Cross-conjugated 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene in cationic cycloaddition and proton-catalyzed cyclodimerization reactions

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Abstract

Cationic cycloaddition of cross-conjugated 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene to 1-ferrocenyl-2-isopropenyl-3,3-dimethylallylium tetrafluoroborate and its proton-catalyzed cyclodimerization result in diferrocenylbicyclo[3.3.1]nonene derivatives. The spatial structure of one of the reaction products, viz., ferroceno[4,5]-{9-ferrocenylmethylidene-1,3,3,8,10-pentamethyltricyclo[6.3.1.0^{2,6}]dodec-2(6)-ene}, was established based on the data from X-ray diffraction analysis.
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1. Introduction

Polyene derivatives of the ferrocene series with a terminal methylidene group [1–4] have gained prominence in recent years by virtue of their exciting structure, chemical reactivity, and potential use as molecular building blocks and in the realm of supramolecular chemistry as redox switching receptors. The most studied compounds of this type are represented by linear ferrocenyl-1,3-dienes (**1**) (Scheme 1).

s-*cis*-Dienes and cross-conjugated trienes bearing ferrocenyl fragments are studied to a much lesser extent. To date, syntheses of 3-ferrocenylmethylidene-2-methylidenecamphane (**2a**) [5,6], 2-ferroicenylmethylidene-3-methylidenequinuclidine (**2b**) [7] 1,3-bisferrocenylmethylidene-2-methylidenecyclohexane (**2c**) and cycloheptane (**2d**) [8,9], and 3,5-bisferrocenylmethylidene-4-methylidene-1-methylpiperidine (**2e**) [10] (Scheme 2) have been carried out and their chemical properties have been studied.

The chemical behavior of compounds **2a–e** has been examined in the following reactions: cycloaddition, dimerization, and cyclodimerization (thermal, proton-catalyzed, and cation-catalyzed) [5–10], which occurred highly diastereoselectively. The stepwise non-synchronous mechanism of proton/cation-catalyzed cyclodimerization has been proven experimentally, this reaction afforded fused polycarbo (or -hetero) cycles of unusual structures with spiro- or "three-petal"-type of fusion [11].

With relation to synthetic and theoretical organic chemistry and chemistry of high-molecular compounds, it was of interest to inquire into a question of a feasibility of synthesizing the simplest representatives of linear cross-conjugated ferrocenyl-substituted trienes and to study their properties.

1
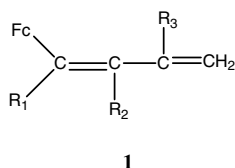
R$_1$,R$_2$,R$_3$=H, Alk, Ar, Fc

Fc= C$_5$H$_5$FeC$_5$H$_4$

Scheme 1.

In our previous publication [12], we reported the preparation of 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene (**3**) by dehydration of the alcohol **4** in ca. 70% yield and a new type of cationic cycloaddition of the triene **3** to the cation **5** leading to 7-ferrocenyl-4-ferrocenylmethylidene-8-isopropylidene-1,3,5-trimethyl-9-oxabicyclo-[3.3.1]non-2-ene (**6**) (Scheme 3).

Naturally, it was suggested that the formation of the cyclodimer **6** is a characteristic feature of cross-conjugated trienes of the type **3**, and the starting Z- and E-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes (**7a,b**) may be regarded as a cross-conjugated heterotriene.

In continuation of our investigations in this field, we examined chemical properties of 3-ferrocenylmethylid-

ene-2,4-dimethylpenta-1,4-diene (**3**) in more details, especially, its behavior in cyclodimerization.

2. Results and discussion

The starting 3-ferrocenylmethylidene-2,4-dimethyl-penta-1,4-diene (**3**) was obtained by dehydration of 3-ferrocenylmethylidene-2,4-dimethylpentane-2,4-diol (**8**) prepared by addition of MeLi in benzene to 3-ferro-cenylmethylidenepentane-2,4-dione (**9**) (Scheme 4).

The diol **8** was isolated in 67% yield following chromatographic purification on alumina, the yield of the triene **3** (storage-stable orange crystals) was 64%. No formation of cyclodimers of the Diels–Alder type **10** from the triene **3** was observed even upon prolonged boiling in xylene (Scheme 5).

However, reactive dienophiles, e.g., N-phenylmalei-mide, smoothly react with the triene **3** to yield an adduct **11** (Scheme 5).
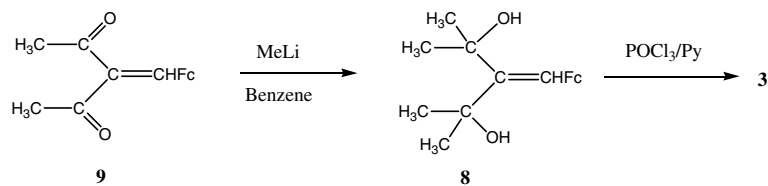
According to data from ^{1}H and ^{13}C NMR data, the adduct **11** was formed as a single diastereomer. Its spatial structure as endo-4-ferrocenyl-5-isopropenyl-6-methyl-2-phenyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione was established by X-ray diffraction analysis of a single

