ELSEVIER

Journal of Organometallic Chemistry 654 (2002) 202–209

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of a new iron Lewis acid catalyst possessing a chelating cyclopentadienyldiphenylphosphinite ligand, (η^5:η^1-$C_5H_4CH(Ph)OPPh_2$)

Michael F. Mayer, M. Mahmun Hossain *

Department of Chemistry, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201, USA

Received 30 January 2002; received in revised form 6 February 2002; accepted 6 February 2002

Abstract

A new iron Lewis acid catalyst, $[(\eta^5:\eta^1\text{-}C_5H_4CH(Ph)OPPh_2)Fe(CO)(THF)]^+[BF_4]^-$ featuring a cyclopentadienyl ring that is tethered to a terminal diphenylphosphinite moiety was created. This is the first complex to contain a chelating η^5:η^1-cyclopentadienyl-phosphinite ligand. This new racemic iron Lewis acid was tested and found to be an effective catalyst in an aziridine-forming reaction. An asymmetric alcohol that is a precursor of the chiral catalyst was synthesized with greater than 95% ee. Upon ligation of the diphenylphosphinite to the iron center, a 3:2 mixture of diastereomers was formed. The diastereomeric mixture of the asymmetric catalysts was utilized in the aziridine-forming reaction and produced the *cis*-aziridine with low enantiomeric excess. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: η^5:η^1-Cyclopentadienyl-phosphinite ligand; Iron Lewis acid catalyst; Aziridines

1. Introduction

We have embarked on the synthesis of a new asymmetric catalyst with the following characteristics; (1) the metal is iron because it is abundant, inexpensive, and relatively non-toxic, (2) it is based upon an achiral complex, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(THF)]^+[BF_4]^-$ (**1**), that is known to be effective for inducing a variety of transformations, and (3) the catalyst has a chiral metal center in order to provide the most effective transfer of chirality.

Previously, the iron Lewis acid complex (**1**) has been shown to catalyze a variety of reactions [1]. A similar complex (**2**), that has a chiral iron center (Fig. 1), was found to be ineffective for inducing the Diels–Alder reaction [2] due, in part, to the reduced Lewis acidity of the complex. However, the more electron-deficient analog (**3**) was found to catalyze the Diels–Alder reaction [2]. Other electron-deficient variants (**4** and **5**) were also shown to be very effective enantioselective Diels–Alder catalyst [3]. The complex **6** (Fig. 1) was synthesized and found to catalyze a cyclopropanation reaction, but no enantioselectivity was observed [4]. The lack of enantioselectivity from **6** was attributed to the free rotation of the chiral cyclopentadienyl (Cp) moiety, with respect to the catalytic binding site. Thus, a further criterion for our new catalyst is to link a chiral Cp moiety to the metal center in order to prevent rotation of the Cp moiety. A linked design of this type is a challenging endeavor [5–7]. Herein, we report the synthesis of a new asymmetric catalyst that embodies the criteria discussed above.

2. Results and discussion

The new synthesis started from the known methyl complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (**7**) [8]. The Cp ring was deprotonated and lithiated with *s*-BuLi. Initially, the lithiated Cp complex was treated with acetyl chloride; however, the reaction did not produce any substituted Cp complexes. We assumed that the reaction was unsuccessful due to the competitive deprotonation of the α-protons of acetyl chloride; therefore, we employed an acid chloride that possessed no α-protons.

* Corresponding author. Fax: +1-414-229-5530.
E-mail address: mahmun@csd.uwm.edu (M.M. Hossain).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01257-3

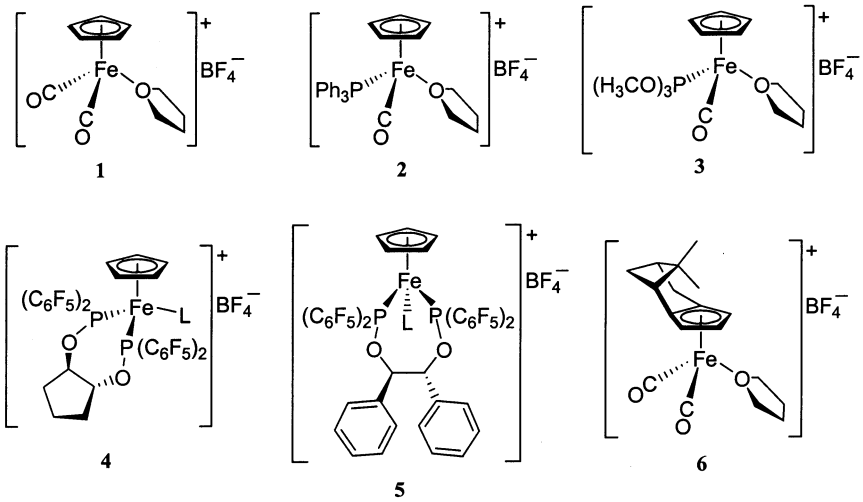
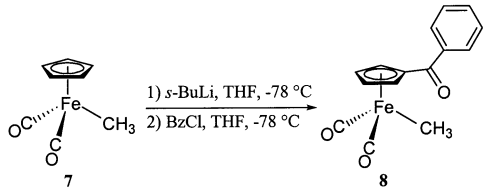


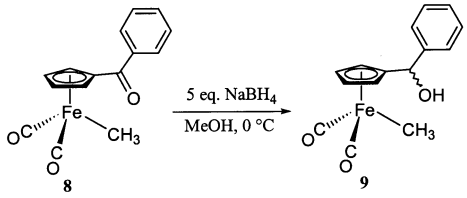
Fig. 1. Selected iron Lewis acid catalysts.

