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Rod-like derivatives of ferrocenylacetylene: syntheses and structure

Vladimir N. Okulov, Marina A. Dyadchenko, Andrei V. Churakov, Evgeny V. Polunin, Dmitrii A. Lemenovskii, Haojie Yu, Li Wang and Victor P. Dyadchenko

Experimental

The following compounds were prepared in accordance with published procedures: 4-dodecyloxybenzoic acid 4-iodophenyl ester [9], 4-iodophenylbutanoic acid [11].

NMR spectra were recorded with VARIAN VXR-400 and Agilent 400-MR instruments for solutions in chloroform-d if otherwise not stated. POM data for compound **8** were obtained using a Polam P-211 microscope (LOMO, Russia) supplied with a Mettler FP 80 hotstage. MALDI-TOF spectra were recorded with a Bruker Daltonics UltraFlex instrument in a dithranol matrix.

***4-Ferrocenylethynylbenzoic acid* 4.** A solution of 2.01 M *n*-butyllithium (2,46 ml; 4.94 mmol) was added to a solution of **1** (1.5 g; 4.11 mmol) in 15 ml dry THF at -60^{o}C in argon purge. The deep brick colored reaction mixture was stirred at -55÷ -60 ^{o}C for 1 h resulting in an orange suspension of 4-ferrocenylethynylphenyllithium. This suspension was poured onto 30 g of crushed solid carbon dioxide. After warming to ambient temperature, 30 ml of THF and 50 ml of water were added and the mixture was acidified with 15% solution of HCl to pH 2-3. The organic phase was separated, washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 1.3 g of acid **4**.

Column chromatography of the product on silica gel (eluent – methanol−dichloromethane 1:9 mixture) gave 1.06 g (78%) of **4**, mp 233 ^{o}C (decomp.). Calc. for $C_{19}H_{14}FeO_2$, %: C 69.12; H 4.27. Found, %: C 68.95; H 4.37.

^{1}H NMR (δ, ppm, dmso-d$_6$): 4.26 s. (5H, C_5H_5), 4.34 m. (2H, C_5H_4), 4.59 m. (2H, C_5H_4), 7.56-7.58 m. (2H, C_6H_4), 7.92-7.94 m. (2H, C_6H_4).

^{13}C NMR (δ, ppm, dmso-d$_6$): 63.67, 69.26 (C_5H_4), 69.83 (C_5H_5), 71.27 (C_5H_4), 84.96 and 91.88 (C≡C), 127.29, 129.49, 130.14, 131.04 (C_{Ar}), 166.9 (COOH).

MALDI-TOF calc. for $C_{19}H_{14}FeO_2$ M$^+$ 330.0343. Found M$^+$ 330.034.

***4-(4'-Ferrocenylethynyl[1,1']biphenyl-4-yl)butanoic acid* 5.** A mixture of boroxine **3** (0.168 g; 0.18 mmol), 4-(4-iodophenyl)butanoic acid (0.157 g; 0.54 mmol), potassium carbonate (0.15 g; 1.08 mmol), $Pd(PPh_3)_4$ (0.012 g; 0.01 mmol), CuI (0.023 g; 0.12 mmol), DMF (7.5 ml) and 1.2 ml of water was stirred at 40 °C for 6 h under argon. After cooling to ambient temperature the reaction mixture was poured into a mixture of dichloromethane (25 ml) and water (25 ml) and acidified to pH 3 with conc. HCl. The organic layer was separated, water layer was extracted with dichloromethane (3 x 20 ml). The combined organic extracts were washed thoroughly with water to remove DMF, dried over Na_2SO_4 and evaporated to dryness. The residue was subjected to column chromatography on silica gel. Using benzene, two yellow bands were eluted and discarded. Subsequent elution with benzene–ethyl acetate 1:1 mixture afforded acid **5** (0.164 g; 67%), mp 151−153 °C. Calc. for $C_{28}H_{24}FeO_2$, %: C 75.01, H 5.39. Found, %: C 75.16; H 5.76.

^{1}H NMR (δ, ppm): 2.00 m. (2H, $CH_2\mathbf{CH_2}CH_2$), 2.40 t. (2H, CH_2), 2.72 t. (2H, CH_2), 4.25 m. (2H, C_5H_4 + 5H, C_5H_5), 4.51 m. (2H, C_5H_4), 7.26 m. and 7.53 m. (4H, C_6H_4), 7.54 m. (4H, C_6H_4).

^{13}C NMR (δ, ppm): 26.16, 29.70 and 34.63 (CH_2), 65.31, 68.83 (C_5H_4), 69.97 (C_5H_5), 71.41 (C_5H_4), 85.65 and 88.97 (C≡C), 116.65, 122.66, 126.76, 126.96, 129.0, 131.75, 138.27, 140.1 (C_{Ar}), 179.32 (COOH).

