Available online at www.sciencedirect.com
ScienceDirect
*Mendeleev Commun.*, 2010, **20**, 312–313
Mendeleev Communications

# Novel intramolecular transformations of amino(diferrocenyl)vinylcarbenes

**Elena I. Klimova,*[a] Tatiana Klimova,[a] Leon V. Backinowsky,[b] Marcos Flores-Alamo,[a] Luis A. Ortiz-Frade[c] and Marcos Martínez García[d]**

[a] *Department of Chemistry, National Autonomous University of Mexico, CP 04510 Mexico DF, Mexico. E-mail: eiklimova@yahoo.com.mx*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328*
[c] *Center of Research and Technological Development in Electrochemistry, SC Technology Park Queretaro, Pedro Escobedo, CP 76703 Queretaro, Mexico*
[d] *Institute of Chemistry, National Autonomous University of Mexico, CP 04510 Mexico DF, Mexico*

DOI: 10.1016/j.mencom.2010.11.002

2,3-Diferrocenyl-1-morpholino- and 2,3-diferrocenyl-1-piperidinocyclopropenylium tetrafluoroborates react with allylmagnesium bromide to give 3-allylidene-1,2-diferrocenylcyclopropene, 1,2-diferrocenylbenzene, 1,3-diferrocenyl-2-morpholino(piperidino)-hexa-1,3,5-trienes and 2,3-diferrocenyl-1-morpholino(piperidino)bicyclo[3.1.0]hex-2-enes.

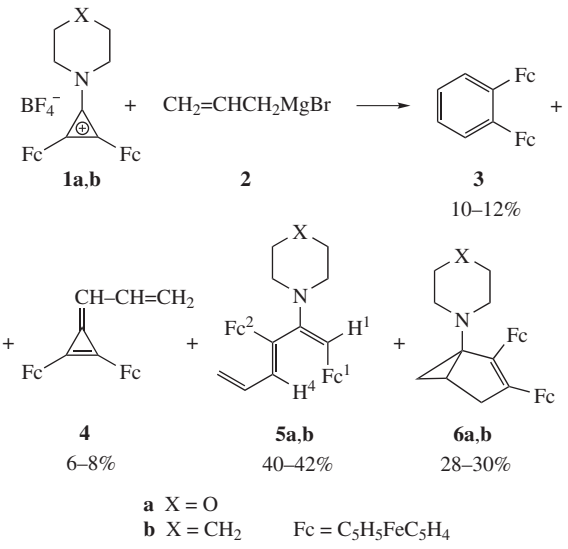
Vinylcarbenes are formed as intermediates upon ring-opening of cyclopropenes with electron-donating substituents, their intramolecular transformations afford products that are difficult to obtain through other synthetic schemes.[1] Transient tetrasubstituted 2,3-diferrocenyl-1-methylsulfanylcyclopropenes[2,3] generated in the reactions of 1,2-diferrocenyl-3-methylsulfanylcyclopropenylium iodide with C- and N-nucleophiles undergo especially smooth regioselective small ring opening[2–9] leading to diferrocenylvinyl(methylsulfanyl)carbenes.[4] Their intramolecular transformations served as the basis for the development of new synthetic procedures for methylsulfanyl-substituted ferrocenylpolyenes,[4,5] carbo- and heterocycles;[4–6] new 1,4-migrations of functional groups such as $CO_2Et$, CN and $NO_2$ were discovered.[6–9]

So far, reactions of 1-amino-2,3-diferrocenylcyclopropenylium salts, which can serve as precursors for 1,2-diferrocenyl-3-methylsulfanylcyclopropenylium salts, with C-nucleophiles have not been studied. At the same time, the introduction of nitrogen-containing fragments into unsaturated ferrocene compounds is of particular interest in view of their applications in pharmacology, electrochemistry, nonlinear optics, *etc*. Comparative analysis of regioselective small ring opening in transient 3-amino-1,2-diferrocenyl- and 1-amino-2,3-diferrocenylcyclopropenes into amino(diferrocenyl)vinylcarbenes and intramolecular transformations of amino(ferrocenyl)carbene intermediates are also of interest.

Here, we investigated the reactions of 2,3-diferrocenyl-1-morpholino- and 2,3-diferrocenyl-1-piperidinocyclopropenylium tetrafluoroborates **1a**,**b** with allylmagnesium bromide **2**.

