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Synthesis and atropisomeric stability of 2,2′-bis(ferrocenylhydroxymethyl)-1,1′-biphenyl

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Abstract—Nickel(0)-mediated homocoupling of (2-bromobenzoyl)ferrocene gave in high yield diketone **4** possessing a biphenyl unit. Its chemical reduction afforded the title compound in three diastereomeric forms **1a**–**c** with sufficient atropisomeric stability to allow their detection and purification. By rotation around the biphenyl bond, enantiomers of **1a** suffered racemization whereas diol **1c** isomerized to **b**, which resulted in being atropisomerically stable since the reverse process from **1b** to **c** did not occur. Activation parameters for both these atropisomerizations were also determined. The observed conformational stability can be explained by both hydrogen bonding and steric interactions.

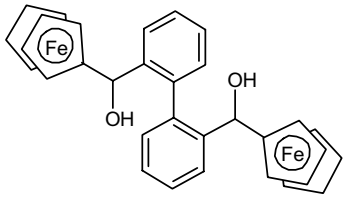
1. Introduction

Biaryl compounds are widely found in nature and exhibit a broad range of biological activities[1] and therefore a continuous effort has been devoted to their synthesis.[2] The main feature of biaryl compounds is their atropisomerism, due to the hindered rotation around the aryl–aryl bond, a consequence of which is that they can exist as molecules with a defined axial chirality.[3]

The majority of tetra-*ortho* substituted biaryls presents a sufficient conformational stability to allow their resolution of the racemates and isolation of single atropisomers;[4] in the case of tri-*ortho* substituted derivatives the interconversion energy barrier is often lower and racemization readily occurs above room temperature.[5]

Configurationally stable biphenyls (and binaphthyls) have been extensively studied with atroposelective synthetic routes[6] developed for their preparation, due to the great interest of their application as highly efficient catalysts[7] in asymmetric synthesis.

'*ortho–ortho*' Substituted biphenyls, synthetically more available than tetrasubstituted counterparts, are usually conformationally flexible unless large substituents are present.[8] However, the twisting of the biphenyl skeleton can be induced by metal complexation and, in some instances, conformationally stable complexes have been prepared and used as catalysts in different asymmetric reactions.[9]



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Our interest in the synthesis of chiral biphenyls as well as ferrocene derivatives[10] prompted us to prepare compound **1**, which combines these two structural characteristics. The presence of a ferrocenyl moiety, which possess peculiar stereochemical and sterical features, on a biphenyl skeleton should lead to interesting ligands. Herein we report the synthesis of **1** and the study of its conformational properties as a preliminary tool for the development of a new class of ligands and further application in asymmetric catalysis.

2. Results and discussion

The synthetic versatility of the hydroxyl group to afford other derivatives, such as amines or phosphines and the

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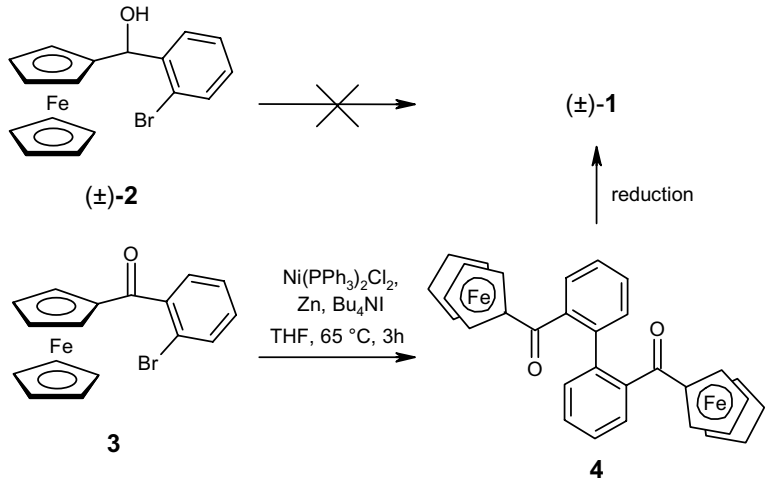
availability of stereoselective procedures for the reduction of ketones[11] mainly dictated the choice of biphenyl **1** as the target compound. Symmetrical biphenyls are usually prepared by metal-assisted homocoupling of suitable halogenated starting materials and among the available methodologies different for aryl–aryl bond formation,[12] we resorted to the Ni(0) catalyzed homocoupling of aryl bromides for the mild conditions required. The active Ni(0) complex was generated in situ from $Ni(PPh_3)_2Cl_2$ and zinc in the presence of Bu_4NI at 60 °C in THF[13] and, after addition of the substrate the reaction proceeded smoothly within a few hours.

