Chiral 1,2,1′-Trisubstituted Ferrocenes: Access to Chiral Oxaferrocenophanes

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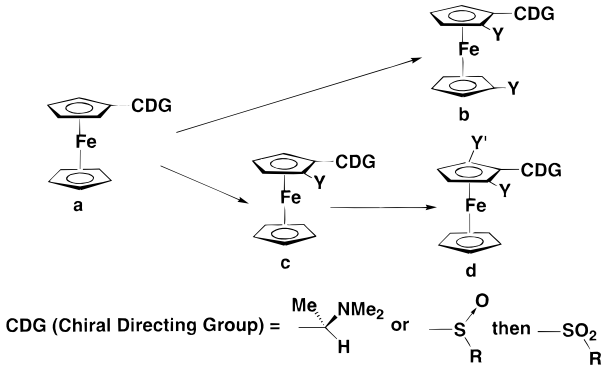
Combining the Kagan method for synthesis of chiral 2-substituted ferrocenecarbaldehydes with our recent method for synthesis of 1′-substituted formylferrocenes, we found easy access to various practically enantiomerically pure ferrocenecarbaldehydes substituted in the 2- and 1′-positions. Furthermore, we have described a general method of synthesis of chiral ferrocenophanes. The X-ray crystal structures for three of them were determined.

Introduction

Ferrocenyl compounds continue to attract the attention of chemists because of their involvement in many fields such as organic synthesis, catalysis, and more recently materials chemistry.[1,2] For example, in the last few years, we and others have described ferrocenyl moieties designed for nonlinear optics (NLO).[3−5] Materials used for SHG (second harmonic generation) need to be noncentrosymmetric. One way to induce the anisotropy of materials is to use chiral, enantiomerically pure compounds to build them up. Therefore, an easy access to chiral polysubstituted ferrocenes as possible precursors for NLO materials is of interest. In addition, more than 200 ferrocenyl derivatives with planar or planar and central chirality have been designed in the quest for asymmetric catalysis for numerous reactions, including asymmetric hydrogenation of alkenes or ketones, hydrosilylation, cross-coupling reactions, and aldol condensation. These recent successes in asymmetric catalysis involving chiral ferrocene ligands have increased the need for an easy access to chiral ferrocenyl molecules.

Until now, chiral trisubstituted ferrocenes have been obtained by only two methods. The first one is the treatment of a chiral amine such as *N*,*N*-dimethyl-1-ferrocenylethylamine (**a**) first with *n*-BuLi and then with *n*-BuLi/TMEDA, followed by an electrophilic attack to obtain the chiral trisubstituted compounds (**b**) with $Y = PPh_2$,[6] SR[7] (Scheme 1). These types of compounds have frequently been used in asymmetric catalysis with sometimes excellent efficiency.[8] However, this method gives no way to obtain, if necessary, three different substituents on ferrocene.

Scheme 1



The second method uses a chiral sulfoxide which is functionalized by a selective lithiation at one of the 2-positions (de >98%) followed by an electrophilic trapping of the organolithium compound. Subsequent oxidation of the sulfoxide moieties into a sulfone followed by lithiation and electrophilic trapping gives 1,2,3-trisubstituted ferrocenes with a sulfone group at the 2-position and two different substituents.[9] In the present paper, we wish to present a new method to obtain chiral, enantiomerically pure 1,2,1′-trisubstituted ferrocenes with three different substituents if necessary.

Results and Discussion

Recently, Kagan et al.[10] reported a general method for preparation of enantiomerically pure 2-substituted ferrocenecarbaldehydes. The key intermediate is the acetal **1**. Deprotonation of **1** with *t*-BuLi, followed by electrophilic attack, gives the 2-substituted acetal **2** in a diastereoisomeric excess (de) greater than 98% (Scheme 2). Acidic hydrolysis of **2** gives the almost enantiomerically pure corresponding 2-substituted ferrocenecarbal-

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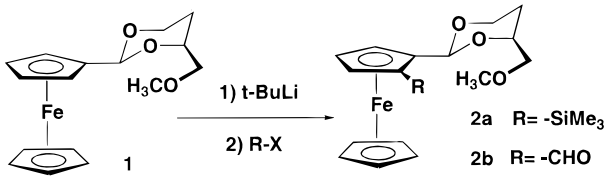
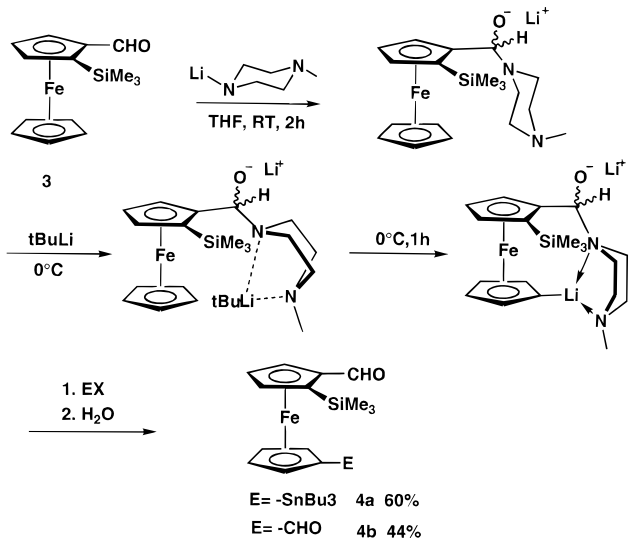
Scheme 2



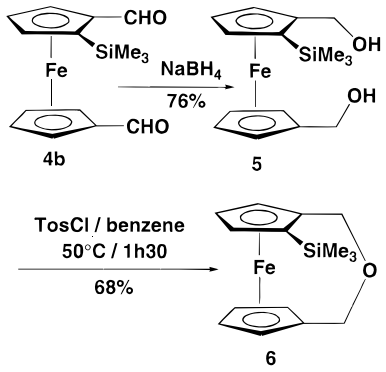
Scheme 3



dehydes. On the other hand, we described recently a new method for the synthesis of 1′-substituted ferrocenecarbaldehydes directly from ferrocenecarbaldehyde by a one-pot procedure, using an amine moiety as a temporary directing group.[11] When there were used together, these two methods led us to a new and general approach for synthesis of chiral, differently trisubstituted ferrocenes **4a**,**b**.

First we prepared the chiral 1,2-disubstituted compounds, following the procedure of Kagan.[9] Using as electrophile trimethylsilyl chloride or DMF, we obtained **2a** and the new compounds **2b** in good yields (85−90%), in a diastereoisomerically pure form. Hydrolysis of **2a** gave the corresponding aldehyde **3** in good yields (>80%). The latter compound **3** was deprotonated with lithium *N*-methylpiperazide (LNMP) followed by electrophilic attack with chlorotributyltin or DMF (Scheme 3). We obtained the trisubstituted compounds **4a**,**b**, in rather good yields of isolated compounds (60% and 44%). The lower yield for the dialdehyde **4b** (44%, isolated product) is related to its poor stability at room temperature. Thus, it was kept under argon in a freezer, before use. The regioselectivity of the reaction in favor of the 1′-position versus the 2-position is especially worth pointing out (>98/2, established by ^{1}H NMR on the crude product, compared with the regioselectivity of similar reactions on ferrocenecarbaldehyde (ca. 90/10)). This high selectivity is probably due to the steric hindrance of groups in the 2-position (trimethylsilyl or methyl). In every case, the major compounds were easily separated by flash chromatography on silica gel. **4a** is, to our knowledge, one of the few examples of an enantiomerically pure 1,2,1′-ferrocene with three different groups.[12] One interesting feature of this compound is the nonequivalence of all the different hydrogens and carbons of both cyclopentadienyl rings by ^{1}H or ^{13}C NMR (see Experimental Section). Furthermore, the three substituents can react independently. Therefore, **4a** can be a feedstock for the synthesis of various new interesting compounds according to the diversity of reactivities of the stannyl group and even more of the formyl group.

