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Substituent Effects on the Catalytic Activity of Bipyrrolidine-Based Iron Complexes

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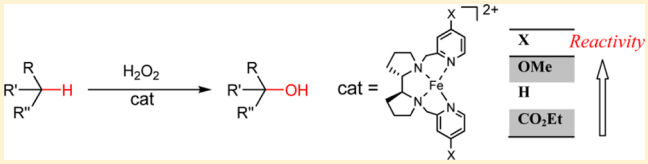
Supporting Information

ABSTRACT: The catalytic activity and the selectivity of the new bipyrrolidine-based Fe(II) complexes **2·Fe**$(OTf)_2$ and **3·Fe**$(OTf)_2$ in the oxidation of a series of alkyl and alkenyl hydrocarbons as well as of an aromatic sulfide with H_2O_2 were tested and compared with the catalytic efficiency of White's parent complex **1·Fe**$(OTf)_2$ in order to evaluate the sensitivity of the reaction to electronic effects.



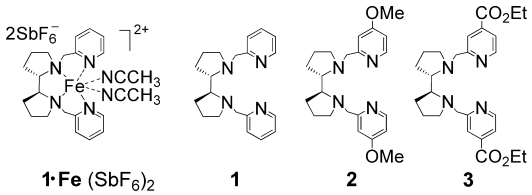
INTRODUCTION

Iron(II) or -(III) nonheme complexes have emerged in the last 10 years as the most promising tools to oxidize nonactivated C−H bonds.[1] This chemical transformation remained elusive to synthetic chemists until recently, because of the inertness of aliphatic C−H bonds, coupled with the difficulty of a selective transformation into the desired oxygenated product. However, a number of high-valent nonheme iron complexes have been recently demonstrated to act as good promoters or catalysts of hydrocarbon oxidation. These complexes usually have simple structures, high catalytic efficiencies, good selectivities and require environmentally friendly and cheap oxidants such as hydrogen peroxide.[2,1d]

The reaction mechanisms of the catalytic processes are still a subject of debate. Nevertheless, it is very likely that in many cases a Fe^{III}−OOH intermediate is involved which, in turn, evolves into the oxoferryl active species Fe^{IV}=O or Fe^{V}=O generated from homolysis or heterolysis of the O−O bond, respectively.[3] The nature of the ligand influences the decomposition pathway of the intermediate. Acid additives were also shown to exert a great influence on the reaction,[4] enhancing both the yield and selectivity of C−H oxidation. The active oxidant is most likely an electrophilic species, as electron-rich C−H bonds, such as tertiary bonds, are the most easily oxidized.

Efforts devoted to elucidation of the features that make a ligand more active than another pointed out that, among other ligands, those based on tetradentate or pentadentate pyridine or tertiary amine N-donors give the most satisfactory results. Furthermore, a high degree of rigidity in the iron complex was found to slow down catalyst degradation. As expected, steric hindrance around the metal ion makes the catalyst more selective toward the oxidation of the most accessible, least sterically encumbered C−H bonds.[5] Rather surprisingly, the effects of the presence of substituents with different electronic properties on the ligands have been far less studied. There are only a few previous investigations[6,5a] which show that substituents on pyridine rings may exert some influence on the catalytic oxidation, whose effectiveness depends on substrate nature.

The past decade has witnessed a growing quest for new and more effective iron(II) catalysts. Among them, the complex **1·Fe**$(SbF_6)_2$, developed by White and co-workers,[7] has certainly reached the degree of ripeness for use in laboratory-scale syntheses in terms of efficiency and selectivity. For instance, it was successfully used in the regio- and stereoselective oxidation of the less hindered tertiary C−H bond in substrates containing different tertiary C−H bonds.



