Reaction of *N*,*N*-dimethylaniline with 1,5-diferrocenyl-3-methyl-2,4-trimethylene-penta-1,4-dienyl carbocation. A nonsynchronous cationic cyclodimerization mechanism in conjugated dienes

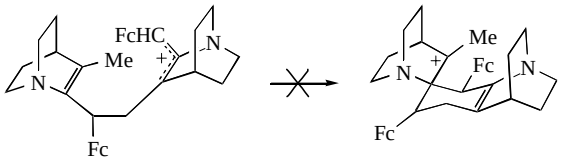
Elena I. Klimova,*[a] Tatiana Klimova Berestneva,[a] Marcos G. Martínez[b] and Lena Ruíz-Ramirez[a]

[a] *Department of Chemistry, National Autonomous University of Mexico, CP 04510 México, México. Fax: +5 25 622 5366; e-mail: klimova@servidor.unam.mx*

[b] *Institute of Chemistry, National Autonomous University of Mexico, CP 04510 México, México*

Reaction of the 1,5-diferrocenyl-3-methyl-2,4-trimethylenepenta-1,4-dienyl tetrafluoroborate cation with *N*,*N*-dimethylaniline affords a mixture of products from the alkylation of *N*,*N*-dimethylaniline at the *para*-position by monomeric and linear and cyclic dimeric carbocations along with linear and cyclic dimers of 1,3-diferrocenylmethylene-2-methylenecyclohexane. These results confirm and illustrate a nonsynchronous cationic cyclodimerization mechanism for ferrocenylbuta-1,3-dienes.

The idea that a stepped mechanism is involved in the cationic cyclodimerization of conjugated dienes was put forward by Hoffmann *et al.*[1–3] in their study on the cyclodimerization reaction of 2,4-dimethylpenta-1,3-diene in the presence of acids. However, up to now this mechanism has not been unambiguously confirmed, although early experimental results are in agreement with it.[4–6] Some recent results[7–16] on the method of synthesis and on the chemical and structural properties of ferrocenyl-containing 1,3-dienes shed additional light on the reaction mechanism. The methylferrocenyl cations are deprotonated during interaction with nucleophiles (*N*,*N*-dimethylaniline, pyridine) resulting in the formation of intermediate ferrocenyl-1,3-dienes followed by their subsequent cationic cyclodimerization. The proposed stepped cationic cyclodimerization mechanism was confirmed by the presence of ferrocenyl-1,3-diene dimers with a terpenoid or condensed polycyclic structure, as final products of the reaction. The presence of the intermediate linear dimeric ferrocenylallyl cation was confirmed in just two cases: in the cationic cyclodimerization of 2-methylene-3-ferrocenyl-methylenecamphane and in 3-methylene-2-ferrocenylmethylene-quinuclidine.[10,11,14] In our opinion, the absence of cyclic dimers in the above cases could be explained by steric hindrance in the camphane and quinuclidine fragments and/or by electronic factors that do not favour the intramolecular alkylation of the dimer cation **1**, which would result in the less stable cation **2** (Scheme 1).



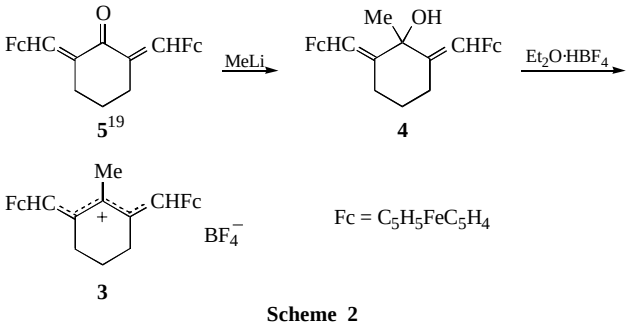
1 **2**

Scheme 1

However, it is worth noting that we could never prove the presence of cyclic intermediate cations, although we obtained cyclic dimers as final products, which indirectly indicates their presence in the intermediate steps of the reaction.

