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Effect of the Structure of the Diamine Backbone of P−N−N−P ligands in Iron(II) Complexes on Catalytic Activity in the Transfer Hydrogenation of Acetophenone

Alexandre A. Mikhailine and Robert H. Morris*

Davenport Laboratory, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

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The asymmetric transfer hydrogenation of aromatic ketones can be efficiently accomplished using catalysts that are based on platinum group metals which are more toxic and less abundant than iron. For that reason the discovery of iron based catalysts for the use in this transformation is important. To address this issue, we synthesized a new series of iron(II)-based precatalysts *trans*-[Fe(Br)(CO)(PPh_2CH_2CH=NCHRCHRN=$CHCH_2PPh_2$)]BPh_4 (**5a**−**5d**) containing P−N−N−P ligands with the diamines (*R,R*)-1,2-diaminocyclohexane (**a**), (*R,R*)-1,2-diphenyl-1,2-diaminoethane (**b**), (*R,R*)-1,2-di(4-methoxyphenyl)-1,2-diaminoethane (**c**), and ethylenediamine (**d**) incorporated in the backbone using a convenient one-pot synthesis using readily available starting materials. All of the complexes, when activated with a base, show a very high activity in the transfer hydrogenation catalysis of acetophenone, using 2-propanol as a reducing agent under mild conditions. A comparison of the TOF of complexes **5a**−**5d** show that the catalytic activity of complexes increase as the size of the substituents in the backbone of ligands increases (**d** < **a** < **b** = **c**).

Introduction

The reduction of pro-chiral ketones to valuable chiral alcohols is an important process for both industrial and academic purposes.[1−3] This transformation can be efficiently accomplished using catalysts that are based on platinum group metals (PGM) in combination with different reducing agents.[3−33] On the other hand, the use of less toxic, more abundant and inexpensive metals would be highly beneficial. Recently, several groups have replaced PGM-containing catalysts with those based on first row transition metals. Iron, in particular, is an interesting alternative because of its chemical properties such as easily varied oxidation states,

*To whom correspondence should be addressed. E-mail: rmorris@chem.utoronto.ca.

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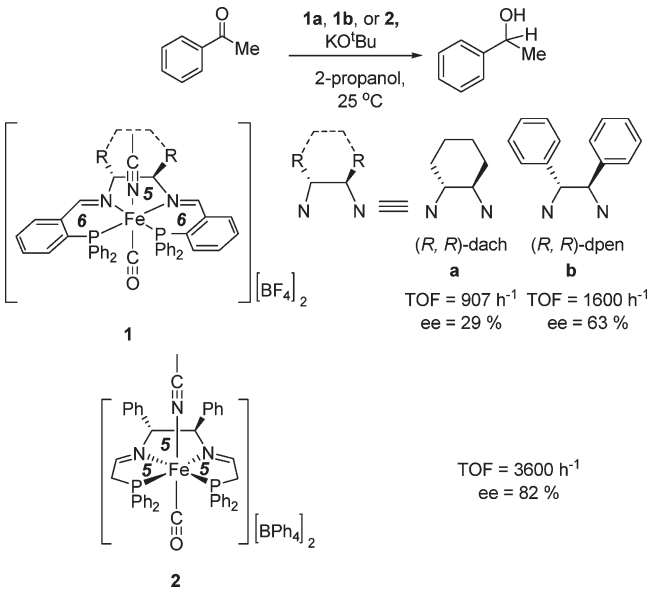
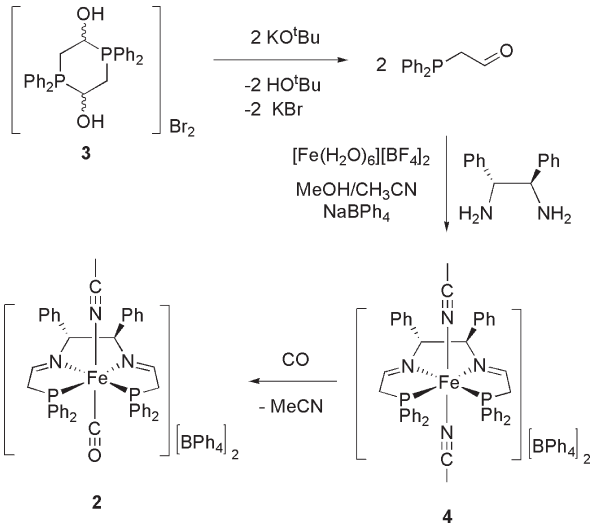
Scheme 1. Examples of Well-Defined Iron-Based Asymmetric Transfer Hydrogenation Precatalysts



well investigated coordination properties and Lewis acidity as well as low toxicity and high abundance.[34−43] Some other reactions such as cross-coupling, cycloadditions, and polymerization that are important for industrial and synthetic applications can now be accomplished using iron-based catalytic systems,[44] although harsh conditions such as high temperature, high catalyst loading, and additives are often required for a successful reaction. Hand-in-hand with the development of new catalytic processes must come studies designed to probe the mechanism of action of these new iron catalysts. Our approach is the preparation and utilization of well-defined homogeneous catalysts to gain an understanding of their mechanism.

