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METALLOCENE POLYMERS

XXVII.* 1,3-TERFERROCENYL

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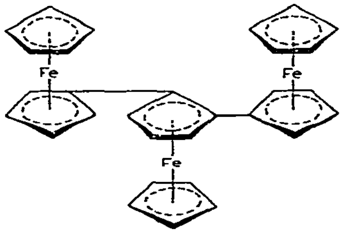
SUMMARY

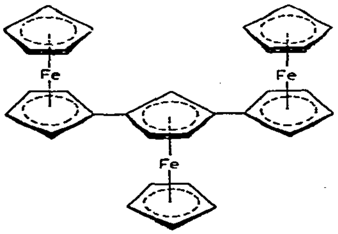
The synthesis of 1,3-terferrocenyl (1,3-diferrocenylferrocene) is accomplished by acylation of ferrocene with 3-(ethoxycarbonyl)propionyl chloride under Friedel–Crafts conditions, followed by condensation of the resulting [3-(ethoxycarbonyl)-propionyl]ferrocene with acetylferrocene in the presence of potassium tert-butoxide. The intermediary diferrocenyl(ethoxycarbonyl)cyclopentadiene (not isolated) is hydrolysed and decarboxylated in boiling aqueous alkali, yielding 1,4-diferrocenylcyclopentadiene. The latter, as the sodium salt, is allowed to react with ferrous chloride in tetrahydrofuran in the presence of excess sodium cyclopentadienide, producing 1,3-terferrocenyl in addition to large quantities of ferrocene. Both the terferrocenyl and its precursor, 1,4-diferrocenylcyclopentadiene, are characterized by IR, UV, PMR, and analytical data.

INTRODUCTION

Previous publications[1,2] were concerned with the isolation and identification of the three isomeric terferrocenyls (I)–(III) formed as by-products in the polyrecombination reaction of ferrocene in the presence of tert-butyl peroxide. Of these



(I)



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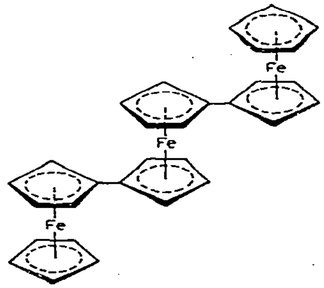

(III)

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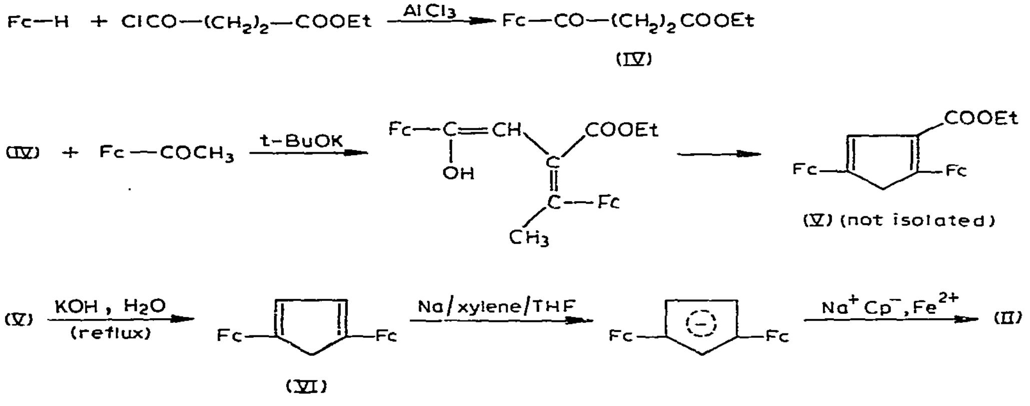
* For Part XXVI, see ref. 2.

isomers, 1,2-diferrocenylferrocene (I) was recently synthesized independently by two groups[3,4] and several reports of the preparation of the heteroannular compound, 1,1'-diferrocenylferrocene (III), are also available[5-8]. The independent synthesis of the remaining isomer, 1,3-diferrocenylferrocene (II), has been achieved in our laboratories, and is described in this communication.