In this work, we studied the reaction of the 1,5-diferrocenyl-3-methyl-2,4-trimethylenepenta-1,4-dienyl tetrafluoroborate cation **1**, which has not been described previously, with *N*,*N*-dimethylaniline. Carbocation **1** is of interest, because at all stages in the cationic cyclodimerization, it should form the stable dimeric (linear and cyclic) allyl carbocations.[17,18] One could therefore expect that these carbocations could be observed in the reaction mixture by reaction with *N*,*N*-dimethylaniline. The final products of this reaction could prove the simultaneous existence of these cations and the stepped mechanism of the cationic cyclodimerization.

In order to verify the validity of the above suggestion we obtained the tetrafluoroborate of carbocation **3** from the corresponding carbinol **4** by treatment with HBF_4 etherate.[7,12] This salt is rather stable upon storage under standard conditions (remains unchanged at room temperature for 10–12 h) (Scheme 2).†



5[19] **4** **3**

Scheme 2

Indeed, treatment of salt **3** with *N*,*N*-dimethylaniline‡ results mainly in the formation of products **6**–**10**§ from the alkylation of *N*,*N*-dimethylaniline at the *para*-position by all allyl (monomeric and dimeric) cations present in the equilibrium reaction mixture (Scheme 3).

In addition, minor quantities of the linear and cyclic dimers **11**, **12** and **13** were isolated from the reaction mixture (Scheme 4).

† *1,5-Diferrocenyl-3-methylpenta-1,4-dienylcation tetrafluoroborate* **3**: yield 87%, black crystals, mp 221–230 °C (decomp.). ^{1}H NMR (CD_2Cl_2) δ: 2.13 (s, 3H), 2.71 (t, 2H, *J* 6.2 Hz), 3.49 (m, 4H, *J* 6.2 Hz), 5.10 (s, 4H, C_5H_4), 5.50 (s, 4H, C_5H_4), 5.31 (s, 5H, C_5H_5), 5.32 (s, 5H, C_5H_5), 8.33 (s, 2H). Found (%): C, 60.59; H, 5.24; F, 12.96; Fe, 19.16. Calc. for $C_{29}H_{29}BF_4Fe_2$ (%): C, 60.46; H, 5.07; B, 1.88; F, 13.20; Fe, 19.39.

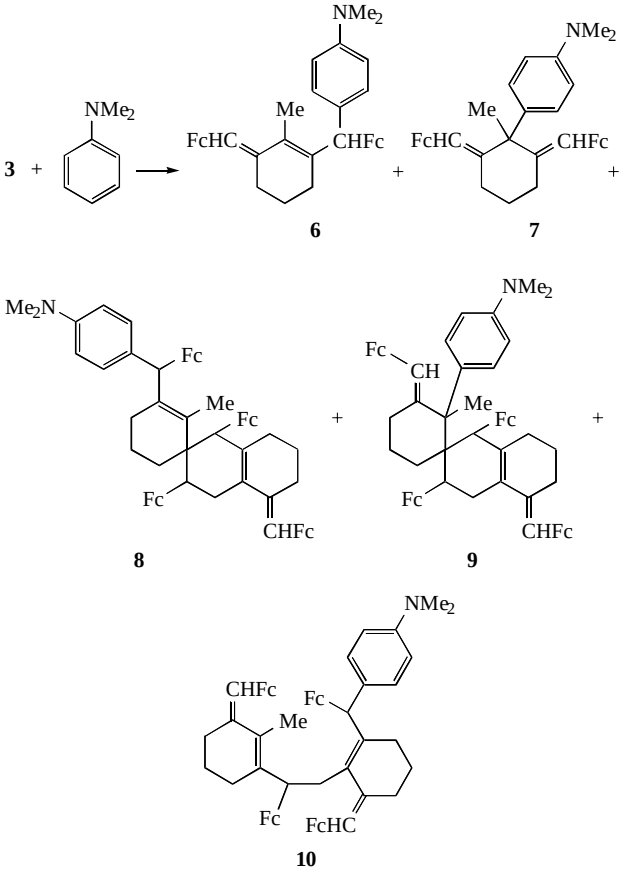
2,6-Diferrocenylmethylene-1-methylcyclohexanol **4**: yield 78%, yellow crystals, mp 156–157 °C. ^{1}H NMR ($CDCl_3$) δ: 1.55 (s, 3H), 1.65 (s, 1H, OH), 2.21 (m, 2H, *J* 10.8, 4.2 Hz), 3.35 (m, 4H, *J* 10.8, 4.2 Hz), 4.1 (s, 10H, $2C_5H_5$), 4.18 (s, 4H, C_5H_4), 4.27 (s, 2H, C_5H_4), 4.31 (s, 2H, C_5H_4), 6.42 (s, 2H). Found (%): C, 68.64; H, 6.12; Fe, 21.93. Calc. for $C_{29}H_{30}Fe_2O$ (%): C, 68.80; H, 5.98; Fe, 22.06.