Scheme 4



We wish to report a direct application of the new chiral dialdehydes described above: the synthesis of chiral β-oxaferrocenophanes bearing a substituent in a 2-position. The enantiomerically pure dialdehyde **4b** was reduced with sodium borohydride in methanol/brine to obtain the diol **5**. By modification of a procedure described by Hillman et al.,[11a] the compound **5** was dehydrated with tosyl chloride (TsCl) in benzene in the presence of 4 Å molecular sieves at 50 °C, yielding (*S*)-2-(trimethylsilyl)-1,1′-(β-oxatrimethylene)ferrocene (**6**) with 68% yield. This new ferrocenophane is, to our knowledge, the first example of a chiral enantiomerically pure oxaferrocenophane obtained by asymmetric synthesis (Scheme 4). Indeed, some (β-oxatrimethylene)ferrocenes were reported in the literature, but there are no examples of chiral compounds of this kind.[13] The deprotonation of 1,1′-(β-oxatrimethylene)ferrocene (**13**) was tried with *n*-BuLi/TMEDA, but the ferrocenophane is totally destroyed without detection of substituted compounds in a 2- or 3-position.[14] Furthermore, to our knowledge, the only examples of synthesis of enantomerically enriched chiral ferrocenophanes are the enantioselective microbial kinetic resolution of racemic 2- and 3-formyl[4]ferrocenophane by bakers' yeast (ee up to 89% in 20% yield)[15] and the functionalization of Ugi's amine by dilithiation with *n*-BuLi/TMEDA and then trapping of the dilithiated intermediate by tetrachlorosilane.[16]

The chiral acetaldehyde **2b** was allowed to react by a similar reaction scheme, affording the dialdehyde **7** in 71% yield (Scheme 5). Once more, the regioselectivity

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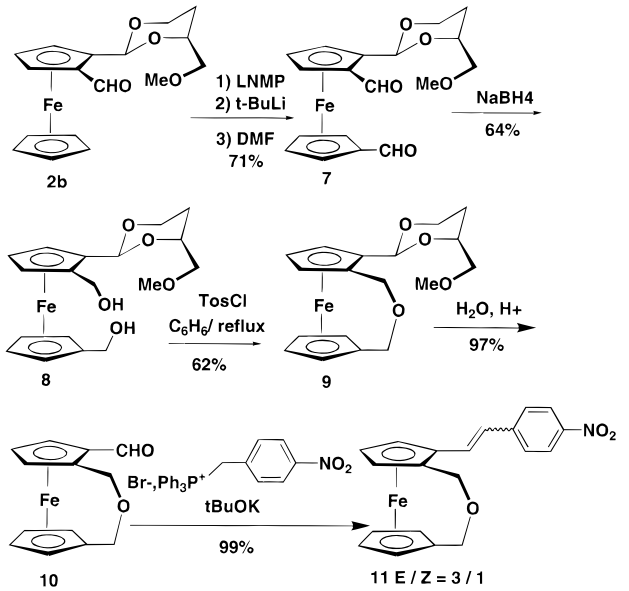
Scheme 5



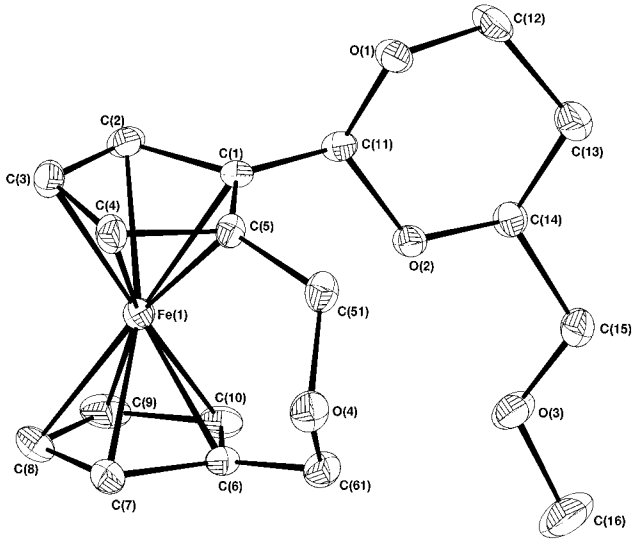


Figure 1. Cameron view of molecule **9**. Ellipsoids represent 30% probability.

during the functionalization at the 1′-position is very high (more than 98%). This dialdehyde was efficiently reduced by sodium borohydride to the diol **8**, which was converted to the chiral enantiomerically pure ferrocenophane **9**. Our modification of Hillman's method by use of 4 Å molecular sieves seems to be valuable, because even an hindered diol such as **8** reacts readily to give the ferrocenophane in fair yield (62%). The hydrolysis of **9** under acidic conditions (PTSA) yields **10**, which is an interesting intermediate for the synthesis of more complicated 1,1′-(*β*-oxatrimethylene)ferrocenes because of its reactive aldehyde group. To illustrate its synthetic value, **10** was converted in one step to **11** by a Wittig reaction in almost quantitative yield (Scheme 5).[17] The *E* isomer can be easily obtained by fractional crystallization in cool pentane. **(*E*)-11** is an interesting chromophore for nonlinear optics because it has the push−pull structure of *trans*-(2-(4-nitrophenyl)ferrocenyl)ethylene (**12**), known to have good molecular non-

(17) Fitjer, L.; Quebeck, U. *Synth. Commun.* **1985**, *15*, 855.

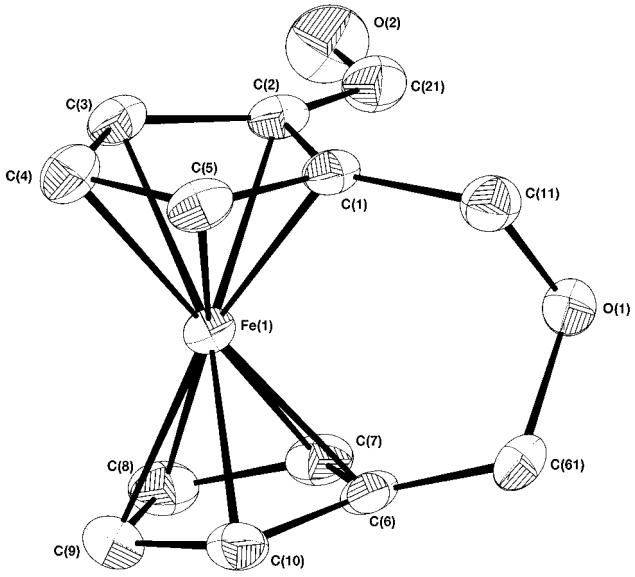


Figure 2. Cameron view of molecule **10**. Ellipsoids represent 30% probability.

linear optical properties. Furthermore, its chirality allows its crystallization in a noncentrosymmetric group so it can have non-linear optical efficiency in solid phase, in contrast to **12**.[18,19]

We were able to obtain crystal structures by X-ray diffraction of the compounds **9**−**11**. The molecular structures (CAMERON)[20] and atom-numbering schemes are shown in Figures 1−3. Selected bond lengths and angles can be found in Table 2.

Each of the three complexes is built up from a ferrocenophane unit containing a *β*-oxatrimethylene bridge. As observed in other ferrocenophane compounds, the presence of the bridge results in ring strain. This strain is conveniently described by the tilt angle α of the rings and the deformation angle *δ* at the iron between the midpoints of the ring (Chart 1).[21] Values observed for complexes **9**−**11** compare well with those for the unsubstituted ferrocenophane compound **13** (Table 3). The occurrence of substituents on one of the ferrocene rings in the 2-position with respect to the *β*-oxatrimethylene bridge does not seem to influence the overall geometry of the ferrocenophane framework. The bonding parameters and geometry within the bridge are identical for all compounds.

All the three complexes are enantiomerically pure and crystallize in noncentrosymmetric space groups. The absolute configuration for each structure was determined by refining the Flack enantiopole parameter *x*,[22] which is defined as

$$F_o^2 = (1 - x)F(h)^2 + xF(-h)^2$$

x is then the fractional contribution of $F(-h)$ to the observed structure amplitude, and it is sensitive to the polarity of the structure. The *x* values for each structure

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(22) Flack, H. *Acta Crystallogr.* **1983**, *A39*, 876.

