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Notes

Selective Functionalization of Chiral Ferrocenyl Acetals. Easy Access to Various Tri- and Tetrasubstituted Ferrocenes with Controlled Geometry

Jérôme Chiffre, Yannick Coppel, Gilbert G. A. Balavoine,
Jean-Claude Daran, and Eric Manoury*

*Laboratoire de Chimie de Coordination, 205 Route de Narbonne,
F-31077 Toulouse Cedex, France*

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Summary: The lithiation of 2-substituted chiral dioxane ***2****, followed by electrophilic trapping of the lithiated intermediate, yields various 1,5-disubstitued acetals with good yields and excellent control of the geometry. These acetals can be easily hydrolyzed into various 1,5-disubstitued ferrocenecarboxaldehydes (in an enantiomerically pure form if the two substituents are different), which can be furthermore substituted on the other Cp ring to yield unprecedented 2,5,1′-ferrocenecarboxaldehydes (in an enantiomerically pure form if they are chiral). The three substituents on ferrocenecarboxaldehyde can be different: this is, to the best of our knowledge, the first example of enantiomerically pure 1,2,3,1′-tetrasubstituted ferrocene with planar chirality only.*

Introduction

The need for efficient synthesis of various ferrocene derivatives drastically increased in the last 10 years because of the booming use of such compounds in numerous fields of science.[1] Indeed, in some applications such as materials science or asymmetric catalysis, an efficient access to ferrocenes with a controlled planar chirality is of great interest. Since the pioneering work of Ugi,[3] many efficient methods to obtain enantiomerically pure 1,2-disubstituted ferrocenes have been developed.[2] Most of them are based on diastereoselective orthometalation of ferrocenyl derivatives containing chiral directing groups. These directing groups may be tertiary amine,[3,4] acetal,[5] sulfoxide,[6] imine,[7] oxazoline,[8] or more recently phosphine oxide.[9] To avoid the sometimes tedious work of synthesizing ferrocenes bearing a chiral directing group, several enantioselective ortholithiations of nonchiral monosubstituted ferrocenes (direct methods) using chiral tertiary amines as additives, to obtain disubstituted ferrocenes with sometimes very high enantioselectivities (up to 99% ee), have been recently developed.[10] In addition, more complex substitution patterns are now available in an enantiomerically pure form: 1,2,1′- or 1,2,3-trisubstituted,[4d,6a,11,12] 1,2,1′,2′-tetrasubstituted,[11e,f,13] or very recently 1,2,3,1′,2′,3′-

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* Corresponding author. Fax: 00 (33) 5 61 55 30 03. E-mail: manoury@lcc-toulouse.fr.

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hexasubstituted ferrocenes.[15] The occurrence of supplementary groups from the classical 1,2-substitution could be very valuable for some applications. For example, in asymmetric catalysis, an additional substitution may increase the selectivity of the catalytic system[16] or allow the tethering of the ligand on various supports like dendrimers.[17] For some years, our group has been involved in the development and the search for synthetic methods leading to various polysubstituted ferrocenes.[2b] In this paper, a highly efficient and general method to obtain 1,2,3-trisubstituted and 1,2,3,1′-tetrasubstituted ferrocenes with only planar chirality will be presented.

Results and Discussion

We have found that these diastereoisomerically pure 2-substituted acetals **1**, prepared and purified according to literature process,[5] could be selectively transformed into the corresponding 1,5-substituted acetals **2** by action of *t*-BuLi at −78 °C followed by electrophilic trapping of the lithiated intermediate. The regioselectivity in favor of the functionalization in the 5 position is complete. No compounds with substitution in the 3 or 1′ position have been observed. Furthermore, no products of polyfunctionalization have been detected so far. A direct reaction between *tert*-butyllithium and a 2-substituted acetal **1**, without precomplexation of *t*-BuLi on the acetal part prior to the deprotonation step, would probably occur on the different available protons of the ferrocenyl moieties without significant selectivity. So, the high regioselectivity is probably due to the precomplexation of *tert*-butyllithium, either on the two oxygen atoms of the acetal part of the molecule as already proposed to explain the selective synthesis of acetals **1** by Kagan et al.[5] or on the other oxygen of the dioxane ring that is not proximal to the methoxymethyl group. In the first case, because the 2 position is already substituted, deprotonation can occur only after rotation of the dioxane ring leading to the attack on the 5 position. In the second case, the base is already proximal to the hydrogen atom in the 5 position and the same lithiated compound should be obtained. So, various 1,5-disubstituted ferrocenylacetals, which are 1,2,3-trisubstituted ferrocenes, could be synthesized with fair to good yields as single enantiomerically pure diastereoisomers as shown in Table 1. However, it should be noted that compounds **2a** and **2g** with the same R^1 and R^2 groups have no planar chirality.