‡ *N*,*N*-dimethylaniline (0.72 g, 6 mmol) was added to a solution of compound **3** (2.30 g, 4 mmol) in anhydrous CH_2Cl_2 (70 ml) with constant stirring in a dry inert atmosphere. The mixture was stirred at room temperature for 1 h, then the excess of *N*,*N*-dimethylaniline was washed out with water, a 1% solution of HCl and water again. The organic layer was separated and dried with Na_2SO_4. The solvent was distilled off *in vacuo*. The residue was chromatographed on a column filled with Al_2O_3 (III Brockmann activity). The following four fractions were obtained:

Hexane as the eluent: fraction I (0.21 g); fraction II (0.56 g). Benzene–hexane (1:2) as second eluent: fraction III (1.02 g). Benzene–hexane (4:1) as third eluent: fraction IV (0.80 g). Then each fraction was chromatographed on SiO_2 plates to obtain: from fraction I, 0.137 g (7%) of dimer **11** (hexane, R_f = 0.7); from fraction II, 0.098 g (5%) of dimer **12** (R_f = 0.63) and 0.195 g (10%) of dimer **13** (R_f = 0.54, benzene–hexane 1:2); from fraction III, 0.29 g (12%) of compound **7**, (R_f = 0.51) and 0.49 g (20%) of compound **6**, (R_f = 0.38, benzene–hexane 2:1); from fraction IV, 0.13 g (6%) of **10** (R_f = 0.41) and 0.20 g (9%) of **9** (R_f = 0.35) and 0.31 g (14%) of **8** (R_f = 0.28, benzene–hexane 3:1).

All reaction products were separated by column chromatography on Al_2O_3 and then by preparative TLC on SiO_2 and characterised by elemental analysis data and ^1H and ^{13}C NMR spectroscopy.

According to the NMR data the dimerization and cyclodimerization occur diastereoselectively. Compounds **8**–**13** were isolated in just one diastereoisomeric form. However, their spatial structures are not established yet.



Scheme 3

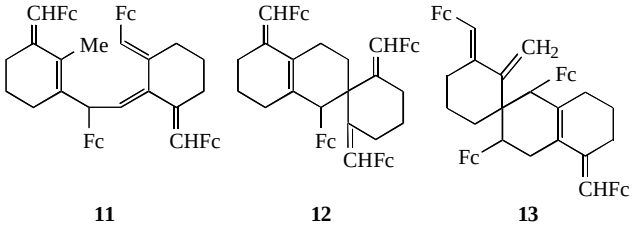
The parameters of the ^1H NMR spectra (number of proton signals, values of chemical shifts and of spin–spin interaction constants) for the aliphatic and olefinic protons in compounds **3**–**13** confirm the suggested chemical structure of these compounds. Additional information on the structure of compounds **8**–**13** is obtained from the ^{13}C NMR spectra. The presence of four quaternary carbon atom signals in the ferrocenyl fragments of compounds **8**–**13**, together with the signals from four C_5H_5 groups, unambiguously prove the formation of dimers. The presence of C_{spiro} signals confirms the suggested cyclic structure of compounds **8**, **9**, **12** and **13**. The number of ^{13}C NMR signals from the C, CH, CH_2 and Me groups in compounds **6**–**13** correspond to their chemical structure.[§,¶]

The formation of compounds **6** and **7** (products of alkylation of *N*,*N*-dimethylaniline) is sufficiently evident and does not require any additional justification. The existence of compounds **8**–**10** is explained well by the schemes discussed in refs. 1–12, which include the following stages:

1) deprotonation of the starting carbocation **3** *via* the intermediate formation of s-*cis*-diferrocenyltriene **14** [Scheme 5, (*a*)];

2) formation of a linear dimeric cation **15** due to the addition of carbocation **3** to the triene **14** at the free methylene group [Scheme 5, (*b*)];

3) formation of the cyclic allyl cation **16** by intramolecular alkylation of cation **15** [Scheme 5, (*c*)].