In spite of the high efficiency shown by **1·Fe** $(SbF_6)_2$ in the oxidation of aliphatic C−H bonds no systematic studies of substituent effects on its catalytic activity have been carried out. Thus, in order to acquire a deeper knowledge of this catalytic system, we considered it worthwhile to investigate the electronic effect of pyridine ring substituents on the catalytic efficiency and selectivity of **1·Fe**$(SbF_6)_2$. In this paper we report on the results of the oxidations of a series of substrates catalyzed by iron(II) complexes of ligands **1**−**3**, with the new complexes of **2** and **3** differing from that of **1** for the presence of a methoxy (ERG) and an ethoxycarbonyl (EWG) group, respectively, in the γ position of the pyridine rings. The substrates selected in this study have been chosen in order to compare the catalytic efficiency and selectivity of the three iron complexes in the oxidation of several types of C−H bonds. In

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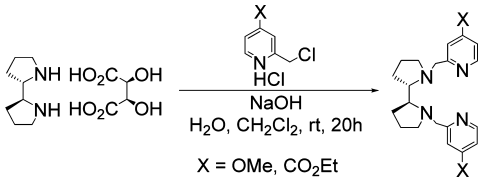
particular, we focused on reactivity toward secondary C−H bonds in the case of cyclohexane, tertiary/secondary selectivity in the case of adamantane, and selectivity toward different kinds of tertiary C−H bonds in the case of *d*-menthyl acetate. In order to widen the scope of this study, we included also the oxidation of the double bond of cyclooctene and the sulfur atom of 4-bromophenyl methyl sulfide.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. The new ligands **2** and **3** were prepared by double N,N′ alkylation of (*S*,*S*′)-2,2′-bipyrrolidine tartrate with 4-methoxy- and 4-ethoxycarbonyl-2-picolyl chloride, respectively, using White's procedure[7] as depicted in Scheme 1. Ligands **2** and **3** were characterized by ^{1}H and ^{13}C NMR, ESI-TOF exact mass, and UV−vis spectroscopy.

Scheme 1. Syntheses of Ligands 2 and 3



The complexes **1**·**Fe**(OTf)$_2$, **2**·**Fe**(OTf)$_2$, and **3**·**Fe**(OTf)$_2$ were prepared in situ by adding equimolar amounts of the ligand and iron(II) triflate (Fe(OTf)$_2$) in acetonitrile solution. In Figure 1 the UV−vis spectra of ligand **3** and of the complex

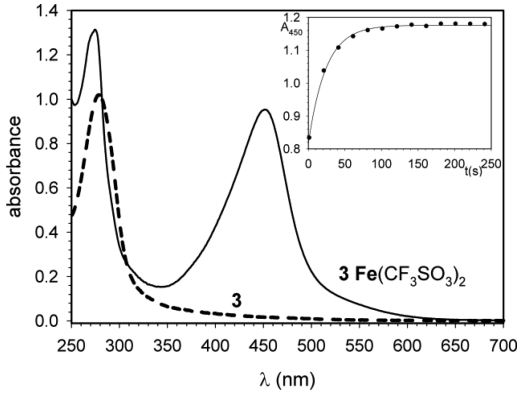


Figure 1. UV−vis spectra of 0.20 mM **3** and 0.20 mM complex **3**·**Fe**(OTf)$_2$ in CH_3CN at 25 °C. Inset: increase of absorbance at λ_{max} 450 nm vs time recorded after the addition of Fe(OTf)$_2$ to a solution of **3**.

3·**Fe**(OTf)$_2$ are reported (UV−vis spectra of ligands **1** and **2** and of the corresponding complexes are reported in the Supporting Information). As reported in the inset of Figure 1, the complexation reaction between ligand **3** and Fe(OTf)$_2$ was fast and binding was complete within 2 min from the addition of the components. Complex formation for ligands **1** and **2** was even faster.