Table 1. Crystal Data

	compound **9**	compound **10**	compound **11**
Crystal Parameters			
formula	$C_{18}H_{22}O_4Fe$	$C_{13}H_{12}O_2Fe$	$C_{20}H_{17}NO_3Fe$
fw	358.2	256.1	376.7
shape (color)	box (dark red)	box (red)	flat (dark red)
size, mm	0.50 × 0.60 × 0.70	0.22 × 0.38 × 0.50	0.15 × 0.80 × 0.83
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C222_1$	$P2_1$
a, Å	8.679(6)	10.462(3)	8.219(8)
b, Å	11.678(6)	11.098(3)	10.195(4)
c, Å	16.145(7)	18.386(4)	19.96(1)
β, deg			99.63(6)
V, Å^3	1636(2)	2134.8(9)	1649(2)
Z	4	8	4
F(000)	753	1058	769
ρ(calcd), g cm^{-3}	1.45	1.59	1.51
μ(Mo Kα), cm^{-1}	9.36	13.89	9.30
Data Collection			
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4F
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range θ, deg	0.9 + 0.345 tan θ	1.2 + 0.345 tan θ	1.1 + 0.345 tan θ
2θ range, deg	$3 < 2\theta < 50$	$3 < 2\theta < 46$	$3 < 2\theta < 50$
no. of rflns collected	3232 (h,k,±l)	1656 (h,k,±l)	6124 (±h,k,±l)
no. of unique rflns	2878	3823	5791
merging R factor	0.041	0.018	no merged rflns
no. of rflns used ($I > 3\sigma(I)$)	2721	1486	4860
Refinement			
R	0.0582	0.0277	0.0569
R_w	0.0692	0.0319	0.0700
weighting scheme	Chebyshev	Chebyshev	Chebyshev
coeff A_r	11.9, 3.29, 10.1	4.49, −1.40, 3.18	11.2, 4.06, 8.84
Flack parameter	0.02(2)	0.002(2)	0.11(29)
goodness of fit	1.37	1.05	1.14
ls params	210	146	462

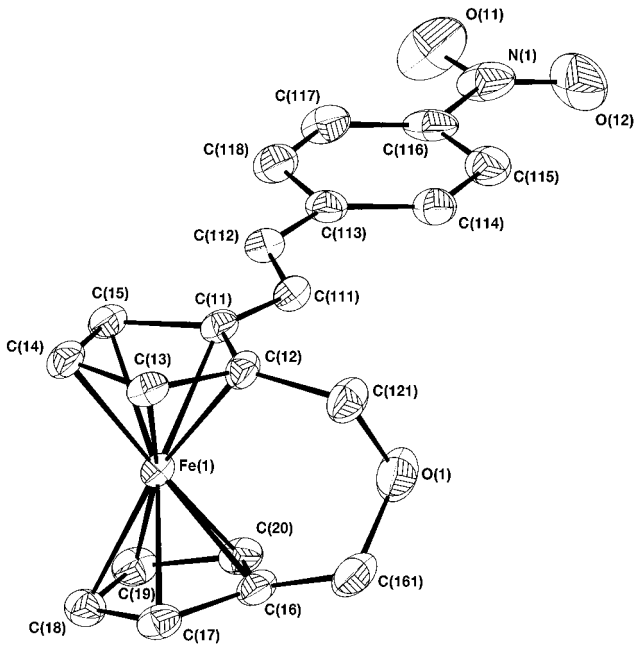
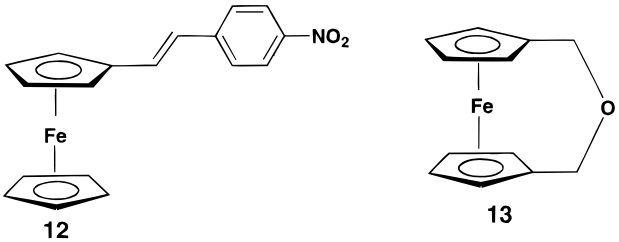


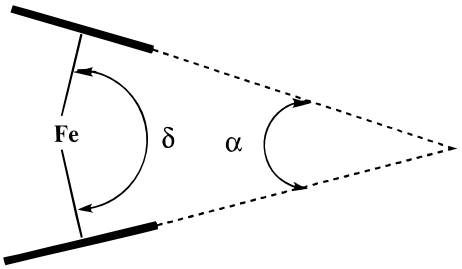
Figure 3. Cameron view of molecule **11**. Ellipsoids represent 30% probability.

Chart 1



12 13

Chart 2



are given in Table 1; they agree with the absolute configuration expected from the synthetic route.

The structure of **9** confirms the configuration of the acetal carbon and the planar chirality which was established by Kagan et al.[9]

Compound **11** crystallizes in the monoclinic space group $P2_1$, with two independent molecules in the asymmetric unit. Except for the disorder observed in the bridge for molecule 2, no significant differences in bonding parameters between these two molecules were found. The nitrophenyl groups are nearly coplanar with the corresponding ferrocene ring; the dihedral angle between these planes is 3.10 and 8.31° for molecules 1 and 2, respectively.

The most interesting and, in view of the NLO properties, the most decisive feature revealed by the crystal structure is the relative positions of these two molecules. As illustrated in Figure 4, they are related by a pseudo-C_2 symmetry axis. The unit cell thus contains two pairs

Table 2. Important Interatomic Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

Compound **9**

Fe(1)−C(1)	2.036(3)	O(4)−C(61)	1.431(5)	Fe(1)−C(10)	2.036(4)	C(6)−C(10)	1.421(5)
Fe(1)−C(2)	2.063(3)	O(1)−C(2)	1.428(5)	O(2)−C(11)	1.408(4)	C(6)−C(61)	1.499(5)
Fe(1)−C(3)	2.064(4)	C(1)−C(5)	1.420(5)	O(2)−C(14)	1.434(4)	C(7)−C(8)	1.439(6)
Fe(1)−C(4)	2.026(4)	C(1)−C(11)	1.490(5)	O(1)−C(11)	1.418(4)	C(8)−C(9)	1.404(7)
Fe(1)−C(5)	2.022(3)	C(2)−C(3)	1.421(6)	O(1)−C(12)	1.428(4)	C(9)−C(10)	1.438(6)
Fe(1)−C(6)	2.007(3)	C(3)−C(4)	1.410(6)	O(3)−C(15)	1.400(5)	C(12)−C(13)	1.508(6)
Fe(1)−C(7)	2.026(4)	C(4)−C(5)	1.464(4)	O(3)−C(16)	1.395(5)	C(13)−C(14)	1.522(5)
Fe(1)−C(8)	2.061(4)	C(5)−C(51)	1.508(5)	O(4)−C(51)	1.426(5)	C(14)−C(15)	1.507(5)
Fe(1)−C(9)	2.069(4)	C(6)−C(7)	1.430(5)				
C(11)−O(2)−C(14)	112.5(2)	C(7)−C(6)−C(61)	125.6(3)	C(2)−C(3)−C(4)	108.5(3)	O(1)−C(12)−C(13)	111.1(3)
C(11)−O(1)−C(12)	110.5(3)	C(10)−C(6)−C(61)	127.2(3)	C(3)−C(4)−C(5)	108.1(3)	C(12)−C(13)−C(14)	108.9(3)
C(15)−O(3)−C(16)	114.3(4)	C(6)−C(7)−C(8)	108.8(4)	C(1)−C(5)−C(4)	106.5(3)	O(2)−C(14)−C(13)	109.1(3)
C(51)−O(4)−C(61)	113.9(3)	C(7)−C(8)−C(9)	107.4(4)	Fe(1)−C(5)−C(51)	119.8(2)	O(2)−C(14)−C(15)	106.8(3)
C(2)−C(1)−C(5)	108.8(3)	C(8)−C(9)−C(10)	108.4(4)	C(1)−C(5)−C(51)	128.7(3)	C(13)−C(14)−C(15)	113.5(3)
Fe(1)−C(1)−C(11)	127.9(2)	C(6)−C(10)−C(9)	108.5(3)	C(4)−C(5)−C(51)	124.3(3)	O(3)−C(15)−C(14)	108.4(3)
C(2)−C(1)−C(11)	123.9(3)	O(2)−C(11)−O(1)	110.9(3)	C(7)−C(6)−C(10)	106.8(3)	O(4)−C(51)−C(5)	115.9(3)
C(5)−C(1)−C(11)	127.3(3)	O(2)−C(11)−C(1)	110.2(3)	Fe(1)−C(6)−C(61)	118.8(2)	O(4)−C(61)−C(6)	114.1(3)
C(1)−C(2)−C(3)	108.1(3)	O(1)−C(11)−C(1)	107.7(3)				

