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Journal of Organometallic Chemistry 681 (2003) 115–119
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of ferrocenylvinylcyclopropene and its transformation into cyclopentadiene

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Received 28 January 2003; received in revised form 24 May 2003; accepted 24 May 2003

Abstract

Dehydrobromination of 2-bromo-1-ferrocenyl-1-(2-ferrocenyl-1-methylvinyl)cyclopropane results in 3-ferrocenyl-3-(2-ferrocenyl-1-methylvinyl)cyclopropene and its transformation product, viz., 1,4-diferrocenyl-5-methylcyclopentadiene. These compounds were characterized by ^{1}H-, ^{13}C-NMR, IR, UV–Vis spectroscopy and mass spectrometry. The structure of diferrocenylcyclopentadiene was determined by X-ray diffraction analysis.

Keywords: Ferrocene; Cyclopropane; Cyclopropene; Cyclopentadiene

1. Introduction

3-Vinylcyclopropenes (**1**) are the subject of thermochemical and photochemical studies; they undergo photochemically induced ring expansion to produce cyclopentadienes (**2**) (Scheme 1) and indenes [1–6]. Some transition metal complexes also effect this ring expansion catalytically and stoichiometrically to give cyclopentadienes η-4-cyclopentadiene complexes and η-5-cyclopentadienyl complexes [7–11]. On treatment with metal–carbonyl complexes yield cyclohexadienones, η-4-cyclohexadienone complexes, and phenols [7–13].

Previously, our group have reported the synthesis of stable ferrocenyl cyclopropenes [14]; the structure of this high-energy systems were confirmed by X-ray diffraction analysis [14–17]. The aim of the present work was to synthesize cyclopropenes having two ferrocenyl substituents, one on the three-membered ring and the other in the geminal vinyl group.

2. Discussion

3-Ferrocenyl-3-(1-ferrocenyl-propenyl)-cyclopropene (**8**) was synthesized starting from 1,3-diferrocenyl-2-methylprop-2-en-1-one (**3**) [18] (Scheme 2). Its methylation (the Wittig reaction) resulted in the corresponding 1-3 diene (**4**). The addition of dibromocarbene to the latter in the presence of transference catalyst Trilon B afforded *gem*-dibromo(vinyl)cyclopropane (**5**).

The vinyl *gem*-dihalogenated cyclopropane (**5**) showed in the ^{1}H-NMR spectrum one singlet at δ 2.11 ppm for the CH_2 group, one singlet at δ 2.33 ppm for the methyl group and one singlet at δ 6.19 ppm assigned to the vinylic proton in addition to the characteristic signals for the ferrocenyl groups.

The reduction of dibromo(vinyl)cyclopropane (**5**) with ethyl magnesium bromide in the presence of titanium tetra(isopropoxide) in dry THF gave the cyclopropane **6** and a mixture of (*Z*)- and (*E*)-isomeric monobromides (**7a** and **7b**). The ^{1}H-NMR spectrum of the (*Z*)-bromide (**7a**) exhibits two doublets of doublets at δ 1.33 and 1.83 ppm corresponding to the protons of the methylene group (the AB part of an ABM spin system). The analogous signals for the (*E*)-isomer (**7b**)

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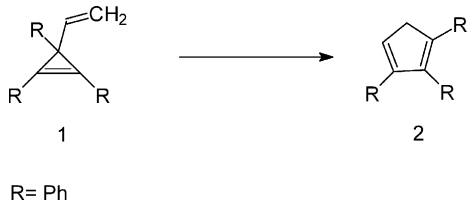
doi:10.1016/S0022-328X(03)00586-2



Scheme 1.

appear at δ 1.61 and 1.80 ppm. The configuration of the isomers was assigned based on the ^{1}H-NMR data [18].

The monobromides (**7a** and **7b**) were treated with Bu^{t}OK in DMSO in order to obtain the vinylcyclopropene **8** (Scheme 3). In addition to the target vinylcyclopropene, yet another compound, viz., diferrocenylcyclopentadiene (**9**), was isolated. Single crystals of the cyclopentadiene (**9**) prepared by crystallization from hexane were studied using X-ray diffraction analysis, which showed that compound **9** has the structure of diferrocenylcyclopentadiene, the crystal structure and crystal packing of compound **9** are shown in Fig. 1.