Consequently, the lithiated Cp complex was treated with benzoyl chloride. The reaction was successful (Eq. (1)) and a 60% yield of the benzoylated cyclopentadienyl–iron–methyl complex **8** was isolated after column chromatography. This reaction was amenable to upscaling on the order of several grams. In a gram scale reaction, it was found to be crucial that the concentrations of the reactants in solution were not increased, otherwise, the product yield dramatically decreased. The benzoylated product was stable to air-transfer and could be stored under nitrogen at 0 °C for several months without decomposition.



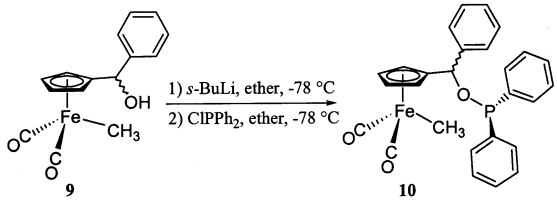
(1)

The ketone **8** was quantitatively reduced to alcohol **9** with five equivalents of $NaBH_4$ (Eq. (2)). Column chromatography was not necessary for purification of this product. Instead, the resulting crude was dissolved into an ether–water mixture and the aqueous layer was further extracted with ether. Upon evaporation of the combined ether extracts under reduced pressure, the pure alcohol **9** was obtained in a 98% yield. The alcohol was stable and could be stored indefinitely under nitrogen at 0 °C.



(2)

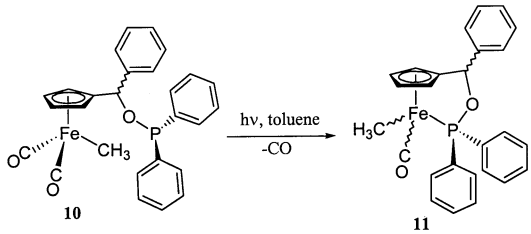
In the next step, the alcohol **9** was deprotonated in order to generate the alkoxide. Subsequent reaction of the alkoxide with chlorodiphenylphosphine produced the diphenylphosphinite complex **10** (Eq. (3)). Several strongly basic reagents were initially employed (NaH, *t*-BuLi, *n*-BuLi) but produced unsatisfactory results. When the deprotonation was performed with *s*-butyl lithium, most of the alcohol was converted to the desired product. After the reaction, the solvent was removed under reduced pressure and the resulting solids were extracted with pentane–ether. Evaporation of the solvents resulted in an orange viscous liquid. Integration of the ^{1}H-NMR spectrum of the resulting liquid showed that it consisted of 70% diphenylphosphinite complex while the remainder was, in equal proportions, unreacted alcohol and one additional unidentified cyclopentadienyl–iron–methyl by-product.



(3)

Photolysis of the terminally substituted diphenylphosphinite complex **10** resulted in the formation of the first complex to possess a chelating η^5:η^1-cyclopentadienyl-linked diphenylphosphinite ligand (Eq. (4)), although many similar η^5:η^1-cyclopentadienyl-linked diphenylphosphine ligands have been reported [5–7]. The ^{1}H-NMR spectrum of the crude reaction mixture showed that the desired product was present as a 1:1 pair of diastereomers. Each diastereomer exhibited a signal near 0 ppm that is characteristic of a methyl group directly connected to iron in complexes of this type. Each signal is split into a doublet due to the three-bond coupling of the methyl protons to the phosphorus atom across the iron center. The coupling constants of the two

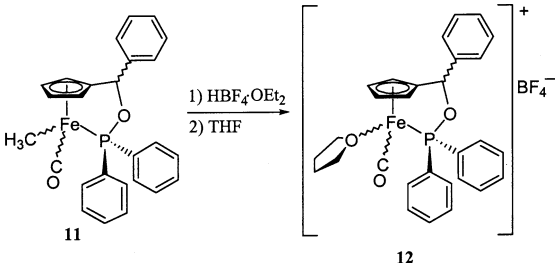
diastereomers are similar but not equivalent, 5.8 and 6.1 Hz, respectively.



(4)

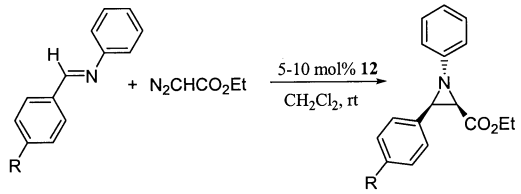
Initially, this photolytic reaction produced a significant amount of the by-product 6-phenylfulvene. In order to suppress the formation of the by-product, the volume of the reaction solution was increased and the reaction solution was placed as close as possible to the light source (400 W mercury vapor lamp). Under these conditions, the reaction was over in about 20 min and a negligible amount of the 6-phenylfulvene was formed.

In the final step of the new synthetic route, the methyl complex **11** was treated with tetrafluoroboric acid–diethyletherate. The reaction mixture was quenched with excess THF and the solvents were removed under reduced pressure resulting in a green powder of racemic iron Lewis acid **12** (Eq. (5)). The crude green product was purified several times by recrystalization from CH_2Cl_2–THF.



