m, 4 H), 7.49 (d, J = 6.75 Hz, 2 H), 7.76 (d, J = 7.25 Hz) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.41, 24.76, 31.33, 33.48, 42.49, 45.66, 54.62, 60.19, 116.01 (q, J = 288.32 Hz), 120.07, 124.34, 124.41, 127.17, 127.30, 127.31, 141.13, 141.19, 146.78, 146.86, 157.44 (q, J = 36.52 Hz) ppm. ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = –75.89 ppm. HRMS: calcd. for $C_{23}H_{25}F_3N_2O$ [M + H]$^+$ 403.1992; found 403.1984 (δ = 1.9 ppm error). $[a]_D^{20}$ = –17.11 (c = 1, CH_2Cl_2). To a solution of **3**–C(O)CF_3 (3.24 g, 8 mmol) in dry ethanol (125 mL) was added in portions at ambient temperature sodium borohydride (1.81 g, 48 mmol). After stirring for 1 h at ambient temperature, the mixture was heated to reflux for 30 min. The solvent was then removed under reduced pressure, and the residue was treated with 1 M aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic extracts were dried with $MgSO_4$, followed by removal of the solvents. The resulting yellow oil was purified by flash chromatography over silica (ethyl acetate/methanol, 9:1, 1% triethylamine) to yield **3** (2 g, 81.6%) as a light yellow oil, which turned brown upon storage at

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ambient temperature. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.88–0.94 (m, 1 H), 1.07–1.26 (m, 4 H), 1.63 (m, 2 H), 1.85–1.97 (m, 3 H), 2.17–2.40 (m, 6 H), 2.69 (m, 1 H), 4.10 (t, J = 5.6 Hz, 1 H), 7.29–7.38 (m, 4 H), 7.53 (d, J = 7.2 Hz, 2 H), 7.75 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 25.12, 25.15, 30.89, 33.23, 35.41, 43.40, 45.78, 54.98, 63.59, 120.00, 124.55, 127.11, 127.14, 127.20, 141.16, 147.00, 147.04 ppm. HRMS: calcd. for $C_{21}H_{26}N_2$ $[M + H]^+$ 307.2169; found 307.2170 (δ = 0.3 ppm error). $[\alpha]_D^{20}$ = –42.07 (c = 1, CH_2Cl_2).

Ligand 4: To a solution of 2-(2,3,4,5-tetramethylcyclopentadienyl)-benzaldehyde (1 g, 4.42 mmol) in dry methanol (35 mL) was added *N*-[(1*R*,2*R*)-2-aminocyclohexyl]-2,2,2-trifluoroacetamide (0.91 g, 4.34 mmol), molecular sieves 4 Å (1.25 g), and glacial acetic acid (2 drops, catalytic) at ambient temperature. After complete formation of the imine (checked by TLC), sodium borohydride (1 g, 26.5 mmol) was added, and the reaction mixture was stirred overnight at ambient temperature. Heating to reflux for 1 h followed. The molecular sieves were then filtered off, and the solvents were removed under reduced pressure. The residue was dissolved in ethyl acetate and then washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude brown oil (1.64 g, 88.2%) of 2,2,2-trifluoro-*N*-{(1*R*,2*R*)-2-[2-(2,3,4,5-tetramethylcyclopentadienyl)benzylamino]cyclohexyl}acetamide [**4**-C(O)CF_3] was used without purification. HRMS: calcd. for $C_{24}H_{31}F_3N_2O$ $[M + H]^+$ 421.2461; found 421.2467 (δ =1.4 ppm error). Ligand **4** was obtained following the same procedure as for **3**. Purification by flash chromatography on silica (ethyl acetate/methanol, 9:1; 1% triethylamine) yielded **4** as a light yellow oil (47.4% over 2 steps). ^{1}H NMR and ^{13}C NMR spectra can be found in the Supporting Information. HRMS: calcd. for $C_{22}H_{32}N_2$ $[M + H]^+$ 325.2638; found 325.2639 (δ = 0.2 ppm error). $[\alpha]_D^{20}$ = –60.35 (c = 1, CH_2Cl_2).