Our group reported the first highly active, well-defined iron-based asymmetric precatalysts for the reduction of pro-chiral aromatic ketones to chiral alcohols (Scheme 1).[35] Gao and co-workers had previously reported the use of a less well-defined system where an iron carbonyl cluster and a

Scheme 2. Reported Synthesis of the Precatalyst **2**



P−N−N−P ligand were mixed in situ to give a catalyst of lower activity.[34] The P−N−N−P ligands in these systems were prepared from a commercially available phosphine aldehyde and enantiopure diamines. In the complexes of our initial study, the tetradentate ligands form 6-, 5-, and 6- membered rings with the iron. Although the catalyst activity was promising, the enantiomeric excess (ee) of the product alcohols were low, and the starting organophosphorus compound was limited in availability. For this reason, we prepared by means of a template synthesis method a second generation of iron precatalyst **2** with a P−N−N−P ligand that has a smaller numbers of atoms in the ligand−metal rings (5, 5, 5).[36] The diamine used in the template synthesis, 1,2-diphenyl-1,2-diaminoethane (dpen), provided the chirality for the catalyst. This turned out to be more active and enantioselective than the first generation catalyst **1b** with (6, 5, 6) rings. In the current report we investigate the effect of incorporating different diamines into the backbone of the P−N−N−P ligand on the activity of the resulting catalysts in the transfer hydrogenation of the aromatic ketones.

Results and Discussion

Synthesis of the Complexes. Imine formation is usually accomplished in organic synthesis via the condensation of aldehydes with amines. Stabilizing groups such as electron-withdrawing substituents on nitrogen, or unsaturated groups in conjugation with the imine group that is formed, favor the reaction.[45] These factors make the synthesis of the P−N−N−P ligand of complex **1** easier than that of **2**. On the other hand, we have reported that iron(II) serves as a template in the condensation of diamines with the unstable phosphine aldehyde PPh_2CH_2CHO released by the action of the strong base from the phosphonium salt **3** (Scheme 2).[36,46] This leads to the efficient formation of the desired complex containing a P−N−N−P ligand and two *trans* acetonitrile ligands. One problem that detracts from the convenience of the method is the separation of the complex *trans*-$[Fe(NCMe)_2(PNNP)]^{2+}$ from stoichiometric

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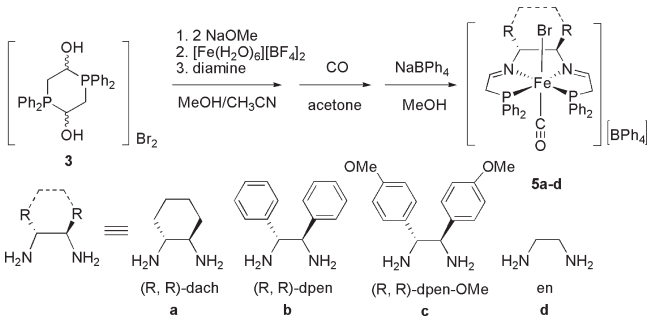
Scheme 3. One Pot Synthesis of Iron(II) Precatalysts **5a**−**5d** Starting from Dimer **3**



amounts of salts that are formed in the reaction. We reported that for the dpen-derived complex this can be overcome by the selective precipitation of the bis(acetonitrile) complex as the tetraphenylborate salt.[36] Then the carbonyl-containing precatalyst was simply prepared by stirring a solution of the bis(acetonitrile) complex **4** in acetone under an atmosphere of carbon monoxide.

An attempt to synthesize similar iron(II) complexes with other diamines using the template procedure led to the formation of a byproduct in the last step of the synthesis as was determined by ^{31}P NMR. The electrospray ionization mass spectrometry (ESI-MS) spectrum of the mixture had a significant peak at 697.0828 m/z, showing that one of the products contained bromide coordinated to the iron along with carbonyl and P−N−N−P ligands. Our group has recently reported the synthesis and characterization by single crystal X-ray diffraction of similar iron(II) complexes with bromide *trans* to carbonyl.[47] This observation directed us to a new optimized one pot synthesis of active iron(II) complexes **5** (Scheme 3).