(5)

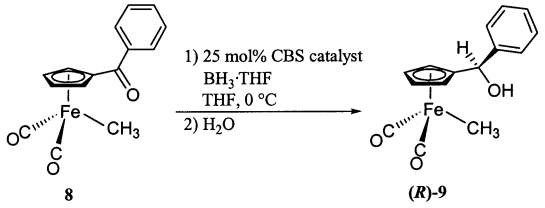
The catalytic activity of the new racemic iron Lewis acid complex (**12**) was tested in an aziridine forming reaction (Eq. (6)). This transformation was chosen because the achiral iron Lewis acid (**1**) is known to catalyze the reaction of imines and diazo compounds to form aziridines [1a]. Further, no general catalytic asymmetric method exists to form aziridines specifically from imines and diazo compounds [9]. Indeed, the Lewis acid **12** was found to be an effective catalyst for the formation of aziridines from aryl imines and ethyl diazoacetate. The reaction of *N*-benzylidene aniline with ethyl diazoacetate afforded 54% yield of *cis*-aziridine. In another reaction, *N*-(4-nitrobenzylidene)aniline and ethyl diazoacetate were reacted in the presence of the racemic Lewis acid (**12**) and produced a 62% yield of *cis* and *trans*-aziridine in a 4:1 ratio. These results were similar to those produced from the achiral dicarbonyl iron Lewis acid catalyst (**1**) [1a]. Thus, knowing that the complex **12** is an effective catalyst for aziridination reaction, the synthesis of an asymmetric version of the catalyst was undertaken.



(6)

In order to introduce asymmetry into the new synthetic scheme, an asymmetric reduction of the ketone **8** was chosen. The chiral oxazaborolidine developed by E.J. Corey et al. (CBS catalyst) [10] seemed most applicable for this particular substrate. The CBS catalyst was prepared by a modified procedure reported by Wright et al. [11].

The benzoyl complex **8** was treated with a THF solution of the CBS catalyst in conjunction with BH_3·THF. The reaction was monitored by TLC and found to take much longer (1 h) than many of the substrates reported by Corey's group (5 min). After the ketone was consumed (monitored by TLC), a couple drops of water were added and the reaction was stirred until the solution ceased to bubble.



(7)

After the reaction, the solvent was removed under reduced pressure and the crude reaction mixture was dissolved in diethyl ether. The solution was passed through a plug of silica gel and dried over sodium sulfate; the solvent was removed under reduced pressure to provide the chiral alcohol **9** in 80% yield with 97% ee (Eq. (7)).

The alcohol illustrated in Eq. (7) is assigned as the (*R*) enantiomer. The stereochemistry of the alcohol was not experimentally determined; rather, its stereochemistry was based upon a transition state model [10] proposed by Corey et al. as shown in Fig. 2.

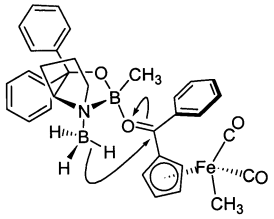
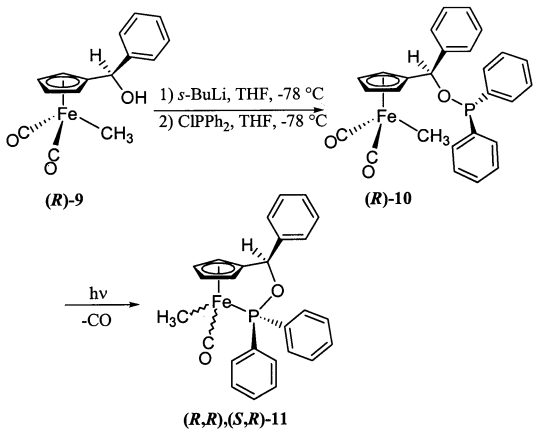


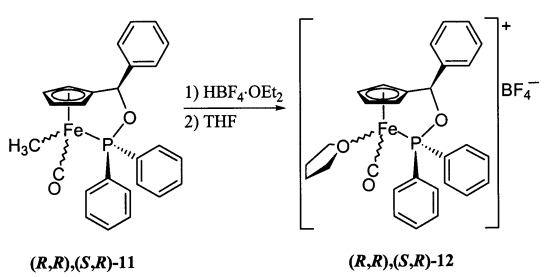
Fig. 2. Transition state model of the enantioselective reduction.

The asymmetric alcohol was subjected to the same treatment as the racemic alcohol in order to convert it into the diphenylphosphinite. The asymmetric terminally functionalized diphenylphosphinite was photolyzed as previously described in order to produce the chelated complex (Eq. (8)). The metal center of this new complex is additionally chiral. Upon ligation of the diphenylphosphinite to the iron center, a 3:2 mixture of diastereomers was formed in contrast to the 1:1 mixture that resulted from photolysis of the racemic diphenylphosphinite. Although disappointing, this result was not unusual. In fact, a 3:2 mixture was also observed by other groups when they synthesized analogous chelated complexes with initial chirality in the Cp-P linker and with secondary chirality at the metal center [6].



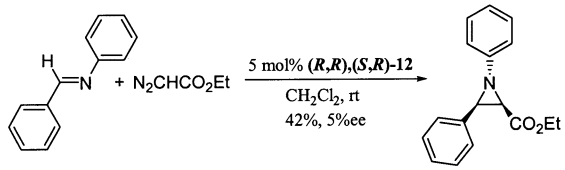
(8)

Since the separation of the diastereomers of the chelated diphenylphosphinite complex was not achieved, the mixture of diastereomers was employed in the final step of the synthesis. The chelated complex was treated with tetraflouroboric acid to produce the iron Lewis acid–THF adduct (Eq. (9)). This product was recrystallized several times and resulted in green powder similar to the racemic one.



(9)

The diastereomeric mixture of the asymmetric iron Lewis acid–THF complexes was employed in the catalytic reaction of ethyl diazoacetate and *N*-benzylidene aniline. The reaction gave, mainly, the *cis*-aziridine in 5% ee (Eq. (10)).