Figure 2 reports as an example the saturation profile obtained in the titration of ligand **1** with Fe(OTf)$_2$ in acetonitrile. The limiting value for the absorbance recorded at λ_{max} 377 nm is attained exactly when 1 equiv of the iron salt is added, as expected for a strong 1:1 binding between ligand and metal ion ($K \geq 10^6$ M^{-1}). A nonlinear increase in absorbance was

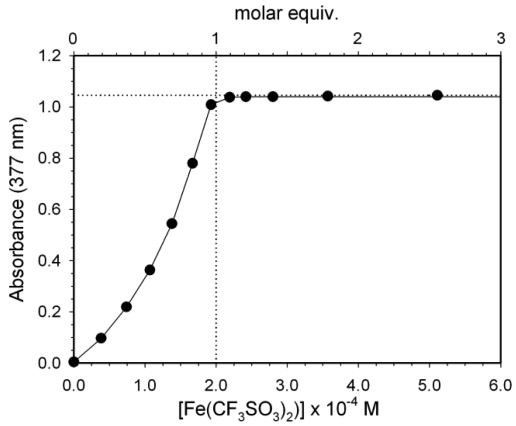


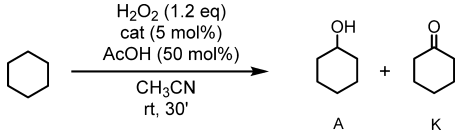
Figure 2. Titration of 0.20 mM ligand **1** with Fe(OTf)$_2$ in CH_3CN at 25 °C.

observed during the titrations of all the ligands. It was attributed to the probable formation of complexes with different stoichiometries formed by a defect of iron(II), which completely disappear when the equivalence is reached.

Oxidation Experiments. In all oxidation experiments the catalyst loading was fixed at 5% molar equiv. The substrate was used at high concentration (0.48−0.66 M), with the sole exception of adamantane, for which a concentration as low as 0.025 M was used due to its low solubility. Catalyst and additive (acetic acid, 0.5 molar equiv) were added to the acetonitrile substrate solution in one shot at the beginning of the reaction, while hydrogen peroxide (1.2 mol equiv) was added over a period of 2 min through a syringe pump. The reaction mixture was then stirred at room temperature for an additional 28 min. After workup, the crude mixture was analyzed by GC or ^{1}H NMR. All results are the average from three independent runs. In the original procedure reported by White,[7a] catalyst, acid, and oxidant were added three times during the reaction course. The simplified procedure adopted in this work was aimed at maximizing reproducibility in oxidation experiments.

The oxidation of cyclohexane affords a mixture of cyclohexanol and cyclohexanone (Scheme 2).[8] The results are

Scheme 2. Oxidation of Cyclohexane to Cyclohexanol (A) and Cyclohexanone (K)



shown in Table 1. It appears that all three catalysts are much more effective than iron(II) triflate, for which low reactivity and

Table 1. Oxidation of Cyclohexane

catalyst	A[a]	K[a]	A + K	A/K
Fe(OTf)$_2$	3.1 ± 0.1	3.5 ± 0.5	7	ca. 1
1·**Fe**(OTf)$_2$	6.5 ± 0.5	53 ± 1	60	0.11
2·**Fe**(OTf)$_2$	7.5 ± 0.5	56 ± 1	64	0.13
3·**Fe**(OTf)$_2$	8.0 ± 0.5	22 ± 1	30	0.36

[a]GC yields defined as (mol of product)/(mol of substrate) × 100. Reactants: cyclohexane (0.66 M), hydrogen peroxide (0.86 M), acetic acid (0.33 M), catalyst (0.033 M). Average of three determinations.

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no selectivity are observed. The catalysts **1·Fe**$(OTf)_2$ and **2·Fe**$(OTf)_2$ display similar catalytic efficiencies in terms of both yield and selectivity, while the catalyst **3·Fe**$(OTf)_2$ is less effective. Thus, while negligible effects on the reaction yield and selectivity are observed in the presence of an electron-releasing group, a significantly lower efficiency is observed in the presence of an electron-withdrawing group. In the case of iron(II) triflate the formation of similar amounts of cyclohexanol and cyclohexanone with low yields is a typical clue of a free radical process, while a completely different scenario is observed for all three PDP-based catalysts.[9] In these cases the low A/K values, comparable with those previously reported by White[7] and Costas,[5b] suggest that the oxidant is not a freely diffusing hydroxyl radical but more probably a metal-based oxidant.

