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Rod-like derivatives of ferrocenylacetylene: syntheses and structure

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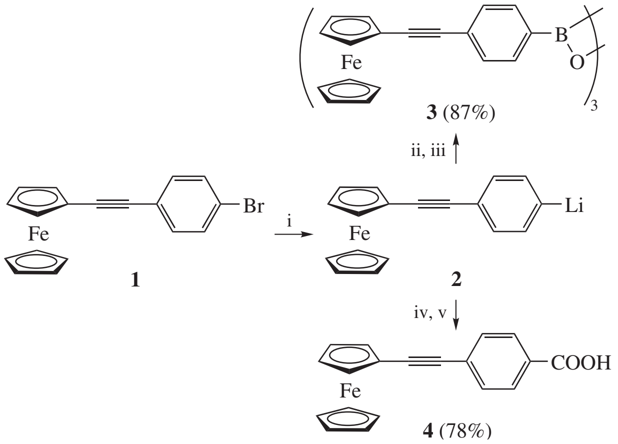
1-Bromo-4-ferrocenylethynylbenzene was transformed into tris(4-ferrocenylethynylphenyl)boroxine and 4-ferrocenylethynylbenzoic acid, which were further converted into new rod-like ferrocenylacetylene and ferrocenylethylene derivatives. Crystal and molecular structures of tris(4-ferrocenylethynylphenyl)boroxine and (*Z*)-4-(2-chloro-2-ferrocenylethenyl)benzoic acid 3-(1-imidazolyl)propylamide were determined by single crystal X-ray analysis.

Ferrocenyl derivatives containing acetylene moiety can serve as semiconductor materials permitting electron transport though a molecule with conjugated bonds by transmission of electron waves through the molecule or by hopping.[1] Ethynylferrocenes are challenging in the construction of redox switchable molecular systems.[2] Metallocene molecular gears,[3] molecular machines[4] and other nanovehicles[5] include acetylene moiety in the frameworks. On the other hand, ferrocenyl derivatives incorporating acetylene fragment are promising in the construction of new rod-like ferrocenylmesogens.[6–9]

In this regard a reaction of ferrocene with terminal alkynes in the presence of copper and iron salts leading to ferrocenylacetylenes[10] can be topical.

Here we report on syntheses of a new generation of precursors based on ethynylferrocene framework appropriate for delicate introducing in complex organic molecules and biomolecules which can serve as photo- and electrochemical sensors.



Scheme 1 *Reagents and conditions*: i, BuLi, –60 °C; ii, $B(OMe)_3$, –60 °C; iii, HCl (aq.) and dehydration; iv, CO_2; v, HCl (aq.).

1-Bromo-4-ferrocenylethynylbenzene **1** is available by alkynylation of ferrocene and seems promising for our purpose since bromine atom permits functionalization of the molecule *via* corresponding lithio derivative **2** (Scheme 1). Previously[11] boroxine **3** was prepared using tri-*n*-butyl borate in 67% yield. We found that application of trimethyl borate significantly elevates yield of **3**.[†] Acidification gave **3** along with the corresponding boronic acid. Azeotropic removal of water with xylenes afforded pure boroxine **3**.

Crystals of compound **3** contain two independent molecules within the unit cell (Figure 1).[‡] The core B_3O_3 fragments represent (Figure 2) almost regular hexagons with B–O–B and O–B–O angles varying from 118.6(8) to 122.5(7)°. The central $(C_6H_4B)_3O_3$

[†] *Tris(4-ferrocenylethynylphenyl)boroxine* **3**. A solution of 2.01 M BuLi (2 ml, 4.02 mmol) was added to a solution of **1** (1.27 g, 3.48 mmol) in a mixture of THF (20 ml) and diethyl ether (6 ml) at –60 °C under argon. The deep brick-colored mixture was stirred at –55 to –60 °C for 1 h resulting in an orange suspension of 4-ferrocenylethynylphenyllithium **2**. Trimethyl borate (0.57 ml, 5.0 mmol) was quickly (2 min) added at –60 °C. The precipitate of lithium derivative dissolved and the mixture became brown. The temperature was gradually raised to –10 °C within 1 h, then to ambient one and after this stirring was continued for 1 h. Water (2 ml) was added followed by a solution of hydrochloric acid (0.7 ml) in water (8.5 ml). The organic layer was separated, diluted with benzene, washed with water, dried over sodium sulfate and evaporated under reduced pressure. Xylenes (25 ml) were added to the residue and the solvent was evaporated again under reduced pressure at bath temperature 93 °C to dryness. The residue was washed with hot light petroleum and dried in air giving boroxine **3** (0.95 g, 87%) as an orange powder, decomp. >205 °C. ^{1}H NMR, δ: 4.24 and 4.27 (m and s, 2H + 5H, C_5H_4, C_5H_5), 4.55 (m, 2H, C_5H_4), 7.60–7.62 and 8.17–8.19 (m, 4H, AA′BB′, C_6H_4). ^{13}C NMR, δ: 64.9 (C_5H_4), 69.1 (C_5H_4), 70.1 (C_5H_5), 71.6 (C_5H_4), 86.0 and 94.50 (C≡C), 128.3, 130.8, 133.4, 135.5 (C_{Ar}). IR (KBr, ν/cm^{-1}): 2206 (C≡C). MS (MALDI-TOF), *m*/*z*: 936.120 [M]$^+$ (calc for [M]$^+$, *m*/*z*: 936.1226). Found (%): C, 69.19; H, 4.29. Calc. for $C_{54}H_{39}Fe_3B_3O_3$ (%): C, 69.30; H, 4.20.

