Acid catalysed condensation reactions of 1,3-dihydroxybenzene with new redox-active metallocene aldehydes

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Abstract

New ferrocene and cobaltocenium acetal and aldehyde containing compounds have been prepared. The acid catalysed condensations of both metallocene bis(aldehydes) (5, 6) with 1,3-dihydroxybenzene yielded complex products. The new metallocene cyclic monoaldehydes (7, 8), differed markedly in their reactions with 1,3-dihydroxybenzene with the ferrocene derivative 8 producing [1 + 1] and [1 + 2] bisphenol: aldehyde adducts, whereas the cobaltocenium analogue gave a cyclic diene compound (16). A single crystal X-ray structure of 16 is also described and the electrochemical properties of some of the new metallocene derivatives reported.

Keywords: Cobalt; Iron; Metallocenes; Crystal structure

1. Introduction

The incorporation of multiple redox-active centres into hydrophobic preorganised macrocyclic compounds may lead to prototypes of new molecular sensory devices capable of electrochemically recognising the inclusion of an organic guest in the host cavity [1]. In addition such components may also ultimately serve as a new class of redox catalyst, polarising included guest species by means of electron density transfer to or from the redox-active centre, thus activating the guest towards reaction with an incoming substrate [2]. The organometallic ferrocene moiety is an attractive redox-active centre to be integrated into preorganised host molecules, and we have achieved this via the use of ferrocenecarboxaldehyde in the acidic condensation reaction with 1,3-dihydroxybenzene to produce the macrocycle 1 [2,3]. This insoluble material was made soluble in organic solvents by ester and ether derivatisation and a cavitand derivative was shown to include dichloromethane in the solid state [3]. As an extension to this initial work we decided to investigate the acid catalysed reactions of new ferrocene and cobaltocenium mono- and bis-aldehydes with 1,3-dihydroxybenzene in

an effort to produce novel mono- and bis-octahydroxy calix[4]arene type molecules.

2. Experimental

NMR spectra were measured using a Bruker AM300 spectrometer at 300 MHz for ^1H and 75.45 MHz for
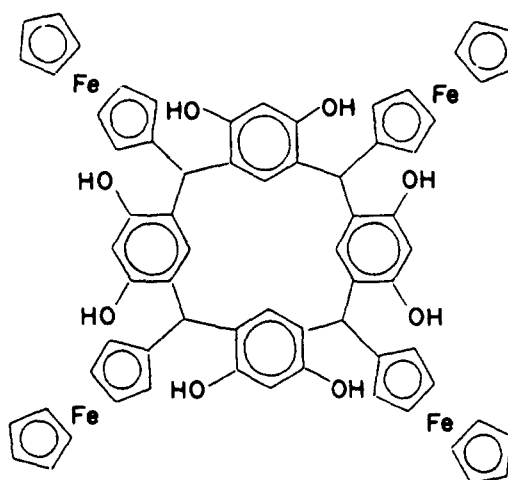
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^{13}C. Elemental analyses were performed by the microanalytical services at the Inorganic Chemistry Laboratory of the University of Oxford. IR spectra were measured using a Mattson Polaris FT spectrophotometer model IR 10410E. Spectra were recorded from 4000–600 cm^{-1} as KBr discs or between NaCl plates (for oils). UV and visible absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV-vis spectrophotometer.

FAB mass spectrometry was undertaken by the SERC mass spectrometry service at University College, Swansea. Cyclic voltammetric studies were performed on a Princeton Applied Research potentiostat/galvanostat model 273. Reference electrode and acquisition parameters are quoted in individual cases. Melting points were recorded in open glass capillary tubes on a Gallenkamp melting point apparatus and are uncorrected. Where necessary, solvents were distilled prior to use. The following drying agents were used before distillation under nitrogen: acetonitrile and dichloromethane were distilled from CaH$_2$; THF was distilled from sodium, using benzophenone as an indicator. Unless stated otherwise, commercial grade reagents were used without further purification.

2.1. (β,β-diethoxyethyl)cyclopentadiene (2)

Freshly distilled cyclopentadiene (33 g, 0.5 mol) was dissolved in THF (30 ml). This solution was carefully added dropwise to a suspension of sodium hydride (15 g, 0.5 mol, 80% in oil) and THF (150 ml) at 10–15°C. The solution was stirred for at least 1 h at room temperature, and then 2-bromo-1,1-diethoxyethane (95 g, 0.5 mol) in 100 ml THF was added slowly to the solution during 1 h, the solution being at 10–20°C. The mixture was stirred overnight under nitrogen. Water (300 ml) was added and the organic layer separated, dried (Na$_2$SO$_4$), and after removal of the volatile organic liquids the residue was distilled to give a colourless liquid, yield 48 g b.p. 65–75/0.1 torr and 17 g liquid b.p. 147–150/0.1 torr, which is the disubstituted Cp ring compound.

^{1}H NMR (CDCl$_3$) δ: 6.6–6.1 (3H, m, olefin), 4.63 (1H, m, -CH-), 3.7–3.4 (4H, m, OCH$_2$), 2.95 (2H, m, CH-CH$_2$-CH=), 2.65 (2H, bd, CH$_2$-CH=), 1.16 (6H, m, CH$_3$.

2.2. 1,1'-bis(β,β-diethoxyethyl)ferrocene (3)

To the (β,β-diethoxyethyl)cyclopentadienylsodium, prepared from the acetal (2) (18 g, 0.1 mol), sodium hydride (3 g, 0.1 mol, 80% in oil) and 75 ml THF, was added iron(II) chloride (6.3 g, 0.05 mol). The resulting mixture was stirred overnight at room temperature and water (5 ml) was slowly added until no more hydrogen was generated. Decolourising charcoal (1 g) was added and the solution was filtered. Water was added to the

residue and the aqueous layer was extracted with chloroform (2 × 150 ml), dried and filtered. Removal of solvent and rapid distillation of the residue gave approximately 9 g (40%) of recovered acetal, b.p. 32–37°C/0.12 mm and 7 g (30%) 1,1'-bis(diethoxyethyl) ferrocene (3), b.p. 156–162°C/0.15 mm. TLC: CH$_2$Cl$_2$: acetonitrile 9 : 1; silica.

