# The behaviour of 2-methylene-3-ferrocenylmethylenecamphane under conditions leading to the cyclodimerization of ferrocenyl-1,3-butadienes

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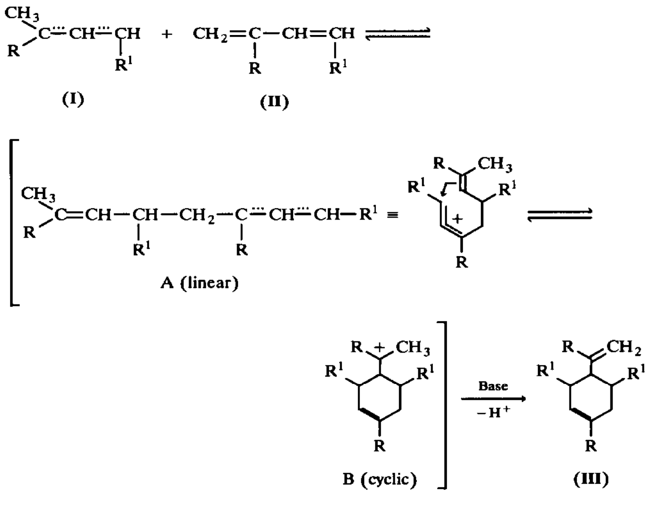
## Abstract

The behaviour of 2-methylene-3-ferrocenylmethylenecamphane under proton cyclodimerization conditions has been investigated. The stage involving the formation of the dimeric linear allylic cation has been confirmed in these interactions by isolating of corresponding diene. Its structure has been established unambiguously by X-ray methods. All substances isolated have been characterized by elemental analyses and $^1H$ and $^{13}C$ NMR spectral data.

*Key words:* Iron; Crystal structure; Cyclodimerization

## 1. Introduction

Earlier we reported [1–3] that ferrocenylallylic cations **I** react with ferrocenyl-1,3-butadienes **II** to form cation [4 + 2]-cycloaddition products, *i.e.* 1,3,4,5-tetrasubstituted cyclohexenes **III**, according to a scheme which involves a number of stages:



($R = R^1 = Fc$; $R = Fc$, $R^1 = Ar$; $R = Ar$, $R^1 = Fc$: $Fc = C_5H_5FeC_5H_4$–)

In our papers we actually postulated the stage in the mechanism of cycloaddition involving formation of the intermediate dimeric linear allylic cation A through the addition of the methylferrocenylallylic cation **I** via a secondary cation centre to the terminal methylene group of diene **II**. In order to complete the reaction we used dimethylaniline (or pyridine) which simply reacted as a deprotonating agent in all cases. However, deprotonation took place at the stage at which the dimeric cyclic tertiary cation B is formed.

This suggested stepwise mechanism for cycloaddition could be proved if the alkylation products of dimethylaniline with the linear dimeric cation A could be isolated, as achieved earlier for a number of monomeric ferrocenylallylic cations [4–7]. However, numerous attempts to isolate such products have proved unsuccessful. As a result, the formation and existence of cation A in the above equilibrium system A ⇌ B should only strictly be considered as hypothetical.

## 2. Results and discussion

In the present work we report that on conducting the proton cyclodimerization of 2-methylene-3-ferrocenylmethylenecamphane (**IV**), *i.e.* the 1,3-diene with an *S-cis* double-bond conformation, we have succeeded

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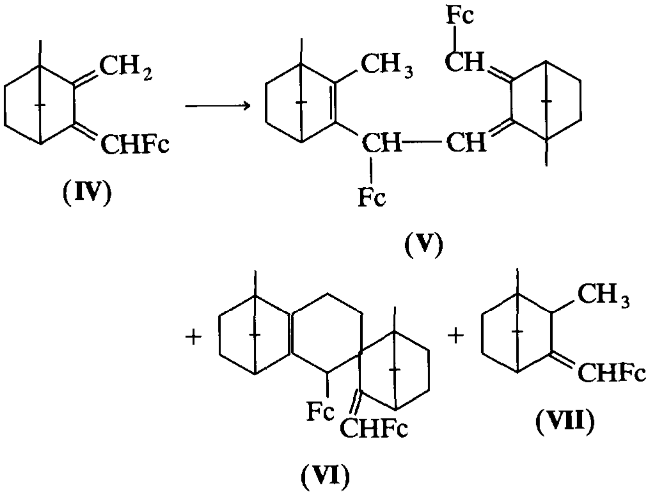
TABLE 1. $^1$H NMR spectral data for compounds **IV**, **V**, **VI**, **VII**, **IXb**, **X** and **XI** [$\delta$ (ppm), multiplicity, integral intensity; $J$ (Hz)]