(10)

3. Conclusions

The new complex, $[(\eta^5{:}\eta^1\text{-}C_5H_4CH(Ph)OPPh_2)Fe(CO)(THF)]^+[BF_4]^-$ (**12**), is the first to feature a chelating $\eta^5{:}\eta^1$-cyclopentadienyl-linked-phosphinite ligand. Furthermore, while the metal was attached, the chelating ligand was synthesized with high ee ($>95\%$). Upon ligation of the diphenylphosphinite to the iron center, a 3:2 mixture of diastereomers was formed. The diastereomeric mixture of the asymmetric catalysts was utilized in the aziridine forming reaction produce the *cis*-aziridine with low enantiomeric excess. The lack of enantioselectivity may stem from the ability of the iron Lewis acid to invert configuration at the metal center after the labile THF ligand dissociates from the complex. Thus, future work is aimed at replacing both CO ligands of **1** with linkages to the Cp ring in order to preclude inversion at the metal center.

4. Experimental

4.1. General considerations

All operations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All reaction vessels were flamed under vacuum and filled with nitrogen prior to use. HPLC grade dichloromethane (EM Science) was distilled under nitrogen from phosphorus pentoxide. Reagent grade benzene (EM Science) and toluene (Mallinckrodt) were distilled under nitrogen from sodium. Reagent grade ether (EM Science) and THF (EM Science) were distilled under nitrogen from the sodium-benzophenone ketyl. Technical grade pentane (Phillips) was mixed with concentrated sulfuric acid, washed with sodium bicarbonate, washed with distilled water, dried over sodium sulfate, and distilled from sodium. HPLC grade methanol (EM Science) was distilled under nitrogen from magnesium iodide. HPLC grade ethyl acetate (Spectrum) was dried over 4*A* molecular sieves. Untreated reagent grade hexanes (EM Science) were used for column chromatography. All other reagents were commercially available and used as received. Flash chromatography was performed using EM Science silica gel 60, 70–230 mesh. Thin-layer chromatography was performed using

EM Science F_{254} silica gel (230–400 mesh). ^{1}H-NMR spectrometry was performed using a Bruker 250 or a 300 MHz spectrometer. ^{13}C-NMR spectrometry was performed at 62.9 MHz. ^{31}P-NMR spectrometry was performed at 121.5 MHz. IR spectra were obtained as described on a Perkin–Elmer 1600 series FTIR. GC–MS (EI) was performed at either 70 or 15 eV. Elemental analysis was performed using a CE Instruments EA 1110 analyzer set up for carbon, hydrogen, and nitrogen analysis.

4.2. (η^5-$C_5H_4COPh)(CO)_2FeCH_3$ (**8**)

A 3.46 g (18.0 mmol) sample of methyl complex **7** was dissolved into 150 ml THF. The solution was cooled to −78 °C. Over 20 min, 1.75 equivalents of 1.3 M *s*-BuLi, 23.5 ml (30 mmol), were added to the THF solution. A separate solution was prepared by adding 5.12 ml (43 mmol) of benzoyl chloride to 75 ml THF and, subsequently, cooled to −78 °C. The (η^5-$C_5H_4Li)(CO)_2FeCH_3$ solution was transferred to the BzCl solution drop-by-drop over 30 min through a cannula. The combined solutions were stirred for 2 more h at −78 °C. The solution was allowed to warm to room temperature (r.t.) and was passed through a pad of silica gel (prewetted with ether) under N_2. The silica was rinsed with 50 ml ether and the combined solutions were evaporated under reduced pressure to provide a brown oil. The crude product was separated on a silica gel column, eluting with 0–20% ether in pentane. The first fraction contained unreacted methyl complex (**7**). The second and third fractions were shown by ^{1}H-NMR to contain the desired product with other impurities (mostly unreacted benzoyl chloride). These last two fractions were combined and chromatographed again on the silica gel. The center of a brown band (fraction 2) that came down when eluted with 8% ether in pentane contained pure product, 3.2 g (60% yield). ^{1}H-NMR ($CDCl_3$): δ 7.79–7.76 (m, 2H), 7.60–7.55 (m, 1H), 7.50–7.45 (m, 2H), 5.43–5.41 (t, $J = 2.3$ Hz, 2H), 4.98–4.96 (t, $J = 2.3$ Hz, 2H), 0.26 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 215.1, 192.2, 138.6, 132.3, 128.5, 128.1, 92.4, 90.8, 85.9, −20.7. IR (CH_2Cl_2): ν_{max} 2968, 2896, 2016, 1961, 1650, 1455, 1294, 708 cm^{-1}. EIMS (15 eV) *m/z* (%): 296 (3) [M$^+$], 268 (23) (M$^+$-CO), 240 (51) (M$^+$-2CO), 225 (86) (M$^+$-2CO, –CH_3), 105 (54) (PhCO$^+$), 77 (42) (Ph$^+$), 56 (100) (Fe$^+$). HRMS Anal. Calc. for $C_{15}H_{12}O_3Fe$ 296.0136, Found: 296.0131. Anal. Calc. for $C_{15}H_{12}O_3Fe$: C, 60.84; H, 4.08. Found: C, 61.17; H, 4.14%.