^{1}H NMR (CD$_3$CN) δ: 4.98 (2H, t, CH), 4.1 (8H, m, Fc-H), 3.7–3.5 (8H, m, OCH$_2$), 2.63 (4H, d, CH$_2$), 1.15 (12H, m, CH$_3$).

^{13}C NMR (Acetone-d_6) δ: 104.3 (CH), 84.64 (Cp-C), 70.42 and 66.74 (Cp-C), 61.74 (CH$_2$O), 35.25 (CH$_2$), 15.73 (CH$_3$).

2.3. 1,1'-bis(β,β-diethoxyethyl)cobaltocenium tetraphenylborate (4a)

A round-bottom flask was equipped with a magnetic stirrer, condenser, dropping funnel and thermometer and placed under a nitrogen atmosphere. The apparatus was flame dried and freshly distilled (β,β-diethoxyethyl)cyclopentadiene (2) (33 g, 0.18 mol) in THF (30 ml) was added slowly to the mixture of sodium hydride (5.4 g, 0.18 mol, 80% in oil) in 150 ml THF at 25°C. The resulting mixture was stirred over 1 h at room temperature and slowly warmed to 50°C until hydrogen was generated. The mixture was cooled in an ice-water bath and cobalt(II) bromide (18 g, 0.08 mol), dissolved in dry DMF (50 ml), was added dropwise via a syringe. The resulting mixture was stirred overnight at room temperature and excess organometallic reagent was decomposed by sequential addition of methanol (200 ml) and water (200 ml). Decolourising charcoal (5 g) was added and the solution was filtered. To the agitated filtrate was added acetic acid (15 ml) and then sodium tetraphenylborate (around 12 g) dissolved in methanol (80 ml). The yellow precipitate was filtered off (48–53 g, 76%) and the sample for analysis was recrystallised from methanol.

M.p. 113°C; IR 2879 cm^{-1} saturated C-H stretch; FAB-MS m/z 421 M$^+$.

^{1}H NMR ((CD$_3$)$_2$CO) δ: 1.14 (12H, m, CH$_3$), 2.82 (4H, d, Cp-CH$_2$), 3.46, 3.67 (8H, 2 × m, OCH$_2$), 4.61 (2H, t, methine CH), 5.50 (4H, t, ^3J = 2 Hz, Fc-H), 5.81, (4H, t, ^3J = 2 Hz, Fc-H), 6.84 (4H, m, BPh$_4$), 6.96 (8H, m, BPh$_4$), 7.39 (8H, bs, BPh$_4$).

^{13}C NMR ((CD$_3$)$_2$CO) δ: 15.61 (CH$_3$), 33.63 (Cp-CH$_2$), 62.88 (OCH$_2$), 85.00, 86.17 (Cp-C), 102.12 (CH$_2$-CH), 103.80 (ipso Cp-C), 122.36, 126.14, 137.07 (BPh$_4$).

Anal. Found: C, 74.40%; H, 7.17%; Co, 7.84% C$_{46}$H$_{54}$BC$_o$O$_4$. Calc.: C, 74.60%; H, 7.34%, Co, 7.95%.

2.4. 1,1'-bis(ferrocenyl)acetaldehyde (5)

To the bis(β,β-diethoxyethyl)ferrocene, (3) (2.1 g, 5 mmol), dissolved in acetonitrile (20 ml) was added

water (2 ml) and Amberlite IR 120(1 g). The mixture was stirred at 55°C for 1 h. The Amberlite was filtered off and the deprotected 1,1'-bis(ferrocenyl)acetaldehyde was used without purification in the next step.

^{1}H NMR (CD$_3$CN) δ: 9.67 (2H, t, ^3J = 2Hz, CH = 0), 4.15–4.00 (8H, m, Fc–H), 3.36 (d, 4H, CH$_2$).

^{13}C NMR (CDCl$_3$) δ: 43.26 (CH$_2$), 68.46, 69.15, 69.50, 69.74, 70.17, 70.40, 71.76 (Fc–C), 78.71 (ipso Fc–C), 199.04 (CHO).

2.5. Compound 9

To diacetal (5) (4.2 g, 10 mmol) in 50 ml 90% acetonitrile in water was added Amberlite IR 120 (2 g), (which had been activated by treatment with 36% hydrochloric acid) and the mixture was heated at 55°C for 1 h. The Amberlite was filtered off and washed with 10 ml acetonitrile. To the filtrate was added base (e.g. 4-aminopyridine (1.8 g, 0.02 mmol) or triethylamine (1.4 ml) dissolved in 50 mL ethanol) and the mixture was stirred at 30°C for 1 day. The dark grey precipitate that formed was filtered and washed with methanol. Yield 95% as a mixture of oligomers and isomers.

FAB-MS m/z 541 M$^+$ (dimer). The ^{1}H and ^{13}C NMR spectroscopic data were both complex, inferring the presence of many components.

2.6. 2,4-(1,1'-ferrocenediyl)-but-2-ene-1-al (8)

Mixture 9 was placed in a sublimation apparatus (cold finger) which was evacuated (0.1 bar) and placed for 1 h in an oilbath that had been preheated to 170–180°C. The sublimed sample was collected to give 0.29 g of product as an orange–yellow solid (11.5% overall yield from 5).

M.p. 147°C; FAB-MS m/z 252 M$^+$.

^{1}H NMR (CDCl$_3$) δ: 3.16 (2H, d ^3J = 4.0 Hz, CH$_2$), 4.09 (2H, t^3J = 1.8 Hz, Fc–H), 4.12 (2H, t^3J = 1.8 Hz, Fc–H), 4.16 (2H, t^3J = 1.5 Hz, Fc–H), 4.23 (2H, t^3J = 1.5 Hz, Fc–H), 7.17 (1H, t^3J = 4.0 Hz, alkene H), 9.71 (1H, s, CHO).

^{13}C NMR ((CD$_3$)$_2$CO) δ: 27.94 (CH$_2$), 70.19, 70.35, 71.19, 72.55 (Fc–C), 81.38, 86.36 (ipso Fc–C) 139.22 (Cp–C–CHO), 164.04 (CH$_2$–CH=), 192.21 (carbonyl C).