Compound **10**

Fe(1)−C(1)	1.990(4)	C(1)−C(2)	1.450(5)	Fe(1)−C(8)	2.051(4)	C(6)−C(7)	1.430(6)
Fe(1)−C(2)	2.007(3)	C(1)−C(5)	1.420(5)	Fe(1)−C(9)	2.055(4)	C(6)−C(10)	1.437(6)
Fe(1)−C(3)	2.047(3)	C(1)−C(11)	1.491(6)	Fe(1)−C(10)	2.023(4)	C(6)−C(61)	1.486(6)
Fe(1)−C(4)	2.061(4)	C(2)−C(3)	1.424(6)	O(1)−C(11)	1.422(6)	C(7)−C(8)	1.403(6)
Fe(1)−C(5)	2.026(3)	C(2)−C(21)	1.444(6)	O(1)−C(61)	1.435(5)	C(8)−C(9)	1.400(7)
Fe(1)−C(6)	2.005(4)	C(3)−C(4)	1.409(6)	O(2)−C(21)	1.219(6)	C(9)−C(10)	1.400(6)
Fe(1)−C(7)	2.020(4)	C(4)−C(5)	1.409(6)				
C(11)−O(1)−C(61)	114.9(3)	C(7)−C(6)−C(10)	105.3(4)	Fe(1)−C(2)−C(21)	120.4(3)	C(8)−C(9)−C(10)	108.6(4)
C(2)−C(1)−C(5)	106.7(3)	Fe(1)−C(6)−C(61)	119.9(3)	C(1)−C(2)−C(21)	125.1(4)	C(6)−C(10)−C(9)	108.8(4)
Fe(1)−C(1)−C(11)	120.4(3)	C(7)−C(6)−C(61)	128.7(4)	C(3)−C(2)−C(21)	126.8(4)	O(1)−C(11)−C(1)	114.7(3)
C(2)−C(1)−C(11)	127.1(4)	C(10)−C(6)−C(60)	125.7(4)	C(2)−C(3)−C(4)	108.0(3)	O(2)−C(21)−C(2)	124.1(5)
C(5)−C(1)−C(11)	126.0(4)	C(6)−C(7)−C(8)	109.3(4)	C(3)−C(4)−C(5)	108.8(4)	O(1)−C(61)−C(6)	114.1(3)
C(1)−C(2)−C(3)	107.7(3)	C(7)−C(8)−C(9)	107.9(4)	C(1)−C(5)−C(4)	108.8(3)		

Compound **11**

molecule 1		molecule 2		molecule 1		molecule 2	
Fe(1)−C(11)	2.035(4)	Fe(2)−C(21)	2.030(4)	C(14)−C(15)	1.410(6)	C(24)−C(25)	1.398(8)
Fe(1)−C(12)	2.002(4)	Fe(2)−C(22)	1.992(6)	C(16)−C(17)	1.431(7)	C(26)−C(27)	1.46(1)
Fe(1)−C(13)	2.034(5)	Fe(2)−C(23)	2.011(5)	C(16)−C(20)	1.416(7)	C(26)−C(30)	1.413(9)
Fe(1)−C(14)	2.059(4)	Fe(2)−C(24)	2.048(6)	C(16)−C(161)	1.517(8)	C(26)−C(261)	1.48(1)
Fe(1)−C(15)	2.046(4)	Fe(2)−C(25)	2.038(5)	C(17)−C(18)	1.402(7)	C(27)−C(28)	1.41(1)
Fe(1)−C(16)	1.986(5)	Fe(2)−C(26)	2.003(7)	C(18)−C(19)	1.409(7)	C(28)−C(29)	1.44(1)
Fe(1)−C(17)	2.032(4)	Fe(2)−C(27)	2.034(5)	C(19)−C(20)	1.409(8)	C(29)−C(30)	1.41(1)
Fe(1)−C(18)	2.056(5)	Fe(2)−C(28)	2.056(6)	C(111)−C(112)	1.299(7)	C(211)−C(212)	1.318(7)
Fe(1)−C(19)	2.044(5)	Fe(2)−C(29)	2.046(7)	C(112)−C(113)	1.466(7)	C(212)−C(213)	1.472(6)
Fe(1)−C(20)	2.015(4)	Fe(2)−C(30)	2.002(6)	C(113)−C(114)	1.404(8)	C(213)−C(214)	1.372(7)
N(1)−O(11)	1.220(9)	N(2)−O(21)	1.211(7)	C(113)−C(118)	1.368(8)	C(213)−C(218)	1.406(7)
N(1)−O(12)	1.193(8)	N(2)−O(22)	1.226(7)	C(114)−C(115)	1.386(8)	C(214)−C(215)	1.378(7)
N(1)−C(116)	1.475(7)	N(2)−C(216)	1.471(6)	C(115)−C(116)	1.396(9)	C(215)−C(216)	1.385(7)
C(11)−C(12)	1.431(6)	C(21)−C(22)	1.441(7)	C(116)−C(117)	1.363(9)	C(216)−C(217)	1.359(7)
C(11)−C(15)	1.448(7)	C(21)−C(25)	1.440(8)	C(117)−C(118)	1.364(8)	C(217)−C(218)	1.387(7)
C(11)−C(111)	1.460(6)	C(21)−C(211)	1.460(8)	C(121)−O(1)	1.380(7)	C(221)−O(2)	1.44(1)
C(12)−C(13)	1.426(7)	C(22)−C(23)	1.454(9)	C(161)−O(1)	1.407(8)	C(221)−O(4)	1.41(2)
C(12)−C(121)	1.501(7)	C(22)−C(221)	1.48(1)			C(261)−O(2)	1.42(1)
C(13)−C(14)	1.405(7)	C(23)−C(24)	1.42(1)			C(261)−O(4)	1.40(2)
O(11)−N(1)−O(12)	124.5(6)	O(21)−N(2)−O(22)	122.6(5)	C(18)−C(19)−C(20)	107.8(4)	C(28)−C(29)−C(30)	107.9(7)
O(11)−N(1)−C(116)	115.8(6)	O(21)−N(2)−C(216)	118.7(6)	C(16)−C(20)−C(19)	108.4(4)	C(26)−C(30)−C(29)	110.8(7)
O(12)−N(1)−C(116)	119.7(7)	O(22)−N(2)−O(216)	118.7(6)	C(11)−C(111)−C(112)	123.6(4)	C(21)−C(211)−C(212)	124.8(5)
C(12)−C(11)−C(15)	106.3(4)	C(22)−C(21)−C(25)	107.1(5)	C(111)−C(112)−C(113)	130.7(5)	C(211)−C(212)−C(213)	126.2(5)
Fe(1)−C(11)−C(111)	126.4(3)	Fe(2)−C(21)−C(211)	126.3(4)	C(112)−C(113)−C(114)	124.3(5)	C(212)−C(213)−C(214)	119.1(4)
C(12)−C(11)−C(111)	127.6(4)	C(22)−C(21)−C(211)	125.2(5)	C(112)−C(113)−C(118)	117.7(5)	C(212)−C(213)−C(218)	122.3(4)
C(15)−C(11)−C(111)	126.1(4)	C(25)−C(21)−C(211)	127.7(5)	C(112)−C(113)−C(118)	117.7(5)	C(212)−C(213)−C(218)	122.3(4)
C(11)−C(12)−C(13)	108.3(4)	C(21)−C(22)−C(23)	106.3(6)	C(114)−C(113)−C(118)	118.0(5)	C(214)−C(213)−C(218)	118.6(4)
Fe(1)−C(12)−C(121)	120.5(3)	Fe(2)−C(22)−C(212)	121.9(4)	C(113)−C(114)−C(115)	121.0(5)	C(213)−C(214)−C(215)	122.2(5)
C(11)−C(12)−C(121)	126.2(4)	C(21)−C(22)−C(221)	127.1(6)	C(114)−C(115)−C(116)	117.8(5)	C(214)−C(215)−C(216)	117.645)
C(13)−C(12)−C(121)	125.2(5)	C(23)−C(22)−C(221)	126.6(6)	N(1)−C(116)−C(115)	118.7(6)	N(2)−C(216)−C(215)	118.3(5)
C(12)−C(13)−C(14)	108.3(4)	C(22)−C(23)−C(24)	109.2(5)	N(1)−C(116)−C(117)	119.8(6)	N(2)−C(216)−C(217)	119.3(5)
C(13)−C(14)−C(15)	108.6(4)	C(23)−C(24)−C(25)	107.4(6)	C(115)−C(116)−C(117)	121.6(5)	C(215)−C(216)−C(217)	122.4(4)
C(11)−C(15)−C(14)	108.5(6)	C(21)−C(25)−C(24)	110.0(6)	C(116)−C(117)−C(118)	119.3(5)	C(216)−C(217)−C(218)	119.2(5)
C(17)−C(16)−C(20)	107.3(5)	C(27)−C(26)−C(30)	104.4(7)	C(113)−C(118)−C(117)	122.3(5)	C(213)−C(218)−C(217)	120.0(4)
Fe(1)−C(16)−C(161)	118.0(4)	Fe(2)−C(26)−C(261)	119.8(5)	C(12)−C(112)−O(1)	115.2(4)	C(22)−C(221)−O(2)	115.6(6)
C(17)−C(16)−C(161)	125.4(5)	C(27)−C(26)−C(261)	126.8(7)	C(16)−C(161)−O(1)	114.5(4)	C(22)−C(221)−O(4)	111.2(7)
C(20)−C(16)−C(161)	126.8(5)	C(30)−C(26)−C(261)	128.4(7)	C(121)−O(1)−C(161)	115.5(5)	C(26)−C(261)−O(2)	117.3(8)
C(16)−C(17)−C(18)	107.6(4)	C(26)−C(27)−C(28)	110.3(6)			C(26)−C(261)−O(4)	113.6(7)
C(17)−C(18)−C(19)	108.9(5)	C(27)−C(28)−C(29)	106.5(7)			C(221)−O(2)−C(261)	115.8(7)
						C(221)−O(4)−C(261)	119.7(12)