The template synthesis starting from the dimer **3**, diamine, and iron(II) precursor was performed in an identical fashion to the previously reported template procedure, but the isolation of the bis(acetonitrile) complex **4** was omitted. The solvent mixture of acetonitrile and methanol was evaporated and replaced with acetone, and the resulting solution was subjected to a CO atmosphere. The Br^-/CO complexes **5** are more thermodynamically stable compared with the CH_3CN/CO complexes **2**, since the formation of **5** was observed when Br^- was present in small quantity in the reaction mixture containing a large excess of acetonitrile. The greater stability of complex **5** compared with that of complex **2** can be explained by the strong, ionic $Fe^{2+}-Br^-$ bond relative to the weaker ion-dipole $Fe^{2+}-N^{\delta-}$ bond of an acetonitrile ligand. The selective precipitation of the resulting complex with $NaBPh_4$ from methanol yielded the desired compounds **5** contaminated with salts. A convenient purification method is the filtration of a dichloromethane solution of the crude product through Celite. This general procedure was used to successfully synthesize and purify complexes **5a**−**5d** in moderate to good yields using a range of diamines as shown in Scheme 3.

Properties of the Complexes. Complexes **5a**−**5d** were isolated as yellow, slightly air-sensitive solids. They demonstrate similar solubility properties: soluble in dichloromethane, acetone, and acetophenone but insoluble in other common solvents. The complexes were characterized by ^{1}H, ^{31}P, ^{13}C NMR, HRMS, and FTIR. Selected properties are listed in Table 1. Complexes **5a**−**5c** that contain a chiral diamine incorporated into the backbone have inequivalent phosphorus atoms because of the lack of symmetry. This was signaled in the ^{31}P{^{1}H} NMR spectra by the appearance of two doublets as opposed to the singlet observed for the C_2- symmetrical bis(acetonitrile) complex **4**. The carbonyl ^{13}C NMR resonance was only detected for complexes **5b** (at 214.9 ppm) and **5c** (215.1 ppm). Complex **5c** gave the expected two doublets due to coupling to two inequivalent phosphorus atoms. The long relaxation time of the carbonyl-carbon of **5a** and **5d** presumably prevented the detection of their carbonyl resonances. On the other hand, the presence of this functionality was supported by the strong peak of the carbonyl stretch in the IR spectrum and the detection of the parent ion peak by mass spectroscopy. The carbonyl stretching wavenumber of the compounds was observed in a range from 1974 to 1981 cm^{-1}. The monocationic bromide-carbonyl complex (**5b**) has a lower carbonyl stretching frequency compared to the dicationic acetonitrile-carbonyl complex **2** at 2001 cm^{-1}, consistent with an increase in iron−carbon backdonation on going from the dication to the monocation. Attempts were unsuccessful in obtaining crystals of complexes suitable for X-ray diffraction analysis.

Table 1. Yields of Complexes **5a**−**5d** Using the Method Described in Scheme 3 and Selected IR and NMR Data

complex	yield (%)	IR CO stretch (cm^{-1})	^{31}P NMR ppm
5a	48	1974	65.2(d), 66.2(d) J_{PP} = 38.2 Hz
5b	53	1975	64.2(d), 65.6(d) J_{PP} = 39.5 Hz
5c	55	1974	64.6(d), 66.0(d) J_{PP} = 39.1 Hz
5d	82	1981	67.6
2[a]		2001	69.3(d), 65.7(d) J_{PP} = 30 Hz

[a] Reference 36.

Catalytic Activity. The catalytic hydrogenation of acetophenone to 1-phenethanol was conducted in an argon glovebox using precatalysts **5a**−**5d**. The reaction was performed at 28−30 °C using acetophenone, catalyst, and base (KO^{t}Bu) in a ratio 6000/1/8, respectively. After precatalysts **5a**−**5d** are activated by the base they become extremely air sensitive and must be handled under N_2 or Ar. Samples were taken by injection of small portions of the reaction mixture into a sealed vial containing air and aerated 2-propanol to ensure successful quenching of the oxygen-sensitive catalyst system. They were then analyzed using gas chromatography. The reaction using each precatalyst was performed three times. The rate of the reaction was obtained by plotting the concentration of 1-phenethanol versus time and determining the slope of the linear part of the graph. The turnover frequency (TOF) values were calculated using least-squared fit equations at 15−50% conversion and are summarized in Table 2.