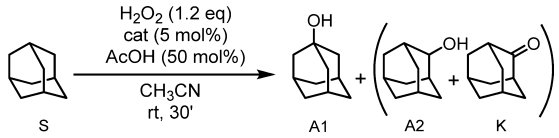
In Table 2 the results related to the oxidation of adamantane (Scheme 3) are reported together with those obtained in the

Table 2. Oxidation of Adamantane

catalyst	A1[a]	A2 + K[a]	total	tert/sec[b]	S[c]
$Fe(OTf)_2$	12.0 ± 0.5	6.1 ± 0.2	18	6	57 ± 2
1·Fe$(SbF_6)_2$	25.5 ± 0.5	6.0 ± 0.2	31	13	61 ± 1
1·Fe$(OTf)_2$	30 ± 1	10 ± 1	40	9	49 ± 2
2·Fe$(OTf)_2$	34 ± 1	5.1 ± 0.1	39	21	53 ± 2
3·Fe$(OTf)_2$	21 ± 1	5 ± 1	26	13	66 ± 2

[a]GC yields defined as (mol of product)/(mol of substrate) × 100. Reactants: adamantane (0.025 M), hydrogen peroxide (0.030 M), acetic acid (0.012 M), catalyst (0.0012 M). Average of three determinations. [b]Normalized tertiary/secondary ratio defined as 3 × [A1/(A2 + K)]. [c]Yield of recovered substrate, in percent.

Scheme 3. Oxidation of Adamantane to 1-Adamantol (A1), 2-Adamantol (A2), and Adamantone (K)



presence of iron(II) triflate and the White's commercially available complex **1·Fe**$(SbF_6)_2$. A good material balance (>97%) was observed in all experiments. As found in the oxidation of cyclohexane, all three complexes are much better catalysts than iron(II) triflate. The catalysts **1·Fe**$(OTf)_2$ and **2·Fe**$(OTf)_2$ have again very similar efficiencies in terms of total yields, while **3·Fe**$(OTf)_2$ is characterized by a lower efficiency. The oxidation catalyzed by **2·Fe**$(OTf)_2$ exhibits a higher selectivity toward tertiary C−H bonds than **1·Fe**$(OTf)_2$. The catalyst **1·Fe**$(OTf)_2$ appears to be more efficient than **1·Fe**$(SbF_6)_2$, indicating that the catalytic process can be affected to some extent by the nature of the counterion. Moreover, all complexes show a tertiary/secondary ratio within the range 10−30 (see Table 2), indicating again the involvement of a metal-based oxidant.[6b]

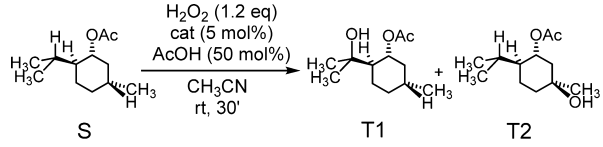
Table 3 reports results related to *d*-menthyl acetate oxidation (Scheme 4). The material balance was again satisfactory (>92%). In this case only two out of three tertiary carbon atoms are oxidized, since the third atom is deactivated by the proximal acetoxy group.[5b,7a] The main product T2 is obtained by attack of the oxidant on the less hindered tertiary C−H bond at the C5 position, which has been shown by DFT

Table 3. Oxidation of *d*-Menthyl Acetate

catalyst	T1[a]	T2[a]	total	T2/T1	S[b]
$Fe(OTf)_2$	1.0 ± 0.5	2.0 ± 0.5	ca. 3		89 ± 2
1·Fe$(OTf)_2$	2.0 ± 0.2	11 ± 1	13	6	84 ± 2
2·Fe$(OTf)_2$	2.0 ± 0.2	22 ± 1	24	11	74 ± 1
3·Fe$(OTf)_2$	3 ± 1	12 ± 1	15	ca. 4	82 ± 1

[a]^{1}H NMR yields defined as (mol of product)/(mol of substrate) × 100. Experimental conditions as in Table 1. [b]Yield of recovered substrate, in percent.