MALDI-TOF calc. for $C_{28}H_{24}FeO_2$ M^+ 448.1126. Found M^+ 448.114.

***4-Ferrocenylethynyl-4'-nitro[1,1']biphenyl* 6.** A mixture of boroxine **3** (0.15 g; 0.16 mmol), 4-nitroiodobenzene (0.12 g; 0.48 mmol), potassium carbonate (0.066 g; 0.48 mmol), $Pd(PPh_3)_4$ (0.01 g; 0.008 mmol), CuI (0.019 g; 0.1 mmol), DMF (10 ml) and 1 ml of water was stirred at 60 °C for 12 h under argon and then poured into a mixture of chloroform (50 ml) and water (50 ml). The organic layer was washed thoroughly with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography of the residue on silica gel was carried out with light petroleum–chloroform 7:3 mixture as eluent. First (orange) and second (yellow) bands were discarded. Product **6** as a red band was collected. After evaporation of the eluate and drying the residue *in vacuo*, **6** (0.18 g; 90%) was obtained as a red solid, mp 215–216 °C, *cf.* [11]: mp 216–217 °C.

^{1}H NMR (δ, ppm): 3.91 s. (5H, C_5H_5), 3.94 m. (2H, C_5H_4), 4.19 m. (2H, C_5H_4), 7.39 – 7.97 m. (8H, C_6H_4); *cf.* [11].

^{13}C NMR (δ, ppm): 64.8, 69.0 (C_5H_4), 70.0 (C_5H_5), 71.5 (C_5H_4), 85.2 and 90.6 (C≡C), 124.2, 124.8, 127.2, 127.6, 132.0, 137.6, 146.8, 147.1 (C_{Ar}); *cf.* [14].

***4'-Ferrocenylethynyl[1,1']biphenyl-4-amine* 7.** A mixture of boroxine **3** (0.156 g; 0.167 mmol), 4-iodoaniline (0.109 g; 0.5 mmol), potassium carbonate (0.066 g; 0.48 mmol), $Pd(PPh_3)_4$ (0.01 g; 0.008 mmol), CuI (0.019 g; 0.1 mmol), DMF (10 ml) and 1 ml of water was stirred at 40 ^oC for 18 h under argon. The following treatment of the reaction mixture was carried out as described for **6.** The residue after removal of the solvent was subjected to column chromatography on silica gel with dichloromethane as eluent. Two first yellow bands were discarded, third (bright red) band gave 0.15 g (79%) of **7**. Calc. for $C_{29}H_{19}FeN$, %: C 76.41, H 5.08, N 3.71. Found, %: C 76.35; H 4.94, N 3.69.

^{1}H NMR (δ, ppm): 3.63 broad signal (2H, NH_2), 4.21 m. (5H, C_5H_5 + 2H, C_5H_4), 4.47 m. (2H, C_5H_4), 7.41-7.65 m. (8H, C_6H_4-C_6H_4).

^{13}C NMR (δ, ppm): 65.2 (C_5H_4), 68.8 (C_5H_4), 69.9 (C_5H_5), 71.4 (C_5H_4), 86.2 and 89.2 (C≡C), 128.3, 128.6, 128.7, 130.4, 131.1, 131.9, 132.0, 134.0 (C_{Ar}).

***4'-Ferrocenylethynyl[1,1']biphenyl-4-yl 4-dodecyloxybenzoate* 8**. A mixture of boroxine **3**, (0.187 g; 0.20 mmol), 4-iodophenyl 4-dodecyloxybenzoate (0.305 g; 0.6 mmol), potassium carbonate (0.22 g; 1.6 mmol), $Pd(PPh_3)_4$ (0.025 g; 0.02 mmol), CuI (0.023 g; 0.12 mmol), DMF (8.5 ml) and 1.4 ml of water was stirred at 60−70 ^oC for 3.5 h under argon. Then the reaction mixture was poured into a mixture of dichloromethane (50 ml) and water (100 ml). The organic layer was washed thoroughly with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel. Elution with light petroleum–benzene 3:1 mixture gave three bright orange bands. First and second bands were discarded, third band (target compound) was eluted with benzene which gave ester **8** (0.28 g; 69%). Recrystallization from dichloromethane by addition of light petroleum gave **8**, mp 130−131 ^oC. Calc. for $C_{43}H_{46}FeO_3$, %: C 77.47, H 6.96. Found, %: C 77.41; H 7.07.

^{1}H NMR (δ, ppm): 0.84 t. (3H, CH_3), 1.23-1.43 m. (16H, $(CH_2)_9$), 1.78 m. (2H, $OCH_2\mathbf{CH_2}$), 4.00 t. (2H, OCH_2), 4.21 m. (5H, C_5H_5 + 2H, C_5H_4), 4.48 m. (2H, C_5H_4), 6.92-6.94 m. and 7.21-7.23 m. (4H, C_6H_4), 7.51 m. (4H, C_6H_4), 7.58-7.61 m. and 8.10-8.13 m. (4H, AA’BB’ O-C_6H_4-CO).