Scheme 4

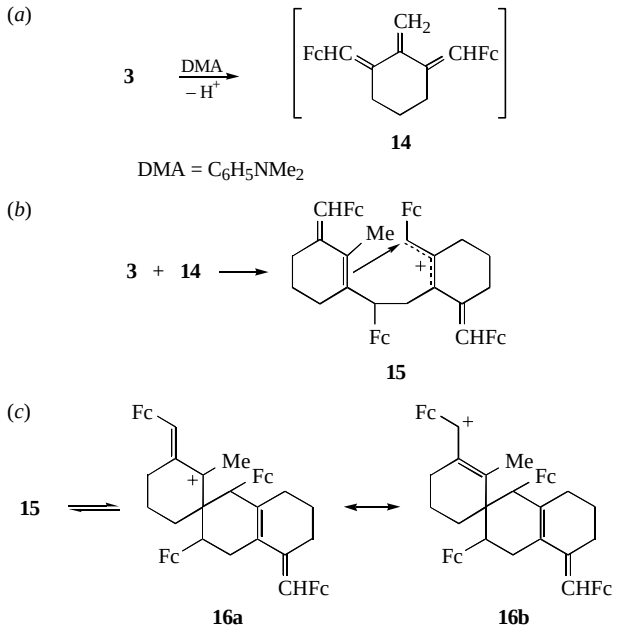
§ *1*-p-*Dimethylaminophenylferrocenylmethyl-3-ferrocenylmethylene-2-methylcyclohexene* **6**: orange crystals, mp 178–179 °C. ^1H NMR ($CDCl_3$) δ: 1.49–1.66 (m, 2H), 1.85–2.04 (m, 2H), 2.4–2.6 (m, 2H), 2.08 (s, 3H, Me), 2.93 (s, 6H, 2Me), 4.10 (s, 5H, C_5H_5), 3.97 (m, 1H), 4.08 (m, 1H), 4.13 (m, 2H), 4.19 (m, 2H), 4.32 (m, 1H), 4.34 (m, 1H, $2C_5H_4$), 5.17 (s, 1H, CH), 6.19 (s, 1H, CH=), 6.69 (d, 2H, *J* 8.2 Hz), 7.14 (d, 2H, *J* 8.2 Hz, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 14.80 (Me), 23.23, 28.30, 28.42 (CH_2), 40.74 (2Me), 47.49 (CH), 68.75 (C_5H_5), 68.98 (C_5H_5), 66.51, 67.35, 68.16, 68.18, 68.46, 69.45, 69.50, 69.72 ($2C_5H_4$), 83.96, 91.78 (C_{ipso}Fc), 112.28 (CH=), 119.46, 127.40, 129.06, 129.07 (C_6H_4), 131.49, 137.26, 139.77, 139.78, 148.89 (C). Found (%): C, 73.11; H, 6.34; Fe, 18.20, N, 2.09. Calc. for $C_{37}H_{39}Fe_2N$ (%): C, 79.92; H, 6.45; Fe, 18.33; N, 2.30.

