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Synthesis of 1,4-(1,1'-Ferrocenediyl)-1,3-butadiene: A Dieno-ferrocenophane.

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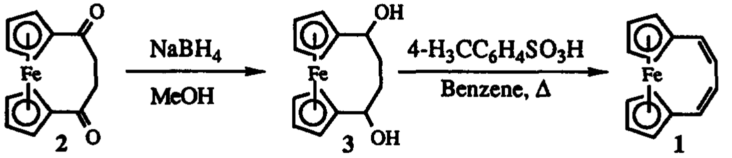
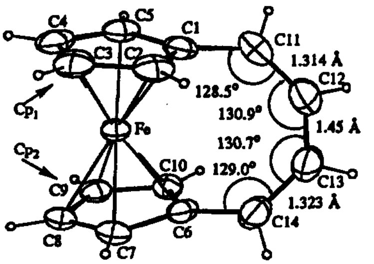
Abstract: Excess sodium borohydride in methanol quantitatively reduces 1,4-(1,1'-ferrocenediyl)-1,4-butanedione to 1,4-(1,1'-ferrocenediyl)-1,4-butanediol which in dilute benzene undergoes tandem dehydration catalyzed by *p*-toluenesulfonic acid to 1,4-(1,1'-ferrocenediyl)-1,3-butadiene in a 61% yield. X-ray crystal structures of 1,4-(1,1'-ferrocenediyl)-1,3-butadiene and 1,4-(1,1'-ferrocenediyl)-1,4-butanedione are compared.

Interest in 1,4-(1,1'-ferrocenediyl)-1,3-butadiene, **1**, stems from its potential as a monomer for Ring Opening Metathesis Polymerization (ROMP) to generate a ferrocene-diene polymer.[1] ROMP studies will be reported later. Herein we report an efficient synthesis of **1** from known diketone, **2**, which is readily prepared from commercially available 1,1'-diacetylferrocene.[2] X-ray crystal structures of **1** and **2** provide insight into the degree of ring strain of these ferrocenophanes.



Reduction of **2** (1.19 g; 4.44 mmol) with sodium borohydride (0.14 g; 3.7 mmol) in methanol (20 mL) gives a diastereomeric mixture of 1,4-(1,1'-ferrocenediyl)-1,4-butanediols, **3**, as a yellow powder[3] (1.21 g; 100% yield). Refluxing a dilute solution of **3** (0.57 g; 2.09 mmol) in benzene (400 mL) with *p*-toluenesulfonic acid (20 mole%) yields **1** with traces of 1,4-(1,1'-ferrocendiyl)-1-butene, **4**, and 2,5-(1,1'-ferrocenediyl)tetrahydrofuran, **5**. The reaction mixture is purified by silica gel column chromatography; hexane elutes **1**[4] (0.30 g; 61% yield) and a trace of **4**;[5] and 1:1 hexane-ethyl acetate elutes a trace of **5**.[6] Recrystallization of **1** by slow cooling from refluxing ethanol, aided by a seed crystal, gives X-ray quality crystals of **1**.



1

<u>Torsion Angles:</u>

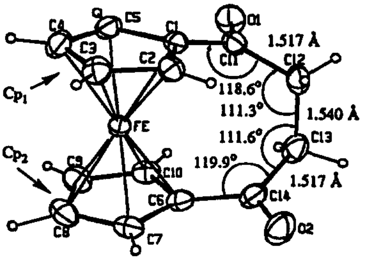
C12-C13-C14-C6	-0.5°
C11-C12-C13-C14	42.2°
C1-C11-C12-C13	1.5°

<u>Dihedral Angle:</u>

Cp_1-Cp_2	10.2°

<u>Twist Angle:</u>

[Fe,C1,C11]=P1
[Fe,C6,C14]=P2
P1-P2 43.6°



2

Torsion Angles:

