Ferrocenoyl-Substituted *Cinchona* Alkaloids: Synthesis, Structure, and Application in Asymmetric Catalytic Oxidation

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Summary: Ferrocenoyl-substituted Cinchona alkaloids were synthesized from ferrocenecarboxylic acid and the free Cinchona alkaloids and represent readily available organometallic auxiliaries. They were employed as a rare example of chiral ferrocenyl ligands in asymmetric oxidation chemistry.

Introduction

Enantiomerically pure ferrocene ligands have played a pivotal role in asymmetric catalysis,[1] and among the many successful examples, the industrial application of planar-chiral bis(phosphino)ferrocenes in the production of Metolachlor emerges as the most efficient one.[2] However, it is noteworthy that the use of chiral ferrocene ligands has been restricted to catalytic reduction chemistry,[1−3] catalyic C−C and C−X bond-forming processes,[1,4] and catalytic cross-coupling reactions.[5] Apparently, their application in asymmetric oxidation catalysis has been prevented by the underlying concern about oxidative decomposition of the ferrocene moiety.[6] On the other hand, asymmetric oxidative synthesis has been largely dominated by *Cinchona* alkaloids and their respective complexes with osmium(VIII) species.[7] The development of catalytic asymmetric dihydroxylation[8,9] and aminohydroxylation[10] reactions and the concept of ligand-accelerated catalysis[11] have been the principal achievements from this chemistry. We here describe the first synthesis of ferrocenoyl-substituted *Cinchona* alkaloids[12] and a preliminary application in asymmetric oxidative double-bond transformation.

Results and Discussion

The representative synthesis of two of the novel compounds is depicted in Scheme 1 for dihydroquinine (**2**; DHQ-H) as a *Cinchona* alkaloid. Thus, sequential reaction of ferrocenecarboxylic acid (**1**) with $SOCl_2$ followed by esterification with DHQ-H gives ferrocenoyldihydroquinine (**3**; (DHQ)Fc) in 76% yield. In an analogous manner, the reaction of 1,1′-dicarboxyferrocene (**4**) with $SOCl_2$ and DHQ-H (**2**) gives rise to the bis(ester) $(DHQ)_2fc$ (**5**) in 52% yield. The respective diastereomeric compounds (DHQD)Fc (**6**) and $(DHQD)_2fc$ (**7**) containing the diastereomer dihydroquinidine (DHQD-H, **8**) as the *Cinchona* alkaloid moiety have been prepared via identical reaction sequences in yields of 74 and 59%, respectively. All novel complexes are air-stable, crystalline, orange to red solids. The crystal structure of (DHQ)Fc (**3**) is depicted in Figure 1. It is in general agreement with other aryl carbonyl substituted *Cinchona* alkaloid structures.[13]

The potential application of these new complexes as ligands for osmium-mediated transformations was investigated for OsO_4 and (DHQ)Fc (**3**). A stoichiometric

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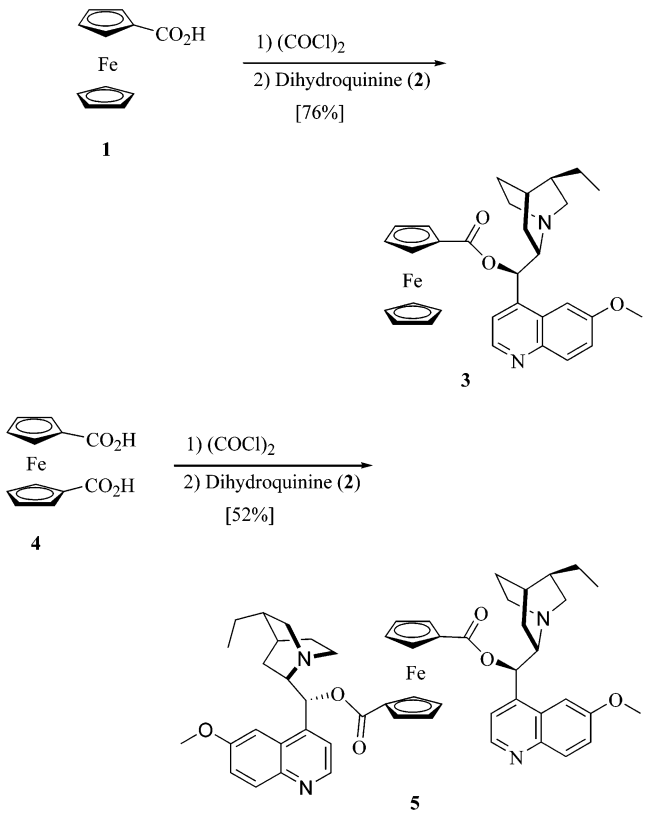
Scheme 1. Synthesis of Ferrocenoyl *Cinchona* Alkaloids 3 and 5