We demonstrated that salts **1a** and **1b** react with an excess of the Grignard reagent **2** affording several products separated by preparative TLC on silica gel, the major products being 1,2-diferrocenylbenzene **3**, 3-allylidene-1,2-diferrocenylcyclopropene **4**, 1,3-diferrocenyl-2-morpholino(piperidino)hexa-1,3,5-trienes **5a**,**b** and 2,3-diferrocenyl-1-morpholino(piperidino)-bicyclo[3.1.0]hex-2-enes **6a**,**b** (Scheme 1).†

The structures of the products were established based on the mass spectrometry, $^1$H and $^{13}$C NMR spectroscopy and elemental analysis data. Thus, the $^1$H NMR spectrum of compound **3** characterizes it as a symmetrical aromatic compound with one singlet for two $C_5H_5$ fragments of two ferrocenyl substituents and two signals (a doublet and a triplet) for four aromatic protons. The $^{13}$C NMR spectrum of this compound contains one signal for $C_5H_5$ and two signals for $C_5H_4$ of the ferrocene fragments, one signal for two $C_{ipso}$Fc, two signals for $C_{ipso}$ and two signals for four C atoms of the $C_6H_4$ fragment. The $^1$H NMR spectroscopic data of this product differ from those reported previously.[10]




**Scheme 1**

† *General reactions of salts* **1a**,**b** *with allylmagnesium bromide* **2**. Allylmagnesium bromide **2** (7.0 ml of a 1 M solution in diethyl ether) was added to a suspension of salt **1a** or **1b** (2.0 mmol) in dry benzene (100 ml) and the mixture was stirred in an inert dry atmosphere until complete dissolution of the salts **1a**,**b** (~8 h). The excess of the organometallic reactant was quenched with water (20 ml), the organic layer was separated, concentrated, and the residue was chromatographed on silica gel (hexane–dichloromethane, 4:1) to give compounds **3**, **4**, **5a**,**b** and **6a**,**b**.

For characteristics of compounds **3**, **4**, **5a**,**b** and **6a**,**b**, see Online Supplementary Materials.

The $^1$H NMR spectrum of cyclopropene **4** exhibits signals for the protons of two ferrocenyl groups and four sets of olefinic protons. The quantity of signals for the carbon atoms not connected to protons in the $^{13}$C NMR spectrum corroborates its structure.

Spectroscopic data suggest that trienes **5a** and **5b** are formed as single geometric isomers, presumably with *E*-arranged Fc[1] and heterocyclic substituents and *Z* configuration of the internal double bond. The 2-position of the heterocycle at the hexatriene system was established by $^1$H NMR spectroscopy with a 1D NOE experiment, which revealed interactions between the olefinic proton H(1) and protons of the Fc[1], as well as between H(4) and protons of the Fc[2] (Scheme 1).

The structures of bicycles **6a**,**b** were established reckoning on the aforementioned physicochemical methods and, for compound **6a**, confirmed by X-ray diffraction analysis, which allowed us to unambiguously identify **6a** as 2,3-diferrocenyl-1-morpholinobicyclo[3.1.0]hex-2-ene (Figure 1).‡ The three-membered ring in **6a** represents an equilateral triangle with virtually equal bond lengths and bond angles.

The tentative mechanisms of formation of compounds **3**–**6** (Scheme 2) imply intramolecular transformations of diferrocenyl- (**7**) and amino(diferrocenyl)vinylcarbenes (**8**, **9**). The nucleophilic attack on C(1) of the cations **1a**,**b** results in compounds **3**, **4** and **6a**,**b**. We failed to isolate the intermediate adducts **10a**,**b** and **11a**,**b**. Cyclopropene **4** is stable in the crystalline state, while in solution it gradually converts into diferrocenylbenzene **3** (20 °C, 10 h). The nucleophilic attack on C(2) of the cations **1a**,**b** affords hexatrienes **5a**,**b**.

In conslusion, the results obtained in the present study demonstrate substantial differences in the regiodirection of the ring-opening of transient diferrocenylcyclopropenes **4**, **10a**,**b** and **11a**,**b** as compared with the MeS-analogues[3–9] and 3-alkyl-3-allyl-1,2-diphenylcyclopropenes.[12,13] The reactions proceed *via* novel types of diferrocenylcarbenes, *viz*., cyclohexadiene **7** and those with a ferrocenyl substituent at the carbene centre, **8** and **9**. The intramolecular transformations of these species

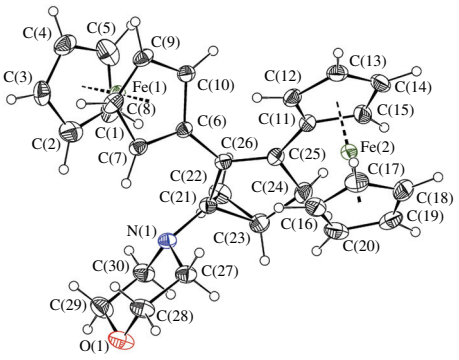
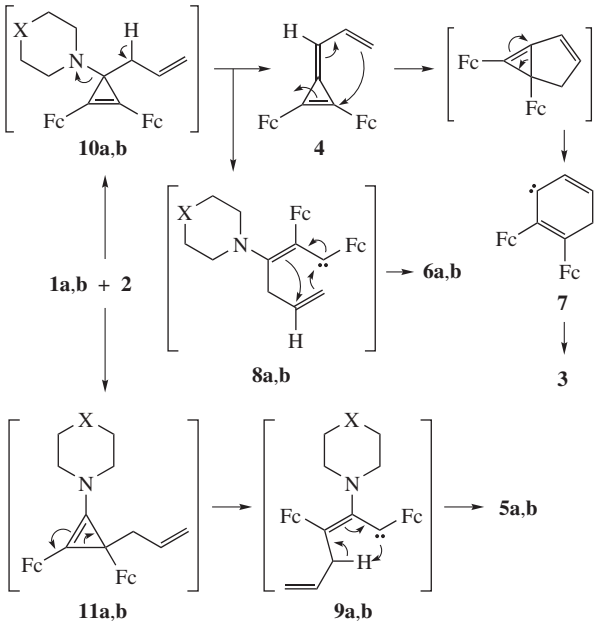