| Compound | $CH_3$ | $CH_2$, OH | CH | $C_5H_5$ | $C_5H_4$ | CH=, AR |
|---|---|---|---|---|---|---|
| **IV** | 0.80 s, 3H; 0.97 s, 3H; 1.05 s, 3H | 1.30–2.00 m, 4H; 4.70 s, 1H; 5.20 s, 1H | 2.83 m, 1H | 4.08 s, 5H | 4.20 m, 2H; 4.40 m, 2H | 6.48 s, 1H |
| **V** | 0.78 s, 3H; 0.80 s, 3H; 1.12 s, 3H; 0.94 s, 6H; 1.14 s, 3H; 1.53 s, 3H | 1.42 m; 1.76 m; 1.95 m, 8H | 2.82 m, 2H; 6.35 d, 1H; $J$ = 6.4 | 4.13 s, 5H<br>4.14 s, 5H | 4.1–4.22 m, 4H; 4.3–4.4 m, 4H | 7.25 s, 1H; 6.58 d, 1H; $J$ = 6.0 |
| **VI** | 0.68 s, 3H; 0.71 s, 3H; 0.86 s, 3H; 0.91 s, 3H; 0.93 s, 3H; 0.94 s, 3H | 1.12–1.43 m; 1.95–2.20 m, 8H | 2.80–2.90 m, 3H | 4.09 s, 5H<br>4.11 s, 5H | 4.0–4.50 m, 8H | 6.09 s, 1H |
| **VII** | 0.73 s, 3H; 0.80 s, 3H; 0.93 s, 3H; 1.30 d, 3H; $J$ = 7.1 | 1.55–2.00 m, 4H | 2.2–2.7 m, 2H | 4.0 s, 5H | 4.1–4.22 m, 4H | 7.20 s, 1H |
| **IXb** | 0.67 s, 3H; 0.91 s, 3H; 1.13 s, 3H; 1.83 s, 3H | 2.15 m; 2.56–2.64 m, 4H | 3.48 m, 1H | 4.59 s, 5H | 4.8–5.2 m; 5.8–6.1 m, 4H | 8.38 s, 1H |
| **X** | 0.93 s, 6H; 1.10 s, 3H; 1.34 s, 3H | 1.32–2.10 m, 4H; 1.52 s, 1H | 2.77 m, 1H | 4.0 s, 5H | 4.13 m; 4.40 m, 4H | 6.13 s, 1H |
| **XI** | 0.60 s, 3H; 0.70 s, 3H; 0.87 s, 3H | 1.23–1.53 m; 2.05–2.20 m, 6H | 2.50 m, 1H; 3.4–3.8 m, 3H | 4.17 s, 5H | 4.05–4.01 m, 4H | 7.0–7.4 m, 5H |

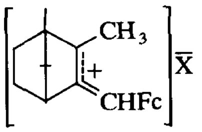
for the first time in isolating the linear dimer **V**. In addition, we have obtained the Diels–Alder adduct **VI** and the alkene **VII**:



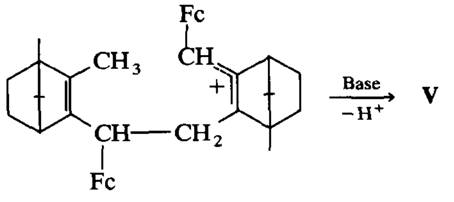
(IV) (V) (VI) (VII)

The structures of the compounds obtained have been confirmed by $^1$H and $^{13}$C NMR spectral data (Tables 1 and 2). Their melting points, yields and elemental analysis data are listed in Table 3.