The catalytic activity of the precatalyst **2** was redetermined under the conditions used for **5b** to identify the effect of the ligand in the *trans* position relative to the

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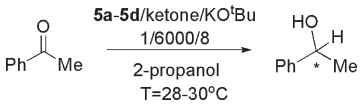
Table 2. Transfer Hydrogenation of Acetophenone Catalyzed by Complexes **5a**−**5d** in Basic 2-Propanol



complexes	TOF (h^{-1})[a]	ee (% *S*)
5a	4.9×10^3	60
5b	2.0×10^4	81
5c	2.0×10^4	82
5d[b]	2.1×10^3	
2	2.1×10^4	82

[a] TOF at 15−50% conversion. [b] 15% conversion.

carbonyl (Table 2). The activation and the maximum constant rate of the transfer hydrogenation using **5b** and **2** were found to be the same within experimental error. A lower TOF of 3.6×10^3 h^{-1} was reported earlier for **2** (Scheme 1), but this refers to a lower temperature and a lower substrate loading than for the present conditions. This observation also shows that the dissociation of the ligand *trans* to carbonyl most likely is taking place during the activation of the precatalyst and that bromide and acetonitrile do not participate in the process of the reduction of acetophenone to 1-phenethanol.

The incorporation of different diamines into the backbone of the ligand of complexes **5a**−**5e** influences both the electronic and the steric properties of the complexes. The basicity of the nitrogen donors decrease in order dach = MeO-dpen = dpen > en as interpreted from the wavenumbers of the carbonyl absorptions listed in Table 1—the more basic the donor, the lower the CO stretching wavenumber. The TOF values of the corresponding complexes do not correlate well with the basicity of the donors. The sterically bulky diamines might be expected to increase the enantioselectivity but decrease the activity of ruthenium complexes. This was the observation when the sterically more crowded precatalyst $RuCl_2$(daipen)(xylBinap) was used in place of $RuCl_2$(dpen)(tolBinap) in the catalytic hydrogenation of acetophenone.[48] However there is also a report where the substitution of the diamine backbone with phenyl groups in the 1- and 2-positions results in an increase in ee and an increase in rate compared to diamines with only monosubstitution at the 1- or 2-positions.[49] No explanation was provided for the rate enhancement. But the activity trend within this group of iron catalysts is different with the more bulky phenyl and substituted phenyl ligands of **5b** and **5c** producing more active precatalysts than the less bulky diaminocyclohexane- and ethylenediamine-derived ligands of **5a** and **5d**. This shows that the steric effect of the diamine has a larger influence on the activity of the catalyst than electronic factors.

To gain a deeper understanding of this process, the conversion of the substrate to the product was monitored by taking samples of the reaction mixture at short time intervals. Catalysts **5a**−**5d** showed similar reaction profiles in the reduction of acetophenone to 1-phenethanol;

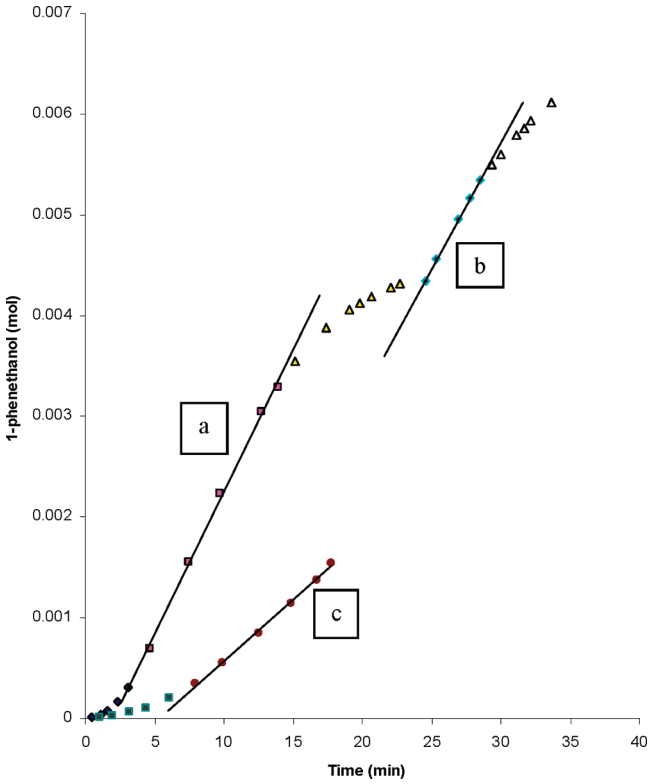


Figure 1. Reaction profile of the catalytic reduction of acetophenone to 1-phenethanol catalyzed by the precatalyst **5b** under Ar at 28−30 °C. [(a) cat/sub/base = 1/6000/8, (b) 4800 equiv of acetophenone was added to the reaction mixture after 23 min of reaction, (c) reaction conducted with cat/sub/acetone/base = 1/6000/6000/8.]

the profile for complex **5a** is depicted in Figure 1a. The reaction starts with the activation of the precatalyst to the so far unknown active catalyst, a process with continuously increasing rate. The activation period varies for different catalysts, but in general takes place during the first 5 min of the reaction. The following turnover step produces 1-phenethanol at a constant rate before the reaction reaches 60% conversion in case of complexes **5a**−**5c** and 15% conversion in case of the complex **5d**. A reduction of the rate is observed later in the reaction to give, at the end, more than 80% of the product in case of the complexes **5a**−**5c** and 40% in case of the complex **5d**.