of molecules in an almost antiparallel arrangement; therefore, the NLO properties in the crystalline state are probably weak. A similar situation was recently reported for some related vinylferrocene complexes.[23]

Table 3. Comparison of Selected Molecular Parameters for the Ferrocenophane Framework

	9	10	11	12
α, deg	11.86	11.68	12.14, 8.31	11.9
δ, deg	171.8	172.6	171.6, 173.2	171.2
iron to ring dist, Å	1.640(3)	1.631(3)	1.633(5), 1.622(5)	1.630(1)
av C−C dist in Cp ing, Å	1.428(6)	1.419(7)	1.419(8), 1.429(8)	1.425(4)
av C−C−C angle in Cp ring, deg	108.0(4)	108.0(3)	108.0(4), 108.0(5)	108.0(2)
C(ring)−C(bridge) ist, Å	1.503(6)	1.489(6)	1.509(7), 1.49(1)	
C−O(bridge) dist, Å	1.428(5)	1.429(6)	1.395(7), 1.42(1)	1.415(4)
C−O−C(bridge) angle, deg	113.9(3)	114.9(3)	115.5(5), 117.7(9)	114.7(4)
C−C−O(bridge) angle, deg	115.0(3)	114.4(3)	114.9(4), 114.4(7)	

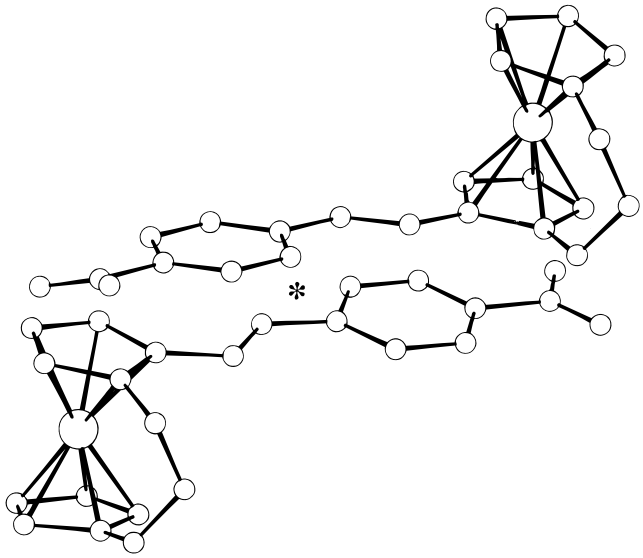


Figure 4. Drawing of the two independent molecules related by the pseudo C_2 axis (*).

Conclusion

We described an efficient method of various 1,2,1′-trisubstituted ferrocenes in an enantiomerically pure form with, in some cases, three different substituents, which pioneers an access to numerous molecules of this kind. We also reported the first general method of synthesis of chiral enantiomerically pure 2-substituted (β-oxatrimethylene)ferrocenes. These compounds were precisely studied, especially by crystal structure. We think that the new compounds described in this paper can widen the range of use of ferrocenic moieties in many fields, especially asymmetric catalysis, materials chemistry, etc. For example, because of the blocked rotation of the cyclopentadienyl ring and the tilting of this rings, which can give them particular stereoelectronic properties, the ferrocenophanes could be especially valuable.

Experimental Section

All of the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. *N*-Methylpiperazine was distilled and stored over sodium carbonate. Iodomethane and chlorotrimethylsilane were distilled on calcium hydride and stored on 3−4 Å molecular sieves. Dimethylformamide was freshly distilled on calcium hydride prior to use. Ph_2PCl was distilled under reduced pressure on carborundum and kept on 3−4 Å molecular sieves. Other compounds were used as commercial samples. All solvents were dried before use. Thin-layer chromatography was carried out on Merck Kieselgel $60F_{254}$ precoated silica gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 (^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR), Hewlett-Packard HP MSD 7590 (GC−MS), Hewlett-Packard HP 8452A (UV−vis), Perkin-Elmer 1725X (FT-IR), Enraf-Nonius CAD4 (X-ray). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse, France.