dihydroxylation of (*E*)-stilbene in the presence of an equimolar amount of (DHQ)Fc (**3**) gave the corresponding diol in 91% isolated yield and 42% enantiomeric excess (Scheme 2). A reaction under catalytic conditions (5 mol % OsO_4, 9 mol % **3**, *N*-methylmorpholine *N*-oxide (NMO) as terminal oxidant) gave 88% of the product diol with 44% ee. In both cases the ferrocene ligand **3** was recovered by column chromatography in more than 90% yield and more than 96% purity according to NMR analysis. These results show that the ferrocene ligand is stable under the oxidative conditions of the catalytic reaction.[14]

In view of the related aminohydroxylation, use of **3** or its bidentate analogue **5** together with the preformed osmium imido species $O_3OsNtBu$[15] led to products with very low enantiomeric purity (up to 9% ee) in the oxidation of stilbene. This result is in agreement with an assumed weaker complexation constant and with the general assumption that the basic free lone pair of the imido nitrogen diminishes the overall electrophilicity of the osmium center and thereby reduces its availability for complexation to **3**.[16b] In agreement with these electronic properties, the related bis(imido) and tris(imido) compounds $O_2Os(NtBu)_2$ and $OOs(NtBu)_3$ did not undergo complexation and only racemic diamines were isolated from the respective diamination reactions with diethyl fumarate in the presence of either **3** or **5**.[16]

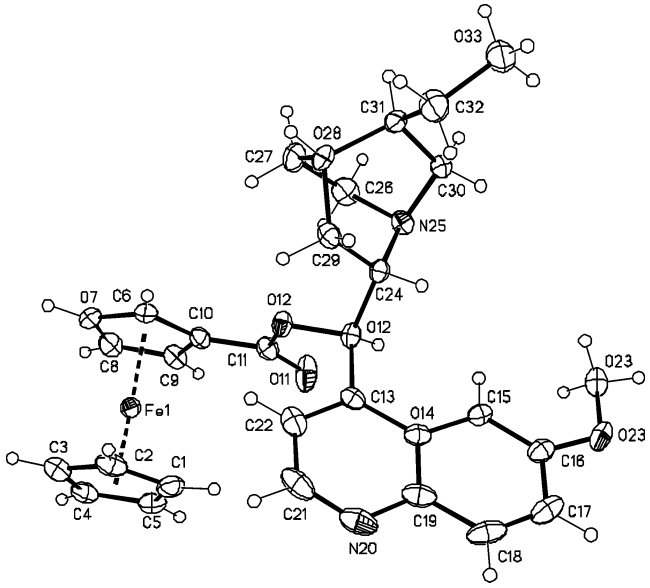
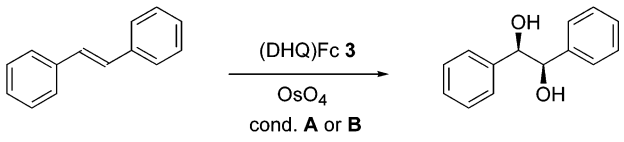


Figure 1. Solid-state structure of ferrocenoyldihydroquinine (**3**) (ORTEP plot). Selected bond lengths (Å) and angles (deg): Fe(1)−C(10), 2.0291(16); C(10)−C(11), 1.468(2); C(11)−O(12), 1.3528(19); O(11)−C(11)−C(10), 124.58(15); O(11)−C(11)−O(12), 123.49(15); C(30)−N(25)−C(24), 107.51(12); N(25)−C(24)−C(29), 112.16(13).

Scheme 2. Dihydroxylation of (*E*)-stilbene (9)[a]



[a] Conditions (A) **3**, OsO_4 (1 equiv, relative to substrate), CH_2Cl_2, room temperature; (B) **3** (9 mol %), OsO_4 (5 mol %), NMO (1.2 equiv, relative to substrate), CH_2Cl_2, room temperature.

Again, the ferrocene ligands **3** and **5** were recovered unchanged, indicating their stability in the presence of the terminal osmium oxidant.

(DHQ)Fc (**3**) worked well for the catalytic aminohydroxylation of stilbene and cyclohexene with chloramine-T as terminal oxidant,[10,17] (28 and 35% ee, respectively). When a change was made to the bidentate ligand **5**, enantioselectivities were increased to 42 and 48% ee, respectively. With regard to other *Cinchona* alkaloid ligands, **3** displays a significantly enhanced solubility, a feature that was also encountered with the bis-*Cinchona* ligands $(DHQ)_2fc$ (**5**) and $(DHQD)_2fc$ (**7**). In view of the sometimes slow dissolution of the Sharpless ligands $(DHQ)_2PHAL$ and $(DHQD)_2PHAL$, this reduced induction period compares advantageously.