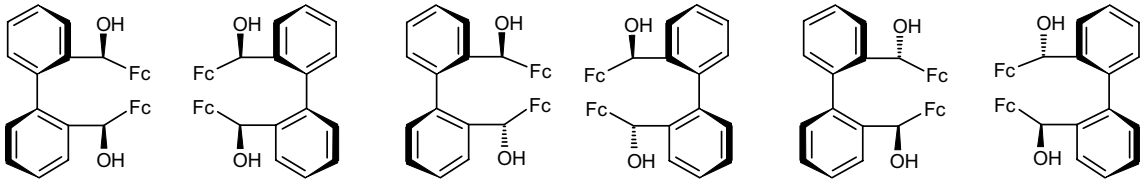
In the hypothesis that diol **1** is atropisomerically stable at room temperature, three different diastereomeric diols were obtained, namely the (*R*,*S*,a*R*)/(*S*,*R*,a*S*)-isomer **1a** and the two C_2-symmetrical (*R*,*R*,a*R*)/(*S*,*S*,a*S*)-**1b** and (*R*,*R*,a*S*)/(*S*,*S*,a*R*)-**1c** diols.

The reduction of **4** with $NaBH_4$ afforded a chromatographically single diol **1a**, whose ^1H and ^{13}C NMR spectra showed distinct resonances for each proton and carbon in the molecule, as would be expected for a compound lacking C_2- or C_s-symmetry. This resonance pattern, reasonable in the case of opposite



Our initial attempts using ferrocenylalcohol **2**, as well as the methoxy- and acetoxyderivatives, gave almost exclusively the hydrodehalogenation product of the starting ferrocene. Conversely, homocoupling of ketone **3** proceeded in excellent yield affording the biphenyl derivative **4**. Chiral HPLC analysis of diketone **4** in different chromatographic systems always showed a single peak, indicating that free rotation around the biphenyl bond occurs, despite the sterical hindrance of the ferrocenyl substituents.

(*R*)- and (*S*)-configurations on the stereogenic carbons in a molecule also possessing a chiral axis,[10b] could imply that diol **1a** is conformationally stable and should exist as a couple of atropisomers. Chiral HPLC analysis of **1a** showed two baseline well-resolved peaks in a 1:1 ratio, supporting this assumption; the absence of broadening or plateau-like region between peaks is consistent with slow atropisomerization on the time scale of HPLC separation.



Although chemical reduction of **4** should provide a *dl*/*meso* mixture of diols, a different stereochemical composition of **1** could be expected when taking into the account that *ortho*-substituents containing sp^3 carbons have a higher capacity to inhibit internal rotation in biphenyls.[3a,6e]

In order to have an evaluation of the atropisomeric stability of **1a** at room temperature, single enantiomers were collected by chiral HPLC analysis and allowed to stand in hexane solution for various lengths of time. Re-injection of the fractions showed complete racemization after about 48 h with an enantiomerization reaction

rate of $k_1 = 7.4 \times 10^{-6}$ (see Scheme 1).[14] Using the same procedure, the values of k_1 at different temperatures and activation parameters were also determined (Table 1).[15]