Scheme 4. Oxidation of *d*-Menthyl Acetate to Tertiary Alcohols T1 and T2



calculations to be also the more electron-rich C−H bond.[7a] The C5 carbon atom configuration is retained during hydroxylation, as shown by a comparison of the ^{1}H NMR spectra (see Figure SI 11 in the Supporting Information) with those reported in the literature,[10] pointing to the probable involvement of a metal-based oxidant. The addition of iron(II) triflate gives practically no reaction, indicating again that a PDP ligand is required for an effective process. The catalysts **1·Fe**$(OTf)_2$ and **3·Fe**$(OTf)_2$ display similar catalytic efficiencies, while the complex **2·Fe**$(OTf)_2$ appears to be the most efficient, with a significantly higher conversion of the substrate into the reaction products. As in the case of adamantane, the catalyst **2·Fe**$(OTf)_2$ results to be more selective than **1·Fe**$(OTf)_2$ (T2/T1 ratio 11/6) toward tertiary C−H bond oxidation. In this case we see an appreciable substituent effect, with the methoxy group enhancing both yield and selectivity.

In Table 4 the results related to the oxidation of cyclooctene (Scheme 5) are reported. A good material balance was observed

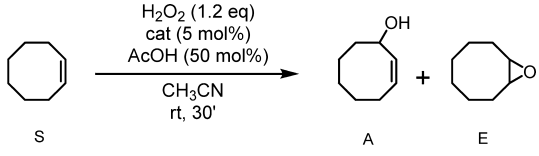
Table 4. Oxidation of Cyclooctene

catalyst	A[a]	E[a]	total	E/A	S[b]
$Fe(OTf)_2$	2.5 ± 0.5	18 ± 2	20.5	8.2	64 ± 1
1·Fe$(OTf)_2$	4.0 ± 0.5	92.5 ± 0.5	96.5	23	<1
2·Fe$(OTf)_2$	3.5 ± 0.5	95.0 ± 0.5	98.5	27	<1
3·Fe$(OTf)_2$	4.5 ± 0.5	83 ± 1	87.5	18	<1

[a]GC yields defined as (mol of product)/(mol of substrate) × 100. Experimental conditions as in Table 1. [b]Yield of recovered substrate, in percent.

in the reactions promoted by **1·Fe**$(OTf)_2$ and **2·Fe**$(OTf)_2$ (>97%) but not in the reactions promoted by iron(II) triflate and **3·Fe**$(OTf)_2$ (<90%). This result can be likely attributed to the formation of other unidentified oxidation products. A

Scheme 5. Oxidation of Cyclooctene to 3-Hydroxycyclooctene (A) and Cyclooctene Oxide (E)



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marked preference for epoxidation over allylic oxidation is shown by all three catalysts, in line with the outcome of other nonheme-catalyzed alkene oxidation processes.[1d] It should be noted that, under the same experimental conditions adopted for the aliphatic C−H oxidation, iron(II) PDP systems display a very high catalytic efficiency in cyclooctene oxidation with an almost quantitative conversion of the alkene into the corresponding epoxide.

In view of the particularly high conversion only small differences should be expected when reactivity data of the three catalytic systems are compared. A slight steady increase of reaction yield and selectivity is indeed observed by enhancing the electron-donating power of the pyridine substituents.

The three iron(II) complexes were also tested in the oxidation of 4-bromophenyl methyl sulfide (Scheme 6). Table 5 shows that all three complexes are very efficient catalysts in the sulfide oxidation process. 4-Bromophenyl methyl sulfoxide is formed as the main product, accompanied by much lower amounts of 4-bromophenyl methyl sulfone, and a good material balance (>97%) was observed in all experiments. As found in cyclooctene oxidation, total yields slightly increase on increasing the electron-donating power of the pyridine substituent, in the order **3**·Fe(OTf)$_2$ < **1**·Fe(OTf)$_2$ < **2**·Fe(OTf)$_2$.