In the AA reactions of cinnamic esters, (DHQ)Fc (**3**) gave no regioselectivity (Table 1; entries 1 and 3) and the bis-*Cinchona* motif was again essential in order to obtain regioselectivity and higher product enantiomeric excess. Thus, when $(DHQ)_2fc$ (**5**) was employed, regioselectivities up to 5:1 were obtained, a result that compares well with $(DHQ)_2PHAL$.[10] An enantiomeric excess up to 51% was obtained for the crude product. When the nitrogen source was altered to the benzyl

(14) However, when the standard AD procedure containing hexacyanoferrate(III)/K_2CO_3 was employed, concomitant ester hydrolysis of **3** and **5**, respectively, took place while the ferrocene moiety was apparently uneffected by the oxidant.

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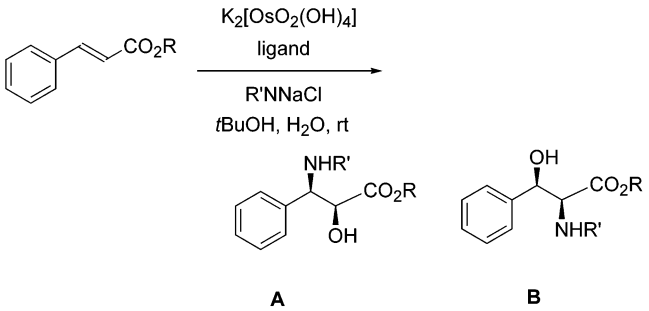
Table 1. Asymmetric Catalytic Aminohydroxylation

entry	R′NNaCL	rest R	ligand	**A**:**B**	ee[a]
1	chloramine-T	CH_3	**3**	1:1	nd[b]
2	chloramine-T	CH_3	**5**	4:1	38[c]
3	chloramine-T	*i*Pr	**3**	1:1	nd
4	chloramine-T	*i*Pr	**5**	5:1	51[c]
5	BnOC(O)NNaCl	CH_3	**5**	1:1.5	nd
6	BnOC(O)NNaCl	*i*Pr	**5**	1:2	59[d]
7	BnOC(O)NNaCl	*i*Pr	**7**	1:2.4	61[e]

[a] Determined from the crude product after aquous workup, extraction with CH_2Cl_2, and column chromatography. [b] nd = not determined. [c] Major regioisomer (**A**). [d] Major regioisomer (**B**). [e] Major regioisomer (*ent*-**B**).

Scheme 3. Asymmetric Catalytic Aminohydroxylation



carbamate nitrene precursor, a reversal in regioselectivity was observed. Now, regioisomer B (Scheme 3) was mainly produced and was obtained in a good enantiomeric excess of 59%. For the diastereomerically configured ligand $(DHQD)_2fc$ (**7**) the opposite enantiomer was obtained with a nearly identical reaction outcome. This proves that the ferrocene ligands behave like pseudoenantiomers,[18] a feature that had to be expected, since it had already been known from the parent ligand systems.[9,10,17] Still, the reversal in regioselectivity is of interest, since such a reversal had so far only been known for the change from the PHAL ligands to the respective AQN ligands.[19] While both the origin of this reversal and the exact mechanism of the catayasis remain unknown, the electronic similarities of the AQN ligands and the present ferrocene systems appear noteworthy. Again, recovery of the ferrocenes by column chromatography indicates that the oxidative nitrene precursors represent no drawback for the use of the organometallic moiety. The somewhat lower enantioselectivities with ligands **5** and **7** as compared to their PHAL and AQN counterparts are reasonable. While the latter display a pronounced binding pocket for the stereo-determining transition state,[9d] the described ferrocenes are conformationally flexible with free rotation of the Cp rings. As a result, simple monocoordination of a single *Cinchona* moiety to Os leads to an active catalyst similar to **3** and thus to diminished regio- and stereoselectivities.

In summary, we have described the convenient one-step synthesis of novel mono- and bidentate *Cinchona* alkaloid substituted ferrocenes from commercially available starting materials and their application in catalytic asymmetric oxidation reactions, which represents the first application of ferrocene-derived ligands in asymmetric catalytic oxidation. Their use as ligands or auxiliaries in related asymmetric transformations[18] is currently under investigation.

