Photochemical transformations of 3-alkyl-3-ferrocenylcyclopropenes

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Photolysis of 3-ferrocenyl-3-methyl- and 3-ferrocenyl-3-isopropylcyclopropenes was studied. Sensitized irradiation (triplet excitation) afforded [2+2]-cycloaddition products, *viz.*, tricyclohexane derivatives. Direct irradiation (singlet excitation) of methyl-substituted ferrocenylcyclopropene gave rise to 2-ferrocenylbut-1-en-3-yne and *trans*-2-ferrocenylbut-2-ene. The isopropyl analog was converted into 1-ferrocenyl-4,4-dimethylcyclobutene. The reaction of this cyclopropene with 2-ferrocenyl-3-methylbut-1-ene afforded 1,3-diferrocenyl-3-isopropyl-6,6-dimethylcyclohexene. The latter compound and 3,6-diferrocenyl-3,6-diisopropyltricyclo[3.1.0.0^{2,4}]hexane were studied by X-ray diffraction analysis. Possible reaction pathways are discussed.

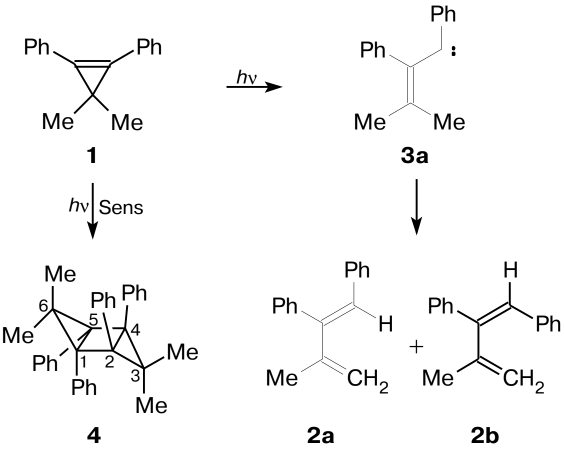
Key words: photolysis, ferrocenylcyclopropene, tricyclohexane, vinylcarbenes, cyclobutene, X-ray diffraction analysis.

The photochemical properties of most compounds of the cyclopropene series containing alkyl or aryl substituents in the small ring depend substantially on the multiplicity of the excited state.[1] Direct irradiation (singlet excitation), like thermolysis, leads to the cleavage of the σ bond of cyclopropenes to form vinylcarbene intermediates, which are then converted into unsaturated compounds. Thus direct irradiation of 3,3-dimethyl-1,2-diphenylcyclopropene (**1**) afforded two isomeric 3-methyl-1,2-diphenylbuta-1,3-dienes **2a** and **2b** (Scheme 1) generated from intermediate vinylcarbene **3a**.[2]

Irradiation of cyclopropene **1** in the presence of sensitizing agents (triplet excitation) gave rise to a [2+2]-cyclodimerization adduct, *viz.*, 3,3,6,6-tetramethyl-1,2,4,5-tetraphenyltricyclo[3.1.0.0^{2,4}]hexane (**4**).[3]

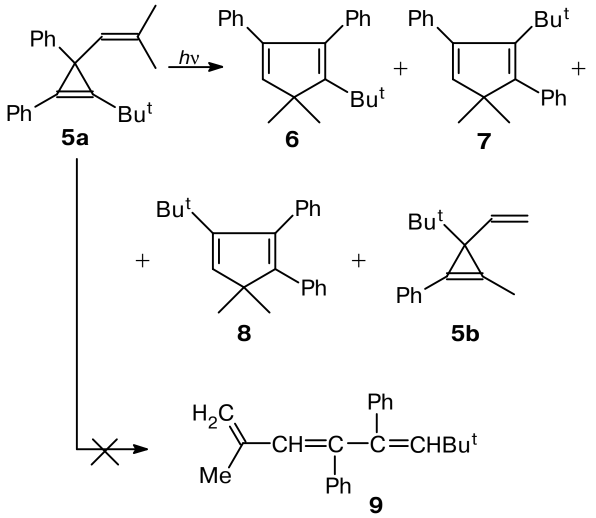
Photolysis of 3-vinyl-substituted cyclopropenes afforded predominantly mixtures of isomeric cyclopentadiene compounds independently of the multiplicity of the excited state. For example, 1-*tert*-butyl-3-isobutenyl-2,3-diphenylcyclopropene (**5a**)[4,5] was converted into three cyclopentadiene products **6**—**8** and isomeric cyclopropene **5b** irrespective of the mode of irradiation (Scheme 2). Triene compounds with a linear structure of type **9** were not found among the photoreaction products.