2.7. 2,4-(1,1'-ferrocenediyl)-but-2-ene-1-ol (10)

Cyclic aldehyde (8) (0.2 g, 0.79 mmol) was dissolved in 10 ml ethanol and sodium borohydride (0.05 g, 1.32 mmol) added. After stirring for 3 h at 65–70°C, the mixture was neutralised with a few drops of dilute HCl and the solvent was removed under vacuum. The residue was purified by column chromatography (silica, CH$_2$Cl$_2$) to yield a yellow–brown solid. A sample for analysis was recrystallised from a minimum amount of hexane. Yield 78%.

M.p. 90–91°C; FAB-MS m/z 254 M$^+$.

^{1}H NMR (CD$_3$CN) δ: 6.02 (1H, m, J = 1.3 Hz, J = 2.6 Hz, CH), 4.15–4.03 (10 H, m, Fc–H and CH$_2$OH), 3.10 (1H, bs, OH), 2.88 (2H, m, J = 1.8 Hz, J = 2.0 Hz, CH).

^{13}C NMR (CD$_3$CN) δ: 26.06 (Cp–CH$_2$), 67.46 (CH$_2$OH), 69.66, 69.76, 70.99, 71.92 (Fc–C), 86.80, 87.68 (ipso Fc–C), 134.26 (Cp–C–CH$_2$OH), 134.52 (Cp–CH$_2$–C=).

Anal. Found: C, 66.36%, H, 5.23%. C$_{14}$H$_{14}$FeO. Calc.: C, 66.17%; H, 5.55%.

2.8. 1,1'-bis(2-[4,4'-bis-1,3-dihydroxyphenyl]ethyl)ferrocene (11)

Resorcinol (6.6 g, 0.06 mol) and bis(β,β-diethoxyethyl)ferrocene (5) (1.26 g, 3 mmol) were dissolved in 40 ml ethanol and hydrochloric acid (1 ml, 36%) added. The mixture was stirred at 70°C and the reaction was followed by TLC, monitoring the disappearance of the diacetal (TLC silica, CH$_2$Cl$_2$: CH$_3$CN 8 : 1.5). Stirring was then continued at ambient temperature for 12 h. Sodium hydrogen carbonate was added to neutralise the acid and the inorganic salts formed were filtered off. The filtrate was concentrated under vacuum and the residue dissolved in a minimum quantity of acetonitrile for purification by column chromatography (silica, CH$_2$Cl$_2$: CH$_3$CN 8 : 2 to remove excess resorcinol, and then acetonitrile only). The yellow band collected was purified again by column chromatography (silica, CHCl$_3$: CH$_3$CN 3 : 1) to yield a yellow oil, about 20% yield.

FAB-MS m/z 675 M$^+$.

^{1}H NMR ((CD$_3$)$_2$CO) δ: 3.03, 3.11 (4H, 2 × d ^3J = 8 Hz, CH$_2$), 3.90 (4H, s, Fc–H), 3.95 (4H, s, Fc–H), 4.64, 4.66 (2H, 2 × t^3J = 8 Hz, methine CH), 6.35 (8H, s, Ar–H), 7.12 (4H, m, Ar–H), 7.95, 8.13, 8.22, 8.42 (8H, 4 z s, OH).

2.9. 2,4-{1,1'-di[η^5-cyclopentadienyl]cobalt(III)}-but-2-ene-1-al hexafluorophosphate (7)

The hexafluorophosphate salt 7b is prepared via the chloride salt 7d.

Diacetal (4a) (2 g, 2.7 mmol) was dissolved in 10 ml acetic acid and 0.5 ml concentrated hydrochloric acid. The mixture was refluxed for 1 h and the organic acid was evaporated under vacuum to dryness. Water (25 ml) and decolourising charcoal were added to the residue and the mixture was filtered. The addition of sodium hexafluorophosphate to the filtrate solution of the chloride salt 7d yielded a yellow precipitate and the solution was decanted off. After drying, the precipitate was chromatographed on silica with 4 : 6 acetone : acetonitrile as eluent to give a dark orange oil (7b) in 59% yield.

^{1}H NMR (CD$_3$CN) δ: 9.70 (1H, s, CHO), 7.39 (1H, t, ^3J = 4.2 Hz, alkene H), 5.70–5.40 (8H, m, Fc–H), 3.43 (2H, d, ^3J = 4.2 Hz, CH$_2$).

2.10. (7e) tosylate salt

Diacetal (**4a**) (2 g, 2.7 mmol) was dissolved in 10 ml toluene to which a few drops of water had been added. *p*-Toluenesulfonic acid (0.7 g, 4.1 mmol) was added and the mixture was refluxed for 2 h. The precipitate that formed was filtered off and washed with toluene and dried (yield 79%). A sample for analysis was recrystalled from acetonitrile.

M.p. 224–226°C; IR 1690 cm^{-1} α,β-unsaturated aldehyde carbonyl stretch.

^{1}H NMR ((CD$_3$)$_2$SO) δ: 2.2 (3H, s, tosylate CH$_3$), 3.43 (2H, d, CH$_2$), 5.70 (1H, s, alkene H), 5.78 (4H, d, Cp–H), 5.88 (4H, d, Cp–H), 7.13 (4H, d, Ts–H), 7.53 (4H, d, Ts–H), 9.70 (1H, s, CHO).

^{13}C NMR ((CD$_3$)$_2$SO) δ: 20.83 (tosylate CH$_3$), 25.37 (CH$_2$), 85.59, 86.91, 87.05 (Cp–C), 97.98 (*ipso* Cp[–CH$_2$]), 103.03 (*ipso* Cp[–C = C], 125.42, 125.54, 128.13, 128.23 (Ts–C), 131.95 (alkene β–C), 137.95, 145.31 (Ts–C), 164.37, 164.53 (alkene α–C), 191.08, 191.18 (CHO).

Anal. Found: C, 78.42%; H, 5.86%, Co, 9.95%. C$_{21}$H$_{19}$CoO$_4$S. Calc. C, 78.35%; H, 5.84%, Co, 10.10%.

2.11. (7c) trifluoroacetate salt

This was prepared as described for the tosylate salt using 2 g of **4a** in 4 ml 30% aq. trifluoroacetic acid. After reflux, the reaction solution was left to stand, with gradual crystallisation of the product.

IR 1690 cm^{-1} α,β-unsaturated aldehyde carbonyl stretch; FAB-MS *m/z* 255 M$^+$.