The linear dimer **V** could obviously be formed as a result of the deprotonation of the intermediate dimeric linear allylic cation **VIII** in a similar manner to cation A:



(IX)

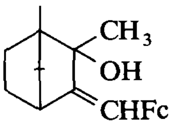


(VIII)

(a) X = BPh$_4$; (b) X = BF$_4$

Considering **V** as the key substance, we have investigated its structure by X-ray methods. Crystals of **V** were triclinic; $a$, 11.59(2); $b$, 11.89(2); $c$, 14.01(2) Å; $\alpha$, 67.85(2); $\beta$, 87.22(2); $\gamma$, 83.00(2)°; $Z = 2$; space group $P\bar{1}$. The intensities of 2489 reflections with $|F| \geqslant 3\sigma|F|$ (total number of reflections, 5890) were measured with a CAD diffractometer ($\lambda$ Mo$K\alpha$) at room temperature. The final discrepancy factor $R$ was 0.062. The positional parameters and their estimated standard deviations are listed in Table 4, with the bond lengths and bond angles in Tables 5 and 6, respectively (see Fig. 1 for details of atomic numbering).

The X-ray data confirm that diene **V** is formed strictly in accordance with the rules for the addition of the monoferrocenylallylic cation **IX** to the monoferrocenyldiene **IV**. The tetraphenylborate of the allylic cation **IXa** may be obtained both from 2-methylene-3-ferrocenylmethylenecamphane (**IV**) and from the allylic carbinol **X** and NaBPh$_4$ in acetic acid solution; the corresponding tetrafluoroborate **IXb** may be obtained by the use of HBF$_4$. The formation of spirane **VI** can be readily explained in terms of the usual cyclodimerization involving the Diels–Alder reaction. Alkene **VII** is the product of the reduction of both the tetraphenylborate **IXa** and the tetrafluoroborate **IXb**.



(X)

It should be stressed, however, that even under conditions sufficient to allow the usual proton cyclodimerization of *S-trans/S-cis*-ferrocenyl-1,3-butadienes [1–3], it has not proved possible to obtain the spirane cyclodimer. Thus, the treatment of salts **IXa,b** with bases at room temperature, for example, leads to the generation of diene **IV** alone in quantitative

TABLE 2. $^{13}$C NMR spectral data for compounds V and VI [$\delta$ (ppm)]

| Atomic group | Compound V | Compound VI |
|---|---|---|
| $C_5H_5$ | 68.64; 69.19 | 68.24; 68.33 |
| $C_5H_4$ | 68.29–69.68 | 66.53–69.90 |
| $C_sFc$ | 83.92; 84.06 | 83.83; 83.85 |
| CH= | 121.28; 121.48 | 120.07 |
| C | 149.24; 149.05; 144.17; 144.14; 48.15; 48.25; 52.70; 52.79 | 143.81; 139.96; 135.50; 47.31; 47.11; 54.85; 55.13; 52.62 |
| CHFc | 68.17 | 52.96 |
| $CH_3$ | 12.72; 13.09; 18.68; 18.72; 20.43; 20.52 | 10.88; 11.83; 13.08; 18.72; 19.42; 19.72 |
| $CH_2$ | 25.62; 26.16; 35.04; 35.68 | 25.78; 26.43; 26.68; 32.33; 32.53; 34.21 |
| CH | 52.14; 52.17 | 52.10; 52.42 |

TABLE 3. Melting points, yields and elemental analysis data for compounds synthesized