Scheme 1



Sens is a sensitizing agent

Scheme 2



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It was suggested[4,5] that photochemical transformations of 3-vinylcyclopropenes proceed according to a mechanism involving the formation of biradical intermediates.[6,7]

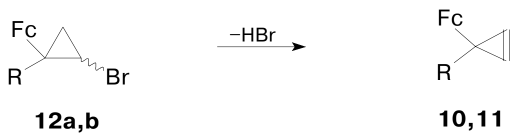
Recently, it has been demonstrated[8–11] that thermolysis of cyclopropenes containing the ferrocene substituent at position 3 of the three-carbon ring also proceeded through the formation of ferrocenylvinylcarbene intermediates followed by their transformations or disproportionation.

Photochemical transformations of ferrocenylcyclopropenes are as yet unknown. Photolysis of compounds of the ferrocene series is characterized by the possibility of cleavage of the iron—cyclopentadienyl ring bond. The cleavage proceeds particularly readily in the case of ferrocene derivatives, which contain an atom bearing the complete or partial positive charge at the α position with respect to the cyclopentadienyl ring.[12–14] In 3-ferrocenylcyclopropenes, the carbon atom possessing high electron density is located at the α position with respect to the cyclopentadienyl ring of metallocene.[15–17] Hence, one would expect that the organometallic system will be retained in photochemical processes upon transformations of the three-carbon ring.

Results and Discussion

In the present work, we studied the photolysis of 3-ferrocenyl-3-methyl- and 3-ferrocenyl-3-isopropylcyclopropenes **10** and **11**, which were prepared by dehydrobromination of the corresponding bromoferrocenylcyclopropanes **12a,b** under the action of Bu^tOK in DMSO [8,9] (Scheme 3).

Scheme 3

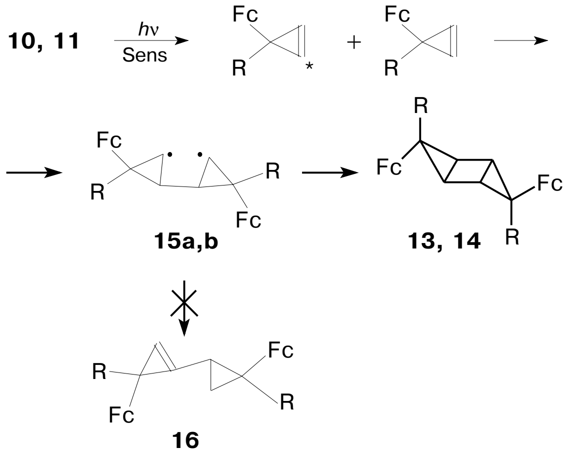


R = Me (**10**, **12a**); Pr^i (**11**, **12b**)

Freshly prepared samples were used for photolysis because compounds **10** and **11** are unstable on storage under ordinary conditions.

Photolysis of 3-alkyl-3-ferrocenylcyclopropenes 10 and 11 in the presence of a sensitizing agent. Analysis of the ^1H NMR spectra of the reaction mixture obtained after irradiation of cyclopropenes **10** and **11** in a solution in acetonitrile in the presence of benzophenone demonstrated that the formation of dimeric products **13** and **14** in both cases (Scheme 4) proceeded stereospecifically to give one of the diastereomeric tricyclohexanes. The formation of dimers was supported by the disappearance of the signals for the olefinic protons of the initial cyclopropenes (at δ 7.15 and 6.95) and the appearance of high-field singlets for the protons of the tricyclohexane fragment (at δ 1.64 and 1.58). Dimers **13** and **14** were isolated by column chromatography on Al_2O_3 in 73 and 70% yields, respectively.