^{1}H NMR ((CD$_3$)$_2$CO) δ: 3.17 (2H, d, CH$_2$), 5.35–5.45 (8H, m, Cp–H), 7.13 (1H, t, alkene H), 9.33 (1H, s, CHO).

2.12. (7a) tetraphenylborate salt

This was prepared by refluxing **4a** with HCl and sodium teteraphenylborate in methanol–water and collecting the yellow precipitate.

2.13. Compounds (12) and (13a)

To a solution of ferrocene cyclic monoaldehyde (**8**) (0.5 g, 1.98 mmol) in 20 ml 95% ethanol was added 0.3 ml hydrochloric acid, (diluted 1 : 1 with water) and resorcinol (0.22 g, 2.0 mmol). The mixture was stirred at about 50°C for 20 h and the solution was neutralised to pH 7 by addition of sodium hydrogencarbonate. The inorganic salts were removed by filtration and the filtrate evaporated to dryness under reduced pressure. The

residue was purified by column chromatography (silica, chloroform as eluent) to afford two fractions. Fraction 1, a yellow–brown powder, was found to be **12** (yield 0.1 g, 15%). Fraction 2, a yellow powder, was compound **13a** (yield 0.25 g, 22%).

2.13.1. Compound 12

M.p. > 220°C (dec.); FAB-MS *m/z* 344 M$^+$.

^{1}H NMR ((CD$_3$)$_2$CO) δ: 2.29 (1H, t$^3J_{AC}$ = 11.9 Hz, $^2J_{BC}$ = –12.5 Hz, CH$_2$), 2.56 (1H, dd $^2J_{BC}$ = –12.8 Hz, $^3J_{AB}$ = 4.2 Hz, CH$_2$), 3.97 (2H, d ^3J = 1.1 Hz, Fc–H), 4.11 (1H, d ^3J = 1.7 Hz, Fc–H), 4.18 (1H, t^3J = 1.8 Hz, Fc–H), 4.22 (1H, d ^3J = 1.4 Hz, Fc–H), 4.40 (2H, s, Fc–H), 4.44 (1H, d ^3J = 1.0 Hz, Fc–H), 5.12 (1H, dd $^3J_{AB}$ = 4.2 Hz, $^3J_{AC}$ = 11.6 Hz, Ar–O–CH), 6.41 (1H, ^4J = 2.0 Hz, Ar–H ortho to alkoxy), 6.45 (^4J = 2.2 Hz, ^3J = 8.1 Hz, Ar–H), 6.57 (1H, s, alkene H), 6.95 (1H, d ^3J = 8.0 Hz, Ar–H *meta* to OH), 8.64 (1H, s, OH).

^{13}C NMR (CD$_3$CN) δ: 32.65 (CH$_2$), 69.34, 69.60, 69.96, 70.61, 71.08, 72.77 (Fc–C), 77.87, 78.11 (CH$_2$–CH–O), 78.00, 79.23 (*ipso* Fc–C), 104.28, 109.17, 116.19, 127.63, 133.04 (Ar–C and alkene C), 153.95, 159.18 (Ar–C *ipso* to OH).

Anal. Found: C, 68.48%; H, 4.61%. C$_{20}$H$_{16}$FeO$_2$. Calc. C, 69.79%; H, 4.69%.

2.13.2. Compound 13a

M.p. 213°C (dec.); FAB-MS *m/z* 578 M$^+$.

^{1}H NMR (CDCl$_3$: CD$_3$CN) two spectra present, *meso*-diastereomer and racemate, the second component (isomer) shown by $'\delta$: 2.38 (2H, t$^2J_{BC}$ = –12.2 Hz, CH$_2$), 2.41 (2H, t$^2J_{BC}$ = –12.0 Hz, CH$'_2$), 2.66 (2H, t$^3J_{AB}$ = 4.3 Hz, CH$_2$), 2.70 (2H, t$^3J_{AB}$ = 4.4 Hz, CH$'_2$), 3.98 (4H, m, Fc–H), 4.02 (4H, m, Fc–H), 4.23 (4H, m, Fc–H), 4.26 (4H, m, Fc–H), 4.32 (4H, m, Fc–H), 4.35 (4H, m, Fc–H), 4.37 (4H, m, Fc–H), 5.05 (2H, t$^3J_{AB}$ = 3.8 Hz, C*H*–CH$_2$), 5.09 (2H, t$^3J_{AB}$ = 3.8 Hz, C*H*–CH$'_2$), 6.47 (2H, s, Ar–H *ortho* to OR), 6.54 (4H, s, alkene H), 6.78 (1H, s, Ar–H'), 6.79 (1H, s, Ar–H).

Anal. Found: C, 71.50%; H, 6.64%. C$_{34}$H$_{26}$Fe$_2$O$_2$. Calc. C, 70.62%; H, 4.53%.

2.14. 1,3-{1,1'-di[η^5-cyclopentadienyl]cobalt(III)}-4-(4'-[1',3'-dihydroxyphenyl])-1,3-butadiene chloride (16)

Cobaltocenium cyclic monoaldehyde (**7a**) (1.15 g, 2 mmol) and resorcinol (0.24 g, 2.2 mmol) were stirred in 30 ml DMSO with 6 drops of hydrochloric acid (diluted 1 : 1 with water) for 12 h at 45–50°C. Water (50 ml) was then added to the mixture and the suspension was filtered. The precipitate was purified by column chromatography (silica, 9 : 1 acetone : methanol as eluent) to yield three fractions. Fraction 1 was unreacted resorcinol, while fraction 2 was unknown and not identified. Fraction 3, a red powder, was found to be **16** and was

formed in 73% yield. A sample for analysis was recrystallised from methanol to give red needles.

M.p. > 250°C (dec.).

^{1}H NMR (CD$_3$OD) δ: 5.67 (2H, t^3J = 1.9 Hz, Cp–H), 5.72 (2H, d ^3J = 1.4 Hz, Cp–H), 5.84 (2H, t^3J = 1.9 Hz, Cp–H), 6.08 (1H, dd, $^3J_{MX}$ = 8.6 Hz, $^4J_{MA}$ = 2.3 Hz, alkene H$_m$), 6.35 1H, d $^4J_{MA}$ = 2.3 Hz, alkene H$_a$), 6.64 (1H, d $^3J_{MX}$ = 8.6 Hz, alkene H$_x$), Ar–CH$_a$ = CCp–CH$_m$ = CH$_x$–Cp, 5.96, 6.88 (2H, AB system, ^3J = 10.9, 10.5 Hz, Ar–H), 7.41 (1H, s, Ar–H).