^{13}C NMR (δ, ppm): 14.1, 22.7, 26.0, 29.0, 29.4, 29.5-29.6 - non-resolved signals, 31.9 ($C_{12}H_{25}$), 68.3, 68.9 (C_5H_4), 70.0 (C_5H_5), 71.5 (C_5H_4), 85.6 and 89.1 (C≡C), 114.3, 121.4, 122.2, 122.9, 126.9, 128.0, 131.8, 132.3, 138.1 139.6, 150.7, 163.6 (C_{Ar}).

MALDI-TOF: calc. for $C_{43}H_{46}FeO_3$ M^+ 666.684. Found M^+ 666.484.

***(Z)-4-(2-Chloro-2-ferrocenylethenyl)benzoic acid* 9**. To a suspension of **4** (0.5 g; 1.51 mmol) in 20 ml of dichloromethane in argon atmosphere, 10 ml of 1.6 M solution of hydrogen chloride in diethyl ether (16 mmol) was added. The mixture was stirred under argon. Within 5 h the precipitate of **4** was gradually dissolved. Volatiles were removed on rotor evaporator and the residue was dried *in vacuo*, which gave 0.52 g (94%) of **11** as red powder, decomp. over 190 ^{o}C. Calc. for $C_{19}H_{15}ClFeO_2$, %: C 62.25; H 4.12; Cl 9.67. Found, %: C 62.11; H 4.30; Cl 9.81.

^{1}H NMR (δ, ppm, dmso-d$_6$): 4.22 m. (5H, C_5H_4), 4.42 m. (2H, C_5H_4) , 4.77 m. (2H, C_5H_4), 7.17 (H, C=CH), 7.82-7.84 m. (2H, C_6H_4), 7.94-7.96 m. (2H, C_6H_4), 13.00 (H, COOH).

^{13}C NMR (δ, ppm, dmso-d$_6$): 67.25, 69.9 (C_5H_4), 69.7 (C_5H_5), 84.58 (C_5H_4), 120.32 (CH=), 129,2 (CCl), 128.90, 129.36, 132.94, 139.4 (CH_{Ar}) 167.1 (COOH).

***(Z)-4-(2-Chloro-2-ferrocenyletheny)lbenzoic acid 3-(1-imidazolyl)propylamide* 10**. Oxalyl chloride (0.56 ml; 6.6 mmol) was added under argon to a stirred solution of **11** (0.8 g; 2.18 mmol) in 20 ml of dry dichloromethane followed with 3 drops of DMF. After gas evolution ceased the reaction mixture was stirred for 1 h and volatiles were removed *in vacuo*. The solid residue was dissolved in dichloromethane and the solvent was removed again *in vacuo*.

The acyl chloride thus obtained was dissolved in dry dichloromethane (10 ml) and a solution of 3-(1-imidazolyl)propylamine (0.3 ml; 2.5 mmol) in 2.5 ml of 1 M NaOH (2.5 mmol) was added. The mixture was stirred at ambient temperature overnight, then poured into 100 ml of water and the product was extracted with chloroform. The extract was thoroughly washed with water, dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was subjected to column chromatography on silica gel using dichloromethane−methanol mixture as eluent. Elution of red band gave 0.7 g (68%) of **10**, mp 161−162 ^{o}C. Calc. for $C_{25}H_{24}ClFeN_3O$, %: C 63.38; H 5.11; Cl 7.48; N 8.87. Found, %: C 63.15; H 5.19; Cl 7.39; N 8.99.

^{1}H NMR (δ, ppm): 2,10 t. (2H, CH_2), 2.43 q. (2H, CH_2), 4.03 (2H, CH_2), 4.21 m. (5H, C_5H_4), 4.33 m. (2H, C_5H_4) , 4.62 m. (2H, C_5H_4), 6.79 s. (H, C=CH), 6.96 s. (1H, CH_{Im}), 7.06 s. (1H, CH_{Im}), 7.19 br. (1H, NH), 7.65 s. (1H, CH_{Im}), 7.71-7.73 m. (2H, C_6H_4), 7.78-7.81 m. (2H, C_6H_4).

^{13}C NMR (δ, ppm): 30.99 (CH_2), 37.11 (CH_2), 44.90 (CH_2), 67.23, 69.7 (C_5H_4), 69.86 (C_5H_5), 85.23 (C_5H_4), 119.1 ($CH_{Imidazole}$), 120.32 (CH=), 127.01 (CH_{Ar}), 128.77 (CCl), 129,02(CH_{Ar}), 129.64 ($CH_{Imidazole}$), 132.38 (C_{Ar}), 136.96 ($CH_{Imidazole}$), 138.65 (C_{Ar}), 167.51 (C(O)NH).