Scheme 4



R = Me (**10**, **13**, **15a**); Pr^i (**11**, **14**, **15b**)

The structure of tricyclohexane **14** was established by X-ray diffraction analysis. The overall view of molecule **14** is shown in Fig. 1. The principal bond lengths and bond angles are given in Table 1. An interesting feature of the crystal structure of **14** is the presence of one molecule per unit cell.

Compound **14** has the structure of 3,6-diferrocenyl-*anti,anti*-3,6-diisopropyltricyclo[3.1.0.0^{2,4}]hexane. The central four-membered ring is planar. The dihedral angle between the three- and four-membered rings is 114°. The C(12)—C(13) and C(12a)—C(13a) bonds are somewhat longer (1.557 Å), whereas the C(12)—C(13a) and C(12a)—C(13) bonds are somewhat shorter (1.500 Å) than the standard values (the standard C—C bond lengths in cyclopropanes and cyclobutanes are ~1.51 [18,19] and

Table 1. Principal bond lengths (*d*) and bond angles (ω) in molecule **14**

Parameter	Characteristic
Bond length	*d*/Å
C(11)—C(12)	1.521(13)
C(11)—C(13)	1.515(12)
C(12)—C(13)	1.557(15)
C(12a)—C(13a)	1.557(15)
C(12)—C(13a)	1.500(11)
C(12a)—C(13)	1.500(11)
Bond angle	ω/deg
C(13a)—C(12)—C(11)	113.9(9)
C(12a)—C(13)—C(11)	114.1(9)
C(11)—C(12)—C(13)	59.0(6)
C(12a)—C(13)—C(12)	90.0(9)

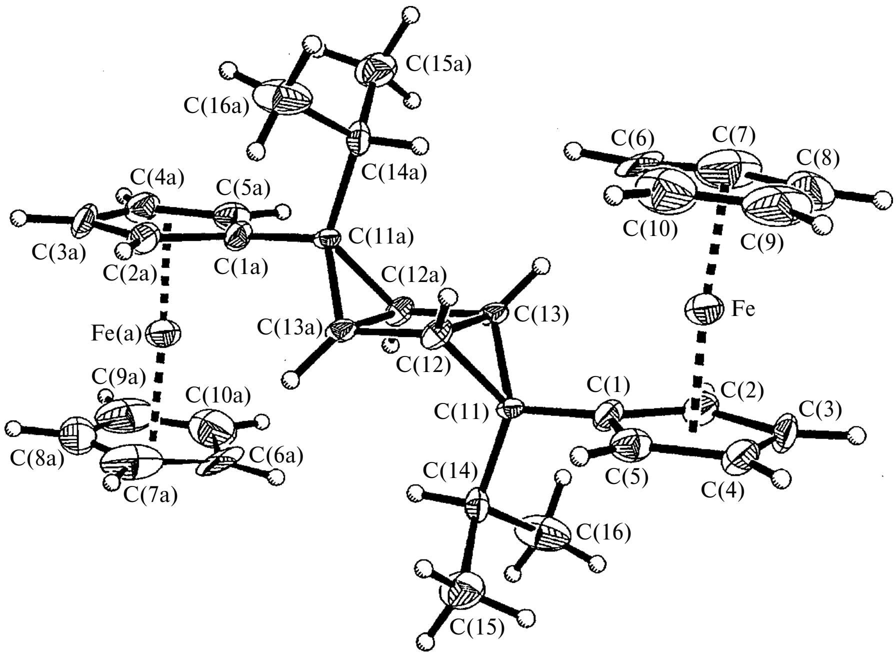


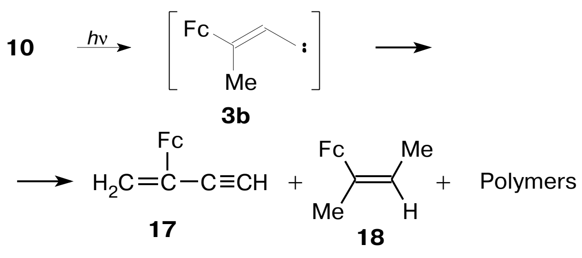
Fig. 1. Molecular structure of compound **14**.