We wondered whether the observed rate reduction is associated with the decomposition of the catalyst after a certain number of turnovers in the catalytic cycle. To check that assumption, extra acetophenone was added after 23 min of the reaction (Figure 1b). Since the rate increases to the value comparable to that observed during the turnover step, we conclude that the catalyst decomposition cannot be the reason for the rate reduction.

As the reaction progresses toward equilibrium, the concentration of the acetophenone decreases as the concentration of the acetone and 1-phenethanol increases. Therefore, the rate of the 1-phenethanol formation can decrease because of its dehydrogenation back to the acetophenone. Another explanation for the rate decrease is that the reduction of the acetone back to the 2-propanol is taking place in a non-productive cycle which competes with the hydrogenation of the acetophenone (Scheme 4). This process is reasonable, especially if the acetone concentration becomes higher than the concentration of the

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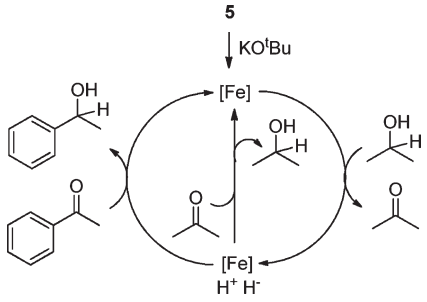
Scheme 4. Catalytic Cycle of the Acetophenone Reduction Where [Fe] and $[Fe]H^+H^-$ Are Unknown Active Iron Complexes



acetophenone. $[Fe]H^+H^-$ in Scheme 4 represents a so-far unknown intermediate in catalytic cycle that transfers an H_2 equivalent from 2-propanol to the acetophenone.

A mixture (50−50% by mol) of acetophenone and acetone was subjected to the catalytic conditions to see how acetone influences the rate of the reaction (Figure 1c). There was almost a 3-fold decrease in rate for the reaction with extra acetone compared to the rate of the initial reaction. This unambiguously shows that acetone is competing with acetophenone for the active site on the catalyst.

Conclusions

In conclusion, we were able to synthesize and characterize iron(II) complexes (**5a**−**5d**) containing P−N−N−P ligands with different diamines incorporated into the backbone to compare their activity and enantioselectivity in asymmetric catalytic transfer hydrogenation of acetophenone to 1-phenethanol using 2-propanol as a reducing agent. A highly efficient one pot procedure allowed us to prepare those compounds in high purity and in moderate to good yields starting from readily available starting materials. Similar activities, previously reported by our group, of precatalyst **2** and **5b** indicate that ligand *trans* to CO has no effect on the reaction rate. All of the complexes show very high TOF (up to 2.0×10^4 h^{-1}) and enantioselectivity (up to 82% ee), using very low catalyst loadings (0.016% relative to the substrate). Monitoring the formation of product in a course of the reaction illustrated that the catalytic process consists of three stages: activation of the precatalyst to an active catalyst (increasing rate of product formation), turnover step (formation of the product at a constant rate), and termination step (decreasing rate of product formation). A series of experiments has proven that the decrease in the rate when approaching the end of the reaction may be associated with the competing reduction by isopropanol of acetone versus acetophenone. The comparison of the TOF of complexes **5a**−**5d** showed that the catalytic activity of the complexes increases as the steric influence of the groups in the backbone of ligand increases.

In an accompanying paper we showed the effect on the activity of such iron catalysts for transfer hydrogenation when the substituents on phosphorus were varied from Ph to Et to ^{i}Pr to Cy.[47] The last two changes produced inactive complexes and therefore indicated that there cannot be too much steric bulk on the phosphorus. The activity of the complexes and the enantioselectivity dropped on going from Ph to Et groups on phosphorus. Thus less donating groups that are not too bulky are required on the phosphorus atoms for activity. Further studies of the mechanism of these interesting catalytic systems are underway.