[‡] Crystals of compound **3** suitable for X-ray investigation were obtained by the following procedure. A suspension of **3** in benzene–toluene mixture was heated till dissolution. The solution was cooled to 40 °C, a layer of light petroleum was added without stirring and the mixture was kept at room temperature.

Crystallographic data for **3** and **10** (*vide infra*) were collected on a Bruker SMART APEX II diffractometer using graphite monochromatized MoKα radiation (λ = 0.71073 Å). Absorption corrections based on measurements of equivalent reflections were applied. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms except disordered C_5H_5 rings and solvent benzene molecules in **3**.[12]

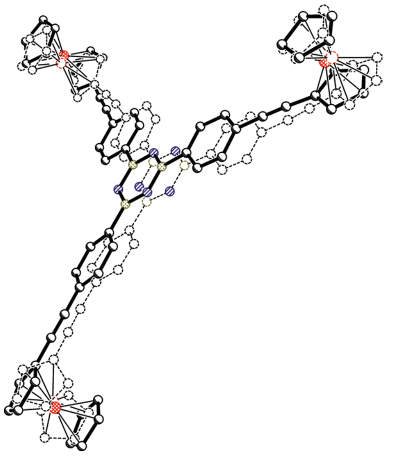


Figure 1 The best orthogonal least-squares fitting of two independent molecules of **3** based on iron, boron and oxygen atoms.

units are planar within 0.237(7) Å. All six ferrocenyl substituents possess nearly parallel cyclopentadienyl rings with interplanar angles less than 4.5°. In both molecules, one of three unsubstituted C_5H_5 ligands are rotationally disordered over two positions with approximately equal occupancies. Four ordered ferrocenyl substituents exhibit eclipsed conformation. In general, both molecules have similar bond lengths and angles. However, these two molecules seriously differ in rotations along ferrocenyl–C_{sp} bonds. In the first molecule (A), substituted C_5H_4 rings form significantly greater interplanar angles with the central ($-C{\equiv}C-C_6H_4-B)_3O_3$ units [12.3(4), 7.2(3) and 27.2(4)°] than in the second molecule (B): 9.4(4), 13.6(4) and 17.1(4)°. These differences are clearly seen from the best orthogonal least-squares fitting based on iron, boron and oxygen atoms (Figure 1). In the cell, the independent molecules are related by pseudosymmetry centers. The closest molecules are linked in pairs by π–π stacking interactions (Figure 3). However, these interactions do not affect dramatically acetylene triple bond because its stretching vibrations in **3** are observed at 2206 cm^{-1}, which is only slightly below two stretching bands 2220 and 2235 cm^{-1} found in **1**. Specific CH–π(alkyne) interactions were determined previously in a series of alkynylferrocenes.[13]

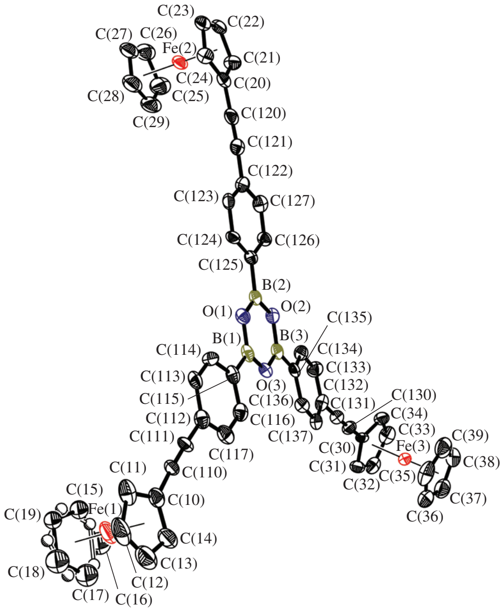


Figure 2 One of the two independent molecules in the structure of **3**. Displacement ellipsoids are shown at 50% probability level. Minor component of disordered C_5H_5 group are drawn with open lines. Hydrogen atoms are omitted for clarity.