2b: Deprotonation of acetal **1** (2.28 g, 7.2 mmol) was carried out as described by Kagan.[8] DMF (1.1 mL, 2 equiv) was added at −78 °C. The mixture was stirred for 30 min and then for 1 h at −45 °C. A 30 mL portion of sodium hydroxide (2 N) was added to quench the excess electrophile; then the product was extracted with ether, washed with water, evaporated, dried on sodium sulfate, and then purified by flash chromatography on silica gel (eluent 1/2 cyclohexane/ether) to give 2.23 g (90%) of **2b** as a red solid. ^{1}H NMR ($CDCl_3$): δ 10.22 ppm (1H, s, CHO); 5.68 ppm (1H, s, OCHO); 4.77 ppm (2H, m, C_5H_3); 4.52 (1H, t, J = 2.6 Hz, C_5H_3); 4.27 ppm (5H, s, C_5H_5); 4.24 ppm (1H, m, CH_2O); 4.04 ppm (1H, m, CHO); 3.94 ppm (1H, td, J = 11.9 and 2.6 Hz, CH_2O); 3.49 and 3.40 ppm (2 × 1H, two dd (J = 10.2 and 5.9 Hz and J = 10.2 and 4.6 Hz), ABX system, CH_2OCH_3); 3.37 ppm (3H, s, OCH_3); 1.77 and 1.50 ppm (2 × 1H, qd (J_{gem} = 12.6 and J = 5.1 Hz) and dtd (J_{gem} = 13.1, 2.4, and 1.4 Hz), CH_2CH_2CH); $[\alpha]_D$ = −427 ($CHCl_3$, c = 0.64). ^{13}C NMR ($CDCl_3$): δ 193.9 ppm (CHO); 98.5 ppm (OCHO); 87.8 ppm (C_5H_3); 76.53, 75.45, 74.79, 72.12, 70.93, 70.0 ppm (C_5H_5); 68.8, 66.2, 58.6 ppm (OCH_3); 27.2 ppm (CH_2CH_2CH). GC−MS (IE, 70 eV): *m/e* 345 (M + 1, 20%); 344 (M, 100%); 279 (M − Cp, 26%); 251 (M − Cp − CO, 50%); 177 ($Fe(C_5H_4CH^+OCH{=}CH_2)$, 94%); 121 (29%); 56 (18%). IR ($CHCl_3$): 1668 cm^{-1} (−CHO). Anal. Calcd for $C_{17}H_{20}FeO_4$: C, 59.30; H, 5.81. Found: C, 59.47; H, 5.85. Mp: 83−84 °C.

General Procedure for 1′-Deprotonation of Aldehydes 2b and 3. Synthesis of 2a. At room temperature, 1.61 mL (1.1 equiv) of a *tert*-butyllithium solution (1.5 M in pentane) was added dropwise to a solution of 0.274 g (1.25 equiv) of *N*-methylpiperazine in 7 mL of anhydrous THF in a Schlenk tube under argon. The solution was stirred for 15 min; then 0.63 g (2.2 mmol) of aldehyde **3** in 7 mL of anhydrous THF was added. After it was stirred at room temperature for 2 h, the mixture was cooled to 0 °C. Then 1.82 mL (1.25 equiv) of a *tert*-butyllithium solution (1.5 M in pentane) was added and the solution was kept for 1 h at 0 °C and afterwards cooled to −78 °C. The electrophile was added by syringe (4−5 equiv), and the mixture was allowed to react at room temperature overnight. Then the solution was hydrolyzed, extracted by dichloromethane, washed with two parts of brine, dried on sodium sulfate, and evaporated with a high-vacuum pump, yielding the crude material as a red oil. Purification by flash chromatography on silica gel with cyclohexane/ether (1/1) yielded 0.76 g (60%) of **4a**. ^{1}H NMR ($CDCl_3$): δ 9.99 ppm (1H, s, CHO); 4.86 ppm (1H, dd, J = 2.4 and 1.2 Hz, C_5H_3); 4.59 ppm (1H, t, J = 2.4 Hz, C_5H_3); 4.46 ppm (2H, m, C_5H_3 and C_5H_4); 4.39 ppm (1H, td, J = 2.2 and 1.0 Hz, C_5H_4); 4.14 ppm (1H, dt, J = 2.2 and 1.0 Hz, C_5H_4); 3.99 ppm (1H, dt, J = 2.2 and 1.0 Hz, C_5H_4); 1.51 ppm (6H, m, $SnBu_3$); 1.35 ppm (6H, m, $SnBu_3$); 1.03 ppm (6H, m, $SnBu_3$); 0.91 ppm (9H, t, J = 7.2 Hz, $SnBu_3$); 0.30 ppm (9H, s, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 194.0 ppm (CHO); 83.3, 79.4, 75.8, 75.6, 74.7, 72.2, 72.1, 71.0, 69.2, 68.1, 29.0 ppm ($SnBu_3$); 27.2 ppm ($SnBu_3$); 13.6 ppm ($SnBu_3$); 10.0 ppm ($SnBu_3$); 0.31 ppm ($SiMe_3$). ^{119}Sn NMR ($CDCl_3$): δ −20.2 ppm. ^{29}Si NMR ($CDCl_3$): δ −2.3 ppm. GC−

(23) Togni, A.; Rihs, G. *Organometallics* **1993**, *12*, 3368.

MS (IE, 70 eV): *m/e* 576 (M, 1.9%), 575 (M − 1, 1.0%), 574 (M − 2, 1.4%), 519 (M − (nBu), 100%), 518 (M − 1 − (nBu), 48%), 517 (M − 2 − (nBu), 82%), 516 (M − 3 − (nBu)x, 37%), 515 (M − 4 − (nBu), 44%), 447 (47%), 255 (59%), 185 ($CpFe(C_5H_4)^+$, 23%), 121 ($CpFe^+$, 8%). $[\alpha]_D = -53$ ($CHCl_3$, $c = 1.09$). IR ($CHCl_3$): 1674 cm^{-1} (CHO). Anal. Calcd for $C_{26}H_{44}FeOSiSn$: C, 54.36; H, 7.71. Found: C, 55.21, H, 7.99.

4b: The reaction was carried out in a way similar to that for **4a** with 0.40 g of **3** (1.4 mmol). The electrophile (DMF) was added dropwise at −78 °C. The mixture was stirred for 30 min at −78 °C and then 1 h at −45 °C, followed by hydrolysis with water. Purification by flash chromatography with cyclohexane/ether (1/2) yielded 0.19 g (44%) of the red oil **4b**. ^1H NMR ($CDCl_3$): δ 9.95 ppm (s, 1H, −CHO); 9.90 ppm (s, 1H, −CHO); 5.02 ppm (dd, $J = 2.5$ and 1.3 Hz, 1H); 4.84 ppm (m, 2H); 4.77 ppm (t, $J = 2.5$ Hz, 1H); 4.65 ppm (m, 1H); 4.59 ppm (m, 1H); 4.53 ppm (m, 1H); 0.30 ppm (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 193.69 ppm (−CHO); 192.80 ppm (−CHO); 84.36, 80.60, 79.81, 75.59, 75.31, 74.09, 70.92, 70.46, 0.12 ppm. GC−MS (IE, 70 eV): 315 (M + 1, 23%); 314 (M, 100%); 299 (M − CH_3, 37%); 284 (56%); 271 (M − CH_3 − CO, 10%), 193 ($C_5H_4(SiMe_3)Fe^+$, 11%); 121 ($CpFe^+$, 11%). $[\alpha]_D = +189.4$ ($c = 0.38$, $CHCl_3$). IR (CH_3OH): 1688 cm^{-1} (−CHO), 1666 cm^{-1} (−CHO).

7: The procedure was similar to that for **4a**, with 3.0 g of **2b** (8.73 mmol). The electrophile (DMF) was added dropwise at −45 °C. The mixture was stirred for 1 h at −45 °C and then 3 h at 0 °C, followed by hydrolysis with water. Purification by flash chromatography with ether yielded 2.29 g (71%) of the red oil **7**. ^1H NMR ($CDCl_3$): δ 10.23 ppm (1H, s, CHO); 9.87 ppm (1H, s, CHO); 5.48 ppm (1H, s, OCHO); 4.85 ppm (1H, br s); 4.80 ppm (2H, br s); 4.75 ppm (1H, br s); 4.60 ppm (2H, br s); 4.52 ppm (1H, br s); 4.16 ppm (1H, m); 3.92 ppm (2H, m); 3.38 ppm (2H, m, CH_2OCH_3); 3.32 ppm (3H, s, OCH_3); 1.78 ppm (1H, m, CH_2CH_2CH); 1.44 ppm (1H, m, CH_2CH_2CH). ^{13}C NMR ($CDCl_3$): δ 194.2 ppm (CHO); 193.5 ppm (CHO); 97.8 ppm (OCHO), 89.3 ppm (subst Cp); 80.7 ppm (subst Cp); 78.0 ppm (subst Cp); 75.9, 75.1, 74.9, 74.8, 73.6, 72.3, 71.7, 71.0, 70.2, 66.6, 59.1 ppm (OCH_3); 27.4 ppm (CH_2CH_2CH). GC−MS (IE, 70 eV): 373 (M + 1, 10%); 372 (M, 44%); 279 (M − Cp − CO, 45%); 251 (M − Cp − 2CO, 46%); 177 ($Fe(C_5H_4CH^+OCH{=}CH_2)$, 100%); 121 ($CpFe^+$, 20%). $[\alpha]_D = +355.9$ ($CHCl_3$, $c = 0.27$). Anal. Calcd for $C_{18}H_{20}FeO_5$: C, 58.06; H, 5.38. Found: C, 58.33; H, 5.96.