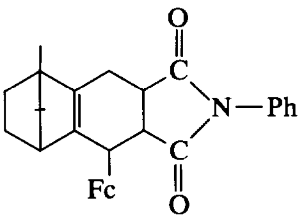
| Compound | M.p. (°C) | Yield (%) | Found (%) | | | Molecular formula | Calculated | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | Fe | | C | H | Fe |
| **IV** | 73–74 | 80 | 76.20 | 7.63 | 16.35 | $C_{22}H_{26}Fe$ | 76.30 | 7.57 | 16.13 |
| **V** [a] | 219–220 | 32 | 76.41 | 7.44 | 16.20 | $C_{44}H_{52}Fe_2$ | 76.30 | 7.57 | 16.13 |
| **V** [b] | 219–221 | 81 | 76.16 | 7.68 | 16.07 | $C_{44}H_{52}Fe_2$ | 76.30 | 7.57 | 16.13 |
| **VI** | 209–210 | 16 | 76.12 | 7.80 | 15.94 | $C_{44}H_{52}Fe_2$ | 76.30 | 7.57 | 16.13 |
| **VII** | 84–85 | 20 | 75.77 | 7.93 | 16.25 | $C_{22}H_{28}Fe$ | 75.86 | 8.10 | 16.04 |
| **IXb** | decomp. | 76 | 61.03 | 6.15 | 12.91 | $C_{22}H_{27}BF_4Fe$ | 60.87 | 6.27 | 12.86 |
| **X** | 96–97 | 43 | 72.48 | 7.80 | 15.28 | $C_{22}H_{28}FeO$ | 72.53 | 7.74 | 15.33 |
| **XI** | decomp. 260 | 83 | 73.71 | 6.52 | 10.84 | $C_{32}H_{33}FeNO_2$ | 74.00 | 6.40 | 10.75 |

[a] From diene **IV** (or carbinol **X**) in the presence of $NaBPh_4$ and $CH_3COOH$.

[b] By mixing solutions containing equimolar quantities of dienes **IV** and fluoroborates **IXb** in $CH_2Cl_2$ followed by base addition.

TABLE 4. Positional parameters and their estimated standard deviations

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ (Å$^2$) |
|---|---|---|---|---|
| $Fe_1$ | 0.0926(1) | 0.7307(1) | 0.2354(1) | 3.36(3) |
| $Fe_2$ | 0.3902(1) | 0.2127(1) | 0.0393(1) | 3.27(3) |
| $C_{01}$ | 0.3935(8) | 0.3325(8) | 0.3929(8) | 3.5(2) |
| $C_{02}$ | 0.4352(9) | 0.2416(9) | 0.4971(8) | 4.2(3) |
| $C_{03}$ | 0.375(1) | 0.119(1) | 0.502(1) | 8.1(5) |
| $C_{04}$ | 0.253(1) | 0.146(1) | 0.513(1) | 7.3(4) |
| $C_{05}$ | 0.2447(9) | 0.290(1) | 0.5107(8) | 4.5(3) |
| $C_{06}$ | 0.2788(7) | 0.3614(7) | 0.4015(7) | 2.9(2) |
| $C_{07}$ | 0.1971(8) | 0.4485(7) | 0.3180(7) | 2.9(2) |
| $C_{08}$ | 0.0782(8) | 0.4025(7) | 0.3279(6) | 2.6(2) |
| $C_{09}$ | 0.0448(7) | 0.3216(7) | 0.2939(6) | 2.6(2) |
| $C_{10}$ | −0.0791(8) | 0.2823(8) | 0.3077(7) | 3.1(2) |
| $C_{11}$ | −0.0651(9) | 0.1498(9) | 0.3879(9) | 4.8(3) |
| $C_{12}$ | −0.003(1) | 0.0756(9) | 0.3296(9) | 5.1(3) |
| $C_{13}$ | 0.0159(9) | 0.1772(9) | 0.2203(8) | 4.6(3) |
| $C_{14}$ | 0.1073(8) | 0.2493(7) | 0.2381(7) | 2.8(2) |
| $C_{15}$ | 0.2189(9) | 0.2359(8) | 0.2151(7) | 3.7(2) |
| $C_{16}$ | 0.561(1) | 0.206(1) | 0.516(1) | 6.9(4) |
| $C_{17}$ | 0.352(1) | 0.271(1) | 0.5680(9) | 7.4(4) |
| $C_{18}$ | 0.353(1) | 0.171(1) | 0.680(1) | 8.7(5) |
| $C_{19}$ | 0.374(2) | 0.393(1) | 0.5708(9) | 8.9(5) |
| $C_{20}$ | −0.1710(9) | 0.3645(9) | 0.3401(8) | 4.4(3) |
| $C_{21}$ | −0.0960(9) | 0.2621(9) | 0.2095(8) | 4.6(3) |
| $C_{22}$ | −0.092(1) | 0.380(1) ' | 0.1138(8) | 5.4(3) |
| $C_{23}$ | −0.206(1) | 0.203(1) | 0.2089(9) | 6.4(3) |
| $C_{24}$ | 0.1879(8) | 0.5737(8) | 0.3248(7) | 3.3(2) |
| $C_{34}$ | 0.2753(8) | 0.1614(7) | 0.1603(7) | 3.2(2) |
| $C_{44}$ | 0.470(1) | 0.374(1) | 0.2989(8) | 5.5(3) |



