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Communication

[2 + 2 + 2] Cyclotrimerisation of bisaryl acetylene bearing ferrocenyl units with planar chirality: synthesis of enantiopure conjugated polyferrocene complexes

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Abstract

A new family of highly symmetric and fully conjugated hexaferrocenyl complexes were prepared by a [2 + 2 + 2] cyclotrimerisation reaction of the corresponding alkyne monomers. The preliminary electrochemical behaviour of the new complexes was also evaluated by cyclic voltametry. © 2001 Elsevier Science B.V. All rights reserved.

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Owing to its accessibility, ferrocene and its derivatives have received great attention in the preparation of molecular devices and its organic chemistry has been extensively developed [1]. Ferrocene derivatives have been used as building units as well as electrochemical markers in supramolecular chemistry [2]. Applications in material sciences include thermotropic liquid crystals [1,3], electroactive polymers [4,6b], and non-linear optics devices [5]. However, the application of ferrocenyl complexes bearing planar chirality was restricted mainly to the design of chiral ligands for enantioselective catalysis. Up to now, very few examples have been reported in the field of material chemistry [5b,6a,6b]. Recent developments [7] in the efficient asymmetric synthesis of planary chiral ferrocene derivatives should provide the impetus for the incorporation of these chiral units in complex systems and in the design of highly symmetrical molecular architectures.

The construction of hexasubstituted benzene derivatives with saturated or unsaturated carbon groups has been investigated by many groups and represents a considerable synthetic challenge for the organic chemist. Various methods including peralkylation of arene–iron complexes [8], palladium catalysed alkenylation [9] and alkynylation [10] of hexabromobenzene, and Wittig–Horner condensation [11] have been reported. A very elegant and most efficient pathway for building a hexaarylbenzene skeleton relies on a transition metal catalysed [2 + 2 + 2] cyclotrimerisation of bisaryl acetylenes [12]. This transformation allows the assembly of three units of a functionalised monomer in a single step and has already found many applications in organic chemistry, notably in the field of material sciences [13]. Pioneer work regarding the cobalt (0) cyclotrimerisation of ferrocenyl acetylenes was reported by Soukup and Schlögl [14]. In this work, the cyclotrimerisation of the various terminal acetylenes bearing ferrocenyl pendants were shown to give unsymmetrical trisubstituted triferrocenylbenzenes. Our aim was to study the construction of a hexaarylbenzene core bearing a chiral ferrocenyl unit at each extremity. In that case, introduction of enantiopure ferrocene building blocks was necessary for the overall symmetry of the target architecture.

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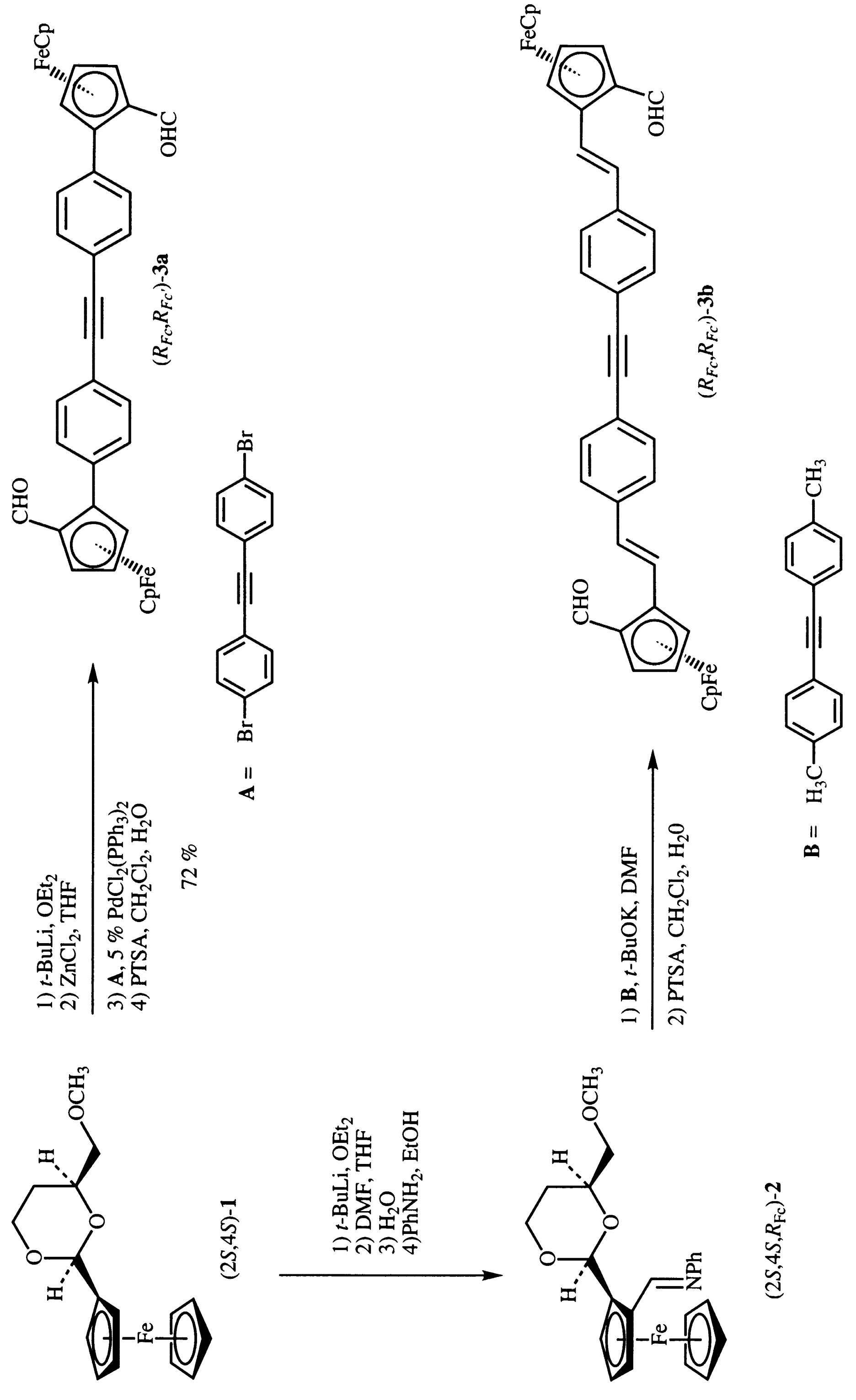