RESULTS AND DISCUSSION

The synthetic steps leading to (II) are depicted in the sequence of Scheme 1. Ferrocene was mono-acylated in 48% yield with 3-(ethoxycarbonyl)propionyl chloride under Friedel–Crafts conditions. In order to suppress polyacylation, it proved necessary to conduct the reaction under conditions allowing for the intermediacy of a Lewis acid–acyl halide complex in dichloromethane solvent. An alternate route involved acylation with succinic anhydride, followed by esterification of the resulting (carboxypropionyl)ferrocene with ethanol. The acyl derivative, [3-(ethoxycarbonyl)propionyl]ferrocene (IV), produced in addition to some heteroannularly diacylated compound and small amounts of diferrocenylmethane resulting from alkylation by the solvent[9], was allowed to condense with acetylferrocene. This furnished the cyclic ester (V). Attempts to enforce this cyclocondensation with sodium hydride in benzene failed; the reaction proceeded satisfactorily, however, in the presence of tert-butoxide. Ester (V), without prior isolation, was hydrolyzed and decarboxylated in boiling aqueous alkali, which produced 1,4-diferrocenylcyclopentadiene (VI) in an overall yield of 16% based on the propionyl derivative (IV).

SCHEME 1. (Fc=ferrocenyl; Cp=cyclopentadienyl.)



The completeness of cyclocondensation and decarboxylation in the sequence (IV) → (V) → (VI) was ascertained by molecular weight, elemental analytical, and spectroscopic data on the diene (VI). No methyl or other open-chain aliphatic protons were detectable in the ^{1}H NMR spectrum, and no carbonyl absorption appeared in the IR. NMR spectroscopy also proved conclusive in the corroboration of the compound's diene structure and substituent disposition. The 60 MHz-spectrum*

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* Spectrum published along with that of (I) in ref. 2.

exhibited a two-proton (allylic methylene) singlet at δ 3.40 ppm and a two-proton (olefinic) singlet at 6.38 ppm. While the latter signal reflects equivalency of the olefinic protons, the former's position, by 0.07 ppm downfield from the corresponding signal in 1,2-diferrocenylcyclopentadiene[3], accounts for the location of the methylene group, flanked by the two ferrocenyl groups and thus placed in two overlapping deshielding zones of the (substituted) cyclopentadienyl rings. These features render other isomer structures with different disposition of double bonds and/or ferrocene substituents highly improbable, as can readily be visualized by consideration of magnetic environments of the four cyclopentadiene protons in the remaining two possible "*meta*" and three "*ortho*" substituent arrangements. Furthermore, the ten unsubstituted cyclopentadienyl ring protons gave a sharp singlet signal at 4.08 ppm, the expected result for a symmetric structure (either 1,4- or 2,3-diferrocenylcyclopentadiene, the latter less likely because of steric crowding and concomitant rotational hindrance of the two ferrocene groups), in which equal average magnetic environments exist for the two unsubstituted ferrocene rings. In contrast, a doublet signal is shown, for example, in the published[3] spectrum of 1,2-diferrocenylcyclopentadiene.

Further confirmation of the 1,4-disposition of the substituents in (VI) derives from the electronic absorption spectrum (in $CHCl_3$), the two highest-wavelength bands of which are recorded in Table 1. The corresponding bands of the open-chain compounds, 1,4-diferrocenyl-1,3-butadiene[10,11] and 1-ferrocenyl-4-phenyl-1,3-butadiene[11,12] are also listed for comparison. Both bands, as expected, are red-shifted in the more rigidly planar (VI) relative to the open-chain compounds; at the same time, a hypochromic effect is observed, in accord with reduced transition-moment change in the cyclic diene. Precedence for this shift pattern is found in the exemplifying two compounds, cyclopentadiene and butadiene, the former having λ_{max} (π–π^*) at 238.5 nm (ε 3,400), and the latter at 217 nm (ε 21,000)[13]. In contrast, assuming 1,3- or 2,5-orientation of the substituents in the diferrocenylcyclopentadiene, one would predict absorption maxima reasonably close to those of vinylferrocene, which exhibits λ_{max} at 223 (ε 16,000), 275 (ε 6,300), 328 (sh) (ε 480), and 447 nm (ε 250)[14].