(XI)

yield. The latter with *N*-phenylmaleinimide gives the adduct **XI**. On refluxing solutions of diene **IV** or

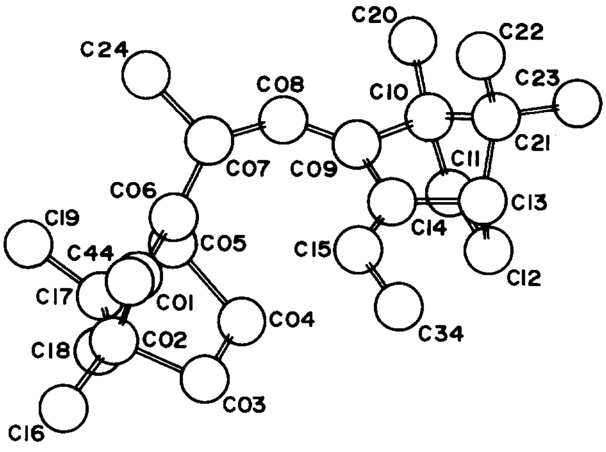


Fig. 1.

TABLE 5. Bond distances (Å)

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| $Fe_1$ | $C_{24}$ | 2.035(8) | $C_{13}$ | $C_{21}$ | 1.52(1) | $C_{13}$ | $H_{13}$ | 0.96(1) |
| $C_{14}$ | $C_{15}$ | 1.32(1) | $C_{15}$ | $C_{34}$ | 1.46(1) | $C_{15}$ | $H_{15}$ | 0.98(1) |
| $C_{16}$ | $H_{16}^{1}$ | 0.97(1) | $C_{16}$ | $H_{16}^{2}$ | 0.98(2) | $C_{16}$ | $H_{16}^{3}$ | 0.93(1) |
| $C_{17}$ | $C_{18}$ | 1.57(2) | $C_{17}$ | $C_{19}$ | 1.52(2) | $C_{01}$ | $C_{02}$ | 1.51(1) |
| $C_{01}$ | $C_{06}$ | 1.34(1) | $C_{18}$ | $H_{18}^{1}$ | 0.96(2) | $C_{01}$ | $C_{44}$ | 1.50(1) |
| $C_{18}$ | $H_{18}^{1}$ | 0.96(2) | $C_{18}$ | $H_{18}^{3}$ | 0.96(1) | $C_{19}$ | $H_{19}^{1}$ | 0.97(2) |
| $C_{19}$ | $H_{19}^{2}$ | 0.95(2) | $C_{19}$ | $H_{19}^{3}$ | 0.97(1) | $C_{02}$ | $C_{03}$ | 1.67(2) |
| $C_{02}$ | $C_{16}$ | 1.47(2) | $C_{20}$ | $H_{20}^{1}$ | 0.96(1) | $C_{20}$ | $H_{20}^{2}$ | 0.945(9) |
| $C_{02}$ | $C_{17}$ | 1.46(2) | $C_{20}$ | $H_{20}^{3}$ | 0.96(1) | $C_{21}$ | $C_{22}$ | 1.53(1) |
| $C_{21}$ | $C_{23}$ | 1.53(2) | $C_{03}$ | $C_{04}$ | 1.42(2) | $C_{03}$ | $H_{03}^{1}$ | 0.98(2) |
| $C_{03}$ | $H_{03}^{2}$ | 0.97(1) | $C_{04}$ | $C_{05}$ | 1.68(2) | $C_{22}$ | $H_{22}^{1}$ | 0.96(1) |
| $C_{22}$ | $H_{22}^{2}$ | 0.97(2) | $C_{04}$ | $H_{04}^{1}$ | 0.99(2) | $C_{22}$ | $H_{22}^{3}$ | 0.97(1) |
| $C_{04}$ | $H_{04}^{2}$ | 0.99(1) | $C_{23}$ | $H_{23}^{1}$ | 0.96(1) | $C_{23}$ | $H_{23}^{2}$ | 0.94(1) |
| $C_{05}$ | $C_{06}$ | 1.51(1) | $C_{05}$ | $C_{17}$ | 1.47(2) | $C_{23}$ | $H_{23}^{3}$ | 0.96(1) |
| $C_{05}$ | $H_{05}$ | 0.97(1) | $C_{06}$ | $C_{07}$ | 1.51(1) | $C_{07}$ | $C_{08}$ | 1.52(1) |
| $C_{07}$ | $C_{24}$ | 1.52(1) | $C_{07}$ | $H_{07}$ | 0.95(1) | $C_{08}$ | $C_{09}$ | 1.33(1) |
| $C_{08}$ | $H_{08}$ | 0.95(9) | $C_{09}$ | $C_{10}$ | 1.54(1) | $C_{09}$ | $C_{14}$ | 1.48(1) |
| $C_{10}$ | $C_{11}$ | 1.55(1) | $C_{10}$ | $C_{20}$ | 1.53(1) | $C_{10}$ | $C_{21}$ | 1.51(2) |
| $C_{11}$ | $C_{12}$ | 1.50(2) | $C_{11}$ | $H_{11}^{1}$ | 0.95(1) | $C_{11}$ | $H_{11}^{2}$ | 0.97(1) |
| $C_{12}$ | $C_{13}$ | 1.58(1) | $C_{12}$ | $H_{12}^{1}$ | 0.96(1) | $C_{12}$ | $H_{12}^{2}$ | 0.95(1) |
| $C_{13}$ | $C_{14}$ | 1.53(2) | $Fe_2$ | $C_{34}$ | 2.054(9) | | | |