General Procedure for Reduction of Dialdehydes with $NaBH_4$. Compound 5. In a Schlenk tube under argon, to a solution of 170 mg (0.54 mmol) of dialdehyde **4b** in 10 mL of methanol, cooled to 0 °C, was added a solution of 330 mg (15 equiv) of $NaBH_4$ in 10 mL of 2 N sodium hydroxide. The mixture was stirred overnight at room temperature; then the methanol was evaporated with a high-vacuum pump. The organic phase was extracted with ether, washed with water, and dried on magnesium sulfate; then the solvent was evaporated. The crude product was purified by flash chromatography on silica gel with ether and gave 130 mg (76%) of a yellow solid. ^1H NMR ($CDCl_3$): δ 4.43 ppm (2H, m); 4.37 ppm (5H, m); 4.30 ppm (1H, t, $J = 2.4$ Hz, subst Cp); 4.17 ppm (2H, m, subst Cp); 4.12 ppm (2H, m, subst Cp); 4.07 ppm (1H, dd, $J = 2.4$ and 1.3 Hz, subst Cp); 0.24 ppm (9H, s, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 93.8 ppm (subst Cp); 89.1 ppm (subst Cp); 74.2 ppm (subst Cp); 70.5 ppm (subst Cp); 69.7 ppm (subst Cp); 69.6 ppm (subst Cp); 68.4 ppm (subst Cp); 67.9 ppm (subst Cp); 67.3 ppm (subst Cp); 66.4 ppm (subst Cp); 60.1 ppm (CH_2-OH); 60.0 ppm (CH_2OH); 0.25 ppm ($Si(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −3.2 ppm. $[\alpha]_D = +8.17$ ($CHCl_3$, $c = 0.93$). Anal. Calcd for $C_{15}H_{22}FeO_2Si$: C, 56.60; H, 6.92. Found: C, 56.20; H, 7.24. Mp: 88−89 °C.

Compound 8. Reaction was carried out as for **5** with 2.29 g (6.1 mmol) of dialdehyde **7** in 40 mL of methanol and with 3.60 g of $NaBH_4$ dissolved in 40 mL of 2 N sodium hydroxide. The purification by flash chromatography on silica gel with ethyl acetate as eluent gave 1.48 (64%) of a yellow solid. ^1H NMR ($CDCl_3$): δ 5.60 ppm (1H, s, OCHO); 4.47 ppm (1H, d, $J = 12.3$ Hz, CH_2OH); 4.35 ppm (1H, dd, $J = 2.4$ and 1.5 Hz, subst Cp); 4.31 ppm (3H, m); 4.22 ppm (3H, m); 4.20−4.04 ppm (5H, m); 3.96 ppm (1H, td, $J = 11.9$ and 2.7 Hz, CH_2O); 3.43 ppm (2H, m, CH_2OCH_3); 3.36 ppm (3H, s, OCH_3); 3.27 ppm (2H, br s, OH); 1.72 ppm (1H, qd, $J_{gem} = 13$ Hz and $J = 5.1$ Hz, CH_2CH_2CH); 1.44 ppm (1H, br d, $J_{gem} = 13$ Hz, CH_2CH_2-CH). ^{13}C NMR ($CDCl_3$): δ 99.6 ppm (OCHO); 90.3 ppm (subst Cp); 86.0 ppm (subst Cp); 83.9 ppm (subst Cp); 75.7, 74.8, 70.0, 68.6, 67.6, 67.5, 66.6, 66.5, 59.7, 59.0 ppm (CH_2OH); 58.9 ppm (CH_2OH); 27.0 ppm (CH_2CH_2CH). $[\alpha]_D = -21$ ($CHCl_3$, $c =$ 0.41). Anal. Calcd for $C_{18}H_{24}FeO_5$: C, 57.45; H, 6.38. Found: C,56.23; H 6.72.

General Procedure for Synthesis of (β-Oxatrimethylene)ferrocenes. 6: Under argon, to a solution of 100 mg (0.31 mmol) of diol **4b** in 30 mL of freshly distilled benzene were added 4 Å molecular sieves and then 70 mg (0.31 mmol) of tosyl chloride. The mixture was heated to 50 °C. After 90 min the reaction was complete, and anhydrous sodium carbonate was added after cooling. The solvent was evaporated, and then the crude product was purified by flash chromatography with pentane/ether (5/1) eluent. A 55 mg (58%) amount of **6** was obtained as an oil at room temperature, which crystallizes on cooling. ^1H NMR (C_6D_6): δ (ppm) 4.28 (2H, m); 4.22 (1H, t, $J = 2.2$ Hz, C_5H_3); 4.13 (4H, massif: 3H Cp and 1H $-CH_2O$, d, $J = 13.0$ Hz); 4.06 (1H, d, $J = 13.0$ Hz, $-CH_2O$); 4,05 (1H, dt, $J = 2.4$ and 1.2 Hz, C_5H_4); 3.67 (1H, d, $J = 13.0$ Hz, $-CH_2O$); 3.62 (1H, d, $J = 13.0$ Hz, $-CH_2O$); 0.37 (9H, s, $-SiMe_3$). ^{13}C NMR (C_6D_6): δ (ppm) 88.3, 84.2, 77.3, 75.0, 73.4, 72.3, 71.1, 70.9, 70.4, 70.3, 64.9, 64.3, 1.28 ($-SiMe_3$). ^{29}Si NMR ($CDCl_3$): δ −3.1 ppm (s). GC−MS (IE, 70 eV): *m/e* 302 (M + 2, 6%); 301 (M + 1, 24%); 300 (M, 100%); 285 (M − CH_3, 20%); 121 ($CpFe^+$, 3%). $[\alpha]_D = +36.2$ ($CHCl_3$, $c = 0.55$). Anal. Calcd for $C_{15}H_{20}FeOSi$: C, 60.00; H, 6.67. Found: C, 59.74; H, 7.02.