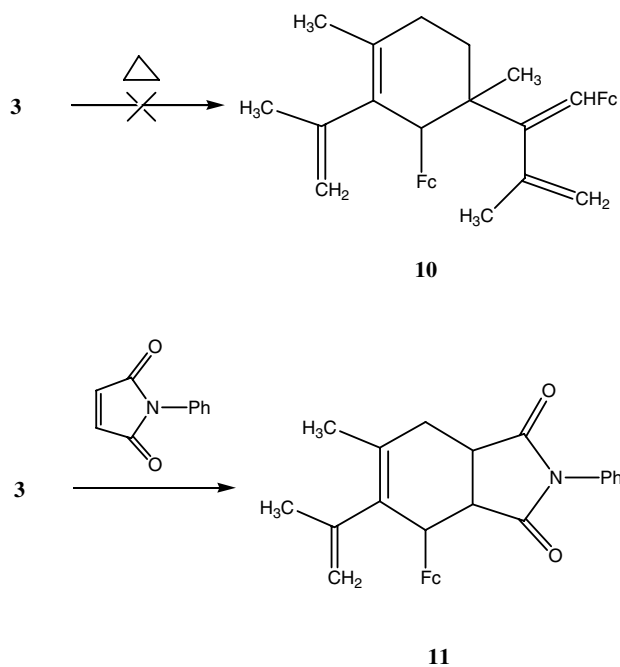**2a**   **2b**   **2c, n=1**   **2e**

2d, n=2
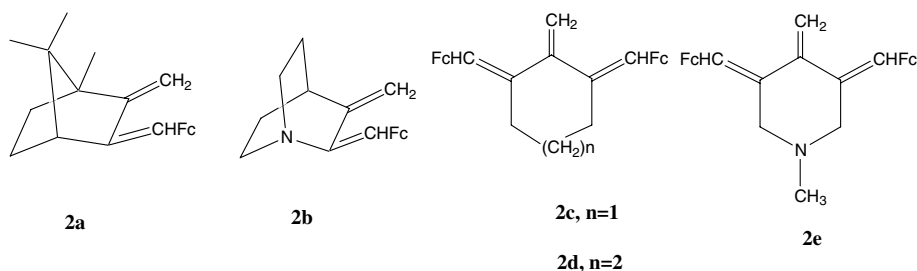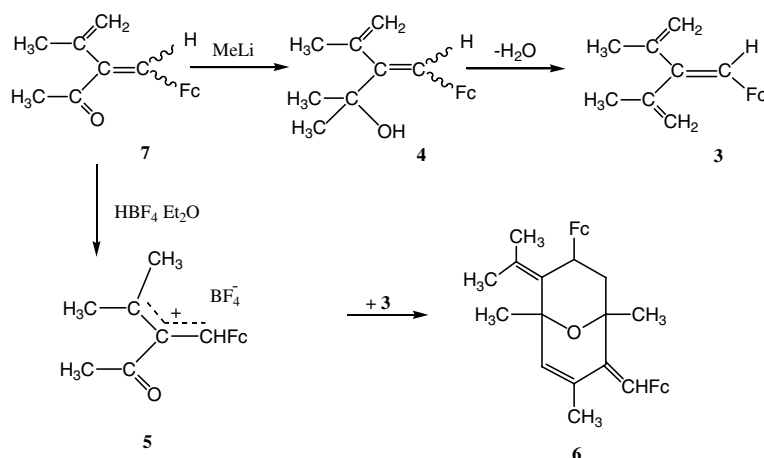
Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

crystal prepared by crystallization from chloroform. The general view of the molecule **11** is shown in Fig. 1. The principal geometrical parameters are listed in Table 1.

Action of tetrafluoroboric acid etherate on the triene **3** afforded crystalline 1-ferrocenyl-2-isopropenyl-3,3-dimethylallilyum tetrafluoroborate (**12**), which is fairly stable on storage in a solid state in an inert dry atmosphere (Scheme 6).

The ^{1}H NMR spectrum of the salt **12** contains signals for three methyl groups and one CH_2= group, which suggests that only one isopropenyl residue underwent protonation.

Treatment of the salt **12** with *N,N*-dimethylaniline afforded the ferrocenyltriene **3** (∼9%) and isomeric cyclodimers **13**–**15** (yields ∼10%, ∼18%, and ∼27%, respectively) isolated by TLC on silica gel (Scheme 7).

The structures of the cyclodimers were established based on the data from mass spectrometry, IR and NMR spectroscopy, and elemental analysis. The characteristic features of the cyclodimers are manifested in their ^{1}H NMR spectra. Thus the spectrum of the dimer **13** contains singlet signals for five methyl groups and two singlets for the olefinic protons, that of compound
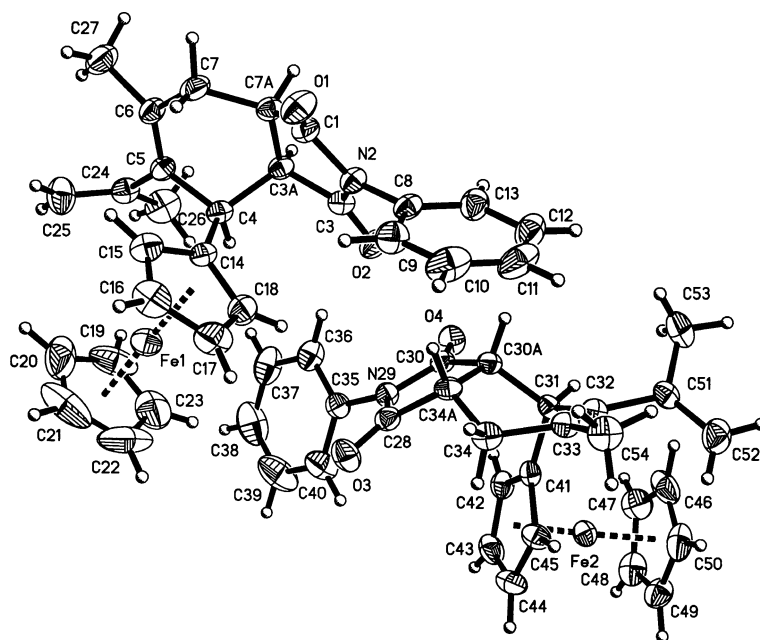

Fig. 1. Crystal structure of compound **11**.