4.3. (η^5-$C_5H_4CH(OH)Ph)(CO)_2FeCH_3$ (**9**)

A 1.91 g (6.4 mmol) sample of benzoyl complex **8** was dissolved into 50 ml of MeOH and cooled to 0 °C. The $NaBH_4$, 1.24 g (32 mmol), was slowly added to the solution to control the rapid evolution of bubbles. The reaction was stirred for 90 min and then the solvent was removed under reduced pressure. The crude solid was dissolved in ether and transferred to a separatory funnel. The ether layer was extracted three times with distilled water and dried over Na_2SO_4. The solvent was removed under reduced pressure to provide relatively pure alcohol in 98% yield. Dissolving the crude alcohol in ether and passing the solution through a pad of silica gel further purified the alcohol. ^{1}H-NMR ($CDCl_3$): δ 7.50–7.30 (m, 5H), 5.46 (d, $J = 3.2$ Hz, 1H, C*H*OH), 4.95 (m, 1H), 4.65 (m, 2H), 4.61 (m, 1H), 2.15 (d, $J = 3.2$ Hz, 1H, CHO*H*), 0.19 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 217.1, 142.7, 128.6, 128.2, 126.3, 84.6, 84.2, 83.1, 70.8, −22.4. IR (CH_2Cl_2): ν_{max} 3590, 2960, 2890, 2004, 1946, 1050 cm^{-1}. EIMS *m/z* (%): 298 (5) [M$^+$], 270 (7) (M$^+$-CO), 242 (31) (M$^+$-2CO), 227 (100) (M$^+$-2CO, –CH_3), 153 (84) (C_5H_4=CPh$^+$). HRMS Calc. for $C_{15}H_{14}O_3Fe$ 298.0292, Anal. Found: 298.0283.

4.4. (η^5-$C_5H_4CH(OPPh_2)Ph)(CO)_2FeCH_3$ (**10**)

The alcohol complex **9**, 680 mg (2.3 mmol), was dissolved into 60 ml ether and the solution was cooled to −78 °C and 1.5 equivalents of 1.3 M *s*-BuLi, 2.63 ml (3.4 mmol), was added to the alcohol solution. The reaction was stirred at −78 °C for 24 h. Then 1.5 equivalents of $ClPPh_2$, 0.65 ml (3.4 mmol), was added and the reaction mixture was stirred for another 24 h at −78 °C. The solvent was removed under reduced pressure. The resulting crude mixture was washed three times with a mixture of pentane and ether (1:3). The combined extracts were reduced under vacuum to oil. The ^{1}H-NMR spectrum showed, by integration, the desired diphenylphosphinite complex, which comprised greater than 70% of the crude extracts. This crude could not be successfully purified further without causing serious degradation. Due to the impurities and instability, this complex was not fully characterized. ^{1}H-NMR ($CDCl_3$): δ 7.7–7.1 (m, 15H), 5.62–5.59 (d, $J = 8.5$ Hz, 1H, C*H*OPPPh$_2$), 4.83 (d, $J = 1.8$ Hz, 1H), 4.59 (s, 2H), 4.49 (d, $J = 1.9$ Hz, 1H), 0.09 (s, 3H). IR (toluene): ν_{max} 3000, 2918, 2005, 1948, 1607, 1489, 1000, 690 cm^{-1}.

4.5. (η^5:η^1-$C_5H_4CH(OPPh_2)Ph)(CO)FeCH_3$ (**11**)

The diphenylphosphinite complex **10** (400 mg) was dissolved into 60 ml toluene in a pyrex photolytic chamber surrounding a quartz, water-jacketed, 400 W mercury vapor lamp. The apparatus was submerged into a bucket of ice water. The solution was continually bubbled with N_2 gas throughout the reaction. The solution (1 ml) was periodically removed and an IR spectrum was obtained in order to monitor the extent of the reaction. The solution was irradiated for a total of 10 h in order for the IR spectrum to show that the

reaction had gone at least halfway. The solvent was removed under vacuum. An ^{1}H-NMR spectrum ($CDCl_3$) was obtained of the crude product and showed the two product diastereomers in addition to the by-product, 6-phenylfulvene, but no starting material remained. The crude product was separated on a silica gel column with pentane. 6-Phenylfulvene: ^{1}H-NMR ($CDCl_3$): δ 7.64–7.60 (m, 2H), 7.45–7.39 (m, 3H), 7.25 (s, 1H), 6.72–6.68 (m, 2H), 6.54–6.52 (m, 1H), 6.37–6.33 (m, 1H). The two diastereomers were obtained and characterized as a 1:1 mixture. Diastereomer 1: ^{1}H-NMR ($CDCl_3$): δ 7.85–7.10 (m, 15H), 5.89–5.86 (d, $J = 7.8$ Hz, 1H, C*H*OP), 4.74–4.72 (m, 2H), 4.52–4.50 (m, 1H), 4.20–4.19 (m, 1H), −0.17–(−0.19) (d, $J = 5.8$ Hz, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, referenced to 80% H_3PO_4): δ 196.6. Diastereomer 2: ^{1}H-NMR ($CDCl_3$): δ 7.85–7.10 (m, 15H), 5.51–5.50 (d, $J = 2.5$ Hz, 1H, C*H*OP), 4.83–4.82 (m, 1H), 4.74–4.72, (m, 1H), 4.52–4.50 (m, 2H), −0.21–(−0.23) (d, $J = 6.1$ Hz, 3H, CH_3). ^{31}P-NMR ($CDCl_3$, referenced to 80% H_3PO_4): δ 195.0. IR of 1:1 mixture (toluene): ν_{max} 1918, 1083, 1000 cm^{-1}.

4.6. $[(\eta^5{:}\eta^1\text{-}C_5H_4CH(OPPh_2)Ph)(CO)Fe(THF)]^+[BF_4]^-$ (**12**)

A 75 mg (0.165 mmol) sample of the complex **11** was dissolved into 8 ml CH_2Cl_2 and cooled to −78 °C. A 0.8 equivalent of HBF_4, 0.02 ml at 54 wt.% in Et_2O (0.132 mmol), was added, and the CH_2Cl_2 solution turned from orange to brown. The solution was stirred for 30 min at −78 °C; then 5 ml THF was added. The solution was stirred for an additional 30 min, the solvent was removed under reduced pressure, leaving a dark green solid. The crude product was purified three times by dissolving the solid in 3 ml THF and cooling to −78 °C, then reprecipitating the complex by addition of 5 ml pentane. Satisfactory NMR spectra were not obtained. IR (CH_2Cl_2): ν_{max} 1991 (CO), 1695, 1424, 1272, 1033, 712 cm^{-1}.