Experimental Section

General Experimental Details. Ferrocenecarboxylic acid, 1,1′-ferrocenedicarboxylic acid, dihydroquinine, and dihydroquinidine were obtained from Fluka Chemical Co. and used as received. All reactions concerning the synthesis of new ferrocene derivatives were carried out under an inert atmosphere employing standard Schlenk techniques. Dichloromethane was distilled from $CaCl_2$ under argon. Triethylamine was distilled from $LiAlH_4$ under argon and stored over 4 Å molecular sieves in the dark. All reagents for catalytic reactions were purchased from Aldrich Chemical Co. and used as received.

***O*-(Ferrocenoyl)dihydroquinine (Fc-DHQ; 3).** Ferrocenecarboxylic acid (**1**; 1.00 g, 4.34 mmol) and triethylamine (1.5 mL) were dissolved in 20 mL of freshly distilled dichloromethane. Oxalyl chloride (0.755 mL, 8.69 mmol) was added via syringe against a positive stream of argon. After all gas evolution had ceased, the deep red solution was stirred for 30 min at room temperature. All volatile components were distilled off under reduced pressure to leave a reddish material. This was dried under reduced pressure at room temperature for 30 min and then dissolved in 20 mL of dichloromethane. Triethylamine (1 mL) and DHQ-H (**2**; 1.77 g, 5.43 mmol) were added successively, and the resulting solution was stirred at room temperature for a period of 14 h. It was quenched by addition of water followed by extraction with ethyl acetate. The organic layer was separated and dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, EtOAc/NEt_3, 95/5 (v/v)) to give the title compound as an orange solid (1.77 g, 3.3 mmol, 76% cy). Mp: 174 °C. $[\alpha_D]^{26}$: −100.2° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, J = 7.1 Hz, 3H), 1.42−1.61 (m, 6H), 1.72−1.90 (m, 2H), 2.66−2.84 (m, 3H), 2.88−2.97 (m, 1H), 3.32−3.42 (m, 1H), 4.00 (s, 3H), 4.02 (s, 5H), 4.40−4.42 (m, 2H), 4.82−4.84 (m, 2H), 6.63 (d, J = 7.4 Hz, 1H), 7.37 (dd, J = 2.6, 9.2 Hz, 1H), 7.45 (d, J = 4.4 Hz, 1H), 7.54 (d, J = 2.6 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 8.75 (d, J = 4.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.97, 23.78, 25.49, 26.02, 27.17, 37.41, 49.95, 50.77, 55.61, 59.22, 69.75, 69.99, 70.12, 70.55, 71.44, 71.50, 73.70, 101.86, 119.02, 121.72, 127.08, 131.78, 144.38, 144.84, 147.31, 157.80, 170.90. MS (EI, eV): *m*/*z* (%) 538 $[M]^+$ (5), 424 (100), 333 (27), 237 (11), 188 (43), 162 (26), 146 (25). HRMS: calcd for $C_{31}H_{34}FeN_2O_3$, 538.1919; found, 538.1911.

***O*-(Ferrocenoyl)dihydroquinidine (Fc-DHQD; 6).** This compound was synthesized from ferrocenecarboxylic acid (**1**; 755 mg, 3.28 mmol), oxalyl chloride (0.57 mL, 6.56 mmol), and DHQD-H (**8**; 1.285 g) and purified as described above for its diastereoisomer **3**. Isolated yield: 1.3 g (2.43 mmol, 74%). Mp: 84 °C. $[\alpha_D]^{26}$: +105.1° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, J = 7.2 Hz, 3H), 1.30−1.86 (m, 8H), 2.32−2.40 (m, 1H), 2.64−2.74 (m, 1H), 3.01−3.10 (m, 1H), 3.20−3.29 (m, 1H), 3.37−3.46 (m, 1H), 4.01 (s, 3H), 4.03 (s, 5H), 4.41−4.43 (m, 2H), 4.84−4.85 (m, 2H), 6.61 (d, J = 6.4 Hz, 1H), 7.38 (dd, J = 2.7, 9.2 Hz, 1H), 7.44 (d, J = 4.5 Hz, 1H), 7.55 (d, J = 2.7 Hz, 1H), 8.02 (d, J = 9.2 Hz, 1H), 8.74 (d, J = 4.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.05, 23.97, 25.37, 27.69, 28.58, 37.39, 42.46, 55.71, 58.41, 59.03, 69.55, 70.02, 70.07, 70.66, 71.43, 71.47, 74.12, 101.81, 118.87, 121.75, 126.91, 131.80, 144.22, 144.86, 147.31, 157.88, 170.77. MS (EI, eV): *m*/*z* (%) 538 $[M]^+$ (5), 424 (100), 333 (27), 237 (11), 188 (43), 162 (26), 146 (25). HRMS: calcd for $C_{31}H_{34}FeN_2O_3$, 538.1919; found, 538.1907.