Hydrolysis of these rather hindered dioxanes could be achieved in a biphasic dichloromethane/water system in the presence of *p*-toluenesulfonic acid[5b] to yield different aldehydes **3** with excellent yields (see Scheme 1 and Table 2). Compounds **3a** and **3g** are not chiral, but aldehydes **3b**, **3c**, **3d**, **3f**, and **3h** are chiral and obtained in an enantiomerically pure form.

Table 1. Functionalization of 2-Substituted Ferrocenyl Dioxanes

entry	R^1	R^2	product	yield
1	$SiMe_3$	$SiMe_3$	**2a**	78%
2	$SiMe_3$	$SnBu_3$	**2b**	50%
3	$SiMe_3$	PPh_2	**2c**	29%
4	$SiMe_3$	SPh	**2d**	68%
5	PPh_2	$SiMe_3$	**2e**	42%
6	PPh_2	$SnBu_3$	**2f**	52%
7	PPh_2	PPh_2	**2g**	37%
8	PPh_2	SPh	**2h**	70%

Scheme 1

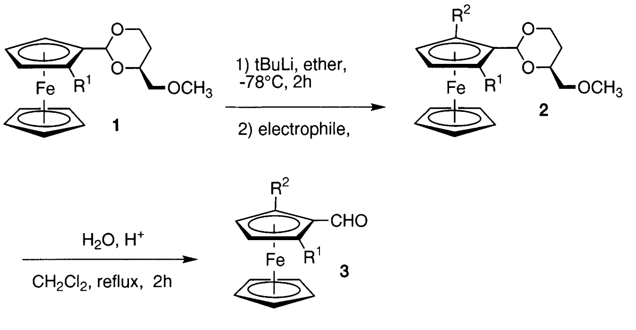
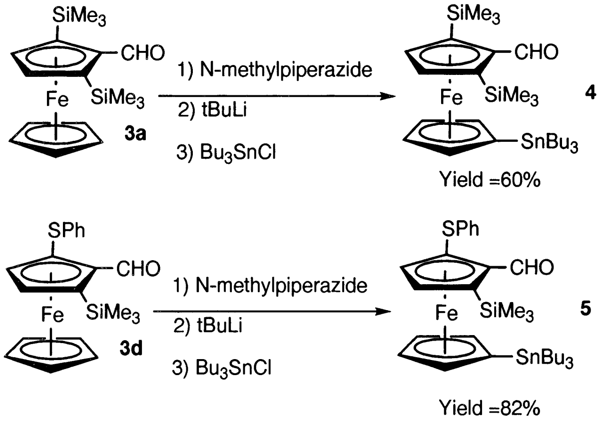


Table 2. Hydrolysis of 2-Disubstituted Ferrocenyl Dioxanes

entry	R^1	R^2	product	yield
1	$SiMe_3$	$SiMe_3$	**3a**	90%
2	$SiMe_3$	$SnBu_3$	**3b**	94%
3	$SiMe_3$	PPh_2	**3c**	88%
4	$SiMe_3$	SPh	**3d**	93%
5	PPh_2	$SnBu_3$	**3f**	94%
6	PPh_2	PPh_2	**3g**	89%
7	PPh_2	SPh	**3h**	95%

Scheme 2



Furthermore, these new enantiomerically pure aldehydes could be efficiently transformed into 1,2,3,1′-tetrasubstituted ferrocenes by successive action of *N*-methylpiperazide, *t*-BuLi, and finally an electrophile (Scheme 2).[11d] Compound **5** is, as far as we know, the first example of an enantiomerically pure 1,2,3,1′-tetrasubstituted ferrocene with four different substituents. The functionalization of 1,5-disubstituted ferrocenecarboxaldehydes (1,2,3-trisubstituted ferrocenes) has been tried in only two cases up to now but could probably be easily extended to some other substrates