^{13}C NMR (CD$_3$OD) δ: 85.94, 86.66, 86.71, 87.46 (Cp–C), 101.60, 103.25, 104.68, 107.68, 114.23, 115.18, 121.04, 130.71, 135.04, 146.62, 158.70 (Ar–C and alkene C).

3. Crystal data

C$_{20}$H$_{16}$ClCoO, M = 382.5, monoclinic, a = 14.803(11), b = 8.636(7), c = 26.857(24) Å, β = 104.0(1)°, U = 4237.3 Å^3, Dc = 1.20 g cm^{-3}, Z = 4, λ = 0.7107 Å, μ = 9.74 cm^{-1}, space group $C2/c$.

A crystal of approximate size 0.30 × 0.30 × 0.30 mm^3 was set up to rotate about the a axis on a Stoe Stadi2 diffractometer and data were collected via a variable width scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of 1.5 + sin μ/tan Θ. 3134 independent reflections were measured, of which 1641 with $I > 3\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. The structure was determined by the heavy atom method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included in calculated positions and refined isotropically. Hydrogen atoms bonded to oxygen could not be located. Data were given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.064 (R_w = 0.065). Calculations were carried out using Shelx76 [4] together with some of our own programs on the Amdahl 5870 at the University of Reading. In the final cycles of refinement, no shift/error ratio was greater than 0.2σ. In the final difference Fourier maps, the maximum and minimum peaks were 0.62 and −0.65 eÅ^{-3}. Atomic coordinates are given in Table 1. Dimensions in the metal coordination sphere are given in Table 2. Thermal parameters, hydrogen atom coordinates, and a complete table of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

4. Results and discussion

4.1. Synthesis of new 1,1'-bis-metallocene acetaldehydes and monoaldehydes

The synthons from which the ferrocene and cobaltocenium acetaldehydes were derived were 1,1'-bis

Table 1
Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
CO(1)	5209.3(11)	2189.4(17)	8912.1(4)
CL(2)	3582(2)	2694(3)	3837(1)
C(31)	5356(7)	1945(12)	8179(3)
C(32)	4514(7)	2757(12)	8183(3)
C(33)	4748(5)	4093(13)	8490(3)
C(34)	5777(5)	4160(11)	8684(3)
C(35)	6123(7)	2721(12)	8521(3)
C(36)	6321(6)	5282(12)	9079(3)
C(37)	6685(6)	6565(11)	8946(3)
C(41)	6651(6)	7169(13)	8431(3)
C(42)	6261(7)	6605(14)	7978(4)
C(43)	6253(7)	7256(13)	7515(3)
C(44)	6722(6)	8682(15)	7513(3)
C(45)	7140(6)	9399(12)	7972(3)
C(46)	7105(5)	8652(13)	8430(3)
O(11)	7545(4)	9359(9)	8893(2)
O(12)	6736(5)	9440(10)	7081(2)
C(51)	6493(7)	5001(16)	9631(3)
C(52)	6214(8)	3879(16)	9884(4)
C(53)	5661(8)	2425(15)	9657(4)
C(54)	6001(7)	1041(13)	9516(3)
C(55)	5241(7)	73(13)	9297(4)
C(56)	4393(7)	927(14)	9255(5)
C(57)	4677(8)	2305(17)	9496(4)

(β,β-diethoxyethyl) ferrocene (3) and 1,1'-bis(β,β-diethoxyethyl) cobaltocenium (4) respectively.

The first step in the synthesis was preparation of (β,β-diethoxyethyl) cyclopentadiene (2) by the addition of 2-bromo-1,1-diethoxyethane to a solution of sodium cyclopentadienide in THF in 50% yield. Using the procedure of Schaaf and Lenk [5], a solution of 2 in THF was deprotonated with sodium hydride and the resulting diacetal cyclopentadienide treated with iron(II) chloride to give (3) as a pale yellow oil in 30% overall yield (Scheme 1).

The new cobaltocenium analogue (4a) was also prepared from 2 using cobalt(II) bromide followed by addition of sodium tetraphenylborate to the aqueous methanolic solution produced in the reaction work-up to precipitate the bright yellow solid product in 74% yield (Scheme 1). A sample of 4a was converted to its hexafluorophosphate salt 4b by addition of ammonium hexafluorophosphate to an aqueous solution of 4a. The hydrolysis of 3 by warming an aqueous acetonitrile solution of this compound with Amberlite IR 120 for 1 h gave the new deprotected 1,1'-bisferrocenyl (acetaldehyde) (5) as a yellow oil (Scheme 2).

The addition of acid to a solution of the cobaltocenium diacetal (4a) resulted in the unexpected isolation of a new cyclic aldehyde (7) whose counteranion was that of the acid employed (Scheme 3). The unprotected bis(aldehyde) (6) was thought to be generated in the reaction though various attempts to isolate this reactive compound failed. Immediately it is produced an in-

Table 2
Selected molecular dimensions (distances, Å; angles, °)