4.7. Test for catalysis using $[(\eta^5{:}\eta^1\text{-}C_5H_4CH(OPPh_2)Ph)(CO)Fe(THF)]^+[BF_4]^-$ (**12**) in the reaction of *N*-benzylidene aniline and ethyl diazoacetate

A 64 mg (0.106 mmol, 10 mol%) sample of racemic complex **12** was dissolved in 4 ml CH_2Cl_2. To the catalyst solution, a 197 mg (1.06 mmol) sample of *N*-benzylidene aniline was added. A separate solution was created by diluting 0.155 ml at 90% (1.33 mmol) ethyl diazoacetate (EDA) to 5 ml with CH_2Cl_2. The EDA solution was added by syringe pump over 5 h to the imine–catalyst solution and stirred for a total of 19 h at r.t. Then, 5 ml THF was added to the reaction and the solution was further stirred for 1 h. The crude mixture was passed through a silica gel plug and eluted with ether in order to remove the catalyst. Silica gel column chromatography of the crude (2–8% EtOAc in pentane) provided 154 mg of the *cis*-aziridine (54%). No *trans*-aziridine was isolated from the reaction.

4.8. Test for catalysis using $[(\eta^5{:}\eta^1\text{-}C_5H_4CH(OPPh_2)Ph)(CO)Fe(THF)]^+[BF_4]^-$ (**12**) in the reaction of (*N*-4-nitrobenzylidene)aniline and ethyl diazoacetate

A 31 mg (0.052 mmol, 5 mol%) sample of racemic complex **12** was dissolved in 4 ml CH_2Cl_2. To the catalyst solution, a 237 mg (1.03 mmol) sample of *N*-(4-nitrobenzylidene)aniline was added. A separate solution was created by diluting 0.150 ml at 90% (1.29 mmol) EDA to 5 ml with CH_2Cl_2. The EDA solution was added by syringe pump over 5 h to the imine–catalyst solution and stirred for a total of 18 h at r.t. Then, 5 ml THF was added to the reaction and the solution was further stirred for 1 h. After the reaction, the crude was passed through a silica gel plug and eluted with ether in order to remove the catalyst. Silica gel column chromatography (2–8% EtOAc in pentane) of the crude mixture provided 200 mg of the *cis* and *trans*-aziridine (62% yield) in 4:1 ratio.

4.9. $(\eta^5\text{-}C_5H_4CH(OH)Ph)(CO)_2FeCH_3$ ((**R**)-**9**)

The oxazaborolidine complex, 40 mg (0.145 mmol, 25 mol%), was dissolved in 2 ml THF and cooled to 0 °C. A 0.145 ml (0.145 mmol, 1 M) sample of $BH_3{\cdot}THF$ was added to the oxazaborolidine solution and stirred for 5 min. A 172 mg (0.58 mmol) sample of **8** was dissolved in 3 ml THF. The solution of **8** and 0.29 ml (0.29 mmol) $BH_3{\cdot}THF$ were added together over 8 min to the oxazaborolidine solution and stirred at 0 °C. The reaction was monitored by TLC (silica gel plate, 20% ether–80% pentane); ketone $R_f = 0.34$, alcohol $R_f = 0.25$. After 105 min, the reaction appeared to be complete. The solvent was removed under reduced pressure and the crude was redissolved in 4 ml of moist ether and dried over anhydrous Na_2SO_4. The supernatant was filtered through glass wool and the solvent removed under reduced pressure. Silica gel chromatography of the crude with 4–14% ether in pentane provided 136 mg (80% yield) of chiral alcohol.

4.10. Chiral HPLC of the alcohol complex $(\eta^5\text{-}C_5H_4CH(OH)Ph)(CO)_2FeCH_3$ ((**R**)-**9**)

A chiral Regis (*S*,*S*)-Whelk-O-1 column was employed. Using a 1% isopropyl alcohol–99% hexanes solvent system at a flow rate of 2 ml min^{-1} and a pressure of 1080 psi, the racemic alcohol complex was resolved. The peaks for the (*R*) and (*S*)-enantiomers (racemic) were baseline resolved with column retention

times of 7.52 and 8.49 min, respectively, and peak area ratio of 49.876:48.838. The peaks for the asymmetric alcohol sample, with the measured specific rotation of 19.5°, came through at 7.59 and 8.65 min and had a peak area ratio of 98.312:1.688, respectively, which corresponds to an enantiomeric excess of 96.6%. From most of the asymmetric reductions, only the one enantiomer was detected using this technique. However, occasional reductions provided the alcohol product with a lower enantiomeric excess (as low as 85% ee).

*4.11. Determination of the optical rotation of the asymmetric alcohol complex ((**R**)-**9**)*

In order to obtain stable optical rotation measurements, a freshly purified sample was required. The sample was purified on a silica gel plug with pentane–ether (1:1) and the solvent was removed under reduced pressure. A portion of the oil (20 mg) was dissolved into freshly distilled methanol (1 ml) that was bubbled with N_2 gas for 20 min prior. The average rotation of ten measurements provided $[\alpha]_D^{25} = 19.5°$.

*4.12. (η^5-$C_5H_4CH(OPPh_2)Ph)(CO)_2FeCH_3$ ((**R**)-**10**)*

The reaction was carried out according to the same procedure described for the racemic complex **10**, using 0.894 g (3.0 mmol) of the complex ***R*-9**, 3.46 ml (4.5 mmol) of 1.3 M *s*-BuLi and 0.85 ml at 95% (4.5 mmol) of chlorodiphenylphosphine at −78 °C. Workup followed by separation of the crude mixture by extraction with pentane–ether (1/3) resulted in 1.658 g (80%) of complex (***R***)-**10** and some unreacted alcohol (∼15%).