Experimental Section

General Comments. All manipulations that involved air- or moisture-sensitive materials were performed using Schlenk techniques or a glovebox under an argon or nitrogen atmosphere. Solvents were degassed and dried using standard procedures prior to all manipulations and reactions. Deuterated solvents were distilled and dried over activated molecular sieves. The phosphonium dimer **3** was synthesized according to the procedure previously reported by our group.[46] Other reagents used were purchased from commercial sources and utilized without further purifications. NMR spectra of the samples that were prepared under argon in degassed solvents were recorded at ambient temperature and pressure using a 400 MHz Varian Gemini [^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz), and ^{31}P{^{1}H} (161 MHz)]. The infrared spectra of the KBr pellets containing precatalysts **5a**−**5d** was measured on Paragon 500 (Spectral Range 4600 cm^{-1} to 400 cm^{-1}) using Perkin-Elmer's SPECTRUM for Windows system for data collection and processing at 25 °C. The ESI-MS data on samples in methanol/water were done on an AB/Sciex QStar mass spectrometer with an ESI source. The elemental analyses were performed at the Department of Chemistry, University of Toronto, on a Perkin-Elmer 2400 CHN elemental analyzer. Some complexes gave a low carbon analysis but acceptable hydrogen and nitrogen contents because of a combustion problem that is common for the compounds containing boron atoms.[50]

(*R*,*R*)-[Fe(Ph$_2$PCH$_2$CHN(C$_6$H$_{10}$)NCHCH$_2$PPh$_2$)(Br)(CO)]-[BPh$_4$] (5a). In an Ar glovebox dimer **3** (5.41 g, 8.75 mmol), $[Fe(H_2O)_6][BF_4]_2$ (4.43 g, 13.1 mmol) and NaOMe (0.946 g, 17.5 mmol) were dissolved in 20 mL of MeOH to give a slightly yellow transparent solution after 15 min of stirring. A solution of (1*R*,2*R*)-diaminocyclohexane (1.00 g, 8.75 mmol) in acetonitrile (5 mL) was added to the reaction mixture to give a bright purple solution instantaneously. After 48 h the solution became orange in color with an orange-pink precipitate. The solvent was removed under vacuum, and the resulting orange-pink solid was washed with diethyl ether (10 mL) and redissolved in 15 mL of acetone. The resulting pink-orange solution with a white precipitate was stirred under 1 atm of carbon monoxide at 30 °C for 48 h to give a bright yellow solution with a white precipitate that was filtered. The solvent of the eluate was removed under vacuum, and the resulting solid was redissolved in 40 mL of MeOH. The solution of $NaBPh_4$ (2.99 g, 8.75 mmol) in 5 mL of MeOH was slowly added to a yellow solution to give yellow precipitate that was filtered and washed with diethyl ether (10 mL) three times. The resulting solid was dissolved in 5 mL of dichloromethane to give a brown-yellow solution and white precipitate that was filtered through the glass frit and then through a bed of Celite. The solvent of eluate was removed under vacuum to give a bright-yellow precipitate that was mixed with diethyl ether, and the mixture stirred for 20 h. The precipitate was filtered and washed with 10 mL of diethyl ether three times to give microcrystals containing diethylether (NMR evidence). Yield: 48% (4.26 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.2−1.4 (m, 1H, NCHCH_2; 2H, NCHCH$_2$CH_2), 1.4−1.6 (m, 1H, NCHCH_2), 1.7−2.8 (m, 1H, NCHCH_2; 2H, NCHCH$_2$CH_2), 2.2−2.5 (m, 1H, NCHCH_2), 3.3−3.5 (m, 1H, NC*H*; 1H, PCH_2), 3.6−3.8 (m, 1H, PCH_2), 3.8−4.0 (m, 1H, NC*H*; 1H, PCH_2), 4.1−4.2 (m, 1H, PCH_2), 6.7−7.8 (m, 40H, Ar*H*), 7.9−7.7 (m, 1H, N=C*H*), 7.9−8.1 (m, 1H, N=C*H*); ^{13}C{H} NMR (100 MHz; CD_2Cl_2) δ: 23.7 (s, *C*H$_2$CH$_2$), 23.7 (s, CH$_2$*C*H$_2$), 29.4 (s, CH*C*H$_2$), 30.0 (s, CH*C*H$_2$), 47.2−47.9 (m, P*C*H$_2$), 70.1 (s, N*C*H), 74.0 (s, N*C*H), 122 (s, BPh*C*H), 126 (m, BPh*C*H), 127−134 (m, Ar*C*H),

(50) Marco, A.; Compano, R.; Rubio, R.; Casals, I. *Microchim. Acta* **2003**, *142*, 13–19.