TABLE 1

ELECTRONIC ABSORPTION MAXIMA OF SOME FERROCENYL DIENES

Compound	λ_{max}, *nm* (*ε in parentheses*)		*Ref.*
	π–π^*	*d–d transition*	
1,4-diferrocenylcyclopentadiene (VI)	368 (11,400)^a	468 (2,400)	Our work
1,4-diferrocenyl-1,3-butadiene	330 (30,400)^b	463 (3,600)	10
	335 (27,800)^a	468 (3,000)	11
1-ferrocenyl-4-phenyl-1,3-butadiene	333 (33,000)^a	465 (1,900)	11
	332 (35,500)^c		12

^{a} In chloroform. ^{b} In tetrahydrofuran. ^{c} In dioxan.

The diene (VI), following conversion to its sodium salt by means of sodium dispersion in xylene [we preferred this over the lithium salt used[3] for the lower-yield synthesis of (I)], was allowed to react with a large excess of sodium cyclopentadienide and ferrous chloride in tetrahydrofuran. Complex formation as shown in Scheme 1 provided the desired 1,3-terferrocenyl (II) (23.5% yield) in addition to copious quantities of ferrocene. The rigorously purified compound melted sharply at 198–200° *.

Terferrocenyl (II) gives an electronic absorption spectrum that reflects the batho- and hyperchromic effects expected for this isomer relative to the sterically strained and, thus, less coplanar 1,2-isomer (I)[2,3], having maxima (in ethanol) at 268 (sh) (ε 13,500), 301 (ε 12,500), 349 (sh) (ε 2200), and 455 nm (ε 1120). The IR spectrum (KBr pellet) is characterized by the simplicity of the spectra of ferrocene and biferrocenyl. In addition to all typical ferrocene bands[15–17], the characteristic substitution peak at 1025 cm^{-1} is shown**, and the CH out-of-plane deformation band [15] at 1050 cm^{-1}, very weak in ferrocene and biferrocenyl and weak in the heteroannular terferrocenyl (III), appears in medium intensity (decreased forbiddenness in going from E_2 modes of ferrocene to a_2 in local C_{2v} symmetry of center ring) as similarly exhibited[2] by the second all-homoannular isomer (I). The band at 1410 cm^{-1} [2,15,20] is of relatively high intensity, and both the 1000 and 1110 cm^{-1} bands (the latter as a doublet)[15,21] appear as strong peaks, indicating a large extent of homoannularity. (A quantitative homoannularity determination[22] proved inconclusive, in accord with Hata's finding[7] that the "9,10-μm rule"[21] breaks down in the spectra of oligoferrocenylenes.)

As in other simple ferrocenes devoid of aliphatic side groups, the mass spectrum of (II) features a very stable parent ion, M^+, at m/e 554 (intensity 100), with an associated $[M+1]^+$ ion in the correct intensity (38) expected for the isotopic composition of a terferrocenyl. The corresponding, highly intense $m/2e$ peaks appear at m/e 277 (30) and 277.5 (11.4), in precisely the same intensity ratio. In contrast to biferrocenyl[23], where loss of cyclopentadienyl (m/e 65) and cyclopentadienyliron (m/e 121) constitutes the principal mode of fragmentation, this pattern is entirely insignificant in (II). Instead, loss of two cyclopentadienyl units is a prominent decomposition path, leading to $[M-2\times65]^+$ with m/e 424 (5) and $[M-2\times65-1]^+$ with m/e 423 (16). Similarly, loss of two cyclopentadienyliron species gives $[M-2\times121]^+$ with m/e 312 (10) and $[M-2\times121-2]^+$ with m/e 310 (11). Whether these eliminations are concerted (conceivably from the molecule with both ferrocene groups in a conformation "*cisoid*" to each other) could not be decided for lack of metastable peaks in the spectrum. A prominent double peak at m/e 366 (16) and 368 (13) points to facile loss of the elements of ferrocene. The stability of the m/e 368 ion (and its m/e 369 satellite), indicated by the appearance of a weak doubly charged peak at m/e