Ligand 5: To a solution of 2-(2,3,4,5-tetraethylcyclopentadienyl)-ethyl acetate (2.64 g, 10 mmol) in dry hexane (20 mL) was added diisobutylaluminium hydride (50 mL, 1 M in hexane) dropwise (drop rate: 1 drop/4 s) over 3 h at –78 °C. After stirring the reaction mixture for another hour at –78 °C, a mixture of methanol and 6 M HCl (1:1, 50 mL) was added dropwise over 3 h. After completion, the cooling bath was removed, and as soon as the aqueous phase was clear, the reaction mixture was washed with deionized water to obtain a neutral pH. The organic phase was dried with $MgSO_4$, and the solvents were removed to yield 2-(2,3,4,5-tetraethylcyclopentadienyl)acetaldehyde (1.98 g, 90%) as a yellow oil, used directly without further purification {The product can be stored in the refrigerator for up to a month. Longer storing times or storing at ambient temperature can lead to the 2-[2,3-(2,3,4,5-tetraethylcyclopent-2-en-1-ylidene)acetaldehyde isomer].} HRMS (EI): calcd. for $C_{15}H_{24}O$ $[M]^+$ 220.1822; found 220.1823 (δ = 0.45 ppm error). To a solution of (1*R*,2*R*)-*N*-(2-aminocyclohexyl)-2,2,2-trifluoroacetamide (2.65 g, 12.64 mmol) in dry dichloromethane (30 mL) was added 2-(2,3,4,5-tetraethylcyclopentadienyl)acetaldehyde (2.53 g, 11.5 mmol) at 0 °C in dry dichloromethane (85 mL), followed by the portionwise addition of sodium triacetoxyborohydride (16.1 g, 75.8 mmol). After stirring for 7 h at 0 °C, NaOH (1 M solution) was added in portions, and the reaction mixture was extracted with dichloromethane. The organic phase was dried with $MgSO_4$, and the solvents were removed under reduced pressure. Purification by gradient flash chromatography over silica (hexane; hexane/ethyl acetate, 10:1; hexane/ethyl acetate, 3:1; 1% triethylamine] yielded **5**-C(O)CF_3 (3.22 g, 70%) as a yellow oil. ^{1}H NMR and ^{13}C NMR spectra can be found in the Supporting Information. ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = –75.96 (main peak), –75.98, –76.00, –76.01 (3 minor peaks) ppm. HRMS: calcd. for $C_{23}H_{37}F_3N_2O$ $[M + H]^+$ 415.2931; found 415.2925 (δ = 1.4 ppm error). $[\alpha]_D^{20}$ = –32.28 (c = 1, CH_2Cl_2). Deprotected **5** was obtained following the same procedure as for **3**. Purification by flash chromatography over silica (ethyl acetate/methanol, 9:1; 1% triethylamine) yielded **5** as a yellow oil (70%). ^{1}H NMR and ^{13}C NMR spectra can be found in the Supporting Information. HRMS: calcd. for $C_{21}H_{38}N_2$ $[M + H]^+$ 319.3108; found 319.3109 (δ = 0.3 ppm error). $C_{21}H_{38}N_2$ (318.54): calcd. C 79.18, H 12.02, N 8.79; found C 78.9, H 11.99, N 8.54. $[\alpha]_D^{20}$ = –51.76 (c = 1, CH_2Cl_2).

Ligand 6: Following the same procedure as for **5**-C(O)CF_3, purification by flash chromatography over silica (cyclohexane/ethyl acetate, 10:1; 1% triethylamine] yielded **6**-C(O)CF_3 (41%). ^{1}H NMR and ^{13}C NMR can be found in the Supporting Information. ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = –66.74 (main peak), –66.83 to –66.94 (minor peaks) ppm. HRMS: calcd. for $C_{31}H_{39}F_3N_2O$ $[MH^+]$ = 513.3087 found 513.3088 (δ = 0.1 ppm error). $[\alpha]_D^{20}$ = –72.29 (c = 1, CH_2Cl_2).

The deprotected ligand **6** was obtained following the same procedure as for **3**. Purification by short flash chromatography on silica [hexane/ethyl acetate (3:2), 1% triethylamine] yielded **6** (70%). ^{1}H NMR and ^{13}C NMR can be found in the Supporting Information. HRMS: calcd. for $C_{29}H_{40}N_2$ $[M + H]^+$ 417.3264; found 417.3264 (δ = 0.1 ppm error). $[\alpha]_D^{20}$ = –9.86 (c = 1, CH_2Cl_2).

Experimental Procedure for Catalytic Asymmetric Hydrosilylation: In a glove box, to $Fe(acac)_2$ (5.08 mg, 0.02 mmol) in an oven dried 10 mL Schlenk was added a ligand (0.02 mmol) in dry and degassed THF (1.5 mL), followed by the addition of acetophenone (60 μL, 0.5 mmol). The Schlenk was removed from the glove box, and then the reaction mixture was stirred under Argon and heated to 60 °C for 10 min. After removing the oil bath, the silane (1.1 mmol) was added, and the reaction mixture was stirred for 24 h at ambient temperature. Aqueous workup by the addition of HCl (1 N solution, 1 mL) at 0 °C was followed by stirring for 1 h. The mixture was extracted with ethyl acetate, washed with saturated $NaHCO_3$ and brine, and then dried with $MgSO_4$. Filtration over 1 cm silica to remove the remaining traces of the catalyst followed by removal of the solvent provided a yellow oil which was analyzed by NMR (acetaldehyde as internal standard) and chiral HPLC without further purification.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra for new compounds.

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