Diketone **4** was then reduced with $LiAlH_4$ with the ^1H NMR analysis of the reaction mixture showing the presence of three diols, as mainly deduced from their methinic resonances at 4.86 and 5.37 ppm for **1a** and 5.32 and 5.20 ppm for diols **1b** and **c**, respectively. The measured ratio **1a**:**b**:**c** was 55:10:35 and chiral HPLC analysis showed two peaks, due to the single atropisomers, for each diol. When the reduction mixture was analyzed after standing in hexane solution at room temperature for some time, a marked decrease in the relative concentration of **1c** was measured, with a concomitant increase in the amount of **1b** and without formation of any other products. Since diastereomers **1b** and **c** only differed in their relative axial configuration, [tentatively assigned on the basis of energy minimization studies (see infra)], it was reasonable to assume that an interconversion between them occurred in some degree, by rotation around the biphenyl bond.

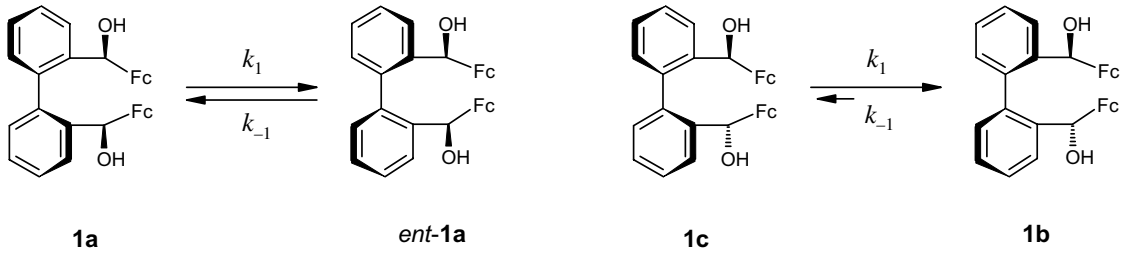
Chromatographic purification of the reduction mixture allowed us to obtain pure **1a** and **b**, whereas fractions containing **1c** were always contaminated by **1b**, allowing different isomerization rates from **1c** to **b** and for the inverse process to be deduced. Samples containing pure **1b** or a mixture of **1b** and **c** in hexane solution were monitored for long periods of time and in both cases the final thermodynamic ratio **1b**:**c** determined as 96:4 so that the rate constant k_{-1} for the isomerization from **1b** to **c** was considered, in the first approximation, as negligible (Scheme 1).

For the determination of activation parameters of this isomerization, freshly prepared mixtures containing **1c** and **b** were maintained at constant temperature in hexane solution and aliquots were analyzed at suitable time intervals by HPLC. Eyring and Arrhenius plots of rate constants against temperature gave experimental values of $\Delta H^{\#}$, $\Delta S^{\#}$ and E_a (Table 1).

The conversion of **1c** into **b** was accelerated in more polar solvents; for the sake of comparison, in THF at 45 °C the isomerization occurred with about two-fold rate with respect to hexane ($k = 35.10 \times 10^{-5}\ s^{-1}$).

For a better understanding of the influence of the axial chirality on the different thermodynamic stabilities of **1b** and **c**, molecular modelling of these diols was accomplished fixing an (*R*,*R*)-configuration on the stereogenic carbons. Monte Carlo conformational searches starting from structures with different C2–C1–C1′–C2′ dihedral angles related with both axial configurations gave the same global minimum showed in Figure 1A possessing an a*R* chirality. The structure with an a*S* chirality was found as a local minimum at about 2.3 kcal/mol higher in energy (Fig. 1B).

In both cases, stabilization by hydrogen bonding between hydroxyl groups was possible and the phenyl rings were in nearly orthogonal relative positions with C2–C1–C1′–C2′ dihedral angles—74.7° and 94.3°, respectively, for the structure shown in Figure 1A and B. The main difference resides in the orientation of the ferrocenyl moiety whose axis Cp–Fe–Cp′ lies almost parallel to the C1–C1′ biphenyl bond in 1A and orthogonal in 1B.