Table 1
Selected bond lengths r (Å) and bond angles ω (°) for compounds **11** and **15**

Selected bond lengths		Selected bond angles	
Compound 11			
C(3A)—C(4)	1.548(3)	C(3A)—C(4)—C(5)	107.5(2)
C(4)—C(5)	1.524(3)	C(4)—C(5)—C(6)	118.4(3)
C(5)—C(6)	1.331(3)	C(5)—C(6)—C(7)	120.9(3)
C(6)—C(7)	1.505(3)	C(7)—C(7A)—C(3A)	115.2(2)
C(7)—C(7A)	1.528(3)	C(7A)—C(3A)—C(4)	112.3(2)
C(3A)—C(7A)	1.530(3)	C(25)—C(24)—C(26)	120.4(3)
C(24)—C(25)	1.334(4)	C(31)—C(32)—C(33)	117.7(3)
C(30A)—C(31)	1.535(3)	C(32)—C(33)—C(34)	120.1(3)
C(32)—C(33)	1.335(3)	C(30A)—C(34A)—C(34)	115.1(2)
C(33)—C(34)	1.516(4)	C(52)—C(51)—C(32)	123.1(3)
C(34A)—C(34)	1.536(3)	C(34A)—C(34)—C(33)	113.1(2)
C(30A)—C(34A)	1.525(3)	C(54)—C(33)—C(34)	11.2(3)
C(51)—C(52)	1.325(4)	N(29)—C(30)—C(30A)	108.3(3)
C(31)—C(32)	1.529(3)	C(32)—C(33)—C(54)	124.6(3)
Compound 15			
C(1)—C(2)	1.407(3)	C(9A)—C(3A)—C(3)	111.3(2)
C(2)—C(3)	1.510(3)	C(3A)—C(4)—C(5)	111.22(19)
C(3)—C(3A)	1.550(3)	C(7)—C(8)—C(9)	109.96(17)
C(3A)—C(9A)	1.343(3)	C(4)—C(10)—C(8)	111.58(18)
C(9A)—C(1)	1.464(3)	C(5)—C(6)—C(7)	112.95(18)
C(3A)—C(4)	1.519(3)	C(9)—C(9A)—C(3A)	125.5(2)
C(4)—C(5)	1.558(3)	C(9A)—C(3A)—C(4)	121.7(2)
C(5)—C(6)	1.547(3)	C(6)—C(7)—C(8)	117.07(18)
C(6)—C(7)	1.520(3)	C(8)—C(7)—C(23)	119.97(19)
C(7)—C(8)	1.533(3)	C(20)—C(3)—C(19)	108.7(2)
C(8)—C(9)	1.535(3)	C(12)—C(13)—C(1)	106.5(2)
C(9)—C(9A)	1.490(3)	C(10)—C(4)—C(21)	108.6(2)
C(8)—C(10)	1.532(3)	C(34)—C(8)—C(10)	109.75(19)
C(4)—C(10)	1.521(3)	C(3A)—C(9A)—C(1)	109.5(2)

14 contains signals for the protons of the $CH_2=$ and $-CH=$ groups and four singlets for the methyl groups, while four singlets and one doublet of the methyl groups and a singlet of one olefinic proton were present in the spectrum of compound **15**. The ^{13}C NMR spectrum of the latter contains three signals for carbon atoms of
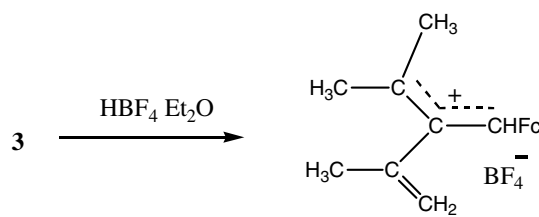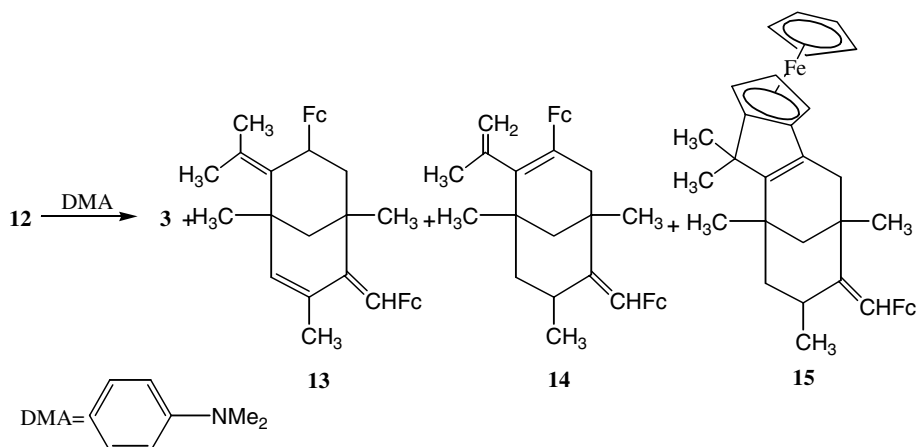

Scheme 6.

the ferrocene fragments bearing no hydrogen atoms (C_{ipso}Fc).

The ^1H and ^{13}C NMR spectroscopic data of the cyclodimers **13**–**15** suggest that they were formed each as only one diastereomeric form. The objective spatial structure of one of the cyclodimers, viz., compound **15**, as ferroceno[4,5]-{9-ferrocenylmethylidene-1,3,3,8,10-pentamethyltricyclo[6.3.1.0^{2,6}]dodec-2(6)-ene}, was established based on the X-ray diffraction data of a single crystal prepared by crystallization from dichloromethane. The general view of the molecule **15** is shown in Fig. 2(a), and the packing pattern, in Fig. 2(b). The principal geometrical parameters are listed in Table 1.

In our opinion, the mechanism of formation of the cyclodimers **13**–**15** can be represented as follows. Deprotonation of the salt **12** by DMA yields the triene **3**, which adds the allylic cation **12** to afford the dimeric linear cation **16** (Scheme 8).

Intramolecular alkylation of the methylidene fragments of the cation **16** results in its consecutive transformation into the cations **17** and **18**. Deprotonation of the latter affords the cyclodimer **13**, which is structurally similar to the cyclodimer **6** [12].