TABLE 6. Bond angles (°)

| | | | | | |
|---|---|---|---|---|---|
| $C_{17}-C_{18}-H_{18}^{1}$ | 112.0(1) | $C_{17}-C_{18}-H_{18}^{2}$ | 110.0(1) | $C_{17}-C_{18}-H_{18}^{3}$ | 111.0(1) |
| $H_{18}^{1}-C_{18}-H_{18}^{2}$ | 108.(1) | $H_{18}^{1}-C_{18}-H_{18}^{3}$ | 108.(2) | $H_{18}^{2}-C_{18}-H_{18}^{3}$ | 108.(1) |
| $C_{17}-C_{19}-H_{19}^{1}$ | 111.(1) | $C_{17}-C_{19}-H_{19}^{2}$ | 112.(1) | $C_{17}-C_{19}-H_{19}^{3}$ | 111.(1) |
| $H_{19}^{1}-C_{19}-H_{19}^{2}$ | 108.(1) | $H_{19}^{1}-C_{19}-H_{19}^{3}$ | 107.(1) | $H_{19}^{2}-C_{19}-H_{19}^{3}$ | 108.(1) |
| $C_{10}-C_{20}-H_{20}^{1}$ | 109.7(8) | $C_{10}-C_{20}-H_{20}^{2}$ | 110.4(9) | $C_{10}-C_{20}-H_{20}^{3}$ | 111.(1) |
| $H_{20}^{1}-C_{20}-H_{20}^{2}$ | 109.(1) | $H_{20}^{1}-C_{20}-H_{20}^{3}$ | 108.(1) | $H_{20}^{2}-C_{20}-H_{20}^{3}$ | 109.1(9) |
| $C_{10}-C_{21}-C_{13}$ | 94.7(8) | $C_{10}-C_{21}-C_{22}$ | 112 (1) | $C_{10}-C_{21}-C_{23}$ | 113.8(9) |
| $C_{10}-C_{21}-H_{13}$ | 118.7(6) | $C_{10}-C_{21}-H_{22}^{1}$ | 137.0(7) | $C_{10}-C_{21}-H_{22}^{2}$ | 98.0(7) |
| $C_{10}-C_{21}-H_{22}^{3}$ | 97.9(7) | $C_{10}-C_{21}-H_{23}^{1}$ | 139.7(7) | $C_{01}-C_{44}-H_{44}^{1}$ | 109.(1) |
| $C_{10}-C_{21}-H_{23}^{2}$ | 99.5(6) | $C_{10}-C_{21}-H_{23}^{3}$ | 99.6(6) | $C_{01}-C_{44}-H_{44}^{2}$ | 109.(1) |
| $C_{01}-C_{44}-H_{44}^{3}$ | 109.(1) | $H_{44}^{1}-C_{44}-H_{44}^{2}$ | 109.(1) | $H_{44}^{1}-C_{44}-H_{44}^{3}$ | 109.(1) |
| $C_{13}-C_{21}-C_{22}$ | 110.9(8) | $C_{13}-C_{21}-C_{23}$ | 114.(1) | $H_{44}^{2}-C_{44}-H_{44}^{3}$ | 109.(1) |
| $C_{13}-C_{21}-H_{13}$ | 24.0(5) | $C_{13}-C_{21}-H_{22}^{1}$ | 102.9(7) | $C_{13}-C_{21}-H_{22}^{2}$ | 134.9(7) |
| $C_{13}-C_{21}-H_{22}^{3}$ | 92.0(6) | $C_{13}-C_{21}-H_{23}^{1}$ | 104.9(8) | $C_{13}-C_{21}-H_{23}^{2}$ | 96.6(6) |
| $C_{13}-C_{21}-H_{23}^{3}$ | 139.9(8) | $C_{22}-C_{21}-C_{23}$ | 110.3(9) | $C_{22}-C_{21}-H_{13}$ | 99.4(7) |