~1.55 Å,[20–22] respectively). The average Fe—C bond length is 2.033 Å and the average C—C bond length in the cyclopentadienyl rings is 1.392 Å.

As expected, the cyclopropene fragments exclusively underwent photochemical transformations (as has been demonstrated for alkyl- and aryl-substituted cyclopropenes[5,23]), whereas the ferrocene fragments of the starting compounds **10** and **11** remained unchanged. A distinguishing feature of the photolysis of ferrocenyl-substituted cyclopropenes is the stereospecificity of the process. Apparently, dimerization proceeded according to an analogous stepwise mechanism involving the formation of biradical intermediates **15a,b**.[23] However, we did not detect cyclopropylcyclopropene dimers **16a,b**, which could support the stepwise character of the process, in the reaction mixture at all.

Direct photolysis of 3-alkyl-3-ferrocenylcyclopropenes 10 and 11. Direct photolysis of cyclopropene **10** gave rise to 2-ferrocenyl-but-1-en-3-yne (**17**) and *trans*-2-ferrocenylbut-2-ene (**18**)[24] in 23 and 30% yields, respectively, as well as to unidentified polymeric products (Scheme 5).

Scheme 5

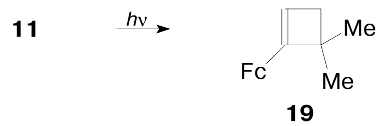


Undoubtedly, the reaction proceeds through the formation of ferrocenylvinylcarbene intermediate **3b** followed by its disproportionation.

Recently, we have described an analogous process in the case of pyrolysis of 3-alkyl-3-ferrocenylcyclopropenes (alkyl = Me, Pr^i, or *cyclo*-Bu).[24] The formation of α-ferrocenylvinylacetylenes and ferrocenylalkenes was the predominant process and occurred due to heterolysis of one of the σ bonds of the small ring to form ferrocenylvinylcarbenes followed by their transformations.

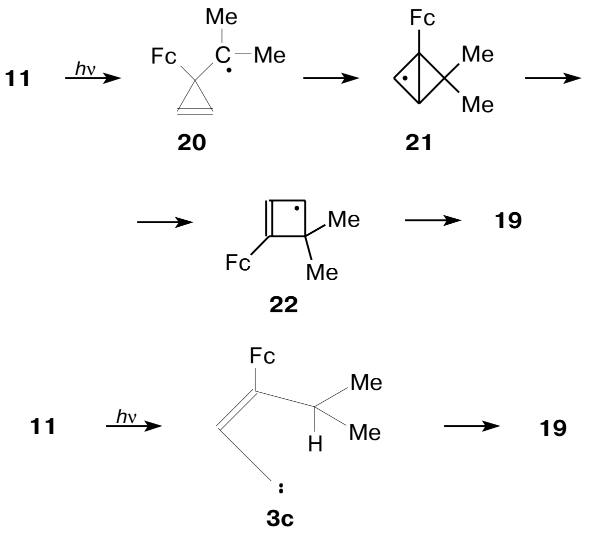
Direct irradiation of cyclopropene **11**, unlike that of cyclopropene **10**, resulted in substantial resinification of the reaction mixture from which only one product was isolated by chromatography (the yield was 27%). Based on the data from ^{1}H and ^{13}C NMR spectroscopy and elemental analysis, the structure of 1-ferrocenyl-4,4-dimethylcyclobutene (**19**) was assigned to the resulting product (Scheme 6). Compound **19** is an orange oily substance, which decomposes rather rapidly on storage even at low temperature.

Scheme 6



In our opinion, the formation of cyclobutene **19** can occur according to one of the two following schemes: *a*) generation of tertiary dimethylcyclopropenylmethyl radical **20** followed by its transformation to form the dicyclobutyl and cyclobutenyl radicals (**21** and **22**, respectively); or *b*) the insertion of intermediate vinylcarbene **3c** into the C—H bond of the isopropyl group (Scheme 7).