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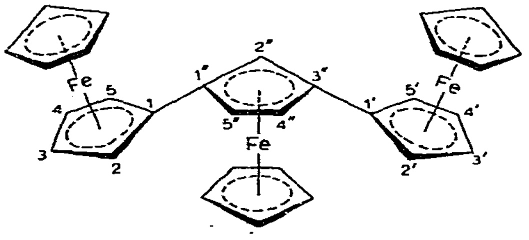
* The terferrocenyls obtained in the earlier quoted polyrecombination studies[1,2] proved extremely difficult to purify owing to the stubborn admixture of methylated dervatives (identified by mass spectroscopy) exhibiting much the same adsorption and solubility characteristics. Coupled with the generally observed difficulty of purifying oligonuclear ferrocenes and obtaining clear-cut and constant melting points[2], this contamination may explain the lower and less sharp m.p. determined for (II) in the earlier study[1]. Later work[2] established a somewhat higher, although no less broad, melting range (198–202°).

** The high intensity suggests this peak to be an a_1 fundamental in local C_{2v} symmetry of the disubstituted center ring and the two monosubstituted rings of the outer units, probably due to a CH in-plane deformation mode. (While absorption at this position in dimethylferrocene had been assigned in an earlier paper[18] to a symmetrical ring-breathing a_1 mode derived from the 1105 cm^{-1} ferrocene band, this assignment was later corrected[19] to apply to a band at 919 cm^{-1} in this compound.)

184 (and 184.5), suggests a [0,0]ferrocenophane structure for this ion. Since hydrogen migration must precede its formation just as in the analogous case involving the 1,2-isomer (I)[2], the intensity of its mass peak is low relative to that exhibited by the heteroannular isomer (III), in which no such migration is required for the cyclization step.

The 60 MHz ^{1}H NMR spectrum of (II) is characterized by two sharp singlets at δ 3.82 ppm (5 H) and 4.02 ppm (10 H) as well as three broad, unresolved absorptions at 4.16 (4 H), 4.36 (6 H), and 4.55 (1 H). Assuming a most probable conformation with the two outer ferrocene units in *cisoid* geometry relative to each other, one may rationalize this absorption pattern by assigning the ten unsubstituted-ring protons of the outer units to the 4.02 singlet, the five unsubstituted-ring protons of the center unit (being in the two shielding cones of the outer units) to the high-field peak at 3.82, and the lone proton 2″, doubly deshielded by the flanking substituted rings of the outer units, to the low-field absorption at 4.55 ppm. The identification of the remaining two absorptions depends on the dihedral angle between the disubstituted center ring and each linked ring of the outer units. Provided that all substituted rings are essentially coplanar, one can ascribe the absorption at 4.36 ppm to the low-field part, and the one at 4.16 ppm to the high-field part, of an AA′BB′ pattern involving the eight protons 2,5 and 3,4 as well as 2′,5′ and 3′,4′, the lower-field signal being enlarged by the contribution of protons 4″ and 5″. Alternately, if, as shown in the drawing, one assumed the two outer units to be slightly declined out of the center-ring plane towards the central unit's unsubstituted ring, the shielding cone arising from this ring will have a more pronounced effect on the outer units than the shielding cones of the outer unit's unsubstituted rings will exert on the center unit. As a result, one would expect the α protons 2,5,2′,5′ to absorb at the upfield position of 4.16 and the less shielded β protons 3,4,3′,4′ at the downfield position of 4.36 ppm, the latter signal again being enhanced by protons 4″ and 5″. The poor resolution of our spectrum does not permit a decision in favour of either alternative; an unambiguous assignment must await re-scanning on a 100 MHz instrument. The entire spectrum, in accord with the analogous behavior shown by biferrocenyl[24], is somewhat shifted to the high-field side relative to mononuclear ferrocene compounds because of mutual shielding effects of the closely arranged ferrocene groups.