1,3-Diferrocenylmethylene-2-p-*dimethylaminophenyl-2-methylcyclohexane* **7**: orange crystals, mp 164–165 °C. ^1H NMR ($CDCl_3$) δ: 1.50–1.68 (m, 2H), 1.81–2.02 (m, 2H), 2.41–2.61 (m, 2H), 2.05 (s, 3H, Me), 3.00 (s, 6H, 2Me), 4.12 (s, 5H), 4.13 (s, 5H, $2C_5H_5$), 3.87 (m, 1H), 3.95 (m, 2H), 3.96 (m, 2H), 4.03 (m, 1H), 4.39 (m, 1H), 4.40 (m, 1H, $2C_5H_4$), 6.28 (s, 2H, CH=), 6.79 (d, 2H, *J* 8.4 Hz), 7.24 (d, 2H, C_6H_4, *J* 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.13 (Me), 22.97, 28.89, 30.32 (CH_2), 40.78 (2Me), 60.39 (C), 68.74 (C_5H_5), 69.05 (C_5H_5), 66.38, 67.19, 68.12, 68.13, 68.26, 69.35, 68.66, 68.90 ($2C_5H_4$), 77.21, 91.50 (C_{ipso}Fc), 112.27 (CH=), 119.45, 127.38, 129.0, 130.01 (C_6H_4), 131.02, 137.02, 137.24, 139.75, 148.79 (C). Found (%): C, 72.81; H, 6.58; Fe, 18.47, N, 2.12. Calc. for $C_{37}H_{39}Fe_2N$ (%): C, 72.92; H, 6.45; Fe, 18.33; N, 2.30.

Spiro[3-p-*dimethylaminophenylferrocenylmethyl-2-methyl-2-cyclohexene-1,2'-(1,3-diferrocenyl-5-ferrocenylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalene)]* **8**: yellow crystals, mp 241–242 °C. ^1H NMR ($CDCl_3$) δ: 1.30–1.85 (m, 4H), 2.42–2.83 (m, 4H), 2.88–3.22 (m, 4H), 3.71 (d, 2H, *J* 7.2 Hz), 2.03 (s, 3H, Me), 2.92 (s, 6H, 2Me), 3.86 (t, 1H, *J* 7.2 Hz), 4.11, 4.15, 4.16, 4.17 (s, $4C_5H_5$), 4.01 (m, 2H), 4.03 (m, 2H), 4.13 (m, 2H), 4.21 (m, 2H), 4.23 (m, 2H), 4.25 (m, 2H), 4.38 (m, 2H), 4.40 (m, 2H, $4C_5H_4$), 4.84 (s, 1H, CHFc), 6.27 (s, 1H, CH=), 6.56 (d, 2H, *J* 8.7 Hz), 6.39 (d, 2H, C_6H_4, *J* 8.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.73 (Me), 22.66, 23.79, 26.16, 28.30, 32.06, 33.91, 40.88 ($7CH_2$), 46.35 (2Me), 41.07, 45.93, 51.85 (3CH), 48.41 (C), 68.38, 68.82, 68.84, 69.07 ($4C_5H_5$), 65.95, 66.33, 66.49, 66.52, 66.68, 66.70, 68.22, 68.41, 68.57, 69.29, 69.37, 69.40, 69.59, 69.64, 70.06, 71.36 ($4C_5H_4$), 83.92, 91.70, 92.14, 93.55 (C_{ipso}Fc), 112.97 (CH=), 128.11, 129.34, 136.11, 136.19 (C_6H_4), 130.39, 132.82, 134.86, 137.06, 137.52, 139.56, 148.54 (C). Found (%): C, 72.43; H, 5.98; Fe, 20.21, N, 1.42. Calc. for $C_{66}H_{67}Fe_4N$ (%): C, 72.22; H, 6.15; Fe, 20.35; N, 1.28.