Scheme 7



With the aim of establishing the most probable scheme of direct photolysis of compound **11**, we carried out the photochemical reaction of cyclopropene **11** with 2-ferrocenyl-3-methylbut-1-ene (**23**) as a possible acceptor both of free radicals and vinylcarbenes. It appeared that the reaction proceeded regioselectively to form a single product in ~100% yield. The ^{1}H NMR spectrum of the resulting compound has signals of two ferrocenyl substituents, two methyl groups, and one isopropyl group, a singlet for one olefinic proton, and two multiplets of two methylene groups of the $CH_2—CH_2$ fragment, which corresponds to compound **24** or **25** (Scheme 8).

Scheme 8

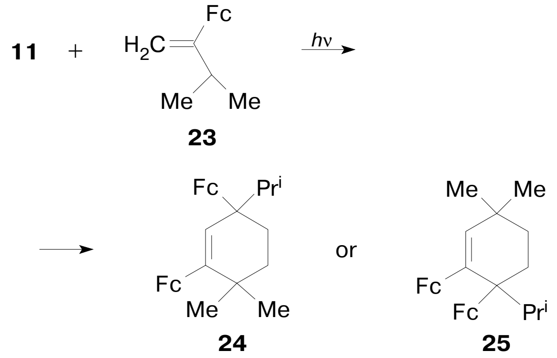


Table 2. Principal bond lengths (*d*) and bond angles (ω) in molecule **24**

Parameter	Characteristic
Bond length	*d*/Å
C(1)—C(2)	1.320(9)
C(2)—C(3)	1.514(8)
C(3)—C(4)	1.549(9)
C(4)—C(5)	1.505(10)
C(5)—C(6)	1.546(9)
C(1)—C(6)	1.528(9)
Bond angle	ω/deg
C(1)—C(6)—C(5)	108.6(6)
C(5)—C(4)—C(3)	112.5(6)
C(2)—C(1)—C(6)	123.0(5)
C(1)—C(2)—C(3)	127.5(6)
C(2)—C(3)—C(4)	107.6(5)
C(4)—C(5)—C(6)	112.3(5)
C(2)—C(1)—C(7)	120.4(6)
C(2)—C(3)—C(17)	108.7(5)
C(20)—C(3)—C(4)	110.1(5)

The crystal structure of the compound synthesized was established by X-ray diffraction analysis of single crystals obtained by crystallization from *n*-hexane. The results of X-ray study demonstrated that the product of direct photolysis of a mixture of compounds **11** and **23** has the structure of 1,3-diferrocenyl-3-isopropyl-6,6-dimethylcyclohexene **24** (Fig. 2). In molecule **24**, the six-membered ring adopts a half-chair conformation. The principal geometric parameters of **24** are given in Table 2. The average Fc_1—C and Fc_2—C distances are 2.035 and 2.051 Å, respectively. The average C—C bond lengths in the cyclopentadienyl rings are 1.406 Å (Fc_1) and 1.401 Å (Fc_2).

It should be noted that we did not detect substituted ferrocenylcyclopentenes of type **28** (whose analogs have been found previously in thermal processes[9]) among the products of the photochemical reaction of compound **11** with **23** (Scheme 9).