Scheme 1. Atropisomeric interconversion in diols **1a** (racemization) and **1c** (isomerization). [**1a** and *ent*-**1a** are here arbitrarily assigned]

Table 1. Experimental determination of the activation parameters

Racemization[a] (+)-**1a** ⇄ (−)-**1a**		Isomerization[b] **1c** → **1b**	
T (°C)	k_1 (s^{-1})	*T* (°C)	k_1 (s^{-1})
23	0.74×10^{-5}	23	1.68×10^{-5}
33	1.81×10^{-5}	35	6.54×10^{-5}
42	3.97×10^{-5}	45	16.34×10^{-5}
52	9.47×10^{-5}	52	27.90×10^{-5}
$\ln(A/s^{-1}) = 16.31$		$\ln(A/s^{-1}) = 20.66$	
$E_a = 69.27$ kJ/mol (16.55 kcal/mol)		$E_a = 77.76$ kJ/mol (18.57 kcal/mol)	
$\Delta H^{\#} = 66.70$ kJ/mol (15.93 kcal/mol)		$\Delta H^{\#} = 75.19$ kJ/mol (17.96 kcal/mol)	
$\Delta S^{\#} = -117.96$ J/mol (−28.18 cal/mol)		$\Delta S^{\#} = -81.83$ J/mol (−19.55 cal/mol)	

[a] Kinetic equation: $2k_1 \times t = \ln(ee_0/ee_t)$ with $k_1 = k_{-1}$.
[b] Kinetic equation: $k_1 \times t = \ln[(x_{1c})_0/(x_{1c})_t]$.

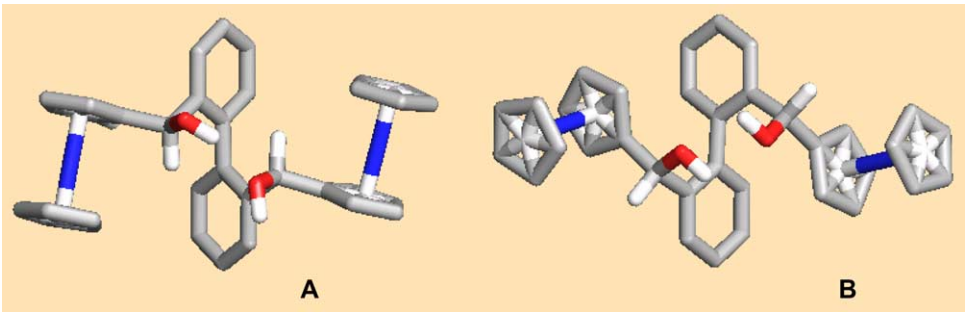
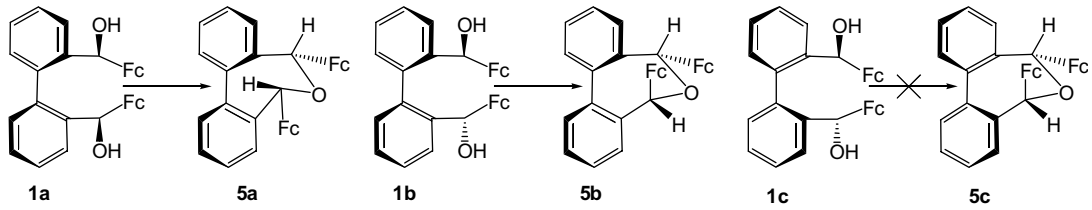


Figure 1. Molecular models of the diastereomeric diols with (*R*,*R*,a*R*)-configuration (A) and (*R*,*R*,a*S*)-configuration (B). Hydrogens on the biphenyl and ferrocenyl moieties are omitted for clarity.



On this basis we assumed the (*R*,*R*,a*R*)/(*S*,*S*,a*S*) combination of configurations more stable with respect to the (*R*,*R*,a*S*)/(*S*,*S*,a*R*) counterpart and tentatively assigned these chiralities to (±)-**1b** and (±)-**1c**, respectively.