|	
Co(1)–C(31)	2.030(7)
Co(1)–C(32)	2.026(7)
Co(1)–C(33)	2.017(7)
Co(1)–C(34)	2.040(6)
Co(1)–C(35)	1.987(8)
Co(1)–C(53)	1.999(8)
Co(1)–C(54)	2.107(7)
Co(1)–C(55)	2.054(8)
Co(1)–C(56)	2.012(7)
Co(1)–C(57)	1.977(8)
C(31)–Co(1)–C(53)	154.7(5)
C(32)–Co(1)–C(53)	156.7(5)
C(33)–Co(1)–C(53)	117.3(5)
C(34)–Co(1)–C(53)	98.1(4)
C(35)–Co(1)–C(53)	113.8(4)
C(31)–Co(1)–C(54)	123.4(4)
C(32)–Co(1)–C(54)	162.3(5)
C(33)–Co(1)–C(54)	154.1(4)
C(34)–Co(1)–C(54)	116.2(4)
C(35)–Co(1)–C(54)	101.7(4)
C(31)–Co(1)–C(55)	113.4(5)
C(32)–Co(1)–C(55)	129.2(4)
C(33)–Co(1)–C(55)	161.8(4)
C(34)–Co(1)–C(55)	155.1(4)
C(35)–Co(1)–C(55)	122.5(4)
C(31)–Co(1)–C(56)	127.6(5)
C(32)–Co(1)–C(56)	110.9(5)
C(33)–Co(1)–C(56)	122.8(4)
C(34)–Co(1)–C(56)	156.9(4)
C(35)–Co(1)–C(56)	160.8(4)
C(31)–Co(1)–C(57)	162.8(4)
C(32)–Co(1)–C(57)	124.2(5)
C(33)–Co(1)–C(57)	105.0(5)
C(34)–Co(1)–C(57)	118.2(5)
C(35)–Co(1)–C(57)	153.4(5)
CG(3)–Co(1)–CG(5)	174.3(8) [a]
C(36)–C(37)	1.309(14)
C(36)–C(51)	1.477(13)
C(37)–C(41)	1.460(12)
C(51)–C(52)	1.316(16)
C(52)–C(53)	1.466(15)
C(34)–C(36)–C(37)	122.7(8)
C(34)–C(36)–C(51)	121.2(8)
C(37)–C(36)–C(51)	116.0(8)
C(36)–C(37)–C(41)	130.6(7)
C(36)–C(51)–C(52)	129.9(9)
C(51)–C(52)–C(53)	128.8(9)

[a] Angle between centroids.
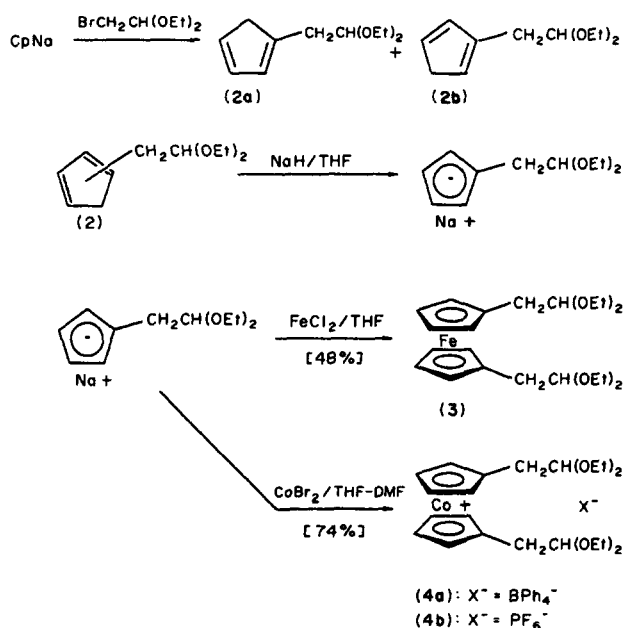
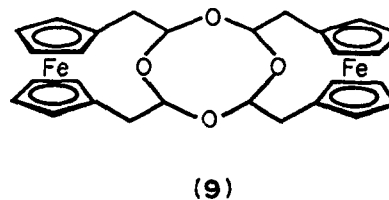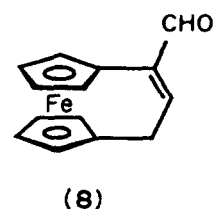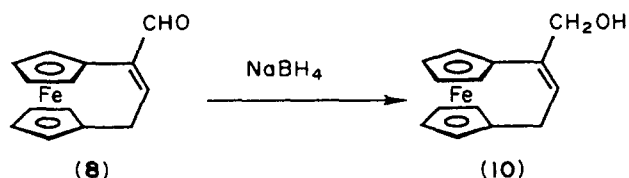

Scheme 1.

Scheme 2.

Scheme 3.

(8)

(9)
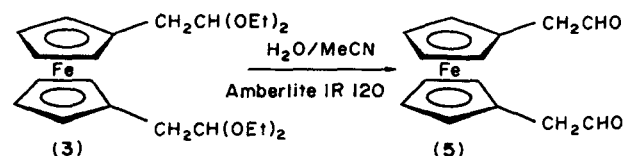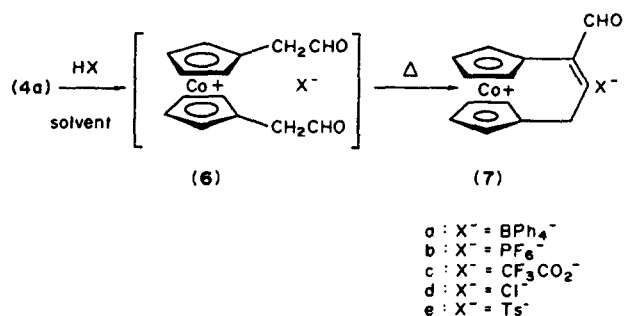
tramolecular aldol condensation reaction is favoured to give the α,β-unsaturated aldehyde (7).

The ferrocene monoaldehyde analogue 8 could be produced by heating 5 in ethanol, although a more convenient synthesis of 8 was found accidentally. When solutions of 5 were treated with organic bases such as pyridine and triethylamine a pale yellow–green precipitate resulted. The ^{1}H and ^{13}C NMR spectra of this material were extremely complex, although the absence of vinylic protons was notable. FAB mass spectra revealed a positive ion at 541 which may be assignable to a tricyclic acetal dimer (9). When this material was

Scheme 4.

subjected to sublimation (120–150°C/1 torr), a pure sample of the cyclic monoaldehyde **8** was isolated.

The reduction of **8** with NaBH$_4$ gave the expected α,β-unsaturated alcohol (**10**) as a yellow solid in 78% yield (Scheme 4). This is a typical reaction of aldehydes and further proof of the structure of **8**.

4.2. Condensation reactions of metallocene bis(aldehydes) with 1,3-dihydroxybenzene

The ethanol-hydrochloric acid catalysed condensation of **5** with equimolar or excess amounts of 1,3-dihydroxybenzene gave many products from which, after careful column chromatographic separation, a [4 + 1] condensation compound (**11**) was isolated (Scheme 5). This compound was characterised by ^{1}H NMR spectroscopy and by FAB-MS ($m/z = 675$). Because **11** could be an intermediate in the formation of the desired calixarene it was reacted further with **5**. Disappointingly, an insoluble green solid was isolated whose FAB mass spectrum suggested the material to be of polymeric origin.