| $H_{22}^{1}-C_{22}-H_{22}^{2}$ | 107.(1) | $H_{22}^{1}-C_{22}-H_{22}^{3}$ | 107.(1) | $H_{22}^{2}-C_{22}-H_{22}^{3}$ | 106.(1) |
| $C_{02}-C_{01}-C_{06}$ | 107.0(8) | $C_{21}-C_{23}-H_{23}^{1}$ | 110.1(1) | $C_{21}-C_{23}-H_{23}^{2}$ | 111.(1) |
| $C_{02}-C_{01}-C_{44}$ | 124.1(8) | $C_{21}-C_{23}-H_{23}^{3}$ | 109.(1) | $H_{23}^{1}-C_{23}-H_{23}^{2}$ | 110.(1) |
| $H_{23}^{1}-C_{23}-H_{23}^{3}$ | 108.(1) | $H_{23}^{2}-C_{23}-H_{23}^{3}$ | 109.(1) | $C_{06}-C_{01}-C_{44}$ | 128.8(8) |
| $Fe_{1}-C_{24}-C_{07}$ | 128.4(7) | $C_{01}-C_{02}-C_{03}$ | 100.6(9) | $C_{01}-C_{02}-C_{16}$ | 119.4(9) |
| $C_{01}-C_{02}-C_{17}$ | 103.0(9) | $C_{03}-C_{02}-C_{16}$ | 108.(1) | $C_{03}-C_{02}-C_{17}$ | 95 (1) |
| $C_{16}-C_{02}-C_{17}$ | 125 (1) | $C_{02}-C_{03}-C_{04}$ | 106.(1) | $H_{03}^{1}-C_{03}-H_{03}^{2}$ | 106.(1) |
| $C_{03}-C_{04}-C_{05}$ | 102.(1) | $H_{04}^{1}-C_{04}-H_{04}^{2}$ | 103.(1) | $C_{04}-C_{05}-C_{06}$ | 102.(1) |
| $C_{04}-C_{05}-C_{17}$ | 96.0(9) | $C_{06}-C_{05}-C_{17}$ | 103.0(8) | $C_{01}-C_{06}-C_{05}$ | 107.1(7) |
| $C_{01}-C_{06}-C_{07}$ | 127.3(8) | $C_{05}-C_{06}-C_{07}$ | 125.6(8) | $C_{06}-C_{07}-C_{08}$ | 111.1(6) |
| $C_{06}-C_{07}-C_{24}$ | 108.5(8) | $C_{08}-C_{07}-C_{24}$ | 111.4(7) | $C_{07}-C_{08}-C_{09}$ | 128.5(8) |
| $C_{08}-C_{09}-C_{10}$ | 124.1(8) | $C_{08}-C_{09}-C_{14}$ | 132.1(8) | $C_{10}-C_{09}-C_{14}$ | 103.(8) |
| $C_{09}-C_{10}-C_{11}$ | 104.6(7) | $C_{09}-C_{10}-C_{20}$ | 115.0(9) | $C_{09}-C_{10}-C_{21}$ | 102.4(8) |
| $C_{11}-C_{10}-C_{20}$ | 112.3(8) | $C_{11}-C_{10}-C_{21}$ | 101.4(9) | $C_{20}-C_{10}-C_{21}$ | 119.3(8) |
| $C_{10}-C_{11}-C_{12}$ | 104.3(8) | $Fe_{2}-C_{34}-C_{15}$ | 127.5(6) | $Fe_{2}-C_{34}-H_{15}$ | 109.1(4) |
| $H_{11}^{1}-C_{11}-H_{11}^{2}$ | 108.(1) | $C_{11}-C_{12}-C_{13}$ | 102.4(8) | $H_{12}^{1}-C_{12}-H_{12}^{2}$ | 108.2(9) |
| $C_{12}-C_{13}-C_{14}$ | 104.7(9) | $C_{12}-C_{13}-C_{21}$ | 100.6(8) | $C_{14}-C_{13}-C_{21}$ | 103.2(8) |