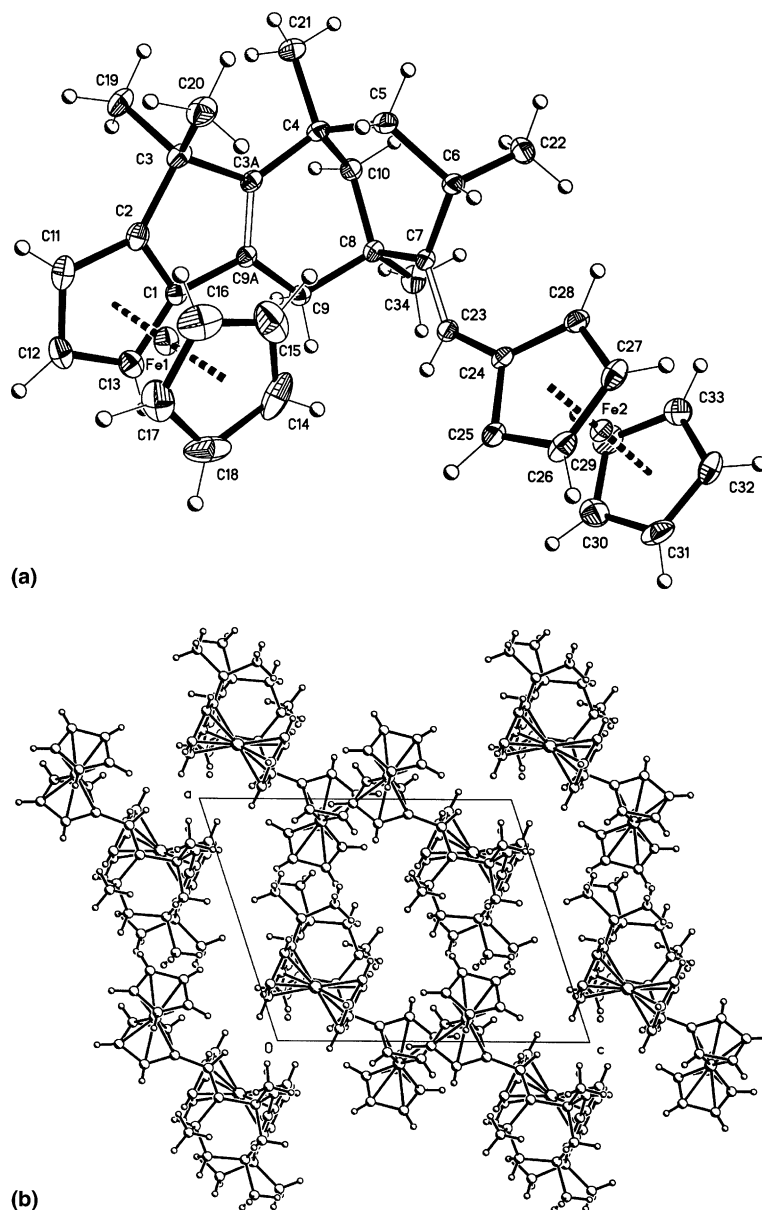Scheme 7.

(a)

(b)

Fig. 2. (a) Crystal structure of compound **15**. (b) Crystal packing of **15**.

The formation of compounds **14** and **15** seems to result from transannular hydride transfer [13] in the cation **18** (Scheme 9).

The allylic cation **19** that formed is further stabilized by either deprotonation leading to the product **14** or *ortho*-alkylation of the substituted cyclopentadiene ring of ferrocene to give compound **15** [11].

Analogous results were obtained in the condensation of the triene **3** with the cation **12** (the ratio of the reagents ~1:1) (Scheme 10).

We have found also that prolonged boiling of the triene or the diol **8** in acetic acid yields the same cyclodimers **13–15**. In addition, a linear dimer **20** could be isolated in ca. 51% yield (Scheme 11).

Apparently, compound **20** is formed as a result of deprotonation of the allylic cation **16**. Its structure was confirmed by the data from ^{1}H and ^{13}C NMR spectra according to which the pentaene **20** is formed as a single geometrical isomer, presumably with *E,E*-configuration analogous to that of *E,E*-4-ferrocenyl-7-ferrocenylmethylidene-3-isopropylidene-6,8-dimethylnona-5,8-dien-2- one [12].

Attention should be paid to high diastereoselectivity of the reactions studied, namely, cycloaddition and cyclodimerization of 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene (**3**). In the cycloaddition reaction studied, high diastereoselectivity in the formation of compound **13–15**, **20** worths special mention. The
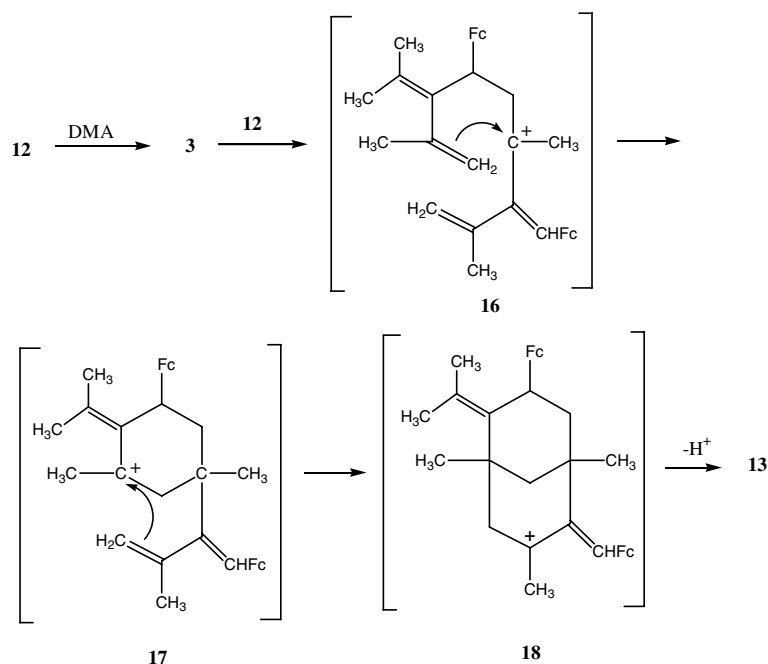
Scheme 8.
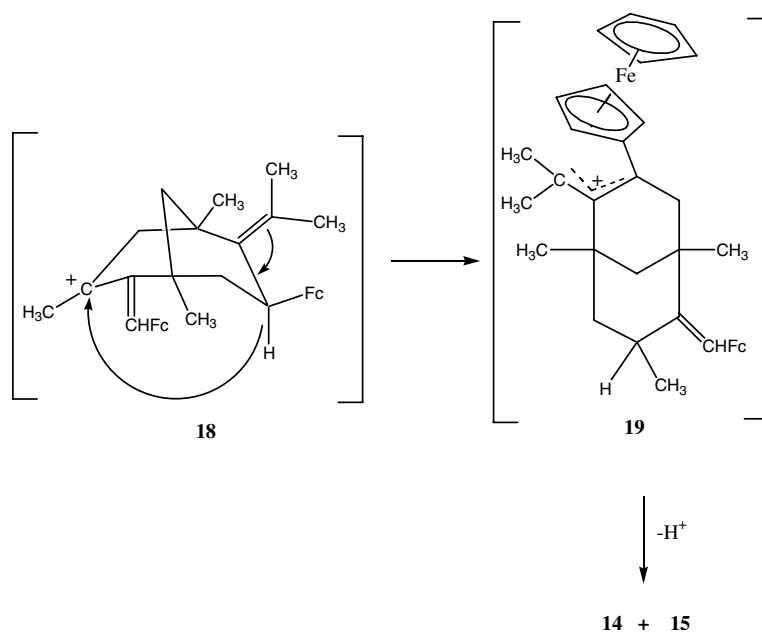
Scheme 9.
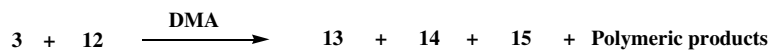
Scheme 10.