(2S,4S)-1
1) t-BuLi, OEt2
2) DMF, THF
3) H2O
4)PhNH2, EtOH
(2S,4S,RFc)-2
1) t-BuLi, OEt2
2) ZnCl2, THF
3) A, 5 % PdCl2(PPh3)2
4) PTSA, CH2Cl2, H2O
72 %
(RFc,RFc')-3a
A =
1) B, t-BuOK, DMF
2) PTSA, CH2Cl2, H20
(RFc,RFc')-3b
B =
CHO
OHC
FeCp
CpFe
Fe
NPh
OCH3
H3C
CH3
Br

Scheme 1.

Starting from a well-defined method for the asymmetric functionalisation of ferrocenyl carboxaldehyde [15], we devised a straightforward preparation of the monomers **3a**–**b** on a multigram scale (Scheme 1). Diastereoselective ortholithiation (98% de) of extensively available acetal (**1**) by tertiobutyl lithium in diethyl ether followed by transmetalation with zinc chloride gave a chiral orthometallated ferrocenyl zinc intermediate. Palladium catalysed coupling of this reagent with bis-(*p*-bromophenyl)acetylene gave the C_2-symmetric bisferrocenyl monomer (**3a**) in a 72% yield after deprotection of the acetal groups. As reported earlier [16], the vinylogue monomer (**3b**) was prepared in a single step from the imine (**2**). Thus, the introduction of a formyl group in the α position of the dioxane ring was conduced by the ortholithiation sequence followed by electrophilic quenching with DMF and aqueous work up in the neutral condition. Finally, quantitative conversion to the desired imine was carried out by the reaction of the aldehyde with aniline in refluxing ethanol. Siegrist condensation [17] of a twofold excess of imine (**2**) and bis-(*p*-tolyl)acetylene in the presence of potassium *tert*-butoxide in DMF furnished the bis condensation adduct, which was in turn deprotected to give the bis aldehyde (**3b**) in a 64% overall yield from the starting imine. [2 + 2 + 2] Cyclotrimerisation of alkynes **3a**–**b** were carried out in refluxing dioxane in the presence of a catalytic amount (10 mol%) of dicobalt octacarbonyl. Clean conversion was observed in both cases and the corresponding cyclotrimers **4a**–**b** were isolated as stable orange crystalline solids after chromatographic purification. During repeated experiments, yields usually ranged in 80–90% and the trimers were fully characterised by standard analytical methods. The ^{1}H and ^{13}C NMR spectra suggest that, for each cyclotrimer, a single conformation is present in the solution. This hypothesis is supported by the examination of molecular models, which shows strong steric interaction between adjacent ferrocenes. Two possible symmetric conformations are thus possible. The first is to arrange all the ferrocenes in an all-*syn* conformation (as shown in Scheme 2) around the central core to form a chiral helical structure. The second possibility is to alternate each ferrocenyl group in an all-*anti* conformation. As the chemical shift of the aldehydic hydrogen (9.96 and 10.06 ppm for **4a** and **4b**, respectively) is closest to that of unshielded α-arylferrocene aldehydes and ferrocene carboxaldehyde itself (9.94 ppm), we favour the hypothesis of a chiral helical structure. However, more work is required to determine the actual conformation of those molecules and efforts are presently underway to obtain single crystals of those trimers, suitable for X-ray analysis.