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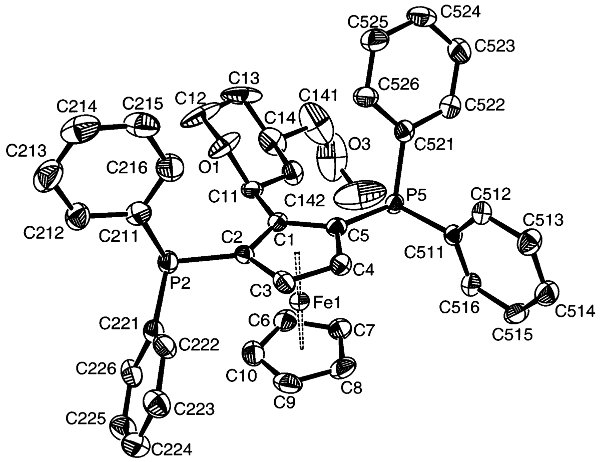

Figure 1. Molecular view of **2g** with atom-labeling scheme. Ellipsoids represent 30% probability.

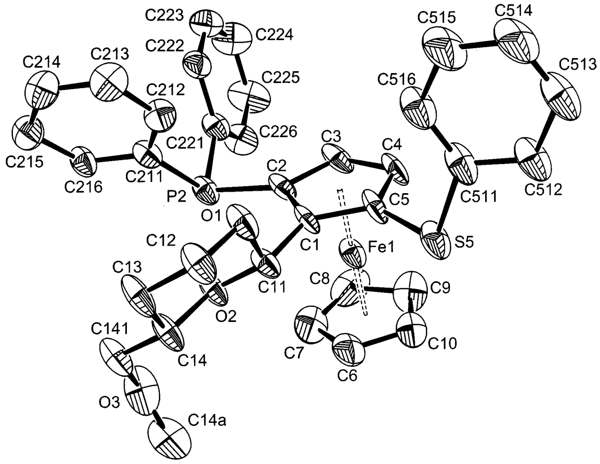

Figure 2. Molecular view of complex **2h** with atom-labeling scheme. Ellipsoids are drawn at 30% probability.

by the method described above. So, various 1,2,3,1′-ferrocenes are now potentially available. The main restriction is the compatibility of both substituents already present in the 1 or 5 position of the carboxaldehyde with the conditions of the functionalization on the other cyclopentadienyl ring (*N*-methylpiperazide and *t*-BuLi; see ref 11d). So, if some achiral 1,2,3,1′-tetrasubstituted ferrocenes have already been described,[17] our method is, to the best of our knowledge, the only one for synthesizing compounds with four different groups in an enantiomerically pure form.

Some crystals suitable for X-ray analysis have been obtained by slow diffusion of hexane into a dichloromethane solution of compounds **2g**, **2h**, or **3c**. Molecular views of these three complexes with atom-labeling schemes are shown in Figures 1, 2, and 3.

In compound **2g**, the two phosphorus atoms are displaced *endo* toward the Fe atom (0.099(1) Å for P(2) and −0.226(1) Å for P(5)). An overall search on the Cambridge Database points out that this situation occurred in roughly 45% of the related structures already reported.[18] All phenyl groups point away from the dioxane moiety. The dioxane ring has a chair conformation with C(11) and C(13) being away from the O(1)−C(12)−C(14)−O(2) mean plane by −0.627(4) and 0.661(7) Å, respectively. This dioxane ring is twisted by 40.6° with respect to the Cp ring to which it is attached. The methoxy group is oriented *endo* toward the Fe, the O(3) atom being −1.625(6) Å below the Cp ring. The two Cp rings are nearly eclipsed with a twist angle of 2.6°.

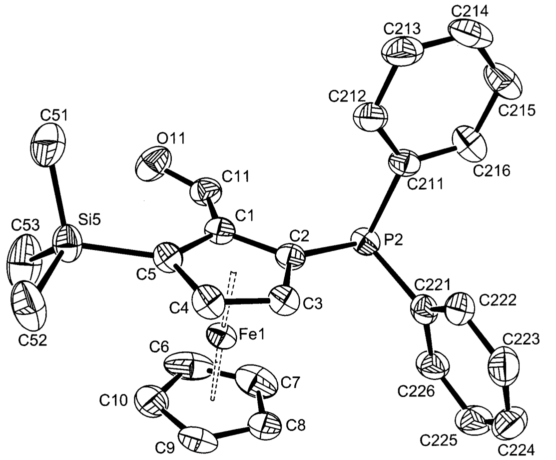

Figure 3. Molecular view of complex **3c** with atom-labeling scheme. Ellipsoids are drawn at 30% probability.