molecules of **13–15**, **20** contains several chiral centers, yet this compounds were isolated as a single diastereomeric forms. One cannot rule out the formation of minor diastereomeric products, however they could not be isolated and characterized. The high diastereoselectivity of this cycloaddition can probably be attributed to configurational features of the dimeric linear allylic cation **16**, where the carbocationic center and
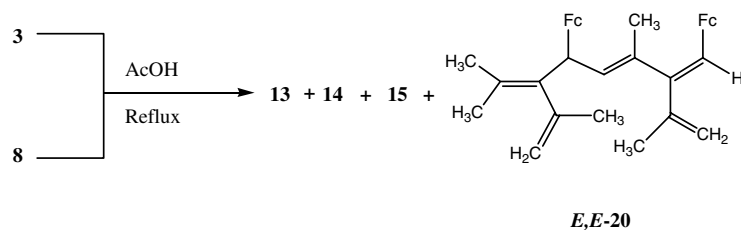
Scheme 11.

the carbon atom of the methylidene group, on the one side, and the terminal methylidene fragment and the carbon atom of the methylidene group, on the other side, become spatially close to enable intramolecular double alkylation.

It is the second time we write about this kind of processes, but they are unprecedented in the literature. Elucidation of the role of varios factors on the characteristics of stepwise cationic dimerization-cyclodimerization involving cross-conjugated trienes and isolation of reation products in each step deserves, in our opinion, special studies.

3. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl$_3$ with Me$_4$Si as the internal standard, the ^{1}H NMR spectra of the tetrafluoroborate **12** was recorded for solutions in CD$_2$Cl$_2$. The IR spectra were measured on a Specord IR-75 instruments for KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elemental Analysis system GmbH was used for elemental analyses. Column chromatography was carried out on Al$_2$O$_3$ (Brockmann activity III) and on plates with a fixed SiO$_2$ layer.

The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD area detector/ω diffractometer. The crystallographic data, the parameters of the X-ray diffraction experiment, and refinements are listed in Table 2. The structures of compounds **11** and **15** were solved by the direct method (SHELXS) and refined using full-matrix least-squares on F^2.

The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; pentane-2,4-dione, 99%; methyllithium, 1.6 M solution in diethyl ether; acetic acid, glacial, 99.99%; *N,N*-dimethylaniline, 99%; piperidine, 99%, *N*-phenylmaleimine, 97%. Tetrafluoroboric acid etherate, 50–52%, was purchased from Alfa AESAR.

3.1. Synthesis of 3-ferrocenylmethylidenepentane-2,4-dione (9)

The title compound was obtained by the condensation of ferrocenecarbaldehyde with pentane-2,4-dione in benzene in the presence of piperidinium acetate. The yield of compound **9** was 72%, m.p. 141–142 °C ([12,14]: m.p. 142 °C).

3.2. Synthesis of 3-ferrocenylmethylidene-2,4-dimethyl-pentane-2,4-diol (8)

A 1.6 M solution of methyllithium in diethyl ether (30.0 ml) was added dropwise in an inert atmosphere to a stirred solution of the diketone **9** (2.86 g, 0.01 mol) in dry benzene (100 ml) for 30 min at 20 °C. The mixture was stirred for an additional 2 h and the excess of methyllithium was quenched by addition of water (50 ml). The organic layer was separated, dried with Na$_2$SO$_4$, the solvent was removed in vacuo, and the residue was chromatographed on alumina (hexane–diethyl ether, 2:1) to give the diol **8** (2.2 g, 67%), orange powder, m.p. 75–77 °C. IR (KBr), v: 799, 885, 1101, 1160, 1245, 1334, 1443, 1527, 1634, 2931, 3084, 3320–3450 cm^{-1}. ^{1}H NMR, δ: 1.48 (6H, s, 2CH$_3$), 1.58 (6H, s, 2CH$_3$), 1.64 (1H, s, OH), 4.11 (5H, s, C$_5$H$_5$), 4.17 (2H, m, C$_5$H$_4$), 4.24 (2H, m, C$_5$H$_4$), 6.34 (1H, s, CH=). ^{13}C, δ: 32.14, 32.71 (4CH$_3$); 68.36, 70.73 (C$_5$H$_4$); 69.60 (C$_5$H$_5$); 76.29 (2C); 84.29 (C$_{ipso}$Fc); 120.79 (CH=); 152.20 (C=). Anal. Calc. for C$_{18}$H$_{24}$FeO$_2$: C, 65.68; H, 7.37; Fe, 17.02. Found: C, 65.71; H, 7.58; Fe, 16.84%. MS: *m/z* 328 [M]$^+$.