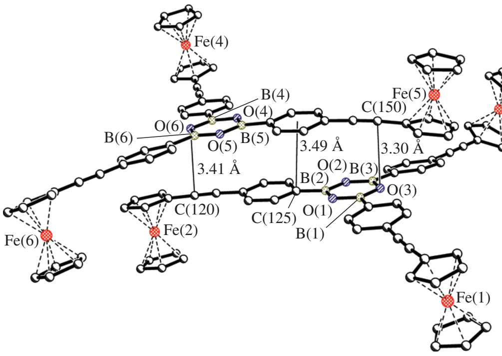
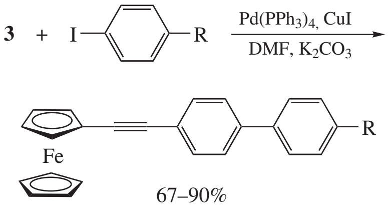


Figure 3 π–π Stacking interactions in the crystal of boroxine **3**.

Starting from boroxine **3**, several rod-like ferrocenyl derivatives (**5**–**8**) containing acetylene moiety were prepared by palladium catalyzed cross-coupling reactions (Scheme 2). Addition of copper(I) iodide as co-catalyst provides better yields of products **5**–**8** as compared with our previous results.[11] Note that yields of biphenyl derivatives of ethynylferrocene prepared by this method are significantly higher than those of similar compounds prepared by Sonogashira coupling between ethynylferrocene and 4-iodo-4′-X-biphenyls.[14]



5 R = $(CH_2)_3COOH$ **7** R = NH_2
6 R = NO_2 **8** R = $OC(O)C_6H_4OC_{12}H_{25}$

Scheme 2

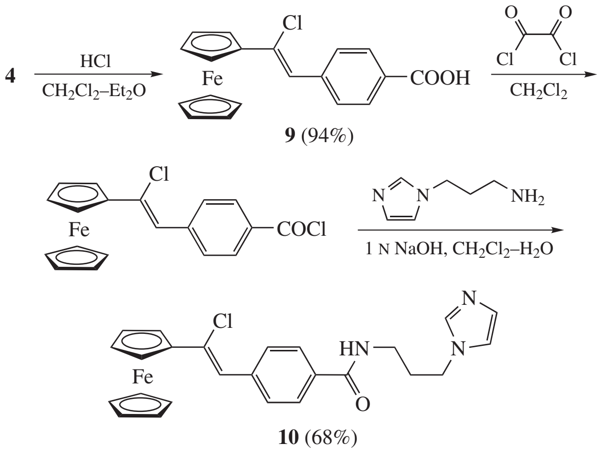
Compounds **5**–**7** may be precursors of liquid crystals with rod-like fragment including acetylene moiety. Compound **8** is a liquid crystal which reveals nematic phase with narrow temperature interval of existence (monotropic transition at 125 °C).

Second path of transformation of bromide **1** is its conversion into acid **4** (see Scheme 1). Carboxylic acid **4** is of interest due to an opportunity for a construction of other rod-like molecules. At the same time, it can be used for the preparation of ethylene derivatives *via* transformation of triple C≡C bond into double one. Double bond is a better conductor of electronic effects as compared with triple bond. For this reason we converted **4** into the corresponding chlorovinyl derivative **9** and then into amide **10** (Scheme 3).

For **3**: crystals of $C_{54}H_{39}Fe_3B_3O_3$ (M = 1248.26) are triclinic, chiral space group $P1$, at 150 K: a = 10.9389(16), b = 14.500(2) and c = 21.107(3) Å, V = 3131.0(8) Å^3, Z = 2, Z' = 2, d_{calc} = 1.324 g cm^{-3}. 25205 reflections were collected from which 21203 unique (R_{int} = 0.0353), F(000) = 1296. Refinement converged to R_1 = 0.1388, wR_2 = 0.1969 (all data) and R_1 = = 0.0752, wR_2 = 0.1683 [$I > 2\sigma(I)$], GOF on F^2 = 1.011.

For **10**: crystals of $C_{28}H_{27}ClFeN_3O$ (M = 512.83) are monoclinic, space group $P2_1/c$ at 183 K: a = 17.479(3), b = 9.1571(17) and c = 15.424(3) Å, V = 2466.9(8) Å^3, Z = 4, d_{calc} = 1.381 g cm^{-3}. 20206 reflections were collected from which 4583 unique (R_{int} = 0.0334), F(000) = 1068. Refinement converged to R_1 = 0.0606, wR_2 = 0.1112 (all data) and R_1 = 0.0393, wR_2 = 0.0985 [$I > 2\sigma(I)$], GOF on F^2 = 1.054.