In compound **2h**, the P(2) and S(5) atoms are also displaced from the Cp ring best planes toward the iron atom by −0.169(3) and −0.087(3) Å, respectively (*endo* structure). As observed in other ferrocenyl thioether derivatives,[19] the phenyl substituent on the sulfur atom is pushed outside from the Fc block. This observation agrees with the EHMO study carried out on Fe(C$_5$H$_4$-SMe)$_2$, which favors the out-of-plane *exo* conformation of R with respect to the out-of-plane *endo*.[20] The two phenyl rings attached to phosphorus are also in *exo* position with respect to the ferrocene moiety. As in **2g**, the dioxane ring has a chair conformation with C(11) and C(13) being away from the O(1)−C(12)−C(14)−O(2) mean plane by −0.63(1) and 0.64(1) Å, respectively, and it is twisted with respect to the Cp ring by 56.9°. The two Cp rings have an intermediate conformation with a twist angle of 14.9°.

As in the previous compounds, the phosphorus atom in **3c** is displaced from the Cp ring best plane toward the iron atom by −0.1042(6) Å, but the Si atom deviates from this plane only by 0.027(1) Å. Of the two phenyl groups, one is *exo*, C(211), and the other, C(221), is *endo* with respect to the Cp ring. The aldehyde group is slightly twisted by 12.4° from this Cp ring. The angles around Si(5) range from 106.1(2)° to 114.3(2)°, the slight distortion observed from ideal tetrahedral geometry may be related to some steric interaction with the CHO group. The Si−C(Cp) distance of 1.878(3) Å is identical within experimental error to related compounds.[21] The two Cp rings are slightly twisted with an angle of 10.4° with respect to the eclipsed conformation.

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In conclusion, we described a new and general method for the synthesis of ferrocenecarboxaldehydes with substituents in positions 2 and 5. If the two substituents are different, the aldehydes are chiral and have been obtained in an enantiomerically pure form. Furthermore, these aldehydes can be transformed by a one-pot reaction in good yields and with complete selectivity into 1,2,1′-substituted ferrocenecarboxaldehydes, eventually with three different substituents, meaning 1,2,3,1′-tetrasubstituted ferrocenes eventually with four different substituents, in an enantiomerically pure form if the compound is chiral.

Experimental Section

General Procedures. All of the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. Chlorotrimethylsilane was distilled on calcium hydride and stored on 3−4 Å molecular sieves. Ph_2PCl was distilled under reduced pressure on carborandum and kept on 3−4 Å molecular sieves. Other compounds were used as commercial samples. *N*-Methylpiperazine was distilled and stored over sodium carbonate. All solvents were dried before use. Thin-layer chromatography was carried out on Merck Kieselgel 60F254 precoated silica gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 or AMX 400 (^1H, ^{13}C, and ^{31}P NMR), Stoe IPDS (X-ray). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France).

General Procedure for the Deprotonation of Acetals 2: Synthesis of (2*S*,4*S*)-4-(Methoxymethyl)-2-[2,5-bis(trimethylsilyl)ferrocenyl]-1,3-dioxane, 2a. In a Schlenk tube, 390 mg of (2*S*,4*S*,S_{Fc})-4-(methoxymethyl)-2-[2-(trimethylsilyl)-ferrocenyl]-1,3-dioxane (**1a**)[5] (1 mmol) was dissolved in 5 mL of anhydrous ether. The yellow solution was cooled to −78 °C, and then 0.63 mL of a 1.7 M *t*-BuLi solution in pentane was added dropwise. The solution was stirred 2 h at −78 °C before adding 0.5 mL of freshly distilled Me_3SiCl (4 mmol). After 15 min stirring at −78 °C, the mixture was allowed to come back at RT and stirred 2 h at this temperature. Isopropylamine (5 mL) was added, and after an additional 5 min stirring, 5 mL of a 2 N sodium hydroxide solution in water was injected. The mixture was extracted with dichloromethane, washed with brine, dried on sodium sulfate, and evaporated to yield an orange oil; the crude material was purified by flash chromatography on silica gel using a pentane/ether mixture. **2a** (360 mg, 78%) as an orange oil was obtained

General Procedure for the Hydrolysis of Acetals 2: Synthesis of 2,5-Bis(trimethylsilyl)ferrocenecarboxaldehyde, 3a. In a Schlenk tube to a solution of acetal **2a** in dichloromethane (ca. 0.15 mol L^{-1}) was added 0.7 equiv of *p*-toluenesulfonic acid monohydrate and ca. 130 equiv of deoxygenated water. The mixture was stirred at dichloromethane reflux during 5 h (bath temperature = 60 °C). After cooling, the solution was diluted with ether, washed with water, dried on sodium sulfate, and evaporated to yield the aldehyde, which was purified by flash chromatography on silica gel using a pentane/ether mixture (9:1, v/v) to yield **3a** as a red-orange solid (90% yield).