*4.13. (η^5:η^1-$C_5H_4CH(OPPh_2)Ph)(CO)FeCH_3$ ((**RR**),(**SR**)-**11**)*

The reaction was carried out according to the same procedure described for the racemic complex **11**, using 1.658 (3.0 mmol) of the complex (***R***)-**10.** Workup followed by separation of the crude mixture by column chromatography at −78 °C resulted in 0.408 g (80%) orange oil of diastereomers (***RR***)-**11** and (***SR***)-**11** in a 3:2 ratio.

*4.14. [(η^5:η^1-$C_5H_4CH(OPPh_2)Ph)(CO)Fe(THF)]^+[BF_4]^-$ ((**RR**),(**SR**)-**12**)*

The reaction was carried out according to the same procedure described for complex **12**, using 0.286 g (0.63 mmol) and 0.07 ml at 54 wt.% in ether (0.50 mmol) at −78 °C. Workup followed by recrystallization resulted in a dry green powder of complexes (***RR***),(***SR***)-**12**.

*4.15. Test for asymmetric catalysis using [(η^5:η^1-$C_5H_4CH(OPPh_2)Ph)(CO)Fe(THF)]^+[BF_4]^-$ ((**RR**),(**SR**)-**12**) in the reaction of N-benzylidene aniline and ethyl diazoacetate*

The asymmetric iron Lewis acid–THF adduct (3:2 mixture of diastereomers), 44 mg (0.073 mmol, 5 mol%), was dissolved in 5 ml CH_2Cl_2. A 270 mg (1.46 mmol) sample of *N*-benzylidene aniline was added to the catalyst solution. An EDA solution (0.231 ml at 90%, 1.83 mmol in 5 ml CH_2Cl_2) was added by syringe pump over 5 h to the imine–catalyst solution and stirred for a total of 18 h at r.t. In order to remove the catalyst, the crude was passed through a silica gel plug and eluted with ether. The solvent was evaporated under reduced pressure and the crude was separated by silica gel column chromatography (2–8% EtOAc in pentane) resulting in 166 mg of the *cis*-aziridine (42%).

4.16. Chiral HPLC of cis-2-ethoxycarbonyl-1,3-diphenylaziridine

A chiral Regis (*S*,*S*)-Whelk-O-1 column was employed. Using a 1% isopropyl alcohol–99% hexanes solvent system at a flow rate of 1 ml min^{-1} and a pressure of 460 psi, the racemic *cis*-2-ethoxycarbonyl-1,3-diphenylaziridine was resolved. The peaks for the two enantiomers of the racemate were baseline resolved with column retention times of 16.89 and 19.00 min and with a peak area ratio of 46.219:53.751, respectively. The inequality in the peak areas most likely stems from the fact that the peak widths are not equal. Utilizing various conditions did not improve the balance in the peak area ratio. Rather, in all cases the peak areas were similar to this ratio and the second peak was consistently shorter and wider than the peak with a shorter retention time. In the determination of the enantiomeric excess of the *cis*-aziridine derived from the asymmetric iron Lewis acid catalyzed reaction, the above conditions were utilized and the above peak ratio was used as the standard for a racemic mixture. The *cis*-aziridine product of the catalytic asymmetric reaction was run and resulted in peaks at 16.71 and 18.80 min. The respective peak areas were 36.16 and 46.05, which translates to a 5% ee.

Acknowledgements

We gratefully thank the NIH for partial financial support of this research project.

References

[1] (a) M.F. Mayer, M.M. Hossain, J. Org. Chem. 63 (1998) 6839;
(b) S.J. Mahmood, M.M. Hossain, J. Org. Chem. 63 (1998) 3333;
(c) S.J. Mahmood, A.K. Saha, M.M. Hossain, Tetrahedron 54 (1998) 349;
(d) J. Picione, S.J. Mahmood, A. Gill, M. Hilliard, M.M. Hossain, Tetrahedron Lett. 39 (1998) 2681;
(e) W.J. Seitz, M.M. Hossain, Tetrahedron Lett. 35 (1994) 7561;
(f) W.J. Seitz, A.K. Saha, M.M. Hossain, Organometallics 12 (1993) 2604;
(g) W.J. Seitz, A.K. Saha, D. Casper, M.M. Hossain, Tetrahedron Lett. 33 (1992) 7755;
(h) M. Rosenblum, D. Scheck, Organometallics 1 (1982) 397.

[2] A.S. Olson, W.J. Seitz, M.M. Hossain, Tetrahedron Lett. 32 (1991) 5299.

[3] (a) M.E. Bruin, E.P. Kündig, Chem. Commun. (1998) 2635.;
(b) E.P. Kündig, B. Bourdin, G. Bernardinelli, Angew. Chem. Int. Ed. Engl. 33 (1994) 1856.

[4] W.J. Seitz, Ph.D. thesis, University of Wisconsin-Milwaukee, 1993.

[5] (a) For reviews see: H. Butenschön, Chem. Rev. 100 (2000) 1527;
(b) U. Siemeling, Chem. Rev. 100 (2000) 1495;
(c) C. Müller, D. Vos, P. Jutzi, J. Organomet. Chem. 600 (2000) 127;
(d) P. Jutzi, T. Redeker, Eur. J. Inorg. Chem. (1998) 663;
(e) P. Jutzi, U. Siemeling, J. Organomet. Chem. 500 (1995) 175;
(f) J. Okuda, Comments Inorg. Chem. 16 (1994) 185;
(g) N.J. Coville, K.E. du Plooy, W. Pickl, Coord. Chem. Rev. 116 (1992) 1.