Analogous condensation reactions with the cobaltocenium acetals **4a** and **4b** gave intractable polymeric products.

4.3. Reactions of metallocene cyclic mono aldehydes with 1,3-dihydroxybenzene

The acid-catalysed condensation of 1,3-dihydroxybenzene with **8** gave two products (**12** and **13**) in yields of 40–45% (Scheme 6). These compounds are the 1 : 1 and 1 : 2 1,3-dihydroxybenzene : aldehyde condensation


(13b)
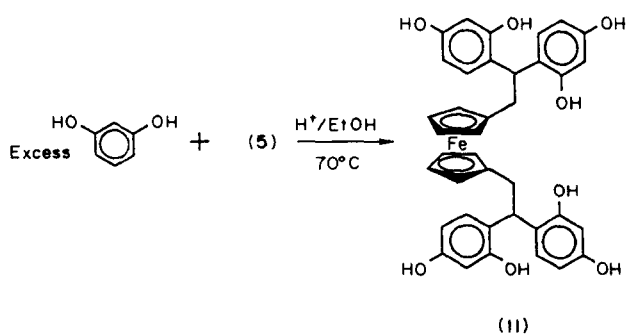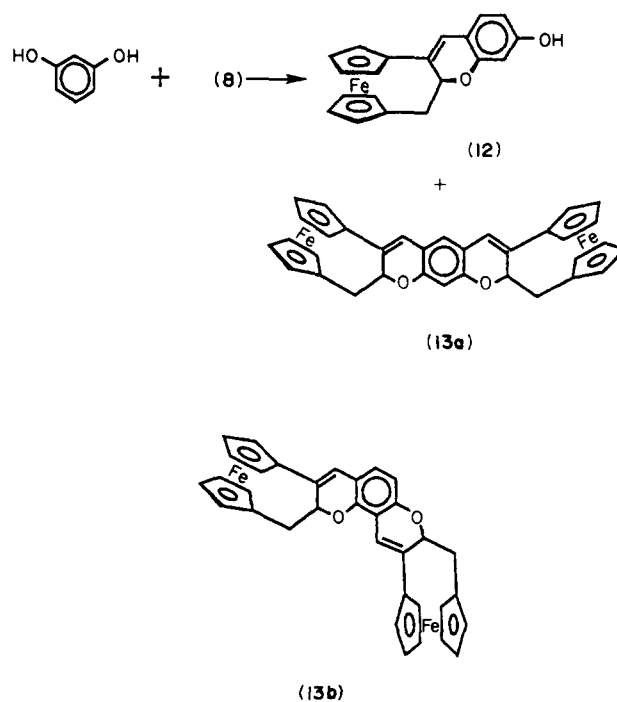
Scheme 6.

products respectively. It is noteworthy that although two regioisomers are possible for the [1 + 2] condensation product, (**13a** and **13b**) the ^{1}H NMR spectrum suggests only **13a** is found, which by virtue of two identical stereocentres is a mixture of *meso* diastereomer and a racemate. A related 1 : 2 condensation product (**15**) has recently been reported prepared via 1,3-dihydroxybenzene and two equivalents of citronellal (**14**) in the presence of acid [6] (Scheme 7). As with **13**, only one geometric isomer was isolated.

The addition of one molar equivalent of 1,3-dihydroxybenzene to a solution of **4a** and hydrochloric acid in ethanol, which had been stirred at ambient temperature for 30 min to generate **7** in situ, led, on continued stirring, to the production of the *cis–cis* conjugated diene isomer **16** (Scheme 8). A possible mechanism for this compound's formation is illustrated in Scheme 9. Protonation of **7** gives the carbocation tautomer **17**. Aromatic electrophilic substitution of **17** at C-4 of
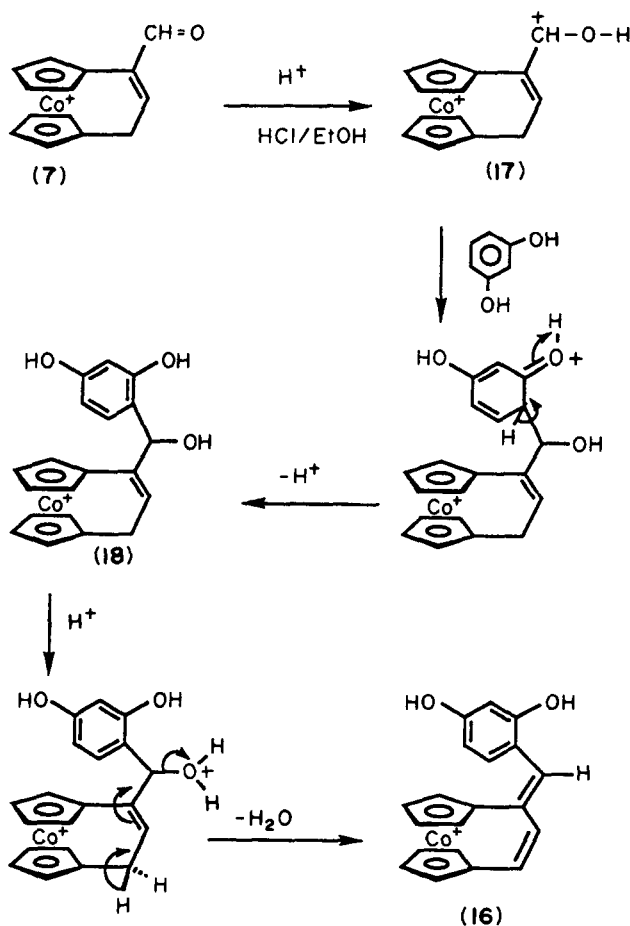

Scheme 5.

Scheme 7.

Scheme 8.