Spiro[2-p-*dimethylaminophenyl-3-ferrocenylmethylene-2-methylcyclohexane-1,2'-(1,3-diferrocenyl-5-ferrocenylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalene)]* **9**: yellow crystals, mp 210–211 °C. ^1H NMR ($CDCl_3$) δ: 1.25–1.49 (m, 4H), 1.72–1.86 (m, 4H), 2.41–2.83 (m, 4H), 2.02 (s, 3H, Me), 2.96 (s, 6H, 2Me), 3.62 (d, 2H, *J* 6.9 Hz), 3.72 (t, 1H, *J* 6.9 Hz), 4.09, 4.12, 4.13, 4.15 (s, $4C_5H_5$), 3.98 (m, 2H), 3.99 (m, 2H), 4.05 (m, 2H), 4.08 (m, 2H), 4.10 (m, 2H), 4.14 (m, 2H), 4.18 (m, 2H), 4.29 (m, 2H, $4C_5H_4$), 4.92 (s, 1H, CHFc), 6.22 (s, 1H, CH=), 6.41(s, 1H, CH=), 6.63 (d, 2H, *J* 9.0 Hz), 6.92 (d, 2H, C_6H_4, *J* 9.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.56 (Me), 23.78, 25.01, 26.18, 28.30, 29.14, 32.60, 34.02 (CH_2), 40.80 (2Me), 47.33, 47.97, 65.74 (CH), 48.43, 50.03 (C), 68.31, 68.71, 68.85, 69.27 ($4C_5H_5$), 66.49, 66.61, 67.90, 67.15, 67.41, 68.17, 68.45, 68.57, 68.65, 68.72, 69.19, 69.40, 69.65, 70.12, 70.74, 71.30 ($4C_5H_4$), 83.93, 90.67, 92.14, 93.52 (C_{ipso}Fc), 112.15, 117.60 (2CH=), 128.11, 129.87, 136.10, 136.20 (C_6H_4), 131.09, 131.12, 134.87, 139.05, 140.83, 148.60 (C). Found (%): C, 72.11; H, 6.23; Fe, 20.56, N, 1.05. Calc. for $C_{66}H_{67}Fe_4N$ (%): C, 72.22; H, 6.15; Fe, 20.35; N, 1.28.

1-p-*Dimethylaminophenylferrocenylmethyl-3-ferrocenylmethylene-2-[2-ferrocenyl-2-(3-ferrocenylmethylene-2-methylcyclohex-1-enyl)]ethylcyclohexene* **10**: orange oil, ^1H NMR ($CDCl_3$) δ: 1.26–1.49 (m, 4H), 1.72–1.86 (m, 4H), 2.52–2.71 (m, 4H), 3.20 (d, 2H, *J* 9.1 Hz), 3.85 (t, 1H, *J* 9.1 Hz), 2.03 (s, 3H, Me), 3.02 (s, 6H, 2Me), 4.74 (s, 1H, CHFc), 4.11, 4.13, 4.16, 4.17 (s, $4C_5H_5$), 3.99–4.29 (m, 16H, $4C_5H_4$), 6.24 (s, 1H, CH=), 6.31 (s, 1H, CH=), 6.62 (d, 2H, *J* 8.3 Hz), 6.79 (d, 2H, C_6H_4, *J* 8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.74 (Me), 19.40, 20.01, 21.35, 24.93, 26.10, 27.18, 30.83 (CH_2), 41.08 (2Me), 47.30, 48.56 (CH), 68.41, 68.56, 68.85, 69.10 ($4C_5H_5$), 65.71, 66.18, 66.58, 66.81, 67.22, 67.89, 68.24, 68.32, 68.76, 69.41, 70.04, 70.31, 70.50, 70.72, 71.26, 71.35 ($4C_5H_4$), 83.81, 83.86, 83.92, 92.14, (C_{ipso}Fc), 112.15 (CH=), 113.60 (CH=), 128.10, 129.87, 130.39, 136.19 (C_6H_4), 129.80, 130.38, 131.20, 131.22, 134.86, 136.20, 138.60, 147.68 (C). Found (%): C, 72.36; H, 5.91; Fe, 20.39, N, 1.41. Calc. for $C_{66}H_{67}Fe_4N$ (%): C, 72.22; H, 6.15; Fe, 20.35; N, 1.28.



Scheme 5

We believe that in this reaction, the alkylation of *N*,*N*-dimethylaniline at the *para*-position by carbocations **3**, **15**, **16a** and **16b**, and deprotonation of the same cations by a base, occur competitively, resulting in the formation of a mixture of all possible reaction products **6**–**13**. We failed to detect the presence of the triene **14** in this process, most likely due to its low stability. However, we isolated the cyclodimer **12**, which is a classic [4+2]-cycloaddition adduct of the Diels–Alder type.

Thus, these results unambiguously confirm the previously suggested scheme[1–12] for the nonsynchronous cationic cyclodimerization of buta-1,3-dienes.