3.3. Synthesis of 3-ferrocenylmethylidene-2,4-dimethyl-penta-1,4-diene (3)

The diol **8** (3.28 g, 0.01 mol) was added to a mixture of dry pyridine (100 ml) and POCl$_3$ (1.0 ml) and stirred at 30–40 °C for 3 h (TLC control). The reaction mixture was treated with water (100 ml) and benzene (100 ml), the organic layer was separated, washed with water (3 × 50 ml) and concentrated in vacuo. The residue was chromatographed on a column with Al$_2$O$_3$ in

Table 2
Crystal data and structure refinement parameters for compounds **11** and **15**

Data	11	15
Molecular formula	$C_{28}H_{27}FeNO_2$	$C_{36}H_{40}Fe_2$
Formula weight (g mol^{-1})	465.36	584.38
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.8148(6)	10.772(1)
b (Å)	14.0494(8)	11.015(1)
c (Å)	16.1159(9)	12.89(1)
α (°)	102.063(1)	98.994(1)
β (°)	98.437(1)	105.450(1)
γ (°)	103.540(1)	101.344(1)
V (Å^3)	2278.2(2)	1409.7(2)
Z	4	2
D_{calc} (Mg mm^{-3})	1.357	1.377
Absorption coefficient (mm^{-1})	0.687	1.053
$F(0\,0\,0)$	976	616
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Monochromator	Graphite	Graphite
θ Range (°)	1.76–25.04	1.68–27.56
Reflections collected	26 830	20 417
Reflections independent	8069	6481
R_{int}	0.0594	0.0386
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0480$, $wR_2 = 0.0526$	$R_1 = 0.0446$, $wR_2 = 0.0903$
R indices (all data)	$R_1 = 0.0964$, $wR_2 = 0.0581$	$R_1 = 0.0623$, $wR_2 = 0.0956$
Refinable parameters	581	348
Goodness-of-fit	0.917	1.040
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2
Minimum maximum residual electron density (e Å^{-3})	−0.316/0.727	−0.185/0.489

hexane to yield 1.87 g (64%) of compound **3** as orange needles, m.p. 78–79 °C ([12]: m.p. 78–79 °C).

3.4. Condensation of the triene 3 with N-phenylmaleimide

A solution of the triene 3 (0.29 g, 1 mmol) and *N*-phenylmaleimide (0.2 g, 1.24 mmol) in toluene (50 ml) was refluxed for 3 h and concentrated. The residue was chromatographed on a column with Al_2O_3 (hexane–dichloromethane, 3:1) to yield 0.32 g (70%) of the adduct **11**, yellow crystals, m.p. 201–202 °C. IR (KBr), *v*: 819, 998, 1104, 1160, 1380, 1432, 1495, 1623, 1682, 1728, 2830, 2938, 3090 cm^{-1}. ^{1}H NMR, δ: 1.98 (3H, d, CH$_3$, $J = 0.8$ Hz), 1.99 (3H, s, CH$_3$), 2.44 (1H, dd, CH$_2$, $J = 9.6$, 16.2 Hz), 2.65 (1H, ddd, CH$_2$, $J = 0.9$, 6.9, 16.2 Hz), 3.08–3.20 (2H, m, 2CH), 4.03 (5H, s, C$_5$H$_5$), 3.95 (1H, m, C$_5$H$_4$), 4.05 (1H, m, C$_5$H$_4$), 4.08 (1H, m, C$_5$H$_4$), 4.20 (1H, m, C$_5$H$_4$), 4.24 (1H, d, CH-Fc, $J = 5.1$ Hz), 4.97 (1H, d, CH$_2$=, $J = 1.8$ Hz), 5.29 (1H, dd, CH$_2$=, $J = 0.8$, 1.8 Hz,), 7.06 (2H, dm, C$_6$H$_5$), 7.31–7.48 (3H, m, C$_6$H$_5$). ^{13}C NMR δ: 21.26, 21.94 (2CH$_3$); 28.34 (CH$_2$); 39.11, 39.27, 48.44 (3CH); 66.96, 67.50, 68.42, 69.32 (C$_5$H$_4$); 69.15 (C$_5$H$_5$); 84.33 (C$_{ipso}$Fc); 116.38 (CH$_2$=); 126.68 (2C), 128.39, 128.86 (2C) (C$_6$H$_5$); 130.22, 131.75, 137.69, 142.98 (4C); 177.59, 178.76 (2C=O). Anal. Calc. for $C_{28}H_{27}FeNO_2$: C, 72.26; H, 5.85; Fe, 12.00; N 3.01. Found: C, 72.43; H, 5.77; Fe, 12.11; N 2.84%. MS: *m/z* 465 [M]$^+$.

3.5. 1-Ferrocenyl-2-isopropenyl-3,3-dimethylallilyum tetrafluoroborate (12)

This salt was prepared by addition of tetrafluoroboric acid etherate (0.5 ml) to a solution of the triene **3** (0.29 g, 1 mmol) in dry diethyl ether (50 ml). The crystalline black product that precipitated was filtered off, washed with dry diethyl ether and dried in vacuo. The yield of the salt **12** was 0.34 g (90%), m.p. 176–177 °C. ^{1}H NMR δ: 1.95 (3H, s, CH$_3$), 1.98 (3H, t, CH$_3$, $J = 1.2$ Hz), 2.24 (3H, s, CH$_3$), 4.88 (5H, s, C$_5$H$_5$), 4.77 (1H, m, C$_5$H$_4$), 4.92 (1H, m, C$_5$H$_4$), 5.45 (1H, m, C$_5$H$_4$), 5.62 (1H, m, C$_5$H$_4$), 6.12 (1H, td, CH$_2$=, $J = 1.2$, 3.0 Hz), 6.25 (1H, m, CH$_2$=), 8.24 (1H, s, CH=). Anal. Calc. for $C_{18}H_{21}BF_4Fe$: C, 56.88; H, 5.57; B, 2.84; F, 20.00; Fe, 14.70. Found: C, 56.67; H, 5.76; F, 19.77; Fe, 14.51%.