Scheme 6. Oxidation of 4-Bromophenyl Methyl Sulfide to the Corresponding Sulfoxide and Sulfone

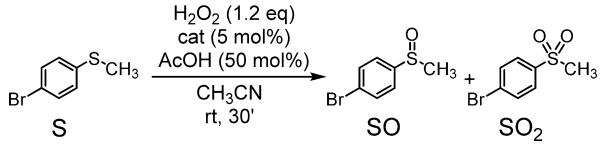

Table 5. Oxidation of 4-Bromophenyl Methyl Sulfide

catalyst	SO[a]	SO$_2$[a]	total	S[b]
none	1.5 ± 0.5	0.6 ± 0.1	ca. 2	98 ± 1
Fe(OTf)$_2$	51 ± 1	2.5 ± 0.5	53.5	46 ± 1
1·Fe(OTf)$_2$	87.5 ± 1.5	3.0 ± 0.2	90.5	7.0 ± 0.5
2·Fe(OTf)$_2$	89.1 ± 0.2	5.1 ± 0.1	94	5.7 ± 0.5
3·Fe(OTf)$_2$	85 ± 1	2.0 ± 0.1	87	12 ± 1

[a]GC yields defined as (mol of product)/(mol of substrate) × 100. Reactants: 4-bromophenyl methyl sulfide (0.48 M), hydrogen peroxide (0.58 M), acetic acid (0.24 M), catalyst (0.024 M). [b]Yield of recovered substrate, in percent.

To sum up, in this study we have reported the synthesis and characterization of two new PDP-type Fe(II) catalysts for the oxidation of unactivated hydrocarbons. The methoxylated complex **2**·Fe(OTf)$_2$ displayed catalytic efficiency and selectivity that are generally higher than or comparable to, depending on the substrate, those of the parent complex **1**·Fe(OTf)$_2$. On the other hand, a significant decrease in the catalytic efficiency and reaction selectivity has been generally observed in the presence of the electron-withdrawing CO_2Et substituent. The beneficial effect on the catalytic process deriving from the introduction of a methoxy substituent in the ligand pyridine ring would suggest that the stabilization of the electrophilic active species by the electron-releasing methoxy group is more important than the decrease of its electrophilic character. In the presence of the electron-withdrawing CO_2Et group a significant destabilization of the active species probably leads to its faster degradation. Further investigations are certainly needed in order to rationalize the PDP Fe(II) substituent effects in a mechanistic framework.

In conclusion, however, in light of the results presented in this report and in other investigations,[6,5a] even considering the slightly higher catalytic efficiency shown by the methoxy-substituted complex, the introduction of a substituent in the γ position of pyridine rings does not seem the right key to improve to a very significant extent the catalytic activity and selectivity of iron(II) nonheme catalysts.

EXPERIMENTAL SECTION

Instruments and General Methods. NMR spectra were recorded on either a 300 or 200 MHz spectrometer. The spectra were internally referenced to the residual proton solvent signal. HR-ESI mass spectra were obtained on an ESI-TOF spectrometer. UV−vis spectra were registered by a double-ray spectrophotometer. GC analyses were carried out on a gas chromatograph equipped with a capillary methylsilicone column (30 m × 0.25 mm × 25 μm), Chrompack CP-Sil 5 CB. GC-MS analyses were performed with a mass detector (EI at 70 eV) coupled with a gas chromatograph equipped with a melted silica capillary column (30 m × 0.2 mm × 25 μm) covered with a methylsilicone film (5% phenylsilicone, OV5).

Materials. All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise stated.