The cyclopropene **8** is an orange oily compound, which decomposes rapidly on storage under ordinary conditions. In solutions (C_6H_6, $CHCl_3$, 20 °C), this isomerises into compounds **9** (up to 30%) and polymeric products. Its structure was established based on the data from ^{1}H-, ^{13}C-NMR spectroscopy and elemental analysis.

In the ^{1}H-NMR spectrum of the vinylcyclopropene **8**, a signal at δ 1.41 ppm for the CH_3 group, a singlet at δ 6.41 ppm for the vinylic proton, and one singlet at δ 7.23 ppm assigned to the two protons of the cyclopropene were present. The characteristic signals for the ferrocenyl groups were also observed.

The formation of cyclopentadienes under these conditions may be rationalized as being due to the lengthy contact of the vinylcyclopropene, which is not sufficiently stable in solutions, with Bu^{t}OK and DMSO. The diferrocenylcyclopentadiene (**9**) is formed via carbene intermediate **10** following pathway A or B. Also, it could by formed via diradical intermediate **11**. It is known following pathway C (Scheme 4). To the best of our knowledge, this kind of transformation has never been hitherto reported.

It is well known that a small cycle of the aryl and alkyl ferrocenyl-substituted cyclopropenes can be easily opened (thermally or photochemically) through the formation of vinylcarbenoid or cyclopropyl diradical intermediates. The intramolecular transformations of the latters lead to the formation of big cycles with different structures. 3-Vinyl cyclopropenes, in general, are transformed into cyclopentadienes that have the terminal part of the vinyl fragment in the position 5.

The principal difference of the cyclopentadiene **9** obtained here as a result of the transformation of the 3-(2-ferrocenyl-1-methylvinyl)cyclopropene (**8**) is the presence of methyl (and not the ferrocenyl as in compound **12**) substituent in the position 5.

Formation of this product can be explained only incorporating into the sequence of the intramolecular transformations a step of 1,2 migration of the hydrogen atom of the final fragment of the vinyl group as hydride ion or free radical toward the carbon joined with the methyl substituent.

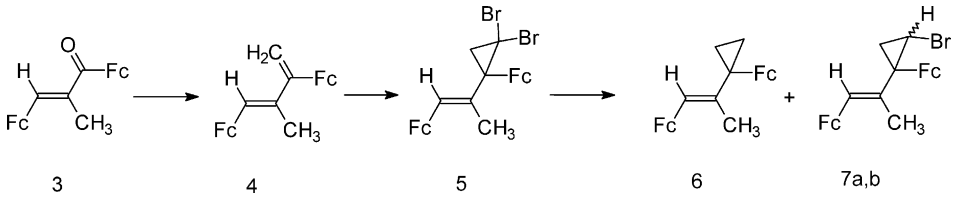
The supposition of the mechanism of intramolecular transformation of the 3,2-ferrocenylvinyl cyclopropene needs further confirmation.

3. Experimental

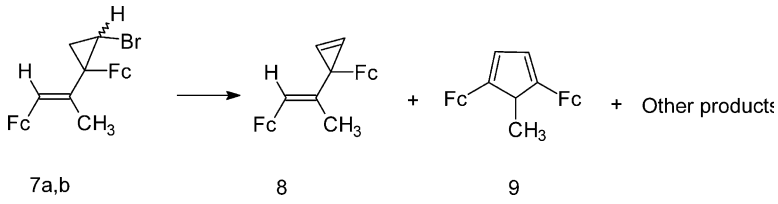
Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H- and ^{13}C-NMR spectra for solutions in $CDCl_3$ were collected on a Varian Unity 500 operating at 500 and 125 MHz, respectively. For both ^{1}H and ^{13}C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me_4Si 0.00 ppm) used as an internal standard. Column chromatography was carried out on alumina (Brockmann activity III). Elemental analyses were performed at Galbraith Laboratories, Inc., Knoxville. FAB$^+$ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystallographic data for the cyclopentadiene **9** were collected at room temperature on a Siemens P/4 diffractometer and are listed in Table 1.