3.6. The reaction of the tetrafluoroborate 12 with N,N-dimethylaniline

N,N-Dimethylaniline (1.5 ml) was added with stirring to a solution of the tetrafluoroborate 12 (1.14 g, 3 mmol) in dry dichloromethane (100 ml). The nearly black solution gradually turns orange in ca. 20 min. The reaction mixture was washed with water (20 ml), 5% HCl (2 × 20 ml) and water (20 ml), the organic layer was dried with CaCl$_2$ and the solvent was distilled off. The

residue was chromatographed on a column with Al_2O_3 (hexane). A fraction of pure triene 3 was isolated in the yield of 0.11 g (9%), m.p. 78–79 °C, followed by a fraction containing a mixture of the dimeric products 13–15 (ca. 1:2:3, ^{1}H NMR data), an orange powder, m.p. 178–183 °C. The dimeric products were separated by TLC on SiO_2 (hexane).

3.6.1. 7-Ferrocenyl-4-ferrocenylmethylidene-8-isopropylidene-1,3,5-trimethyl-bicyclo[3.3.1]non-2-ene (13)

Yield 0.12 g (10%), $R_f = 0.74$, orange powder, m.p. 204–205 °C. ^{1}H NMR δ: 1.24 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.78 (3H, s, CH_3), 1.84 (3H, d, CH_3, $J = 0.9$ Hz), 2.28 (1H, dd, CH_2, $J = 6.3, 12.6$ Hz), 2.46 (2H, s, CH_2), 2.60 (1H, dd, CH_2, $J = 3.3, 12.6$ Hz), 3.87 (1H, dd, CH, $J = 3.3, 6.3$ Hz), 4.00 (2H, m, C_5H_4), 4.09 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.17 (2H, m, C_5H_4), 4.20 (1H, m, C_5H_4), 4.26 (1H, m, C_5H_4), 4.38 (2H, m, C_5H_4), 6.03 (1H, q, CH=, $J = 0.9$ Hz), 6.10 (1H, s, FcCH=). ^{13}C NMR: 20.44, 21.48, 22.53, 25.48, 27.16 ($5CH_3$); 35.39, 36.41 ($2CH_2$); 40.39 (CH); 41.52, 45.73 (2C); 68.34, 68.73, 69.21, 69.52 ($2C_5H_4$); 68.59, 69.17 ($2C_5H_5$); 73.38, 82.28 ($2C_{ipso}Fc$); 118.19, 130.72 (2CH=); 121.78, 128.01, 132.72, 141.80 (4C). Anal. Calc. for $C_{36}H_{40}Fe_2$: C, 73.99; H, 6.90; Fe, 19.11. Found: C, 74.15; H, 6.71; Fe, 19.29%. MS: m/z 584 [M]$^+$.

3.6.2. 3-Ferrocenyl-6-ferrocenylmethylidene-2-isopropenyl-1,5,7-trimethyl-bicyclo[3.3.1]non-2-ene (14)

Yield 0.22 g (18%), $R_f = 0.67$, orange powder, m.p. 196–198 °C. IR (KBr), ν: 796, 820, 878, 1001, 1034, 1110, 1195, 1264, 1334, 1387, 1430, 1607, 1661, 2923, 3073 cm^{-1}. ^{1}H NMR, δ: 1.16 (3H, s, CH_3), 1.26 (3H, d, CH_3, $J = 5.4$ Hz), 1.33 (3H, s, CH_3), 1.49 (1H, dd, CH_2, $J = 4.2, 12.6$ Hz), 1.68 (3H, s, CH_3), 1.72 (1H, dd, CH_2, $J = 2.7, 12.3$ Hz), 2.24 (1H, d, CH_2, $J = 15.3$ Hz), 2.35 (1H, d, CH_2, $J = 15.3$ Hz), 2.43 (2H, s, CH_2), 3.16 (1H, m, CH), 4.04 (2H, m, C_5H_4), 4.11 (5H, s, C_5H_5), 4.15 (5H, s, C_5H_5), 4.17 (2H, m, C_5H_4), 4.20 (1H, m, C_5H_4), 4.24 (1H, m, C_5H_4), 4.27 (1H, m, C_5H_4), 4.54 (1H, m, C_5H_4), 4.86 (1H, d, CH_2=, $J = 1.2$ Hz), 5.19 (1H, bs, CH_2=), 6.05 (1H, s, FcCH=). ^{13}C NMR δ: 19.89, 21.18, 22.65, 27.12 ($4CH_3$); 34.23, 36.43, 37.14 ($3CH_2$); 39.17 (CH); 41.33, 43.19 (2C); 68.42, 68.53, 69.22, 69.29 ($2C_5H_4$); 68.64, 69.11 ($2C_5H_5$); 81.43, 83.32 ($2C_{ipso}Fc$); 111.10 (CH_2=); 126.71 (CH=); 119.13, 122.21, 132.16, 140.18 (4C). Anal. Calc. for $C_{36}H_{40}Fe_2$: C, 73.99; H, 6.90; Fe, 19.11. Found: C, 73.75; H, 6.67; Fe 18.95%. MS: m/z 584 [M]$^+$.