131 (s, BPh*C*H), 136 (s, BPh*C*H), 164 (m, J_{CB} = 49.3 Hz, BPh*C*H), 169−170 (m, N=*C*H); $^{31}P\{H\}$ NMR (161 MHz; CD_2Cl_2): 65.2 (d, J_{PP} = 38.2 Hz), 66.2 (d, J_{PP} = 38.2 Hz); HRMS (ESI-TOF) *m*/*z* calculated for $[C_{35}H_{36}N_2P_2FeOBr]^+$: 697.0830, found: 697.0828 *m*/*z*. Anal. Calcd for $C_{59}H_{56}N_2P_2FeBrOB\ C_4H_{10}O$: C, 69.31; H, 6.09; N, 2.56. Found: C, 70.79; H, 6.06; N, 2.93.

(*S*,*S*)-[Fe(Ph$_2$PCH$_2$CHNC(Ph)HC(Ph)HNCHCH$_2$PPh$_2$)(Br)(CO)][BPh$_4$] (5b). Complex **5b** was synthesized similarly to the complex **5a** using the following amounts of starting materials: dimer **3** (5.24 g, 8.47 mmol), $[Fe(H_2O)_6][BF_4]_2$ (4.29 g, 12.7 mmol), NaOMe (0.916 g, 16.9 mmol), (1*S*,2*S*)-1,2-diphenyldiaminoethane (1.80 g, 8.47 mmol), and $NaBPh_4$ (2.90 g, 8.47 mmol). Yield: 53% (5.01 g); ^1H NMR (400 MHz, CD_2Cl_2) δ: 3.41−3.55 (m, 1H, PCH_2), 3.59−3.74 (m, 1H, PCH_2), 3.76−3.91 (m, 1H, PCH_2), 3.99−4.13 (m, 1H, PCH_2), 5.15−5.25 (m, 1H, NC(Ph)*H*), 5.62−5.72 (m, 1H, NC(Ph)*H*), 6.70−7.57 (m, 50H, Ar*H*), 7.52−7.66 (m, 1H, NC*H*), 7.73−7.87 (m, 1H, NC*H*); $^{13}C\{H\}$ NMR (100 MHz; CD_2Cl_2) δ: 47.05−47.71 (m, P*C*H$_2$), 78.07 (s, N*C*(Ph)H), 81.42 (s, N*C*(Ph)H), 122.03 (s, BPh), 125.96 (m, BPh), 127.9−129.7 (m, Ar*C*H), 130.17 (s, BPh), 130.3−136.52 (m, Ar*C*H), 136.2 (s, BPh), 164.62 (m, J_{CB} = 49.3 Hz, BPh), 174.2−174.5 (m, N*C*H), 214.89 (s, weak, *C*O); $^{31}P\{H\}$ NMR (161 MHz; CD_2Cl_2): 64.24 (d, J_{PP} = 39.5 Hz), 65.62 (d, J_{PP} = 39.5 Hz); HRMS (ESI-TOF) *m*/*z* calculated for $[C_{43}H_{38}N_2P_2FeOBr]^+$: 795.0986, found: 795.0983. Anal. Calcd for $C_{67}H_{58}N_2P_2FeBrOB$: C, 72.13; H, 5.24; N, 2.51. Found: C, 69.21; H, 5.30; N, 2.75.

(*R*,*R*)-[Fe(Ph$_2$PCH$_2$CHNC(*p*-MeO-Ph)HC(*p*-MeO-Ph)HNCHCH$_2$PPh$_2$)(Br)(CO)][BPh$_4$] (5c). Complex **5c** was synthesized similarly to the complex **5a** using the following amounts of starting materials: dimer **3** (2.25 g, 3.64 mmol), $[Fe(H_2O)_6][BF_4]_2$ (1.83 g, 5.45 mmol), NaOMe (0.393 g, 7.27 mmol) (1*R*,2*R*)-1,2-di(4′-methoxyphenyl)-1,2-diaminoethane (0.990 g, 3.64 mmol) and $NaBPh_4$ (1.24 g, 3.64 mmol). Yield: 55% (2.35 g); ^1H NMR (400 MHz, CD_2Cl_2) δ: 3.40−3.57 (m, 1H, PCH_2), 3.60−3.90 (m, 2H, PCH_2), 3.74 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.94−4.11 (m, 1H, PCH_2), 5.00−5.23 (m, 1H, NC(Ph)*H*), 5.50−5.73 (m, 1H, NC(Ph)*H*), 6.50−7.70 (m, 48H, Ar*H*), 7.73−7.97 (m, 1H, NC*H*), 7.48−7.72 (m, 1H, NC*H*); $^{13}C\{H\}$ NMR (100 MHz; CD_2Cl_2) δ: 47.14−47.84 (m, P*C*H$_2$), 55.8 (s, O*C*H$_3$), 55.9 (s, O*C*H$_3$), 77.36 (s, N*C*(Ph)H), 81.00 (s, N*C*(Ph)H), 122.1 (s, BPh), 124.9−136.2 (m, Ar*C*H), 125.4 (m, BPh), 136.16(s, BPh), 164.62 (m, J_{CB} = 49.3 Hz, BPh), 173.7−174.5 (m, N*C*H), 215.1 (dd, J_{CP} = 30.2 Hz, *C*O); $^{31}P\{H\}$ NMR (161 MHz; CD_2Cl_2): 64.6 (d, J_{PP} = 39.1 Hz), 66.0(d, J_{PP} = 39.1 Hz); HRMS (ESI-TOF) *m*/*z* calculated for $[C_{45}H_{42}N_2P_2FeO_3Br]^+$: 855.1197, found: 855.1196 *m*/*z*. Anal. Calcd for $C_{69}H_{62}N_2P_2FeBrO_3B$: C, 70.49; H, 5.32; N, 2.38. Found: C, 68.49; H, 5.48; N, 2.34.