CCDC 1021605 and 1052915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



Scheme 3

Z-Configuration of the double bond in **10** was determined by single crystal X-ray diffraction experiment (Figure 4).‡ Ferrocenyl moiety exhibits eclipsed conformation. In **10**, all bond lengths and angles demonstrate ordinary values. Of interest, the central Cp–C(Cl)=C(H)–C_6H_4 fragment is planar within 0.161(2) Å but forms large angle 34.5° with conjugated amide group. In crystal, adjacent molecules are combined in chains passing along *c*-axis by moderate N–H···N hydrogen bonds (Figure 5).

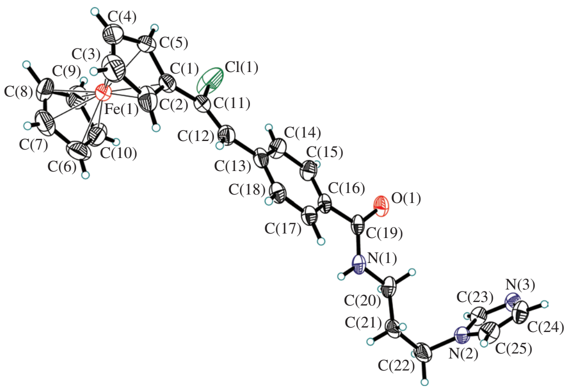


Figure 4 Molecular structure of **10**. Displacement ellipsoids are shown at 50% probability level.

In conclusion, the synthetic approach based on conversion of 1-bromo-4-ferrocenylethynylbenzene into the corresponding carboxylic acid and boroxine is a convenient access to rod-like derivatives of ferrocenylacetylene containing terminal functional groups. These functional groups provide introducing the rod-like ferrocenylethynyl moieties in complex organic molecules and biomolecules creating new photo- and electrochemical sensors.

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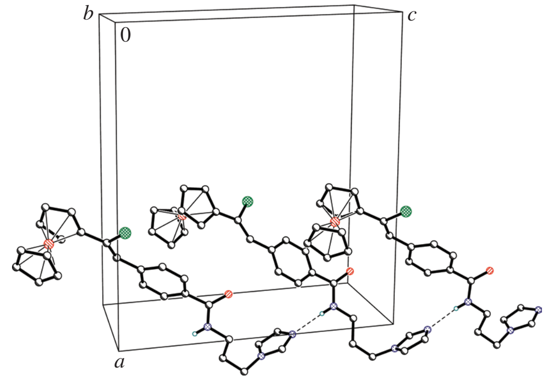

Figure 5 Hydrogen-bonded chains in the structure of **10**.

Online Supplementary Materials

Supplementary data associated with this article (experimental procedures and characterization data for compounds **4–10**) can be found in the online version at doi:10.1016/j.mencom.2015.05.003.

References

1 M. S. Inkpen, T. Albrecht and N. J. Long, *Organometallics*, 2013, **32**, 6053.

2 G. Grelaud, G. Argouarch, M. P. Ciffuentes and M. G. Hunphrey, *Tetrahedron*, 2013, **69**, 3316.

3 A. M. Stevens and C. J. Richards, *Tetrahedron Lett.*, 1997, **38**, 7805.

4 G. Rapenne and G. Jimenes-Bueno, *Tetrahedron*, 2007, **63**, 7018.

5 Y. Shirai, J.-F. Morin, T. Sasaki, J. M. Guerrero and J. M. Tour, *Chem. Soc. Rev.*, 2006, **35**, 1043.

6 C. Imrie, P. Engelbrecht, C. Loubser and C. W. McCleland, *Appl. Organomet. Chem.*, 2001, **15**, 1.

7 T. Chen, D. Wang, L.-H. Gan, Y. Matsuo, J.-Y. Gu, H.-J. Yan, E. Nakamura and L.-J. Wan, *J. Am. Chem. Soc.*, 2014, **136**, 3184.

8 O. N. Kadkin, E. H. Kim, S. Y. Kim and M.-G. Choi, *Polyhedron*, 2009, **28**, 1301.

9 M. V. Makarov, D. A. Lemenovskii, A. E. Bruce, M. R. M. Bruce and V. P. Dyadchenko, *Liq. Cryst.*, 2006, **33**, 485.

10 V. P. Dyadchenko, M. A. Dyadchenko, V. N. Okulov and D. A. Lemenovskii, *J. Organomet. Chem.*, 2011, **696**, 468.

11 V. N. Okulov, D. A. Popov, A. V. Panfilova, M. A. Dyadchenko, D. A. Lemenovskii and V. P. Dyadchenko, *Mendeleev Commun.*, 2015, **25**, 111.

12 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

13 C. J. McAdam, S. A. Cameron, L. R. Hanton, A. R. Manning, S. C. Moratti and J. Simpson, *CrystEngComm*, 2012, **14**, 4369.

14 S. Quan-Ling, B. Yue-Guang, W. Yi-Bing, H. Li-Min and W. Lin-Hong, *Polyhedron*, 2007, **26**, 3153.

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