3.1. 1,3-Diferrocenyl-2-methylbuta-1,3-diene (*4*)

To a solution of 3.96 g (11.13 mmol) of $MePPh_3Br$ in THF (100 ml), a solution of *n*-BuLi in *n*-hexanes (60 ml, 11.33 mmol), and the mixture was stirred for 40 min. Then a solution of the enone **3** (3.9 g, 9 mmol) in 20 ml of THF was added and the mixture was stirred at room



Scheme 2.



Scheme 3.

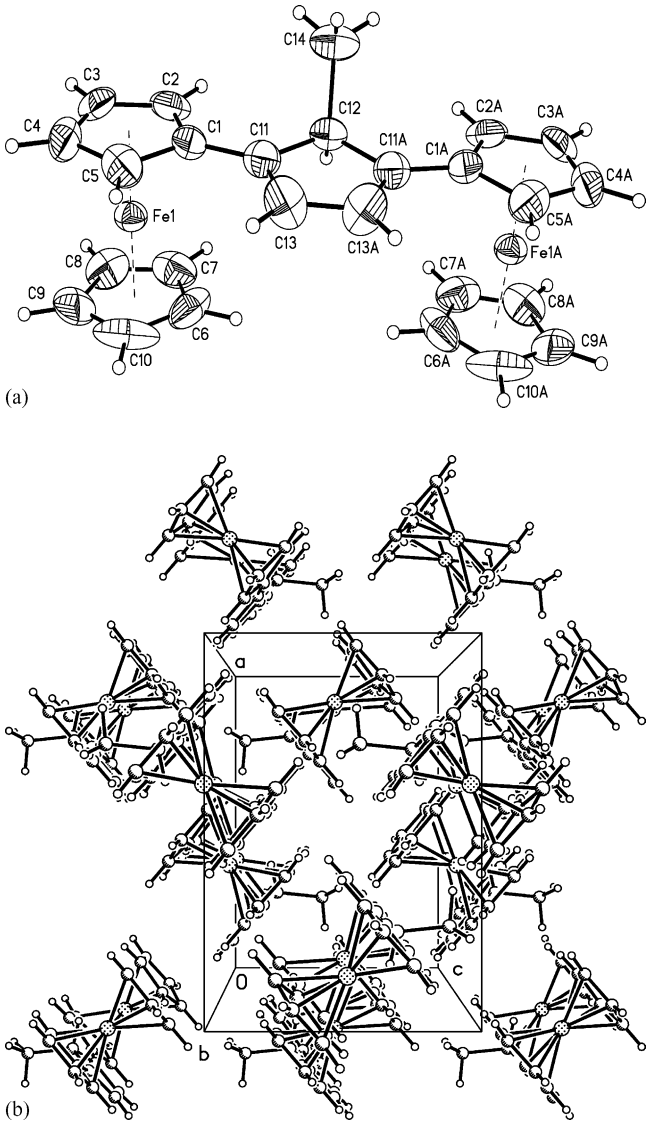


Fig. 1. Crystal structure and crystal packing of compound **9**. Selected bond lengths (Å): C(11)–C(13) = 1.380(8), C(13)–C(13) = 1.407(12), C(11)–C(12) = 1.503(7), C(12)–C(14) = 1.551(11).