Table 1
Formal electrode potentials (in mV vs. SCE) for the ferrocenyl-centered oxidation processes of ferrocene carboxaldehyde and compounds **3**–**4** and **5b**

Compound	FcCHO	**3a**	**3b**	**4a**	**4b**	**5b**
$E_{1/2}$	830	850	800	836	661	450

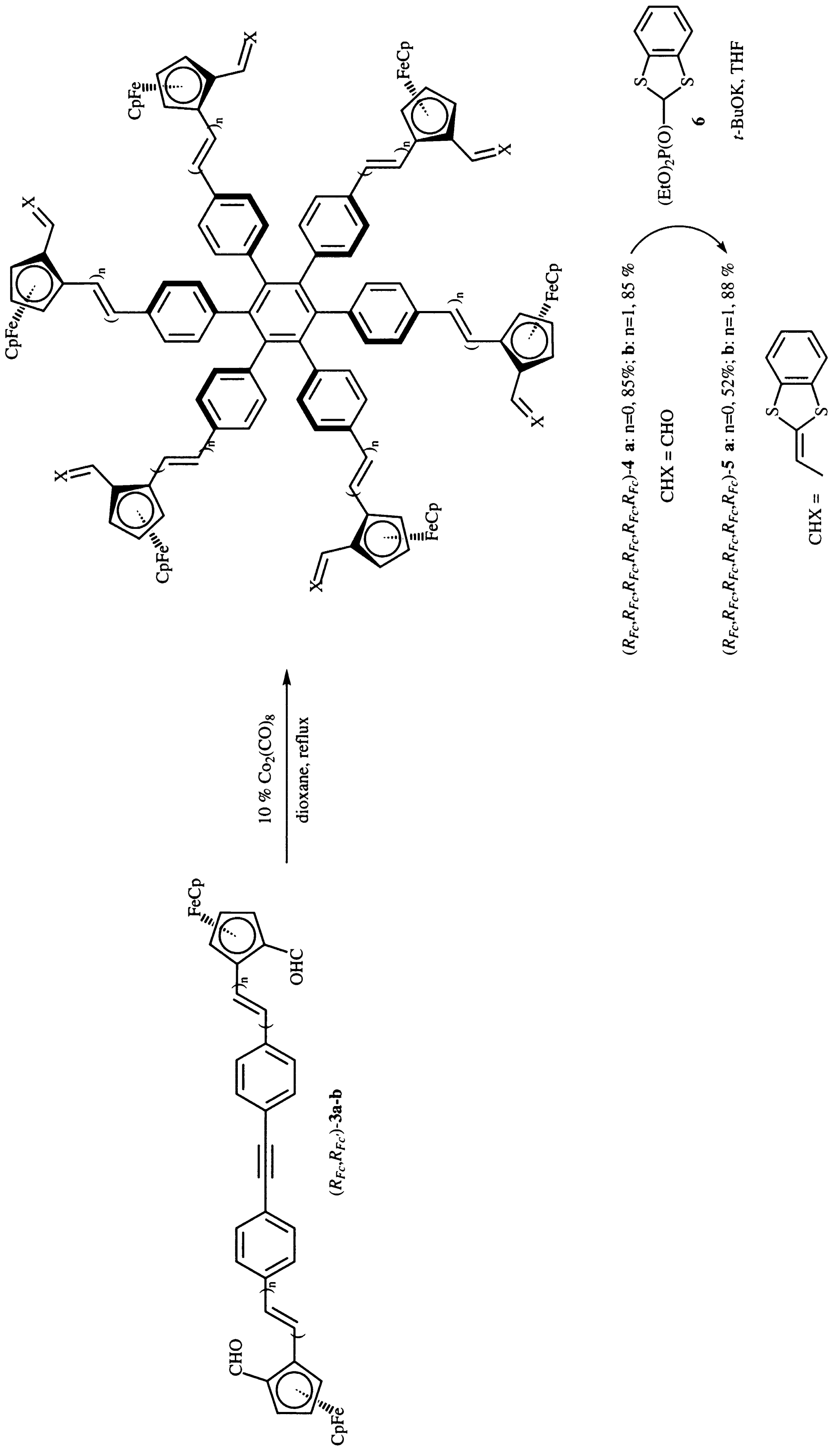
Experimental conditions: CH_2Cl_2–CH_3CN–Bu_4NClO_4 (0.1 M), 2 mm^2 glassy carbon working electrode; SCE reference; 100 mV s^{-1} sweep rate, 20 °C. A shoulder corresponding to an irreversible process was also observed.