In order to study the thermal stability of **1b**, it was heated at 110 °C in toluene and after 24 h the solution contained unchanged **1b** in addition to a new product, in about 40% yield, whose spectroscopic and mass properties were in agreement with the structure **5b**, as a result of an intramolecular dehydration. Since the ^{1}H NMR spectrum of **5b** again showed resonances for half the number of the protons present in the molecule, it is easy to deduce that the symmetry of the substrate is retained and **5b** is a *trans*-cyclic ether, whose formation occurs with retention of the configuration. Indeed, the heating of **1a** gave a different ether **5a** with a *cis* relationship between the ferrocenyl moieties and the same spectroscopic features of the parent diol. Faster conversion of **1a** into **5a** or **1b** into **5b** occurred in dichloromethane at 60 °C in the presence of a catalytic amount of silica.

Compound **5b** was thermally stable and the atropisomerization to the other possible *trans* ether **5c** was not observed. The formation of **5c** was never observed starting from diol **1c**; the heating of solutions containing **1c** always gave mixtures of **1b** and **5b** indicating that the isomerization of **1c** into **b** was faster than the dehydration reaction.

The observed stereochemical outcome in the formation of ethers **5a** and **b** is in agreement with the known reactivity of α-substituted alkylferrocenes,[16] taking into account that in the starting diols **1a** and **b**, one hydroxyl group could act as a nucleophile while the other one as a leaving group.

From the data herein reported, it could be deduced that the presence of two hydroxyl groups and two sterically demanding ferrocenyl substituents is effective in the induction of axial chirality in diol **1**. Both hydrogen bonding and steric interactions have been invoked as the origin of atropisomerism in other sterically congested 2,2′-substituted biphenyl carbinols.[8b] Although all the diols **1a**–**c** possess sufficient atropisomeric stability to allow their detection and separation, differences in their conformational flexibility were noticed. Due to the noncompletely hindered rotation around the biphenyl bond, diol **1a** suffered racemization and the conversion of kinetically preferred atropisomer **1c** into the thermodynamically stable diastereomer **1b** was also observed, this isomerization being probably driven by the achievement of the matched central and axial configuration.[17]

3. Conclusions

We have investigated the conformational behaviour of a biphenyl substituted on the 2,2′-position with ferrocenylhydroxymethyl groups, diol **1**, which was obtained in three diastereoisomeric forms depending on the different combinations of central and axial chirality. Taking into the account the reactivity and metal complexation properties of carbinolic compounds, diol **1** appears as a useful starting material for the development of a new class of ferrocenyl-biaryl ligands. The study of a suitable asymmetric reduction process for the preparation of **1b** in optically active form is currently in progress.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance™ 400 spectrometer at 400.13 and 100.62 MHz, respectively. Chemical shifts (δ) are given as parts per million relative to the residual solvent peak

and coupling constants (J) are in hertz. Cp′ refers to unsubstituted cyclopentadienyl ring in ferrocene. Melting points are uncorrected. THF was distilled under argon from sodium benzophenone ketyl. Column chromatography was performed on silica gel 60 (70–230 mesh) using the specified eluants. Chiral HPLC analyses were carried out on Chiracel® OD column (Daicel Chemical Industries) using *n*-hexane/EtOH mixtures as a mobile phase and detection by UV–vis detector at 225 nm. ESI-MS spectra were acquired in positive mode on a Waters Micromass ZQ2000, using a 30 V cone voltage and 150 °C source temperature. (2-Bromobenzoyl)ferrocene was prepared by conventional Friedel–Crafts acylation of ferrocene.[18]