4-Methoxy-2-chloromethylpyridine hydrochloride was prepared in several steps following literature procedures (see the synthetic scheme in the Supporting Information). Commercially available 2-picoline was first oxidized to its *N*-oxide,[11] which was subsequently reacted with a HNO_3/H_2SO_4 mixture to obtain 4-nitro-2-picoline *N*-oxide.[12] This compound was then reacted with methanol in the presence of potassium *tert*-butoxide to give 4-methoxy-2-picoline *N*-oxide.[13] Reaction of the latter with trifluoroacetic anhydride and subsequent hydrolysis provided us 4-methoxy-2-hydroxymethylpyridine,[14] which was finally transformed into 4-methoxy-2-chloromethylpyridine hydrochloride by reaction with thionyl chloride. 4-Ethoxycarbonyl-2-chloromethylpyridine hydrochloride was prepared from pyridine-2,4-dicarboxylic acid following a literature procedure (see the synthetic scheme in the Supporting Information).[15] The above chloromethyl derivatives were used as alkylating agents for the preparations of ligands **2** and **3** using White's protocol.[7a] The complex **1**·Fe(SbF$_6$)$_2$ was purchased from Aldrich and used as such without further purification. Ligand **1** was purchased from Aldrich as a hydrochloride salt. The related base was obtained by extraction of a basic aqueous solution (1 M NaOH) with dichloromethane.

2-({(*S*)-2-[(*S*)-1-(4-Methoxypyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl}methyl)-4-methoxypyridine (Ligand 2). (*S,S*′)-2,2′-Bipyrrolidine tartrate trihydrate (500 mg, 1.45 mmol) and NaOH (550 mg, 13.8 mmol) were dissolved in a biphasic mixture of CH_2Cl_2 (4.6 mL) and water (4.6 mL). Then, 4-methoxy-2-chloromethylpyridine hydrochloride (680 mg, 3.50 mmol) was added and the reaction mixture was stirred for 46 h. The resulting mixture was diluted with 1 M NaOH and extracted with CH_2Cl_2 (6 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and filtered, and the solvent was removed. Purification by column chromatography was carried out on the crude product (SiO_2, CH_2Cl_2 MeOH 1% NH_4OH 0.5%). Fractions containing the desired product were washed with 1 M NaOH and dried over Na_2SO_4. After evaporation the procedure yielded pure ligand **2** as a yellow oil (340 mg, 0.89 mmol, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (m, 6H), 1.87 (m, 2H), 2.32 (m, 2H), 2.88 (m, 2H), 3.04 (m, 2H), 3.58 (d, 2H, J = 15 Hz), 3.79 (s, 6H), 4.19 (d, 2H, J = 15 Hz), 6.63 (m, 2H), 6.98 (s, 2H), 8.29 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 23.7, 24.4, 55.0, 55.1, 61.1, 65.9, 108.29, 108.34, 150.0 166.2. HRMS (ESI-TOF): calcd for $C_{22}H_{31}N_4O_2$ 383.2447 ($M + H^+$), found 383.2426. UV−vis: λ_{max} 260 nm, shoulder (ε = 1465 L mol^{-1} cm^{-1}).

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2-({(*S*)-2-[(*S*)-1-(4-Ethoxycarbonylpyridin-2-ylmethyl)-pyrrolidin-2-yl]pyrrolidin-1-yl}methyl)-4-ethoxycarbonylpyridine (Ligand 3). (*S*,*S*)-2,2′-Bipyrrolidine tartrate trihydrate (430 mg, 1.26 mmol) and NaOH (370 mg, 9.2 mmol) were dissolved in a biphasic mixture of CH_2Cl_2 (3.3 mL) and water (3.3 mL). To this mixture was added 4-ethoxycarbonyl-2-chloromethylpyridine hydrochloride (710 mg, 3.03 mmol), and the reaction mixture was stirred for 46 h. The resulting mixture was diluted with 1 M NaOH and extracted with CH_2Cl_2 (6 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and filtered, and the solvent was removed. Purification by column chromatography was carried out on the crude product (SiO_2, CH_3CN/MeOH 1/1). After evaporation of the selected fractions ligand **3** was obtained as a yellow oil (210 mg, 0.45 mmol, 36% yield). ^{1}H NMR (300 MHz, $CDCl_3$, containing a trace of trifluoroacetic acid): δ 1.40 (t, J = 6 Hz, 6H), 1.76−1.84 (m, 2H), 1.92−1.99 (m, 4H), 2.19 (m, 2H), 3.03 (m, 2H), 3.41 (m, 2H), 3.6 (m, 2H), 4.41 (q, J = 6 Hz, 4H), 4.50 (d, J = 15 Hz, 2H), 4.63 (d, J = 15 Hz, 2H), 7.82 (d, J = 3 Hz, 2H), 8.06 (s, 2H), 8.73 (d, J = 3 Hz, 2H). ^{13}C NMR (300 MHz, $CDCl_3$, in the presence of a trace of trifluoroacetic acid): δ 14.1, 23.5, 27.8, 54.0, 59.2, 62.0, 66.8, 122.3, 123.8, 138.8, 150.0, 156.3, 164.7. HRMS (ESI-TOF): calcd for $C_{26}H_{35}N_4O_4$ 467.2658 ($M + H^+$), found 467.2686. UV−vis: λ_{max} 279 nm (ε = 5095 L mol^{-1} cm^{-1}).