EXPERIMENTAL

Melting points (uncorrected), were taken in sealed and evacuated capillaries. IR spectra (KBr pellet) were recorded on a Perkin–Elmer, Model 521, spectrophotometer. Electronic spectra, in chloroform or ethanol solutions, were recorded on a Cary, Model 14, spectrophotometer. ^{1}H NMR spectra, in deutero-chloroform solution, were taken on a Varian A-60 NMR spectrometer operating at 60 MHz;

chemical shifts, δ, in ppm relative to TMS. Molecular weights, in benzene solution, were determined with the use of a Mechrolab, Model 301A, vapor pressure osmometer. Mass spectra were recorded on Varian-Mat CH5 mass spectrometer at 70 eV, 150° inlet temperature.

[3-(*Ethoxycarbonyl*)*propionyl*]*ferrocene* (*IV*)

An acyl halide/$AlCl_3$ complex was prepared by the action of 60.0 g (0.45 mol) of anhydrous aluminum chloride on 41.15 g (0.25 mol) 3-(ethoxycarbonyl)propionylchloride dissolved in 500 ml of dry methylene chloride precooled to 0° and maintained under a blanket of prepurified nitrogen. After stirring for 0.5 h at ice-bath temperature, the complex solution was freed from unreacted Lewis acid by filtration and was added dropwise, again under N_2, to the stirred solution of 93.02 g (0.50 mol) of reagent-grade ferrocene in 1500 ml of dry methylene chloride at 0–5°. The resulting purple solution was stirred for 1 h at the same low temperature, followed by 1 h at room temperature. It was then hydrolyzed with ice, care being taken to keep the temperature below 10–15° to avoid co-hydrolysis of the ester group. Following the addition of 20 g of $SnCl_2$ dissolved in 1 *M* aqueous HCl, the mixture was stirred until the aqueous phase had turned colourless, indicating complete reduction of ferricenium species. The organic phase, washed repeatedly with water, $NaHCO_3$ solution and, again, water to neutrality, was dried over anhydrous $MgSO_4$ and freed from solvent *in vacuo*. The resulting reddish crystalline mass was taken up in hexane/ethyl ether (3/1 v/v). The extract, filtered from an orange residue containing the diacyl derivative (see below), was chromatographed on alumina, activity grade II, with the use of the same solvent mixture. After removal of the first eluate containing 45 g of unreacted ferrocene and some diferrocenylmethane (0.81 g, m.p. 144–145°, undepressed on admixture of authentic compound, separated upon repeated chromatography of the crude ferrocene fraction on alumina, activity grade I), the eluent was changed to ethyl ether. This produced a fast-moving orange-red band, which upon elution and recrystallization of the solute from hexane gave 34.7 g of orange plates, m.p. 58–60°. A second crop yielded 3.0 g of the same compound, bringing the total crude yield to 37.7 g (48%). An analytically pure sample had m.p. 60.5–62°. (Found C, 60.62; H, 5.81%. $C_{16}H_{18}FeO_3$ calcd.: C, 61.17; H, 5.77%.)

From a higher band on the alumina column, extraction with ethanol and solvent stripping *in vacuo* gave some crude 1,1'-bis[3-(ethoxycarbonyl)propionyl]-ferrocene, which, after combination with the residue remaining from hexane extraction of the crude major reaction product (see above) and recrystallization from ethanol appeared as orange needles (polymorphic) melting at 131–133°. The yield was 12.1 g. (Found C, 59.42; H, 6.02. $C_{22}H_{26}FeO_6$ calcd.: C, 59.75; H, 5.93%.)