**Figure 1** Crystal structure of compound **6a**.

‡ *Crystallographic data for* **6a**. Crystals of $C_{30}H_{31}Fe_2NO$ ($M$ = 533.26) are triclinic, space group $P\bar{1}$, at 298(2) K: $a$ = 7.5080(7), $b$ = 10.0160(16) and $c$ = 16.585(3) Å, $\alpha$ = 73.790(12)°, $\beta$ = 80.510(10)°, $\gamma$ = 85.340(9)°, $V$ = 1180.4(3) Å$^3$, $Z$ = 2, $d_{calc}$ = 1.500 g cm$^{-3}$, $\lambda$(MoK$\alpha$) = 0.71073 Å, $F$(000) = 556, $\mu$ = 1.253 mm$^{-1}$; index ranges $-1 \le h \le 10$, $-13 \le k \le 13$, $-23 \le l \le 23$, scan range $2.12 \le \theta \le 29.99°$; 6793 independent reflections, $R_{int}$ = 0.0255; 8145 total reflections, 307 refinable parameters; final $R$ indices [$I > 2\sigma(I)$] $R_1$ = 0.0439, $wR_2$ = 0.1064; $R$ indices (all data) $R_1$ = = 0.0643, $wR_2$ = 0.1174, goodness-of-fit on $F^2$ 1.019, largest difference peak and hole 0.586/–0.399 eÅ$^{-3}$. The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The structure was solved by the direct method (SHELXS-97)[11] and refined using full-matrix least-squares on $F^2$.

CCDC 776979 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.




**Scheme 2**

form the basis for the new methods of synthesis of *vic*-diferrocenylarenes, 2-amino-1,3-diferrocenylpolyenes and amino(diferrocenyl)bicyclo[3.1.0]hex-2-enes.

This work was supported by the DGAPA-UNAM (Mexico, grant IN 214209) and by the CONACyT (Mexico, grant no. 100970). The authors are grateful to E. A. Vázquez López for his technical assistance.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.11.002.

## References

1 K. Komatsu and T. Kitagawa, *Chem. Rev.*, 2003, **103**, 1371.
2 T. Klimova, M. Martínez García, L. Ortiz-Frade, S. Hernández Ortega, R. A. Toscano and E. I. Klimova, *J. Organomet. Chem.*, 2006, **691**, 2872.
3 E. I. Klimova, T. Klimova, M. Flores Alamo, L. V. Backinowsky and M. Martínez García, *Molecules*, 2009, **14**, 3161.
4 E. I. Klimova, T. Klimova, S. Hernandez Ortega, D. Mèndez Iturbide, A. Garcia Marquez and M. Martínez García, *J. Organomet. Chem.*, 2005, **690**, 3333.
5 T. Klimova, E. I. Klimova, J. M. Mèndez Stivalet, S. Hernández Ortega and M. Martínez García, *Eur. J. Org. Chem.*, 2005, 4406.
6 E. I. Klimova, T. Klimova, S. Hernández Ortega, L. Ortiz-Frade, L. V. Backinowsky and M. Martínez García, *J. Organomet. Chem.*, 2008, **693**, 1215.
7 T. Klimova, E. I. Klimova, M. Flores-Alamo, L. V. Backinowsky and M. Martínez García, *Synthesis*, 2006, 3706.
8 E. I. Klimova, M. Martínez García, T. Klimova, C. Alvarez Toledano, R. A. Toscano and L. V. Backinowsky, *Eur. J. Org. Chem.*, 2006, 4755.
9 E. I. Klimova, J. M. Mendez Stivalet, T. Klimova Berestneva, M. Flores Alamo, L. V. Backinowsky, L. Ortiz Frade and M. Martínez García, *Synth. Commun.*, 2010, **40**, 839.
10 C. Patoux, C. Coudret, J.-P. Launay, C. Joachim and A. Gourdon, *Inorg. Chem.*, 1997, **36**, 5037.
11 G. M. Sheldrick, *SHELXS-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1994.
12 A. Padwa, T. J. Blacklock, D. M. Cordova and R. Loza, *J. Am. Chem. Soc.*, 1980, **102**, 5648.
13 A. Padwa, T. J. Blacklock, D. M. Cordova and R. Loza, *J. Am. Chem. Soc.*, 1981, **103**, 7202.

*Received: 20th May 2010; Com. 10/3529*