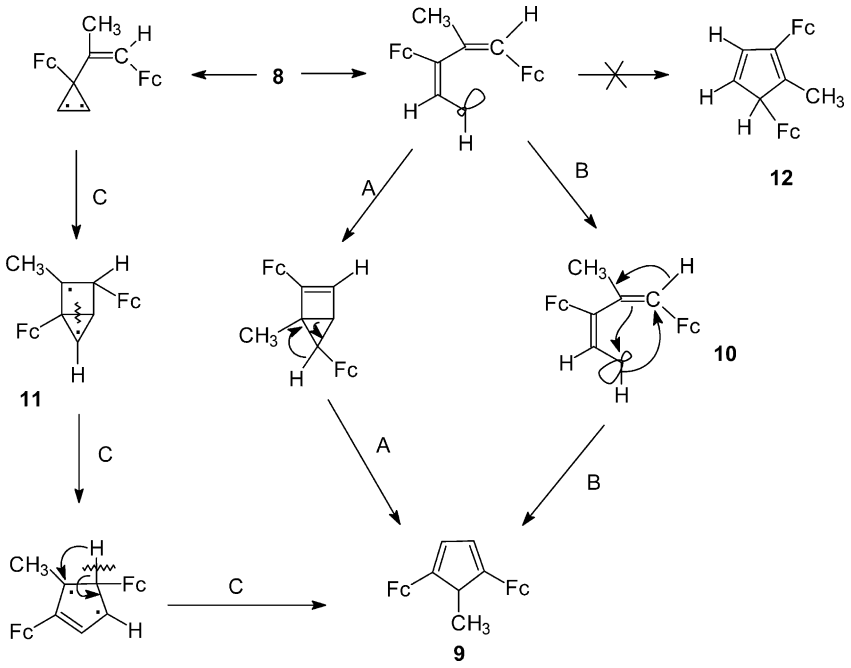
temperature for 2 h. The reaction mixture was partitioned between benzene and water and the organic layer was separated and washed with water. After evaporation of the solvent, the residue was chromatographed on alumina (Brockmann activity III) using hexane as eluent to give 2.74 g (70%) of the diene **4**, orange oil. IR (in KBr, cm^{-1}) 1598 (C=C), 878 (C=CH_2), ^{1}H-NMR ($CDCl_3$) δ: 0.76 (m, 2H, CH_2), 0.92–1.51 (m, 2H, CH_2), 1.96 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.48 (m, 4H, C_5H_4), 5.81 (s, 1H, =CH). ^{13}C-NMR ($CDCl_3$) δ: 18.28 (CH_3), 68.97 (C_5H_5), 69.64 (C_5H_5), 68.05–69.37 (C_5H_4), 82.87 ipso, 85.75 ipso (2C, C_5H_4), 110.15 (=CH_2), 125.90 (=C(Fc)H), 135.10 (=C–CH_3), 150.44 (Fc–C=CH_2) ppm. MS *m*/*z* (I_{rel}, %): 436 (100) $[M]^+$. Anal. Calcd. for $C_{25}H_{24}Fe_2$: C, 68.81; H, 5.54. Found: C, 68.76; H, 5.44%.

3.2. 1,1-Dibromo-2-ferrocenyl-2-(2-ferrocenyl-1-methylvinyl)cyclopropane (5)

The diene **4** (2.74 g, 6.28 mmol) and bromoform (4 ml) were added to a aqueous solution of sodium hydroxide (40%, 10 ml) in the presence of transfer catalyst Trilon B (0.137 g). The reaction mixture was vigorously stirred for 4 h at room temperature, and the mixture was then poured into water and extracted with CH_2Cl_2. The solvent was evaporated and purified on alumina (hexane; CH_2Cl_2). Unchanged diene **4** was eluted first, the second fraction gave pale-yellow crystals 3.43 g (5.65 mmol, 90% yield) of the *gem*-dibromocyclopropane. IR (KBr, in cm^{-1}) 1444 (C=C–CH_3), ^{1}H-NMR ($CDCl_3$) δ: 2.11 (s, 2H, CH_2), 2.33 (s, 3H, CH_3), 4.09–4.53 (m, 18H, 2Fc), 6.19 (s, 1H, =CH). ^{13}C-NMR ($CDCl_3$) δ: 19.64 (CH_3), 36.14 (CH_2), 36.54 (C–Fc), 43.41 (C–Br), 65.96–69.59 (Fc), 126.28 (=C(Fc)H), 135.36 (=C–CH_3) ppm. MS *m*/*z* (I_{rel}, %): 608 (37.5), 606 (21.25), 526 (8.75), 448 (25), 382 (3.75), 326 (100) $[M]^+$. Anal. Calcd. for $C_{26}H_{24}Br_2Fe_2$: C, 51.35; H, 3.97. Found: C, 51.30; H, 3.98%.