¶ *1,3-Diferrocenylmethylene-2-[2-ferrocenyl-2-(3-ferrocenylmethylene-2-methylcyclohex-1-enyl)]ethylidenecyclohexane* **11**: orange crystals, mp 226–227 °C. ^{1}H NMR ($CDCl_3$) δ: 1.30–1.65 (m, 4H), 1.83–2.10 (m, 2H), 2.21–2.40 (m, 2H), 2.51–3.05 (m, 4H), 1.76 (s, 3H, Me), 4.52 (d, CHFc, *J* 8.2 Hz) 4.02, 4.12, 4.15, 4.17 (s, 4C_5H_5), 3.62 (m, 2H), 3.78 (m, 2H), 3.87 (m, 2H), 3.90 (m, 2H), 4.30 (m, 4H), 4.35 (m, 4H, 4C_5H_4), 6.16 (d, 1H, CH=, *J* 8.24 Hz), 6.32 (s, 1H, CH=), 7.35 (s, 2H, CH=). Found (%): C, 71.43; H, 5.56; Fe, 23.03. Calc. for $C_{58}H_{56}Fe_4$ (%): C, 71.34; H, 5.78; Fe, 22.88.

Spiro[2,6-diferrocenylmethylenecyclohexane-1,2'-(1-ferrocenyl-5-ferrocenylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalene)] **12**: yellow crystals, mp 236–237 °C. ^{1}H NMR ($CDCl_3$) δ: 1.80–2.00 (m, 4H), 2.12–3.15 (m, 12H), 4.21 (s, 1H, CHFc), 4.05, 4.06, 4.09, 4.13 (s, 4C_5H_5) , 3.96 (m, 1H), 3.98 (m, 1H), 4.01 (m, 1H), 4.02 (m, 1H), 4.11 (m, 2H), 4.14 (m, 1H), 4.16 (m, 2H), 4.18 (m, 4H), 4.24 (m, 1H), 4.31 (m, 1H, 4C_5H_4), 5.56 (s, 1H), 5.91 (s, 1H), 6.15 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ: 22.68, 23.55, 26.13, 26.92, 28.19, 29.58, 31.88, 33.56 (CH_2), 46.55 (C), 52.28 (CHFc), 68.73, 68.87, 69.00, 69.05 (4C_5H_5), 65.59, 67.42, 67.48, 67.68, 67.75, 67.79, 67.83, 68.02, 68.11, 68.78, 68.96, 69.19, 69.26, 69.28, 69.32, 69.40, 69.64 (4C_5H_4), 83.88, 84.08, 84.28, 89.32 (C_{ipso}Fc), 116.48, 117.71, 118.78 (3CH=), 129.36, 135.60, 136.49, 144.02, 145.43 (C). Found (%): C, 71.49; H, 5.52; Fe, 23.01. Calc. for $C_{58}H_{56}Fe_4$ (%): C, 71.34; H, 5.78; Fe, 22.88.

Spiro[3-ferrocenylmethylene-2-methylenecyclohexane-1,2'-(1,3-diferrocenyl-5-ferrocenylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalene)] **13**: yellow crystals, mp 262–263 °C. ^{1}H NMR ($CDCl_3$) δ: 1.68–2.06 (m, 4H), 2.18–2.42 (m, 2H), 2.51–2.74 (m, 4H), 2.78–2.86 (m, 2H), 3.09 (d, 2H, *J* 6.1 Hz), 4.08 (t, 1H, *J* 6.1 Hz), 4.17 (s, 1H, CHFc), 4.04, 4.05, 4.15, 4.18 (s, 4C_5H_5), 3.63 (m, 1H), 3.74 (m, 2H), 3.78 (m, 1H), 3.82 (m, 1H), 3.87 (m, 1H), 3.96 (m, 2H), 4.22 (m, 2H), 4.26 (m, 1H), 4.30 (m, 1H), 4.36 (m, 2H), 4.44 (m, 1H), 4.49 (m, 1H, 4C_5H_4), 4.58 (d, 1H, CH_2=, *J* 1.5 Hz), 5.06 (d, 1H, CH_2=, *J* 1.5 Hz), 6.18 (s, 1H, CH=), 6.33 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ: 28.18, 29.05, 31.57, 34.35, 36.68, 47.72, 47.83 (CH_2), 52.26 (C), 65.32, 65.58 (CHFc), 68.47, 68.97, 69.19, 69.20 (4C_5H_5), 66.17, 66.58, 68.06, 68.19, 68.28, 68.31, 68.40, 68.53, 68.78, 69.09, 69.25, 69.42, 69.72, 70.01, 70.51, 72.49 (4C_5H_4), 83.06, 83.07, 83.92, 90.78 (C_{ipso}Fc), 109.52 (CH_2=), 117.76, 121.51 (CH=), 128.32, 135.86, 136.01, 141.25, 159.47 (C). Found (%): C, 71.18; H, 5.99; Fe, 23.04. Calc. for $C_{58}H_{56}Fe_4$ (%): C, 71.34; H, 5.78; Fe, 22.88.