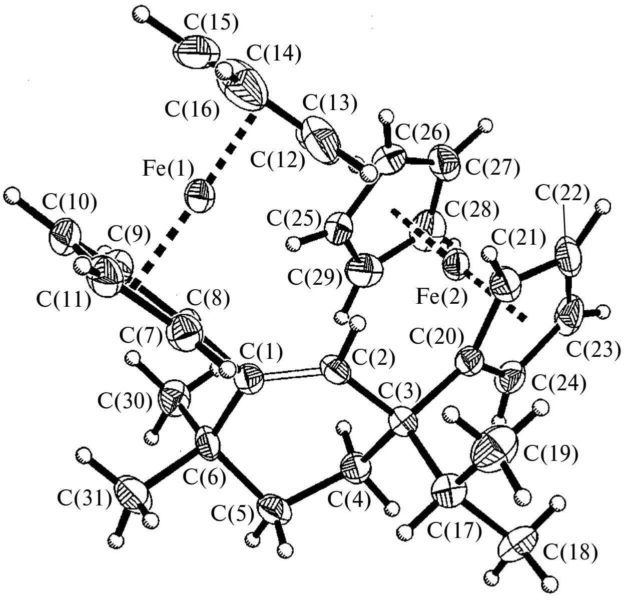
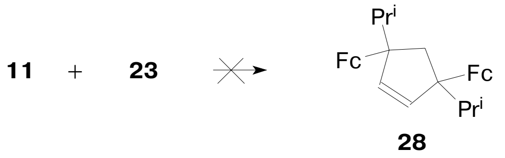


Fig. 2. Molecular structure of compound **24**.

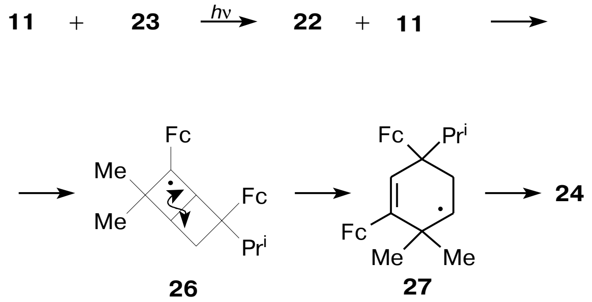
Scheme 9



At the same time, direct irradiation of cyclobutene **19** in the presence of alkene **23** did not give rise to cyclohexene **24**. We isolated the original components and unidentified polymeric products from the reaction mixture.

Based on the results of the present study, we concluded that direct photolysis of cyclopropene **11** follows the path *a*. Apparently, the appearance of dimethylcyclopropenylmethyl radical **20** is more favorable than the formation of vinylcarbene **3c**. The mechanism (Scheme 10) involving generation of the intermediate bicyclohexane and cyclohexene radicals (**26** and **27**, respectively) was proposed for the photochemcial reaction of cyclopropene **11** with butene **23**.

Scheme 10



It should be noted that data on studies of photochemical reactions of cyclopropene compounds in the presence of potential free-radical scavengers are lacking in the literature. In our opinion, the characteristic features of these processes and their mechanisms merit detailed investigation.

To summarize, our results demonstrate that the character of photochemical transformations of 3-alkyl-3-ferrocenylcyclopropenes **10** and **11** is affected both by the multiplicity of the excited state and the nature of the alkyl substituent, the metallocene fragment remaining intact in all photochemical reactions.

Experimental

The solvents were dried according to standard procedures and distilled before use. Column chromatography was carried out on Al_2O_3 (Brockmann activity III). The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz, respectively) in solutions in $CDCl_3$ with Me_4Si as the internal standard. All photochemical reactions were carried out under an atmosphere of dry nitrogen with the use of solvents which have been dried and freshly distilled under an inert atmosphere.

3-Alkyl-3-ferrocenylcyclopropenes 10 and 11 were synthesized by dehydrobromination of *Z*/*E*-1-alkyl-2-bromo-1-ferrocenylcyclopropanes **12a,b** under the action of Bu^tOK in DMSO.[8,9]

3-Ferrocenyl-3-methylcyclopropene (10) was obtained as an orange oil in 44% yield. ^1H NMR, δ: 1.46 (s, 3 H); 4.01 (m, 4 H, C_5H_4); 4.15 (s, 5 H, C_5H_5); 7.15 (s, 2 H, CH=).

3-Ferrocenyl-3-isopropylcyclopropene (11) was obtained as orange crystals in 61% yield, m.p. 62 °C. ^1H NMR, δ: 0.79 (d, 6 H, Me, J = 6.8 Hz); 2.41 (m, 1 H, CH, J = 6.8 Hz); 4.02 (m, 4 H, C_5H_4); 4.12 (s, 5 H, C_5H_5); 6.95 (s, 2 H, CH=).