3.3. Reductive debromination of gem-dobromo(vinyl)cyclopropane (5)

The dihalogenated vinylcyclopropane (**5**) (3.42 g) and titanium isopropoxide (1 ml) were dissolved in dry THF (20 ml), and EtMgBr in ether 7.34 mmol was added slowly dropwise with stirring. Stirring was continued for 3 h at 25 °C, and the mixture was then poured into water and extracted with CH_2Cl_2. The extract was washed with 10% HCl, the solvent was evaporated in vacuo and the residue was chromatographed on alumina (hexane; CH_2Cl_2) to give 1-ferrocenyl-1-(2-ferrocenyl-1-methylvinyl)cyclopropane (**6**) and (*Z*)- and (*E*)-isomers 2-bromo-1-ferrocenyl-1-(2-ferrocenyl-1-methylvinyl)cyclopropane (**7a** and **7b**).



Scheme 4.

Table 1
Crystallographic data and structure refinement parameters for compound **9**

Molecular formula	$C_{26}H_{24}Fe_2$
Formula weight	448.15
Temperature (K)	291(2)
Mo–K_α radiation, λ (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pnma*
Unit cell dimensions	
α (°)	90
β (°)	90
γ (°)	90
a (Å)	10.7928(13)
b (Å)	24.913(3)
c (Å)	7.4916(5)
V (Å^3)	2014.4(4)
Z	4
Density calc. (g cm^{-3})	1.478
Absorption coefficient (mm^{-1})	1.448
F(0 0 0)	928
θ range for data collection (°)	2.84–29.99
Reflections collected	3889
Independent reflections	3003 [$R_{int} = 0.0483$]
Completeness to $\theta = 29.99°$	100.0%
Absorption correction	Integration
Max. and min. transmission	0.8092 and 0.7358
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3003/0/131
Goodness-of-fit on F^2	0.883
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0613$, $wR_2 = 0.1194$
R indices (all data)	$R_1 = 0.1559$, $wR_2 = 0.1405$
Extinction coefficient	0.00116(18)
Largest diff. peak and hole (e Å^{-3})	0.425 and −0.468

3.3.1. 1-Ferrocenyl-1-(2-ferrocenyl-1-methylvinyl)cyclopropane (**6**)

Yield 0.77 g (30%), yellow crystals, m.p. 109–110 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.27, 1.52, 2.11 (m, 4H, CH_2), 2.32 (s, 3H, CH_3), 4.16 (s, 5H, C_5H_5), 4.41 (s, 2H, C_5H_4), 4.43 (s, 2H, C_5H_4) ppm. ^{13}C-NMR ($CDCl_3$) δ: 18.14 (CH_3), 28.02 (CH_2), 68.52 (C_5H_4), 69.80 (C_5H_5), 70.73 (C_5H_5), 72.73 (C_5H_4), 86.41 (ipso-C_5H_4), 124.49 (CH=), 138.05 (=C–CH_3) ppm. MS m/z (I_{rel}, %): 450 $[M]^+$. Anal. Calcd. for $C_{26}H_{25}Fe_2$: C, 69.33; H, 5.77. Found: C, 69.30; H, 5.65%.

3.3.2. (*Z*)-Isomer **7a**

1.00 g (33% yield), yellow crystals, m.p. 119–120 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (dd, 1H, $J = 5.7$ Hz, CH_2), 1.83 (dd, 1H, $J = 6.6$ Hz, CH_2), 2.06 (s, 3H, CH_3), 4.15 (s, 5H, C_5H_5), 3.56, 4.05, 4.07 (s, 4H, C_5H_4), 6.18 (s, 1H, =CH) ppm. ^{13}C-NMR ($CDCl_3$) δ: 18.86 (CH_3), 28.83 (CH_2), 32.49 (CHBr), 34.68 (C–Fc), 66.32–69.33 (C_5H_4), 68.52 (C_5H_5), 68.82 (C_5H_5), 82.07 (ipso-C_5H_4), 90.06 (ipso-C_5H_4), 126.10 (=C(Fc)H), 135.59 (=C–CH_3) ppm. MS m/z (I_{rel}, %): 529 $[M]^+$. Anal. Calcd. for $C_{26}H_{25}Br_1Fe_2$: C, 58.97; H, 4.72. Found: C, 58.93; H, 4.70%.