1,4-*Diferrocenylcyclopentadiene* (*VI*)

[3-(Ethoxycarbonyl)propionyl]ferrocene, 12.56 g (0.04 mol), and 9.12 g (0.04 mol) of acetylferrocene (Research Inorganic/Organic Chemicals Co; chromatographic purification required to remove some 10% impurities) were added to a solution of potassium tert-butoxide (prepared from 3.20 g of potassium) in 180 ml of anhydrous tert-butanol with stirring under N_2. The mixture was maintained at gentle reflux for 1.5 h with moisture protection under N_2. The butanol was then distilled off, to be replaced by successive portions of water until the head temperature reached 100°. To the reaction product, cooled to room temperature, was added 10.0 g of KOH in 50 ml of water, and the mixture was refluxed for another hour. A dark brown precipitate formed slowly, which, after cooling, was separated by filtration and repeatedly recrystallized from benzene. The main fractions yielded a total of 2.81 g (16.2%) of yellow platelets of the diene, m.p. 231–232° *. Occasionally, the compound crystallized as dark reddish needles exhibiting the same m.p. (Found C, 69.26; H, 5.07; Fe, 25.10; mol.wt., 445. $C_{25}H_{22}Fe_2$ calcd.: C, 69.16; H, 5.11; Fe, 25.73%; mol.wt., 434.13.)

1,3-*Diferrocenylferrocene* (*II*)

All manipulations were performed under Ar, and glass-ware was flamed and allowed to cool in a desiccator prior to use; sodium dispersions were transferred by means of hypodermic syringes and serum caps.

1,4-Diferrocenylcyclopentadiene, 2.17 g (0.005 mol), dissolved in 50 ml of tetrahydrofuran (dried over Linde molecular sieves A-4) and cooled to 0°, was converted to its sodium salt through the addition of 2.0 ml of a sodium dispersion in xylene with magnetic stirring. The pyrophoric dispersion, containing 0.46 g (0.02 mol) of sodium per ml, had been prepared by conventional techniques[25] (3 drops of pyridine per 50 ml of xylene added as a dispersing agent). Stirring for 1 h at 0° was followed by stirring overnight at 20–25° and heating for 0.5 h at reflux temperature. The purplish-black solution was allowed to cool to room temperature prior to further use.

In a separate reaction vessel sodium cyclopentadienide was prepared under N_2 from 42 ml (0.5 mol) of freshly distilled cyclopentadiene, 200 ml of dry tetrahydrofuran and 25 ml of the aforementioned sodium dispersion in xylene by a published procedure[25]. To this solution, combined with the sodium 1,4-diferrocenylcyclopentadienide solution of the preceding step and stirred for 0.5 h at 0–5°, was slowly added an ice-cold solution of 64.64 g (0.51 mol) of $FeCl_2$ in 200 ml of dry tetrahydrofuran (prepared[26] from anhydrous $FeCl_3$ and 325-mesh iron powder). The mixture was gently heated to reflux temperature and there maintained for 2.5 h. The crude reaction product was freed from solvent *in vacuo* and the residue was Soxhlet-extracted with hexane for two days. The concentrated extract was chromatographed on alumina, activity grade II, with hexane as the eluent. Following the recovery of 40 g of ferrocene from the first band, elution was continued with hexane/ethyl ether (3/1 v/v). Solvent stripping of the eluate yielded 1.22 g of crude terferrocenyl contaminated with biferrocenyl**. Purification by a second chromatographic treatment (0.18 g of contaminant eluted first; repeated recrystallization from heptane furnished a product with m.p. 236–239°, no depression on admixture of authentic biferrocenyl) produced 0.65 g (23.5%) of (II) as orange-yellow needles melting at 197–199°. After several recrystallizations from heptane, the terferrocenyl had m.p.

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* The high m.p. contrasts sharply with that of the isomeric 1,2-diferrocenylcyclopentadiene recently prepared and described[3] as an oily liquid.

** We are unable to rationalize the formation of this dinuclear compound in terms other than by assuming that traces of the (very unstable) bicyclopentadiene (9,10-dihydrofulvalene[27]) contaminating the cyclopentadiene starting material entered the complex-forming reaction step, thus producing biferrocenyl as an artifact. This point needs further clarification.

198–200°. (Found C, 64.83; H, 4.75; Fe, 30.59; mol.wt., 578. $C_{30}H_{26}Fe_3$ calcd.: C, 65.03; H, 4.73; Fe, 30.24%; mol.wt., 554.12.)

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