[6] (a) For asymmetric complexes containing (η^5:η^1-Cp(linker)PPh_2) ligands see: S. Ciruelos, U. Englert, A. Salzer, C. Bolm, A. Maischak, Organometallics 19 (2000) 2240;
(b) Y. Matsushima, K. Onitsuka, S. Takahashi, Chem. Lett. (2000) 760;
(c) N. Dodo, Y. Matsushima, M. Uno, K. Onitsuka, S. Takahashi, J. Chem. Soc. Dalton Trans. (2000) 35;
(d) A.A.H. van der Zeijden, J. Jimenez, C. Mattheis, C. Wagner, K. Marzweiler, Eur. J. Inorg. Chem. (1999) 1919;
(e) B.M. Trost, B. Vidal, M. Thommen, Chem. Eur. J. 5 (1999) 1055;
(f) T.A. Mobley, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 3253;
(g) Y. Nishibayashi, I. Takei, M. Hidai, Organometallics 16 (1997) 3091;
(h) Y. Kataoka, Y. Iwato, A. Shibahara, T. Yamagata, K. Tani, Chem. Commun. (2000) 841;
(i) Y. Kataoka, Y. Iwato, T. Yamagata, K. Tani, Organometallics 18 (1999) 5423;
(j) Y. Kataoka, Y. Saito, K. Nagata, K. Kitamura, A. Shibahara, K. Tani, Chem. Lett. (1995) 833.

[7] (a) For non-asymmetric complexes containing (η^5:η^1-Cp(linker)PR_2) ligands see: H.H. Karsch, V.W. Graf, W. Scherer, J. Organomet. Chem. 604 (2000) 72;
(b) D.P. Krut'ko, M.V. Borzov, E.N. Veksler, R.S. Kirsanov, A.V. Churakov, Eur. J. Inorg. Chem. (1999) 1973;
(c) L. Weber, M.H. Scheffer, H.-G. Stammler, B. Neumann, Inorg. Chim. Acta 291 (1999) 311;
(d) L. Lefort, T.W. Crane, M.D. Farwell, D.M. Baruch, J.A. Kaeuper, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 3889;
(e) B.E. Bosch, G. Erker, R. Fröhlich, O. Meyer, Organometallics 16 (1997) 5449;
(f) J.R. Butchard, O.J. Curnow, S.J. Smail, J. Organomet. Chem. 541 (1997) 407;
(g) I. Lee, F. Dahan, A. Maisonnat, R. Poilblanc, J. Organomet. Chem. 532 (1997) 159;
(h) T.-F. Wang, J.-P. Juang, Y.-S. Wen, J. Organomet. Chem. 503 (1995) 117;
(i) R.T. Baker, J.C. Calabrese, R.L. Harlow, I.D. Williams, Organometallics 12 (1993) 830;
(j) A.M.Z. Slawin, D.J. Williams, J. Crosby, J.A. Ramsden, C. White, J. Chem. Soc. Dalton Trans. (1988) 2491;
(k) T. Kauffmann, J. Olbrich, Tetrahedron Lett. 25 (1984) 1967;
(l) C. Charrier, F. Mathey, J. Organomet. Chem. 170 (1979) C41;
(m) M.I. Bruce, R.C.F. Gardner, B.L. Goodall, F.G.A. Stone, R.J. Doedens, J.A. Moreland, J. Chem. Soc. Chem. Commun. (1974) 185;
(n) V.G. Andrianov, Y.A. Chapovskii, V.A. Semion, Y.T. Struchkov, Chem. Commun. (1968) 282.

[8] See [1b] or T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 3 (1956) 104.

[9] (a) J.C. Antilla, W.D. Wulff, Angew Chem. Int. Ed. 39 (2000) 4518;
(b) J.C. Antilla, W.D. Wulff, J. Am. Chem. Soc. 121 (1999) 5099;
(c) K. Juhl, R.G. Hazell, K.A. Jørgensen, J. Chem. Soc. Perkin Trans. 1 (1999) 2293;
(d) K.G. Rasmussen, R.G. Hazell, K.A. Jørgensen, Acta Chem. Scand. 52 (1998) 1056;
(e) T.B. Gunnoe, M. Surgan, P.S. White, J.L. Templeton, L. Casarrubios, Organometallics 16 (1997) 4865;
(f) K.G. Rasmussen, K.A. Jørgensen, J. Chem. Soc. Perkin Trans. 1 (1997) 1287;
(g) V.K. Aggarwal, A. Thompson, R.V.H. Jones, M.C.H. Standen, J. Org. Chem. 61 (1996) 8368;
(h) K.G. Rasmussen, K.A. Jørgensen, J. Chem. Soc. Chem. Commun. (1995) 1401;
(i) K.B. Hansen, N.S. Finney, E.N. Jacobsen, Angew. Chem. Int. Ed. Engl. 34 (1995) 676.

[10] (a) E.J. Corey, C.J. Helal, Tetrahedron Lett. 37 (1996) 4837;
(b) E.J. Corey, C.J. Helal, Tetrahedron Lett. 36 (1995) 9153;
(c) E.J. Corey, R.K. Bakshi, S. Shibata, C.-P. Chen, V.K. Singh, J. Am. Chem. Soc. 109 (1987) 7925;
(d) E.J. Corey, R.K. Bakshi, S. Shibata, J. Am. Chem. Soc. 109 (1987) 5551.

[11] J. Wright, L. Frambes, P. Reeves, J. Organomet. Chem. 476 (1994) 215.