References

1 H. M. R. Hoffmann and H. V. Ernst, *Chem. Ber.*, 1981, **114**, 1182.
2 H. V. Ernst and H. M. R. Hoffmann, *Angew. Chem.*, 1980, **92**, 861.
3 R. J. Giguere, G. Ilsemann and H. M. R. Hoffmann, *J. Org. Chem.*, 1982, **47**, 4948.
4 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 6085.
5 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 7993.
6 W. R. Roush, H. R. Gillis and A. P. Essenfeld, *J. Org. Chem.*, 1984, **49**, 4674.
7 E. I. Klimova, A. N. Pushin and V. A. Sazonova, *J. Organomet. Chem.*, 1984, **270**, 319.
8 A. N. Pushin, E. I. Klimova and V. A. Sazonova, *Zh. Obshch. Khim.*, 1987, **57**, 1102 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1987, **57**, 984].
9 E. G. Perevalova, E. I. Klimova, V. V. Kryuchkova and A. N. Pushin, *Zh. Obshch. Khim.*, 1989, **59**, 873 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1989, **59**, 770].
10 E. I. Klimova, L. R. Ramirez, M. M. Garcia, N. N. Meleshonkova and A. M. Becerra, *Dokl. Ross. Akad. Nauk*, 1996, **351**, 776 [*Dokl. Chem.* (*Engl. Transl.*), 1996, **351**, 320].
11 E. I. Klimova, L. R. Ramirez, M. M. Garcia and N. N. Meleshonkova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2743 (*Russ. Chem. Bull.*, 1996, **45**, 2602).
12 E. G. Perevalova, A. N. Pushin, E. I. Klimova, Yu. L. Slovokhotov and Yu. T. Struchkov, *Metalloorg. Khim.*, 1989, **2**, 1405 (*Organomet. Chem. USSR*, 1989, **2**, 745).
13 V. N. Postnov, E. I. Klimova, M. M. Garcia and N. N. Meleshonkova, *J. Organomet. Chem.*, 1994, **476**, 189.
14 V. N. Postnov, E. I. Klimova, A. N. Pushin and N. N. Meleshonkova, *Metalloorg. Khim.*, 1991, **4**, 116 (*Organomet. Chem.*, 1991, **4**, 61).
15 V. N. Postnov, E. I. Klimova, N. N. Meleshonkova and M. M. Garcia, *Dokl. Ross. Akad. Nauk*, 1992, **326**, 113 [*Dokl. Chem.* (*Engl. Transl.*), 1992, **326**, 184].
16 V. N. Postnov, E. I. Klimova, N. N. Meleshonkova and M. M. Garcia, *J. Organomet. Chem.*, 1993, **453**, 121.
17 M. J. A. Habib, J. Park and W. E. Watts, *J. Chem. Soc. C*, 1970, 2556.
18 W. E. Watts, *J. Organomet. Chem.*, 1979, **17**, 399.
19 M. Salisova, M. Puciova, V. N. Postnov and S. Toma, *Chem. Papers, Chem. Zvesti*, 1990, **44**, 201.

Received: Moscow, 7th July 1998
Cambridge, 29th September 1998; Com. 8/05572F