Crystal Data for 2g: [$C_{40}H_{38}FeO_3P_2$]; $M_r = 684.49$; orthorhombic; space group $P2_12_12_1$; $a = 10.0638(9)$ Å, $b = 14.8937(13)$ Å, $c = 22.594(2)$ Å, $V = 3386.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.343$ Mg/m^3, $\mu = 0.578$ mm^{-1}, empirical absorption correction applied, $T_{min} = 0.3558$, $T_{max} = 0.7723$; Mo Kα radiation; $T = 180(2)$ K; φ scan (Stoe IPDS diffractometer); $2\theta_{max} = 52.2°$; reflections collected/unique/used, 33 401/6639($R_{int} = 0.113$)/5044($I > 2\sigma(I)$); parameters refined, 416; $R/R_w^2(I > 2\sigma(I)) = 0.0595/0.1033$, R/R_w^2(all data) = 0.0904/0.1133; GOF = 1.106; $\Delta/\sigma_{max} = 0.09$; $[\Delta\rho]_{min}$, $[\Delta\rho]_{max}$, −0.42, 0.63; Flack's parameter = 0.02(2).

Crystal Data for 2h: [$C_{34}H_{33}FeO_3PS$]; $M_r = 608.48$; orthorhombic; space group $P2_12_12_1$; $a = 8.711(5)$ Å, $b = 16.986(5)$ Å, $c = 19.351(5)$ Å, $V = 2863(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.412$ Mg/m^3, $\mu = 0.690$ mm^{-1}, semiempirical absorption correction applied, $T_{min} = 0.6540$, $T_{max} = 0.7981$; Mo Kα radiation; $T = 160(2)$ K; φ scan (Stoe IPDS diffractometer); 2θmax = 49.4°; reflections collected/unique/used, 25016/4728($R_{int} = 0.113$)/3897($I > 2\sigma(I)$); parameters refined, 375; $R/R_w^2(I > 2\sigma(I)) = 0.0928/0.1962$, R/R_w^2(all data) = 0.1087/0.2055; GOF = 1.09; $\Delta/\sigma_{max} = 0.07$; $[\Delta\rho]_{min}$, $[\Delta\rho]_{max}$, −0.49, 0.62; Flack's parameter = 0.10(5).

Crystal Data for 3c: [$C_{26}H_{27}FeOPSi$]; $M_r = 470.39$; orthorhombic; space group $P2_12_12_1$; $a = 12.3089(11)$ Å, $b = 12.9052(15)$ Å, $c = 15.0422(16)$ Å, $V = 2389.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.308$ Mg/m^3, $\mu = 0.763$ mm^{-1}, semiempirical absorption correction applied, $T_{min} = 0.7912$, $T_{max} = 0.8885$; Mo Kα radiation; $T = 160(2)$ K; φ scan (Stoe IPDS diffractometer); $2\theta_{max} = 52.1$; reflections collected/unique/used, 23619/4680($R_{int} = 0.069$)/4041($I > 2\sigma(I)$); parameters refined, 274; R/R_w^2-($I > 2\sigma(I)$) = 0.0347/0.0768, R/R_w^2(all data) = 0.0454/0.0811; GOF = 1.02; $\Delta/\sigma_{max} = 0.001$; $[\Delta\rho]_{min}$, $[\Delta\rho]_{max}$, −0.24, 0.33; Flack's parameter = 0.03(2).

Structure solution and refinement were carried out with the programs SIR97[22] and SHELXL97.[23] The absolute configurations were determined by refining the Flack's enantiopole parameter.[24] Molecular views were realized with the program ORTEP-III for Windows.[25]

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Supporting Information Available: Experimental procedures, detailed spectroscopic characterization, and crystallographic information files (CIF) are available free of charge via the Internet at http://pubs.acs.org.

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