4.2. Synthesis of 2,2′-bis-(ferrocenylcarbonyl)-1,1′-biphenyl, 4

In a flame dried flask, under an argon atmosphere, $NiCl_2$ $(PPh_3)_2$ (916 mg, 1.4 mmol, 1 equiv), freshly activated Zn dust (458 mg, 7 mmol, 5 equiv) and Bu_4NI (517 mg, 7 mmol, 5 equiv) were suspended with THF (30 mL). The resulting greenish suspension turned dark red upon warming at 60 °C. After 15 min stirring, a THF solution (25 mL) of ketone **3** (516 mg, 1.4 mmol) was added and the suspension left to react for 3 h at 60 °C. The solution was then filtered on Celite and the filtrate taken to dryness. The residue was chromatographed on Si gel column (*n*-hexane/EtOAc 4:1, R_f 0.24) to give pure **4** (688 mg, 85% yield); mp 195–196°C; ^{1}H NMR: δ 4.20 (5H, s, Cp′), 4.45 (2H, s, Cp), 4,83 (2H, s, Cp) 7.24 (1H, m, Ar), 7.25 (1H, m, Ar), 7.76 (1H, m, Ar); ^{13}C NMR: δ 70.05, 71.28, 72.13, 79.73, 126.80, 128.62, 129.34, 131.51, 138.65, 140.04, 202.16; HPLC: *n*-hexane/EtOH 90:10, flow rate 0.5 mL/min, t_R/min = 19.2. ESI-MS (+): m/z 578.1 $(M)^+$. Anal. Calcd for $C_{34}H_{26}Fe_2O_2$: C, 70.62; H, 4.53. Found: C, 70.53; H, 4.49.

4.3. Reduction of 4 with $NaBH_4$

To a solution of **4** (100 mg, 0.173 mmol) in THF/MeOH (4:1 v/v, 10 mL), $NaBH_4$ (133 mg, 3.5 mmol) was added and the suspension stirred at rt. The reaction course was monitored by TLC analysis until quantitative conversion of the substrate was observed. The excess of $NaBH_4$ was quenched with H_2O and the reaction mixture extracted with AcOEt (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified on Si gel column (*n*-hexane/AcOEt 85:15) to give compound (±)-**1a** as a yellow solid (86 mg, 85% yield).

4.3.1. (*R*,*S*,a*R*/*S*,*R*,a*S*)-2,2′-bis-(hydroxymethylferrocenyl)-1,1′-biphenyl, (±)-1a. R_f 0.28 (*n*-hexane/AcOEt 85:15); ^{1}H NMR: δ 2.18 (1H, br s, –OH), 2.47 (1H, br s, –OH), 3.84 (1H, t, J = 1.0, Cp), 3.95 (1H, t, J = 1.0, Cp), 4.06 (1H, br s, Cp), 4.10 (1H, br s, Cp), 4.12 (5H, s, C′p), 4.15 (1H, br s, Cp), 4.18 (2H, m, Cp), 4.21 (5H, s, C′p), 4.30 (1H, br s, Cp), 4.86 (1H, s, –C*H*OH), 5.37 (1H, s, –C*H*OH), 6.95 (1H, d, J = 7.5, Ar), 7.15 (1H, d, J = 7.5, Ar), 7.22 (1H, dt, J = 7.5 and 1.0, Ar), 7.29 (1H, dt, J = 7.5 and 1.0, Ar), 7.39 (2H, m, Ar), 7.68 (1H, d, J = 7.8, Ar), 7.72 (1H, d, J = 7.8, Ar); ^{13}C NMR: δ 65.65, 66.25, 67.40, 67.60, 67.71, 67.83, 67.94, 68.33, 68.45, 68.55, 94.96, 126.56, 126.63, 126.89, 127.88, 127.93, 129.56, 130.77, 138.33, 138.62, 140.98, 142.46. HPLC: *n*-hexane/EtOH 90:10, flow 0.5 mL/min, t_R/min = 17.6 and 23.8. ESI-MS (+): m/z 582.2 (M^+); 604.4 $[(M{\cdot}Na)–H^+]$. Anal. Calcd for $C_{34}H_{30}Fe_2O_2$: C, 70.13; H, 5.19. Found: C, 70.08; H, 5.12.