| $C_{09}-C_{14}-C_{13}$ | 104.5(8) | $C_{09}-C_{14}-C_{15}$ | 130.(1) | $C_{13}-C_{14}-C_{15}$ | 125.(1) |
| $C_{14}-C_{15}-C_{34}$ | 128.(1) | $H_{16}^{1}-C_{16}-H_{16}^{2}$ | 105.(1) | $H_{16}^{1}-C_{16}-H_{16}^{3}$ | 110.(2) |
| $H_{16}^{2}-C_{16}-H_{16}^{3}$ | 109.(1) | $C_{02}-C_{17}-C_{05}$ | 99.(1) | $C_{02}-C_{17}-C_{18}$ | 115.(1) |
| $C_{02}-C_{17}-C_{19}$ | 109.(1) | $C_{05}-C_{17}-C_{18}$ | 114.(1) | $C_{05}-C_{17}-C_{19}$ | 108.(1) |
| $C_{18}-C_{17}-C_{19}$ | 111.(1) | | | | |

carbinol **X** in excess of acetic acid, only the reduction product **VII** is obtained. Below 20°C in the presence of small amounts of acetic acid, a polymer was obtained. Its structure has not been established to date.

The peculiarities in the behaviour of 2-methylene-3-ferrocenylmethylenecamphane (**IV**) under conditions which normally lead to the proton cyclodimerization of ferrocenylbutadienes and, in particular, the high stereoselectivity of its reactions, are related in many respects to the spatial effects of the camphane moiety as well as to the high stability of ferrocenyl carbocations. The combination of these two factors, however, has allowed us in turn to establish the intermediate stage in the addition of the methylferrocenylallylic cation **IX** to diene **IV**.

## 3. Experimental details

NMR spectra were obtained using a WXR-400 instrument with $CDCl_3$ solutions using TMS as an internal standard. Glacial acetic acid was used in the various experiments whereas the tetraphenyl- and tetrafluoro-borates of the allylic cations **IXa,b** were dissolved in $CH_2Cl_2$. The products of the reactions were separated and purified by chromatography on $Al_2O_3$-II. For the various melting points, yields and elemental analysis data, see Table 3. Carbinol **X** was prepared by a standard method [1] starting from ferrocenylmethylenecamphor and methyllithium.

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