Photolysis of cyclopropenes 10 and 11 in the presence of a sensitizing agent. A solution of cyclopropene **10** (0.24 g, 1 mmol) or cyclopropene **11** (0.27 g, 1 mmol) and benzophenone (5 mg) in MeCN (100 mL) was placed in a Pyrex container and irradiated using a 200 W Hanovia medium pressure lamp for 5 h. Then the solvent was distilled off *in vacuo* and the residue was chromatographed on a column with Al_2O_3 (hexane was used as the eluent) to obtain 3,6-diferrocenyl-3,6-dimethyltricyclo[3.1.0.0^{2,4}]hexane (**13**) or 3,6-differrocenyl-3,6-diisopropyltricyclo[3.1.0.0^{2,4}]hexane (**14**) in a yield of 0.18 g (73%) or 0.19 g (70%), respectively. Compound **13** was obtained as orange crystals, m.p. 131—132 °C. ^1H NMR, δ: 1.64 (s, 4 H, CH); 1.66 (s, 6 H, Me); 4.01 and 4.03 (both m, 4 H each, C_5H_4); 4.15 (s, 10 H, C_5H_5). Found (%): C, 70.53; H, 5.89; Fe, 23.56. $C_{28}H_{28}Fe_2$. Calculated (%): C, 70.62; H, 5.93; Fe, 23.44.

Compound **14** was obtained as orange crystals, m.p. 157—158 °C. ^1H NMR, δ: 0.85 (d, 12 H, Me, J = 6.8 Hz); 1.58 (s, 4 H, CH); 2.64 (m, 2 H, $C\underline{H}Me_2$, J = 6.8 Hz); 3.96 and 4.03 (both m, 4 H each, C_5H_4); 4.13 (s, 10 H, C_5H_5). Found (%): C, 72.16; H, 6.73; Fe, 21.07. $C_{32}H_{36}Fe_2$. Calculated (%): C, 72.21; H, 6.81; Fe, 20.98.

Direct photolysis of 3-ferrocenyl-3-methylcyclopropene (10). Cyclopropene **10** (0.24 g, 1 mmol) was dissolved in benzene (100 mL) and irradiated under an atmosphere of dry nitrogen for 4 h using a 250 W Hanovia medium pressure lamp with a Vycor filter. Then the solvent was distilled off and the residue was chromatographed in a thin layer on Al_2O_3 (hexane was used as the eluent) to obtain 2-ferrocenylbut-1-en-3-yne (**17**)[24] and *trans*-2-ferrocenylbut-2-ene (**18**)[24] in yields of 0.065 g (23%) and 0.076 g (30%), respectively. Compound **17**, R_f 0.72, orange oil. Found (%): C, 71.38; H, 5.03; Fe, 23.75. $C_{14}H_{12}Fe$. Calculated (%): C, 71.22; H, 5.12; Fe, 23.66.

Compound **18**, R_f 0.65, orange oil. Found (%): C, 69.87; H, 6.93; Fe, 23.41. $C_{14}H_{16}Fe$. Calculated (%): C, 70.02; H, 6.72; Fe, 23.26.

Direct photolysis of 3-ferrocenyl-3-isopropylcyclopropene (11). A solution of compound **11** (0.27 g, 1 mmol) in benzene (150 mL) was irradiated analogously to compound **10** for 5 h. Then the solvent was distilled off *in vacuo* and the residue was chromatographed in a thin layer on Al_2O_3 (hexane was used as the eluent) to obtain 1-ferrocenyl-4,4-dimethylcyclobutene (**19**) as an orange oil in a yield of 0.07 g (27%). ^1H NMR, δ: 1.83 and 2.07 (both s, 3 H each, Me); 2.93 (d, 2 H, CH_2, J = 7.8 Hz); 4.15 and 4.19 (both m, 2 H each, C_5H_4); 4.10 (s, 5 H, C_5H_5); 5.81 (t, 1 H, CH=, J = 7.8 Hz). ^{13}C NMR, δ: 26.12 and 27.03 (both Me); 38.57 (CH_2); 68.25, 68.49, 69.43, 69.72 (C_5H_4); 69.21 (C_5H_5); 81.69 (C_{ipso}Fc); 118.20 (CH=); 126.13 (C). Found (%): C, 72.09; H, 7.03; Fe, 20.85. $C_{16}H_{18}Fe$. Calculated (%): C, 72.21; H, 6.81; Fe, 20.98.