Fig. 1. Structure of 16.
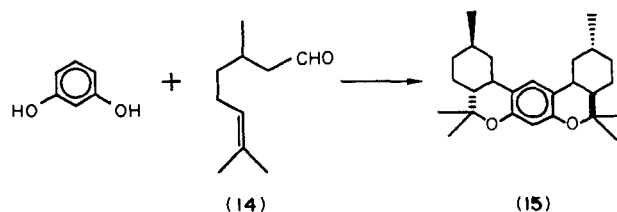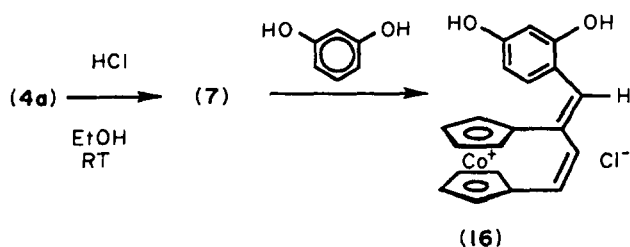
1,3-dihydroxybenzene leads to the intermediate **18** on loss of a proton. Protonation of the aliphatic hydroxyl group of **18** and subsequent elimination of water gives the product **16**. The absence of cyclisation in this reaction compared with the analogous ferrocene system may be due to the relatively greater activation of the alkene double bond of **7** (and therefore **18**) as a result of the electron-withdrawing influence of the positively charged cobaltocenium unit.
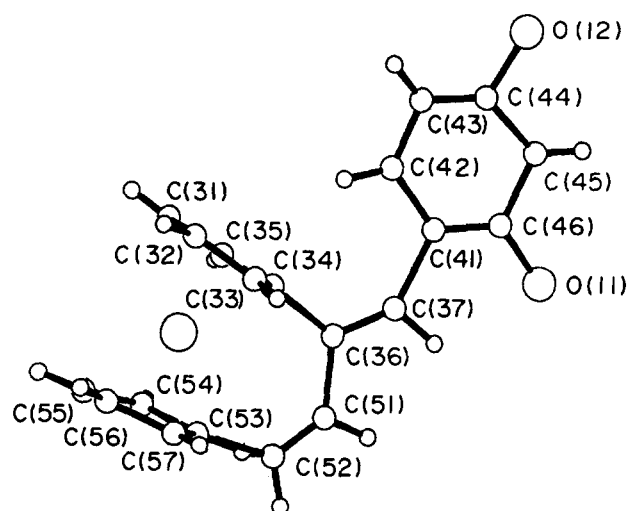
4.4. Single-crystal X-ray structure of 16

Crystals of **16** suitable for analysis by X-ray crystallography were grown from acetonitrile solutions.

The structure contains discrete cations and chloride anions. The cation is shown in Fig. 1, together with the

'Scheme 9.

atomic numbering scheme. There is good evidence from the dimensions that the structure of the cation is significantly strained in order to satisfy the conflicting requirements of the Co(cyclopentadiene)$_2$ moiety and the conjugated system. Usually in the Co(cyclopentadiene)$_2$ moiety, the two rings will be parallel, but this is not possible in the present cation as the two rings are connected to two atoms C(36) and C(52) that are only 2.52 Å apart. This is clearly far too close for two rings sandwiching a cobalt atom.

In order to make room for the cobalt atom, the two cyclopentadiene rings are bent away from each other so that they intersect at an angle of 9.7°. This angle is concomitant with distortion in the conjugated system, thus the C(36)-C(51)-C(52) and C(51)-C(52)-C(53) angles are 129.9(9) and 128.8(9) respectively. The 9.7° bend provides enough space for the cobalt atom and the Co-C distances, as expected, range from 1.96 to 2.04 Å. The two cyclopentadienyl rings are perforce eclipsed.

The remaining atoms in the cation form a conjugated planar system. Thus the six carbon atoms in the phenyl ring, the two oxygen atoms, and atoms C(37), C(36), C(34), C(51), C(52), C(53) are all coplanar to within 0.03 Å. This plane intersects the two cyclopentadienyl rings at angles of 87.8 and 87.2° respectively. There are further distortions in some of the angles in the conjugated system in order to provide space for the adjacent cyclopentadiene ring. Thus C(36)-C(37)-C(41) and C(37)-C(41)-C(42) are 130.6(7) and 127.4(8)° respectively. This ensures that H(42) is not too close to the adjacent cyclopentadiene ring and indeed the closest distance is H(42) · · · C(34) 2.36 Å.

The chloride anion is hydrogen bonded to both -OH groups with Cl · · · O(11) and Cl · · · O(12) distances of 2.99 and 3.02 Å. There are no other intramolecular distances less than the sum of the van der Waals radii between atoms in the structure.

Table 3
Electrochemical data

Compound	$E_{\frac{1}{2}}(V)$ [a]
5	0.50
8	0.71
12	0.64
13a	0.64
4a	−0.87
7a	−0.77
16	−0.92

[a] Obtained in dichloromethane solution containing 0.2 mol dm^{-3} Bu$_4$NPF$_6$ as supporting electrolyte. Solutions were 2×10^{-3} mol dm^{-3} in compound and potentials were obtained with reference to SCE.

4.5. Electrochemical properties of the new metallocene derivatives

The electrochemical properties of some of the new ferrocenyl and cobaltocenium derivatives were studied using cyclic voltammetry in dichloromethane solutions using Bu$_4$NPF$_6$ as supporting electrolyte. All ferrocene systems exhibited a quasi-reversible one electron oxidation wave (Table 3) and all had a tendency to coat or electropolymerise at the electrode surface. In particular cyclic voltammograms of 12 and 13a revealed pronounced adsorption waves which are highly likely to be due to the polymerisation of the alkene group present in both compounds.

The cobaltocenium derivatives displayed quasi-reversable one electron reduction waves (Table 3) and they also showed a tendency to coat the electrode surface.

5. Conclusions

New ferrocene and cobaltocenium acetal and aldehyde containing compounds have been prepared. Disap-

pointingly the acid-catalysed condensation reactions of both metallocene bis(aldehydes) with 1,3-dihydroxybenzene did not produce macrocyclic calixarene type derivatives but afforded complex mixtures of acyclic products.

The new metallocene cyclic monoaldehydes (7 and 8) differed markedly in their reactions with 1,3-dihydroxybenzene. The ferrocene compound 8 gave both [1 + 1] and [1 + 2] resorcinol : aldehyde cyclic adducts (12 and 13a), whereas the cobaltocenium analogue produced the diene 16. This difference in reactivity between 7 and 8 aldehydes may be attributed to the relatively strong electron-withdrawing effect of the positively charged cobaltocenium moiety, compared with the neutral ferrocene unit.

Acknowledgements

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