Oxidation Procedure. In the oxidation of cyclohexane, *d*-menthyl acetate, cyclooctene, and 4-bromophenyl methyl sulfide, the complexes **1·Fe**$(OTf)_2$, **2·Fe**$(OTf)_2$ and **3·Fe**$(OTf)_2$ were prepared in situ by dissolving 2.3 mg (7 μmol) of iron(II) triflate in an acetonitrile solution (0.066 M) of the given ligand (100 μL, 7 μmol). After 2 min, to the resulting solutions were added the following: (i) 30 μL of acetonitrile, 4 μL of AcOH (66 μmol, 50 mol %), 7 μL of $PhNO_2$ used as an internal standard (66 μmol, 50 mol %), and 12 μL of cyclohexane (134 μmol, 100 mol %); (ii) 37 μL of acetonitrile, 4 μL of AcOH (66 μmol, 50 mol %), and 26 mg of *d*-menthyl acetate (136 μmol, 100 mol %); (iii) 25 μL of acetonitrile, 4 μL of AcOH (66 μmol, 50 mol %), 7 μL of $PhNO_2$ as an internal standard (66 μmol, 50 mol %), and 17 μL of cyclooctene (134 μmol, 100 mol %); (iv) 4 μL of AcOH (66 μmol, 50 mol %), 7 μL of $PhNO_2$ as an internal standard (66 μmol, 50 mol %), and 100 μL of a 1.33 M solution of 4-bromophenyl methyl sulfide (134 μmol, 100 mol %).

After the addition of the above reagents, 70 μL of a 2.4 M solution of H_2O_2 in acetonitrile freshly prepared from commercial 30% aqueous H_2O_2 was added by a syringe pump over a period of 2 min, and the reaction mixture was stirred for an additional 28 min. Then 1.0 mL of a saturated $NaHCO_3$ solution was added and the mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and analyzed by GC chromatography.

In the case of adamantane oxidation, the complexes **1·Fe**$(OTf)_2$, **2·Fe**$(OTf)_2$, and **3·Fe**$(OTf)_2$ were prepared in situ by dissolving 0.18 mg of iron(II) trifluoromethanesulfonate (0.51 μmol) in an acetonitrile solution (0.066 M) of the given ligand (7.5 μL, 0.51 μmol). To the resulting solutions were added the following: 10 μL of a 0.5 M AcOH solution in acetonitrile (5 μmol, 50 mol %) and 330 μL of a 0.033 M solution of adamantane (10 μmol, 100 mol %). After the addition of the above reagents, 40 μL of a 0.30 M solution of H_2O_2 in acetonitrile was added by a syringe pump over a period of 2 min, and the reaction mixture was stirred for 28 min. Then 10 μL of a 0.50 M PhCl solution (as an internal standard, 5 μmol, 50 mol %) and 1 mL of a saturated $NaHCO_3$ were added, and the mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, and analyzed by GC chromatography.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving the synthetic scheme followed in 2-chloromethylpyridine derivatives preparation, ^{1}H and ^{13}C NMR and UV−vis spectra of the new ligands, GC chromatograms and ^{1}H NMR spectra of selected crude products of some oxidation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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