Photochemical reaction of cyclopropene 11 with 2-ferrocenyl-3-methylbut-1-ene (23). A solution of compound **11** (0.27 g, 1 mmol) and alkene **23** (0.25 g, 1 mmol) in benzene (200 mL) was irradiated for 6 h. Then the solvent was distilled off *in vacuo* and the residue was chromatographed on a column

Table 3. Crystallographic data and details of X-ray diffraction analysis of compounds **14** and **24**

Parameters	**14**	**24**
Molecular formula	$C_{32}H_{36}Fe_2$	$C_{31}H_{36}Fe_2$
Molecular weight/g mol^{-1}	532.30	520.30
Temperature/K	293	293
Crystal system	Monoclinic	
Space group	$P2_1/n$	$C2/c$
a/Å	6.064(1)	20.483(3)
b/Å	21.328(2)	8.665(1)
c/Å	10.138(1)	30.293(4)
α/deg	90.0	90.0
β/deg	100.54(1)	109.68(1)
γ/deg	90.0	90.0
V/Å^3	1289.1(3)	5062.5(12)
Z	2	8
d_{calc}/g cm^{-3}	1.371	1.365
Absorption coefficient/mm^{-1}	1.144	1.163
F(000)	560	2192
Radiation	Mo-Kα	Mo-Kα
λ/Å	0.71073	0.71073
Monochromator	Graphite	
θ/deg	1.50—25.00	1.50—25.0
Overall number of reflections	2484	4599
Number of independent reflections with R ($I > 2\sigma(I)$)	2263	4464
R_1	0.0955	0.0587
wR_2	0.1323	0.1106
R_{int}	0.0859	0.1322
Number of parameters in the refinement	154	298
Goodness of fit (full-matrix least-squares based on F^2)	0.993	1.065
Residual electron density/e Å^{-3}, ρ_{min}/ρ_{max}	−0.451/0.383	−0.380/0.386
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (0.0735P)^2$, where $P = (F_0^2 + 2F_0^2)/3$	

with Al_2O_3 (hexane was used as the eluent) to obtain 1,3-diferrocenyl-3-isopropyl-6,6-dimethylcyclohexene (**24**) as orange crystals in a yield of 0.43 g (83%), m.p. 164—165 °C. ^{1}H NMR, δ: 0.67 and 0.80 (both d, 3 H each, Me, J = 6.8 Hz); 0.97 and 1.07 (both s, 3 H each, Me); 1.65 (dd, 2 H, CH_2, J = 5.2 and 7.1 Hz); 1.88 (dd, 2 H, CH_2, J = 7.1 and 12.2 Hz); 1.98 (m, 1 H, CH); 4.04 and 4.11 (both m, 1 H each, C_5H_4); 4.16 and 4.18 (both m, 2 H each, C_5H_4); 4.21 and 4.24 (both m, 1 H each, C_5H_4); 4.19 and 4.27 (both s, 5 H each, C_5H_5); 6.48 (s, 1 H, CH=). Found (%): C, 71.43; H, 7.06; Fe, 21.51. $C_{31}H_{36}Fe_2$. Calculated (%): C, 71.56; H, 6.97; Fe, 21.47.

X-ray diffraction study of compounds 14 and 24. The unit-cell parameters and the intensities of reflections were measured on a Siemens P4/PC diffractometer. The structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of all hydrogen atoms were revealed from the difference Fourier synthesis and refined isotropically. The crystallographic parameters and details of X-ray data collection and structure refinement are given in Table 3. The coordinates of atoms are deposited in the Cambridge Structural Database.

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