4.4. Reduction of 4 with $LiAlH_4$

To a solution of **4** (100 mg, 0.173 mmol) in dry ether (10 mL), $LiAlH_4$ (66 mg, 1.73 mmol) was added and the mixture stirred at room temperature for 1 h. At completion, the reaction was quenched by dropwise addition of water (2 mL) and extracted with AcOEt (3 × 30 mL). The organic layers were pooled, washed with brine, dried over Na_2SO_4 and taken to dryness under vacuum to give a residue that was purified on LiChroprep® Si gel 60 column eluting with *n*-hexane/AcOEt 85:15 and collecting three main fractions. The first fraction contained (±)-**1a** (52 mg, 51% yield); the intermediate fraction gave pure (±)-**1b** in 8% yield (8 mg) and the last fraction contained a mixture of (±)-**1c** as the main component and (±)-**1b** (33 mg, 32% yield). The last fraction was left to stand in *n*-hexane solution at 40 °C overnight to convert quantitatively (±)-**1c** into (±)-**1b**.

4.4.1. (*R*,*R*,a*R*/*S*,*S*,a*S*)-2,2′-bis-(hydroxymethylferrocenyl)-1,1′-biphenyl, (±)-1b. R_f 0.26 (*n*-hexane/AcOEt 85:15); ^{1}H NMR: δ 3.28 (2H, br s, –OH), 3.87 (2H, br s, Cp), 4.11 (12H, br s, Cp and C′p), 4.17 (2H, br s, Cp), 4.42 (2H, br s, Cp), 5.35 (2H, s, –C*H*OH), 7.10 (2H, d, J = 7.5, Ar), 7.30 (2H, m, Ar), 7.38 (2H, m, Ar), 7.57 (2H, d, J = 7.7, Ar); ^{13}C NMR: δ 65.86, 67.56, 67.66, 67.77, 68.48, 68.58, 93.10, 127.08, 127.20, 128.03, 129.65, 139.23, 141.92. HPLC: *n*-hexane/EtOH 90:10 flow 0.5 mL/min, t_R/min = 12.6; *n*-hexane/EtOH 98:2, flow 0.5 mL/min, t_R/min = 46.3 and 52.8. ESI-MS (+): m/z 582.2 (M^+); 604.4 $[(M{\cdot}Na)–H^+]$. Anal. Calcd for $C_{34}H_{30}Fe_2O_2$: C, 70.13; H, 5.19. Found: C, 70.08; H, 5.13.

4.4.2. (*R*,*R*,a*S*/*S*,*S*,a*R*/)-2,2′-bis-(hydroxymethylferrocenyl)-1,1′-biphenyl, (±)-1c. R_f 0.24 (*n*-hexane/AcOEt 85:15); ^{1}H NMR: δ 2.34 (2H, d, J = 2.6, –OH), 3.67 (2H, br s, Cp), 4.09 (4H, m, Cp), 4.16 (10H, s, C′p), 4.32 (2H, br s, Cp), 5.20 (2H, d, J = 2.5, –C*H*OH), 7.10 (2H, d, J = 7.4, Ar), 7.36 (4H, m, Ar), 7.60 (2H, d, J = 7.4, Ar); ^{13}C NMR: δ 66.18, 67.56, 67.66, 67.79, 68.07, 68.48, 94.03, 127.08, 127.15, 127.60, 130.87, 139.30, 140.88. HPLC: *n*-hexane/EtOH 90:10, flow 0.5 mL/min, t_R/min = 14.0 and 38.1.

4.5. Determination of kinetic rate constants

Diol **1a** was analyzed by chiral HPLC (*n*-hexane/EtOH 90:10, flow 0.5 mL/min) and the fractions containing single enantiomers were collected separately and, after removal of the solvent, stored at −20 °C. For kinetic measurements the isolated enantiomers were dissolved in hexane and maintained at constant temperature. At different intervals of time, aliquots were directly analyzed by HPLC and data of enantiomeric excess plotted

against time according to the kinetic equation: $2k_1 \times t = \ln(ee_0/ee_t)$.