[Fe(Ph$_2$PCH$_2$CHNCH$_2$CH$_2$NCHCH$_2$PPh$_2$)(Br)(CO)][BPh$_4$] (5d). Complex **5d** was synthesized similarly to the complex **5a** using the following amounts of starting materials: dimer **3** (1.20 g, 1.94 mmol), $[Fe(H_2O)_6][BF_4]_2$ (0.98 g, 2.91 mmol), NaOMe (0.21 g, 3.88 mmol), ethylenediamine (0.12 g, 1.94 mmol) and $NaBPh_4$ (0.66 g, 1.94 mmol). Yield: 82% (1.53 g); ^1H NMR (400 MHz, CD_2Cl_2) δ: 3.47−3.59 (m, 2H, NCH_2), 3.58−3.69(m, 2H, PCH_2), 3.75−3.86 (m, 2H, PCH_2), 3.85−3.97 (m, 2H, NCH_2), 6.75−7.68 (m, 40H, ArH; 2H, NC*H*); $^{13}C\{H\}$ NMR (100 MHz; CD_2Cl_2) δ: 48.3−48.8 (m, P*C*H$_2$), 61.1 (s, N*C*H$_2$), 121.6 (s, BPhCH), 125.4 (m, BPhCH), 127.5 (PPhCH), 128.3 (PPhCH), 130.7 (PPhCH), 131.0 (PPhCH), 131.4 (PPhCH), 133.3 (PPhCH), 135.3 (s, BPhCH), 162.9 (m, J_{CB} = 48.5 Hz, BPhCH), 172.5 (s, N*C*H); $^{31}P\{H\}$ NMR (161 MHz; CD_2Cl_2): 67.58 ppm (s); HRMS (ESI-TOF) *m*/*z* calculated for $[C_{31}H_{30}N_2P_2FeOBr]^+$: 643.0360 *m*/*z*. Found: 643.0356 *m*/*z*. Anal. Calcd for $C_{55}H_{50}N_2P_2FeBrOB$: C, 68.56; H, 5.23; N, 2.91. Found: C, 66.70; H, 5.55; N, 3.27.

General Procedure for the Catalytic Reduction of the Acetophenone Using Catalysts 5a−5d and 2-Propanol As a Reducing Agent. In an Ar glovebox, two stock solutions were prepared. The stock solution 1 (1SS) contains 4.48×10^{-6} moles of the catalyst (**5a**−**5d**) dissolved in 4.64×10^{-3} mole of the acetophenone. The stock solution 2 (2SS) contains 8.91×10^{-5} mole of the KO^{t}Bu dissolved in 1.70×10^{-2} moles of 2-propanol. For every catalytic run, 0.110 g of 1SS was diluted with acetophenone (0.527 g) and 2-propanol (8.0 g). The 0.081 g 2SS was diluted with 2-propanol (0.50 g). Resulting solutions were mixed to initiate the reaction. Final concentrations of reagents in the reaction mixture were as follows: [cat] = 7.7 (mol/L), [substrate] = 0.64 (mol/L). Samples were taken by injection of small portions of the reaction mixture into a sealed vial containing air and aerated 2-propanol to ensure successful quenching of the oxygen-sensitive catalyst system. They were then analyzed using gas chromatography using a Perkin-Elmer Autosystem XL chromatograph with a chiral column (CP chirasil-Dex CB 25 m × 2.5 mm). Hydrogen was used as a mobile phase at a column pressure of 5 psi. The injector temperature was 250 °C, a FID temperature was 275 °C, and an oven temperature was 130 °C. GC retention times were 5.02 min, 8.73, and 9.42 for ketone, alcohol R-isomer, and alcohol S-isomer, respectively.

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Supporting Information Available: Further details are provided in Tables 1S−4S and Figures 1S−3S. This material is available free of charge via the Internet at http://pubs.acs.org.