C12-C13-C14-C6	88.8°
C11-C12-C13-C14	-80.9°
C1-C11-C12-C13	93.0°

Dihedral Angle:

Cp_1-Cp_2	6.7°

Twist Angle:

[Fe,C1,C11]=P1
[Fe,C6,C14]=P2
P1-P2 44.0°

Comparisons of the X-ray crystal structures of 1^7 and 2^8 are revealing. The bridge imposes a nearly equal twist angle 43.6° and 44.0° while the dihedral angle of cyclopentadienyl planes is slightly greater in 1 than in 2. Most striking is the approximate 10° distortions for the bridge sp^2 carbon bond angles in 1 which are absent in 2. Relief of this strain could provide the primary driving force for ROMP of 1.

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References and Notes

(1) Klavetter, F.L.; Grubbs, R.H. *J. Am. Chem. Soc.*, **1988**, *110*, 7807.

(2) Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.*, **1977**, *99*, 1487.

(3) Data for 3: mp. dec>165° C. ^1H NMR (200 MHz, DMSO-d_6) δ 1.68 (m), 2.17 (m), 4.03 (m), 4.31 (m), 4.68 (m); ^{13}C NMR (50 MHz, DMSO-d_6) 31.44, 66.66, 67.38, 67.91, 91.53 ppm; IR (thin film, cm^{-1}) 3331, 3086, 2940, 2858. Note: 2 is not stable under GC/MS conditions, fragmenting into three peaks of M^+ 236, 238 and 254. The MS of the peaks matched those of 1, 4, and 5.

(4) Data for 1: mp: 65° C, ^1H NMR (200 MHz, $CDCl_3$) δ 4.16 (m, 2 H), 4.45 (m, 2 H), 5.54 (m, 1 H), 6.27 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) 67.85, 69.90, 78.10, 126.84, 129.78 ppm. IR (thin film, cm^{-1}) 3111, 3086, 3013; MS, m/z 236 (M^+), 178, 152, 121, 56; HRMS, Calcd. for $^{12}C_{13}{}^{13}CH_{12}{}^{56}Fe$ 237.0322, found 237.0320; Anal. Calcd. for $C_{14}H_{14}Fe$: C, 71.22; H, 5.12. Found C, 71.09; H, 5.15.

(5) Spectra match those reported by Pudelski, J.K.; Callstrom, M.R. *Organometallics*, **1992**, *11*, 2757.

(6) Data for 5: ^1H NMR (200 MHz, $CDCl_3$) δ 2.03 (m, 2 H), 4.05 (m, 1 H), 4.16 (m, 2 H), 4.86 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) 27.02, 68.43, 68.82, 70.43, 70.82 ppm. MS, m/z 254 (M^+), 225, 158, 121, 56.

(7) Crystallographic Data for 1: red needle fragment; T = 299 K; monoclinic, space group $P2_1/n$, with a = 10.4137 (4) Å, b = 21.8611 (9) Å, c = 13.9521 (13) Å, β = 90.488 (5)°; V = 3176.1 (6) $Å^3$, and Z=12 (D_c = 1.481 g cm^{-3}); μ(MoKα) 13.8 cm^{-1} absorption corrected by ψ scans; 7291 unique data; 3380 data with I > 3σ(I) were used in the refinement; R = 0.042, Rw = 0.041, GOF = 1.506.

(8) Crystallographic Data for 2: red needle fragment; T = 296 K; triclinic, space group $P\bar{1}$, with a = 5.8224 (3) Å, b = 8.6463 (3) Å, c = 11.4661 (4) Å, α = 99.188 (3)°, β = 95.589 (3)°, γ = 106.794 (3); V = 538.6 (1) $Å^3$, and Z=2 (D_c = 1.653 g cm^{-3}); μ(MoKα) 13.81 cm^{-1} absorption corrected by ψ scans; 5451 unique data; 4886 data with I > 3σ(I) were used in the refinement; R = 0.025, Rw = 0.036, GOF = 2.013.

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