For the study of the isomerization of **1c** into **b**, ketone **4** (10 mg) was reduced with $LiAlH_4$ as above and the reaction mixture extracted with AcOEt. The organic phase was dried over Na_2SO_4 and taken to dryness to give a residue that was stored at −20 °C. This residue was used without purification since the presence of diol **1a** did not interfere with the quantitative determination of both **1b** and **c**. For kinetic measurements the mixture containing diols was dissolved in hexane and maintained at constant temperature. At different times, aliquots of the solution were directly analyzed by chiral HPLC (*n*-hexane/EtOH 90:10, flow 0.5 mL/min) to determine the relative amounts of **1b** and **c** which were plotted against time according to the kinetic equation: $k_1 \times t = \ln[(x_{1c})_0/(x_{1c})_t]$.

4.6. (*R*,*S*,a*R*/*S*,*R*,a*S*)-3-oxa-2,4-diferrocenyl-1,5(1,2)-dibenzenacyclopentaphane, (±)-5a

To a solution of (±)-**1a** (50 mg,0.085 mmol) in CH_2Cl_2 (5 mL) a catalytic amount of silica was added and the suspension stirred at 60 °C for 6 h. After filtration, the solvent was evaporated under reduced pressure and the residue purified on Si gel column (*n*-hexane/CH_2Cl_2 9:1) to give pure (±)-**5a** as yellow solid (40 mg, 82% yield), mp 197–198 °C (dec), R_f 0.22 (*n*-hexane/CH_2Cl_2 90:10). ^{1}H NMR: δ 3.23 (1H, s, Cp), 3.73 (1H, s, Cp), 3.78 (1H, s, Cp), 3.82 (1H, br s, Cp), 4.05 (1H, s, Cp), 4.18 (5H, s, C′p), 4.25 (5H, s, C′p), 4.32 (1H, s, Cp), 4.64 (1H, s, Cp), 5.41 (1H, s, –CH–O), 6.04 (1H, s, –CH–O), 6.90 (1H, d, J = 7.6, Ar), 7.18 (1H, t, J = 7.3, Ar), 7.29 (1H, m, Ar), 7.36 (1H, d, J = 7.4, Ar), 7.47 (4H, m, Ar); ^{13}C NMR: δ 66.48, 66.86, 67.01, 67.50, 67.56, 67.80, 68.73, 68.95, 73.00, 81.54, 88.52, 92.58, 126.30, 127.47, 127.63, 128.09, 128.16, 128.36, 129.29, 130.05, 138.83, 139.67, 140.44, 141.71. ESI-MS (+): *m*/*z* 564.2 (M^+). Anal. Calcd for $C_{34}H_{28}Fe_2O$: C, 72.37; H, 5.00. Found: C, 72.18; H, 4.92.

4.7. (*R*,*R*,a*R*/*S*,*S*,a*S*)-3-oxa-2,4-diferrocenyl-1,5(1,2)-dibenzenacyclopentaphane, (±)-5b

Using the procedure described above diol (±)-**1b** gave (±)-**5b** in 85% yield, mp 220°C (dec), R_f 0.44 (*n*-hexane/CH_2Cl_2 90:10). ^{1}H NMR: δ 3.98 (2H, s, Cp), 4.17 (2H, s, Cp), 4.27 (10H, s, C′p), 4.33 (2H, s, Cp), 4.68 (1H, s, Cp), 5.05 (2H, s, –CH–O), 7.00 (2H, d, J = 7.6, Ar), 7.30 (2H, t, J = 7.6, Ar), 7.46 (2H, t, J = 7.6, Ar), 7.55 (2H, d, J = 7.6, Ar); ^{13}C NMR: δ 67.23, 67.61, 67.75, 69.00, 73.60, 88.18, 127.02, 127.76, 128.17, 139.23, 140.23. ESI-MS (+): *m*/*z* 564.2 (M^+). Anal. Calcd for $C_{34}H_{28}Fe_2O$: C, 72.37; H, 5.00. Found: C, 72.25; H, 5.04.

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