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Bis(dihydroquininyl) Ferrocenyl-1,1-dicarboxylate (fc-(DHQ)$_2$; 5). Ferrocenedicarboxylic acid (**4**; 0.819 g, 3.00 mmol) and triethylamine (1.5 mL) were dissolved in 20 mL of freshly distilled dichloromethane. Oxalyl chloride (0.52 mL, 6.00 mmol) was added via syringe against a positive stream of argon. After all gas evolution had ceased, the deep red solution was stirred for 30 min at room temperature. All volatile components were distilled off under reduced pressure to leave a reddish material. This was dried under reduced pressure at room temperature for 30 min and then dissolved in 20 mL of dichloromethane. Triethylamine (1 mL) and DHQ-H (**2**; 2.6 g, 8.00 mmol) were added successively, and the resulting solution was stirred at room temperature for a period of 14 h. All solvents were removed under reduced pressure, and the crude product was purified by column chromatography (SiO_2, EtOAc/NEt_3, 80/20 (v/v)) to give the title compound as an orange foam (1.39 g, 1.56 mmol, 52% cy). Mp: 104 °C. $[\alpha_D]^{26}$:−55.4° (c = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 7.0 Hz, 6H), 1.39−1.60 (m, 12H), 1.74−1.85 (m, 4H), 2.62−2.96 (m, 8H), 3.19−3.39 (m, 2H), 3.98 (s, 6H), 4.05−4.10 (m, 2H), 4.11−4.16 (m, 2H), 4.72−4.75 (m, 4H), 6.65 (d, J = 7.0 Hz, 2H), 7.36 (dd, J = 2.6, 9.2 Hz, 2H), 7.39 (d, J = 4.5 Hz, 2H), 7.52 (d, J = 2.6 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 8.72 (d, J = 4.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.82, 23.54, 25.33, 25.80, 26.82, 37.11, 49.74, 50.57, 53.31, 55.65, 59.07, 70.89, 71.18, 71.85, 73.26, 73.46, 101.72, 118.81, 121.75, 126.96, 131.72, 143.86, 144.93, 147.20, 157.87, 169.48. MS (EI, eV): m/z (%) 890 $[M]^+$ (2). Anal. Calcd for $C_{52}H_{58}FeN_4O_6$: C, 70.11; H, 6.56; N, 6.29. Found: C, 70.02; H, 6.61; N, 6.09.

Bis(dihydroquinidinyl) Ferrocenyl-1,1-dicarboxylate (fc-(DHQD)$_2$; 7). This compound was synthesized from ferrocenedicarboxylic acid (**4**; 500 mg, 2.00 mmol), oxalyl chloride (0.38 mL, 4.33 mmol), and DHQD-H (**8**; 0.857 g) and purified as described above for its diastereoisomer **5**. Isolated yield: 1.3 g (0.997 mg, 1.18 mmol, 59%). Mp: 92 °C. $[\alpha_D]^{26}$: +81.3° (c = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, J = 7.3 Hz, 6H), 1.26−1.85 (m, 12H), 2.32−2.39 (m, 3H), 2.63−2.75 (m, 3H), 3.06 (dd, J = 9.8, 13.6 Hz, 2H), 3.10−3.42 (m, 4H), 3.99 (s, 6H), 4.08−4.14 (m, 2H), 4.15−4.20 (m, 2H), 4.74−4.76 (m, 4H), 6.65 (d, J = 5.5 Hz, 2H), 7.37 (dd, J = 2.6, 9.2 Hz, 2H), 7.40 (d, J = 4.5 Hz, 2H), 7.53 (d, J = 2.6 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 8.72 (d, J = 4.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.93, 23.66, 25.18, 27.55, 28.18, 37.08, 42.60, 55.84, 58.15, 58.84, 71.01, 71.10, 71.93, 73.21, 74.01, 77.21, 101.68, 118.70, 121.81, 126.75, 131.77, 143.60, 144.79, 147.20, 158.00, 169.35. MS (EI, eV): m/z (%) 890 $[M]^+$ (2). Anal. Calcd for $C_{52}H_{58}FeN_4O_6$: C, 70.11; H, 6.56; N, 6.29. Found: C, 70.39; H, 6.69; N, 5.96.

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Supporting Information Available: Text giving experimental details for catalytic reactions, figures giving reproductions of NMR spectra of all four ferrocene derivatives, and tables giving X-ray crystallographic data for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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