9 was prepared as for **6** in benzene (270 min of benzene reflux), starting from 480 mg (1.28 mmol) of diol **8**. Flash chromatography of the crude material with ether gave 280 mg (61%) of **9** as a yellow oil at room temperature, which was crystallized in methylene dichloride/hexane and gave crystals suitable for X-ray diffraction. ^1H NMR (C_6D_6): δ (ppm) 5.67 (1H, s, OCHO); 4.76 (1H, dd, $J = 2.4$ and 1.6 Hz, C_5H_3); 4.64 (1H, d, $J = 12.9$ Hz, $-CH_2O$); 4.40 (1H, td, $J = 2.3$ and 1.3 Hz, C_5H_4); 4.33 (1H, dt, $J = 2.3$ and 1.3 Hz, C_5H_4); 4.25 (1H, d, $J = 12.9$ Hz, $-CH_2O$); 4.07 (4H, m, 2H C_5H_4 and 2H C_5H_3); 4.02 (1H, ddd, $J = 11.4$, 6.3, and 1.4 Hz, $-OCH_2-$, dioxane); 3.91 (1H, dddd, $J = 6.0$, 5.1, 4.7, and 2.5 Hz, −CHO); 3.58 (1H, ddd, $J = 12.4$, 11.4, and 2.5 Hz, $-OCH_2-$, dioxane); 3.41 (1H, dd, $J = 10.0$ and 6.0 Hz, AB, $-CH_2OCH_3$); 3.21 (1H, dd, $J = 10.0$ and 4.7 Hz, AB, $-CH_2OCH_3$); 3.19 (s, 3H, $-OCH_3$); 1.68 (1H, dddd, $J_{gem} = 13.1$ Hz; $J = 12.4$, 6.6, and 5.1 Hz, CCH_2C); 1.07 (1H, dtd, $J_{gem} = 13.1$ Hz; $J = 2.5$ and 1.4 Hz; CCH_2C). ^{13}C NMR ($CDCl_3$): δ (ppm) 99.9, 85.9, 83.7, 81.3, 75.9, 75.5, 73.5, 71.4, 70.8, 70.14, 69.75, 69.24, 68.61, 66.84, 64.01, 62.95, 59.19, 27.95. GC−MS (IE, 70 eV): *m/e* 359 (M + 1, 22%); 358 (M, 100%); 235 (16%); 205 ($Fe(C_5H_3(CHO)CH^+OCH{=}CH_2)$, 10%); 177 ($Fe(C_5H_4CH^+OCH{=}CH_2)$, 15%); 121 ($CpFe^+$, 6%). $[\alpha]_D = -89.5$ ($CHCl_3$, $c = 0.28$). Mp: 82 °C.

10: In a Schlenk tube 75 mg (0.21 mmol) of acetal **9** was dissolved in 4 mL of deoxygenated methylene chloride, under argon. A 2 mL portion of deoxygenated water was added, followed by 20 mg of *p*-toluenesulfonic acid. The mixture was heated to 60 °C for 90 min; then the organic phase was diluted with ether, washed twice with water, and dried on sodium sulfate and the solvent was evaporated. Flash chromatography on silica gel with ether gave 50 mg (97%) of **10** as an orange solid. ^1H NMR ($CDCl_3$): δ (ppm) 10.01 (1H, s, −CHO); 4.78 (1H, dd, $J = 2.6$ and 1.4 Hz, C_5H_3); 4.61 (1H, dd, $J = 2.6$ and 1.4 Hz, C_5H_3); 4.53 (1H, d, $J = 13.4$ Hz, $-CH_2O$); 4.52 (1H, t, $J = 2.6$ Hz, C_5H_3); 4.39 (1H, td, $J = 2.4$ and 1.3 Hz, C_5H_4); 4.24 (1H, dt, $J = 2.4$ and 1.3 Hz, C_5H_4); 4.16 (1H, dt, $J = 2.4$ and 1.3 Hz, C_5H_4); 4.13 (1H, td, $J = 2.4$ and 1.3 Hz, C_5H_4); 3.97 (1H, d, $J = 13.1$ Hz, -CH_2-O); 3.96 (1H, d, $J = 13.4$

Hz, -CH_2-O); 3.85 (1H, d, J = 13.1 Hz, −CH_2O). ^{13}C NMR ($CDCl_3$): (ppm) 194.7 (CHO); 85.4, 84.7, 78.6, 75.7, 73.6, 73.1, 72.8, 71.4, 71.1, 71.0, 63.9, 62.9. GC−MS (IE, 70 eV): *m/e* 257 (M + 1, 16%); 256 (M, 100%); 200 (M − 2CO, 16%); 199 (M − CO − CHO, 13%); 177 (M − ($C_5H_4CH_3$), 10%); 134 ($Fe(C_5H_3CH_2)^+$, 18%); 121 (16%). IR ($CHCl_3$): 1676 cm^{-1} (−CHO). [α]$_D$ = +214 ($CHCl_3$, c = 0.19). Anal. Calcd for $C_{13}H_{12}FeO_2$: C, 60.94; H 4.68. Found: C 60.20; H 4.90.

11: Into a distillation apparatus were added 93 mg (0.8 mmol) of tBuOK and 330 mg (0.67 mmol) of (4-nitrobenzyl)-triphenylphosphonium bromide. The system was purged with argon, and to the mixture of solids was added 7 mL of dry toluene. The mixture was warmed, and after 1 h, 6 mL of toluene was distilled and then the solution was kept at reflux for another 2 h. After cooling, a solution of 70 mg (0.27 mmol) of aldehyde **10** in 7 mL of toluene was added; this solution was warmed again, and after 1 h, 6 mL of toluene was distilled. Then the solution was kept at reflux for another 2 h. After it was cooled to room temperature, the organic phase was extracted with methylene chloride and then washed with brine and dried on sodium sulfate and the solvents were evaporated. Flash chromatography first with pentane/ethyl acetate (10/1) then with pentane/ethyl acetate (7/1) gave 110 mg (100%) of **11** as a mixture of two isomers (E/Z = 3/1), which were separated by fractional crystallization in cooled pentane. Isomer E: ^{1}H NMR ($CDCl_3$): δ (ppm) 8.16 (2H, d, J = 8.8 Hz, C_6H_4); 7.53 (2H, d, J = 8.8 Hz, C_6H_4); 7.16 (1H, d, J = 16.2 Hz, vinyl); 6.70 (1H, d, J = 16.2 Hz, vinyl); 4.61 (1H, m, subst Cp); 4.51 (1H, d, J = 13.4 Hz, CH_2); 4.40 (1H, m, subst Cp); 4.36 (1H, d, J = 13.8 Hz, CH_2); 4.32 (2H, m, subst Cp); 4.11 (1H, m, subst Cp); 4.05 (1H, m, subst Cp); 3.79 (1H, m, subst Cp); 3.64 (1H, d, J = 13.8 Hz, CH_2); 3.57 (1H, d, J = 13.4 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 146.0, 144.2, 131.1, 126.1, 124.9, 124.1, 84.0, 82.8, 81.1, 74.2, 73.6, 71.3, 71.1, 70.4, 69.6, 67.8, 64.3, 63.3. [α]$_D$ = −721 ($CHCl_3$, c = 0.005). Anal. Calcd for $C_{20}H_{17}FeNO_3$: C, 64.00; H, 4.53; N, 3.73. Found: C, 63.47; H, 4.82; N, 3.66. Mp: 161 °C. UV: λ_{max} = 474 nm ($CHCl_3$).

X-ray Structure Determination. For **9**−**11**, data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite oriented monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). The final unit cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections that had been accurately centered on the diffractometer. Only statistical fluctuations were observed in the intensity monitored over the course of the data collections for compound **10**, whereas for **9** and **11** reorientations were observed.

The three structures were solved by direct methods (SIR92) and refined by least-squares procedures on F_o. H atoms were introduced in calculations in idealized positions (d(CH) = 0.96 Å), and their atomic coordinates were recalculated after each cycle.[24] They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Among the two independent molecules of compound **11**, one presents a disorder in the β-oxatrimethylene bridge with the oxygen distributed on two sites. In the first step, it was assumed that the thermal parameters of the corresponding oxygen atoms in the disordered positions were equal and the occupancies were allowed to vary with the constraint that the sum of the occupancies equals unity. Additional distance and angle restraints (mean C−O and C−O−C values) were used during this procedure. When the occupancy factors were well-defined, all the restraints were released and the disordered oxygen atoms were refined anisotropically. No hydrogen placing was done for the C atoms of this disordered β-oxatrimethylene bridge. The absolute configuration was confirmed by the refinement of the Flack enantiopole parameter. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - (\Delta F/6\sigma(F_o)^2]_2$, where $w' = 1/\Sigma_1{}^r A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was F_c/F_c(max).[25] Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$; the values are listed in Table 1. Criteria for a satisfactory complete analysis was a ratio of rms shift to standard deviation less than 0.1 and no significant features in the final difference maps. Details of data collection and refinement are given in Table 1.

The calculations were carried out with the CRYSTALS package programs[26] running on a PC486 DX266. Fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and atomic coordinates for H atoms have been deposited at the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Tables of positional and thermal parameters for compounds **9**−**11** (6 pages). Ordering information is given on any current masthead page.

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