3.6.3. Ferroceno[4,5]-{9-ferrocenylmethylidene-1,3,3,8,10-pentamethyltricyclo[6.3.1.0^{2,6}]dodec-2(6)-ene} (15)

Yield 0.32 g (27%), $R_f = 0.60$, orange powder, m.p. 214–216 °C. IR (KBr), ν: 799, 867, 1002, 1026, 1105, 1185, 1256, 1331, 1355, 1383, 1429, 1605, 1649, 2968,

3086 cm^{-1}. ^{1}H NMR, δ: 1.22 (3H, s, CH_3), 1.24 (3H, d, CH_3, $J = 3.6$ Hz), 1.26 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.42 (1H, dd, CH_2, $J = 2.4, 12.6$ Hz), 1.67 (1H, dd, CH_2, $J = 3.2, 12.6$ Hz), 1.84 (1H, d, CH_2, $J = 4.2$ Hz), 2.01(1H, d, CH_2, $J = 4.2$ Hz), 2.19 (1H, d, CH_2, $J = 15.9$ Hz), 2.57 (1H, d, CH_2, $J = 15.9$ Hz), 3.00 (1H, m, CH), 3.90 (5H, s, C_5H_5), 3.98 (2H, m, C_5H_4), 4.04 (2H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 4.13 (1H, m, C_5H_4), 4.19 (1H, m, C_5H_4), 4.39 (1H, m, C_5H_4), 6.33 (1H, s, FcCH=, $J = 0.9$ Hz). ^{13}C NMR δ: 20.02, 22.49, 23.54, 25.42, 27.10 ($5CH_3$); 31.49, 35.64, 36.23 ($3CH_2$); 38.91 (CH); 40.32, 42.25, 44.12 (3C); 68.56, 68.67, 69.16, 69.59, 70.21 (C_5H_3, C_5H_4); 68.43, 69.01 ($2C_5H_5$); 73.58, 82.14, 82.48 ($3C_{ipso}Fc$); 129.25 (CH=); 122.63, 135.92, 143.07 (3C). Anal. Calc. for $C_{36}H_{40}Fe_2$: C, 73.99; H, 6.90; Fe, 19.11. Found: C, 74.08; H, 7.04; Fe, 18.93%. MS: m/z 584 [M]$^+$.

3.7. Condensation of the tetrafluoroborate 12 with the triene 3

The triene 3 (0.29 g, 1 mmol) was added to a solution of the tetrafluoroborate 12 (0.38 g, 1 mmol) in dichloromethane (60 ml) and the mixture was stirred at 20 °C for 1 h. N,N-Dimethylaniline (0.6 ml) was then added and stirring was continued for 30 min. The reaction mixture was washed with water, 5% HCl, water and dried with $CaCl_2$. The solvent was removed in vacuo and the reaction products were separated by TLC on SiO_2 (hexane). The following compounds were obtained: compound 13, yield 0.06 g (10%), $R_f = 0.74$, m.p. 203–205 °C; compound 14, yield 0.12 g (20%), $R_f = 0.68$, m.p. 197–198 °C; compound 15, yield 0.31 g (54%), $R_f = 0.60$, m.p. 215–216 °C.

3.8. Dimerization of 3-ferrocenylmethylidene-2,4-dimethylpenta-1,4-diene (3)

A solution of the triene 3 (0.58 g, 2 mmol) or the diol 8 (0.66 g, 2 mmol) in glacial acetic acid (100 ml) was refluxed for 4 h, cooled to ambient temperature, and diluted with water (100 ml). The reaction products were extracted with benzene (3 × 50 ml), the combined extract was washed with water (2 × 50 ml), 5% aqueous $NaHCO_3$, and water and dried with Na_2SO_4. The solvent was distilled off and the residue was subjected to preparative TLC on silica gel (hexane). The following compounds were obtained: compound 13, yield 0.05 g (8%), $R_f = 0.74$, m.p. 204–205 °C; compound 14, yield 0.06 g (10%), $R_f = 0.67$, m.p. 196–198 °C; compound 15, yield 0.07 g (12%), $R_f = 0.60$, m.p. 215 °C; compound 20, orange powder, yield 0.3 g (51%), $R_f = 0.78$, m.p. 171–172 °C.

6-Ferrocenyl-2-ferrocenylmethylidene-7-isopropylidene-2,4,8-trimethyl-nona-1,4,8-triene (20): IR (KBr), ν: 792, 812, 823, 874, 1006, 1029, 1115, 1181, 1263, 1331,

1375, 1389, 1427, 1605, 1648, 1668, 2965, 3076 cm^{-1}. ^{1}H NMR, δ: 1.50 (3H, s, CH$_3$), 1.61 (3H, s, CH$_3$), 1.90 (3H, s, CH$_3$), 2.02 (3H, d, CH$_3$, J = 0.9 Hz), 2.04 (3H, d, CH$_3$, J = 1.2 Hz), 4.05 (1H, m, C$_5$H$_4$), 4.08 (5H, s, C$_5$H$_5$), 4.10 (2H, m, C$_5$H$_4$), 4.11 (5H, s, C$_5$H$_5$), 4.14 (2H, m, C$_5$H$_4$), 4.21 (1H, m, C$_5$H$_4$), 4.29 (1H, m, C$_5$H$_4$), 4.51 (1H, m, C$_5$H$_4$), 4.55 (1H, q, CH$_2$=, J = 0.9 Hz), 4.73 (1H, d, CH, J = 10.2 Hz), 4.86 (1H, q, CH$_2$=, J = 1.2 Hz), 4.91 (1H, q, CH$_2$=, J = 0.9 Hz), 5.30 (1H, q, CH$_2$=, J = 1.2 Hz), 5.97 (1H, d, CH=, J = 10.2 Hz), 6.13 (1H, s, FcCH=). ^{13}C NMR δ: 21.82, 22.64, 23.27, 25.02, 31.57 (5 CH$_3$); 40.43 (CH); 66.57, 66.98, 67.30, 67.76, 68.26, 68.61, 68.67, 69.32 (2C$_5$H$_4$); 68.44, 69.12 (2C$_5$H$_5$); 82.28, 92.76 (2C$_{ipso}$Fc); 114.14, 115.70 (2CH$_2$=); 120.66, 130.15 (2CH=); 123.72, 132.23, 139.27, 143.49, 144.65, 145.02 (6C). Anal. Calc. for C$_{36}$H$_{40}$Fe$_2$: C, 73.99; H, 6.90; Fe, 19.11. Found: C, 74.12; H, 7.01; Fe, 18.97%. MS: m/z 584 [M]$^+$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 235357 for compound **15** and no. 235358 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambrige CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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