3.3.3. (*E*)-Isomer **7b**

0.77 g (25% yield), yellow crystals, m.p. 125–126 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.61 (dd, 1H, $J = 4.8$ Hz, CH_2), 1.80 (dd, 1H, $J = 6.3$ Hz, CH_2), 2.08 (s, 3H, CH_3), 4.19 (s, 5H, C_5H_5), 4.24, 4.36, 4,42 (s, 4H, C_5H_4), 6.21 (s, 1H, =CH) ppm. ^{13}C-NMR ($CDCl_3$) δ: 18.67 (CH_3), 22.54 (CH_2), 31.47 (CHBr), 34.92 (C–Fc), 66.38–69.33

(C_5H_4), 68.47 (C_5H_5), 68.75 (C_5H_5), 82.07 (ipso-C_5H_4), 94.11 (ipso-C_5H_4), 127.52 (=C(Fc)H), 133.42 (=C–CH_3) ppm. MS *m/z* (%): 529 $[M]^+$. Anal. Calcd. for $C_{26}H_{25}Br_1Fe_2$: C, 58.97; H, 4.72. Found: C, 58.99; H, 4.75%.

3.4. Dehydrobromination of monobromocyclopropanes (*7a* and *7b*)

A mixture of monobromocyclopropanes (**7a** and **7b**) (1.77 g, 3.34 mmol) and of Bu^tOK (10.05 mmol) in 10 ml of dry DMSO was stirred for 48 h at room temperature. 50 ml of benzene and 50 ml of water were then added. The organic layer was separated and concentrated. The residue was chromatographed on Al_2O_3 (hexane) to give compounds **8** and **9**.

3.4.1. 3-Ferrocenyl-3-(2-ferrocenyl-1-methylvinyl)cyclopropene (*8*)

Yield 0.93 g (62%), red crystals, m.p. 135–136 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.43 (s, 3H, CH_3), 4.02, 4.13, 4.17 (m, 4H, C_5H_4), 4.27, 4.40, 4.49 (m, 4H, C_5H_4), 4.07 (s, 5H, C_5H_5), 6.14 (s, 1H, =CH), 7.23 (s, 2H, CH=CH) ppm. ^{13}C-NMR ($CDCl_3$) δ: 19.21 (CH_3), 31.21 (C–), 64.84, 66.50, 67.20, 67.50 (C_5H_4), 69.17 (C_5H_5), 69.19 (C_5H_5), 93.38 (ipso-C_5H_4), 124.55 (HC=CH), 149.47 (=C–CH_3) ppm. MS *m/z* (I_{rel}, %): 448 $[M^+]$. Anal. Calcd. for $C_{26}H_{24}Fe_2$: C,69.41; H, 5.35. Found: C, 69.36; H, 5.30%.

3.4.2. 1,4-Diferrocenyl-5-methylcyclopentadiene (*9*)

Yield 0.56 g (35%), red crystals, m.p. 142–143 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.56 (d, 3H, CH_3), 3.27 (bs, 1H, CH), 4.08 (m, 10H, C_5H_4), 4.15–4.49 (m, 8H, C_5H_4), 6.41 (2 = CH) ppm. ^{13}C-NMR ($CDCl_3$) δ: 19.45 (CH_3), 30.01 (C–CH_3), 64.82, 66.45, 67.16, 67.50, 68.17, 68.42, 68.61 (C_5H_4), 69.13 (C_5H_5), 69.10 (C_5H_5), 81.38 (ipso-C_5H_4), 124.55 (C=C), 149.47 (=C–Fc) ppm. MS *m/z* (I_{rel}, %): 448 $[M^+]$. Anal. Calcd. for $C_{26}H_{24}Fe_2$: C, 69.41; H, 5.35. Found: C, 69.36; H, 5.30%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201533 for compound **9**. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the grant CONACyT No. 34862-E. The author thanks M.L. Velasco, J. Perez, H. Rios, A. Acosta and E.R. Patiño for their technical assistance.

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