Further functionalisation of cycloadducts can be easily considered as the formyl groups on each ferrocene give a wide array of possible transformations. As a first example, we chose to introduce an electroactive benzodithiolene groups on each ferrocene using a standard Wittig–Horner condensation. The six-fold condensation of phosphonate **6** on the hexaaldehydes **4a**–**b** were conduced using *t*-BuOK as a base in THF and gave the new derivatives **5a**–**b** bearing 12 electroactive units in moderate to good yields.

Preliminary studies on the electrochemical behaviour of the new complexes were performed by cyclic voltametry (CV) (Table 1). For all new hexaferrocene derivatives, CV show a reversible one-electron oxidation in which all the ferrocenes appears to be equivalents. In the case of complex **5b** where each ferrocene bears an electron-donating group, the oxidation occurs at a lower potential. In that latter case, a second irreversible wave was attributed to the irreversible oxidation of the benzodithiolene group. However, more studies are required for the unambiguous attribution and the quantification of the electrochemical processes of those new complexes [18]. We are currently studying the chemistry and the electrochemical behaviour of those enantiopure polymetallic complexes as well as the introduction of various electroactive groups on the ferrocenes.

1. Experimental

A dry Schlenck tube was charged with alkyne **3a** (500 mg, 0.83 mmol) and $Co_2(CO)_8$ (30 mg, 0.087 mmol) under argon. Freshly distilled dioxane (10 ml) was injected and the solution was refluxed overnight. After the evaporation of the solvent, the crude reaction mixture was purified by flash chromatography on silica gel (diethyl ether–cyclohexane–CH_2Cl_2, 2:1:1). Cyclotrimer **4a** was isolated as an air stable orange solid. Yield: 85%; m.p. (dec.) > 250 °C ; $[\alpha]_D$ +450 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 4.04$ (30 H, s, C_5C_5), 4.56 (6H, m, C_5H_3), 4.66 (6H, m, C_5H_3), 4.85 (6H, m, C_5H_3), 6.91 (12H, d, $J = 7.7$ Hz, Ar), 7.12 (12H, d, $J = 7.7$ Hz, Ar), 9.96 (6H, s, CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 68.5$, 71.1, 71.95, 74.55, 77.2, 91.9, 128.1, 131.25, 133.25, 139.4, 140.1, 193.64; IR ($CHCl_3$, cm^{-1}): 2928 and 2851 (C–H), 1665.5 (C=O); FABMS; *m*/*e*: 1807.2 (M$^+$). Cyclotrimer **4b** was syn-


CpFe
FeCp
CHO
OHC
n
$(R_{Fc},R_{Fc'})$-3a-b
10 % $Co_2(CO)_8$
dioxane, reflux
X
$(R_{Fc},R_{Fc},R_{Fc},R_{Fc},R_{Fc},R_{Fc})$-4 a: n=0, 85%; b: n=1, 85 %
CHX = CHO
$(EtO)_2P(O)$
S
6
t-BuOK, THF
$(R_{Fc},R_{Fc},R_{Fc},R_{Fc},R_{Fc},R_{Fc})$-5 a: n=0, 52%; b: n=1, 88 %
CHX =

Scheme 2.

thesised using the same procedure. Yield: 85%; m.p. (dec.) >250 °C; $[\alpha]_D$ −625 (*c* 0.064, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 4.16$ (30H, s, C_5H_5), 4.57 (6H, d, $J = 2$Hz, C_5H_3), 4.76 (6H, m, C_5H_3), 4.87 (6H, m, C_5H_3), 6.63 (6H, d, $J = 16.0$ Hz, CH=C), 6.85 (6H, d, $J = 16.0$ Hz, CH=C), 7.05 (12H, d, $J = 8.0$ Hz, Ar), 7.20 (12H, d, $J = 8.0$ Hz, Ar), 10.09 (6H, s, CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 70.1$, 71.45, 72.55, 77.2, 86.4, 122.8, 124.9, 129.5, 131.7, 134.1, 139.85, 140.2, 193.4; IR ($CHCl_3$, cm^{-1}): 2927 and 2851 (C–H), 1672 (C=O); FABMS; *m*/*e* 1963.1 (M^+).

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