***Molecular parameters for* 3 *and* 10.**

Table S1 Selected bond lengths (Å) and angles (°) in **3**.

Molecule A		**Molecule B**	
B(1)-O(3)	1.371(11)	B(4)-O(4)	1.391(11)
B(1)-O(1)	1.385(12)	B(4)-O(6)	1.396(11)
B(1)-C(115)	1.541(13)	B(4)-C(145)	1.538(13)
B(2)-O(1)	1.382(12)	B(5)-O(5)	1.366(12)
B(2)-O(2)	1.383(12)	B(5)-O(4)	1.379(11)
B(2)-C(125)	1.532(13)	B(5)-C(155)	1.542(13)
B(3)-O(2)	1.372(11)	B(6)-O(5)	1.350(11)
B(3)-O(3)	1.401(11)	B(6)-O(6)	1.372(11)
B(3)-C(135)	1.540(13)	B(6)-C(165)	1.539(14)
C(110)-C(111)	1.170(11)	C(140)-C(141)	1.186(11)
C(120)-C(121)	1.188(12)	C(150)-C(151)	1.222(12)
C(130)-C(131)	1.191(12)	C(160)-C(161)	1.205(13)
Fe(1)-Pl(C10-C14)*	1.635(5)	Fe(5)-Pl(C50-C54)	1.641(4)
Fe(1)-Pl(C15a-C19a)	1.68(1)	Fe(5)-Pl(C55a-C59a)	1.65(1)
Fe(1)-Pl(C15b-C19b)	1.62(1)	Fe(5)-Pl(C55b-C59b)	1.66(1)
Fe(2)-Pl(C20-C24)	1.638(4)	Fe(4)-Pl(C40-C44)	1.641(4)
Fe(2)-Pl(C25-C29)	1.635(4)	Fe(4)-Pl(C45-C49)	1.653(4)
Fe(3)-Pl(C30-C34)	1.638(4)	Fe(6)-Pl(C60-C64)	1.638(4)
Fe(3)-Pl(C35-C39)	1.633(4)	Fe(6)-Pl(C65-C69)	1.638(4)
O(3)-B(1)-O(1)	119.4(8)	O(4)-B(4)-O(6)	118.8(8)
O(3)-B(1)-C(115)	120.8(8)	O(4)-B(4)-C(145)	119.0(8)
O(1)-B(1)-C(115)	119.8(8)	O(6)-B(4)-C(145)	122.2(8)
O(1)-B(2)-O(2)	118.6(8)	O(5)-B(5)-O(4)	118.6(8)
O(1)-B(2)-C(125)	121.6(8)	O(5)-B(5)-C(155)	121.4(8)
O(2)-B(2)-C(125)	119.8(9)	O(4)-B(5)-C(155)	120.0(9)
O(2)-B(3)-O(3)	118.9(8)	O(5)-B(6)-O(6)	119.7(9)
O(2)-B(3)-C(135)	120.6(8)	O(5)-B(6)-C(165)	121.1(8)
O(3)-B(3)-C(135)	120.5(8)	O(6)-B(6)-C(165)	119.2(8)
B(2)-O(1)-B(1)	121.1(7)	B(5)-O(4)-B(4)	120.4(7)
B(3)-O(2)-B(2)	121.5(7)	B(6)-O(5)-B(5)	122.5(7)
B(1)-O(3)-B(3)	120.5(7)	B(6)-O(6)-B(4)	120.0(7)
C(111)-C(110)-C(10)	176.5(9)	C(141)-C(140)-C(40)	178.3(10)
C(110)-C(111)-C(112)	174.2(9)	C(140)-C(141)-C(142)	177.5(9)
C(121)-C(120)-C(20)	177.6(10)	C(151)-C(150)-C(50)	175.6(10)
C(120)-C(121)-C(122)	176.5(9)	C(150)-C(151)-C(152)	178.2(10)
C(131)-C(130)-C(30)	175.2(10)	C(161)-C(160)-C(60)	178.5(11)
C(130)-C(131)-C(132)	177.5(10)	C(160)-C(161)-C(162)	178.5(11)

* Fe(x)-Pl(Cx0-Cx4) denotes the distance between Fe atom and the least-squares plane of substituted Cp-ring; Fe(x)-Pl(Cx5-Cx9) denotes the distance between Fe atom and the least-squares plane of C_5H_5 ring; x = 1-6.

Table S2 Selected bond lengths (Å) and angles (°) in **10**.

Cl(1)-C(11)	1.748(3)	C(19)-N(1)-C(20)	121.6(2)
O(1)-C(19)	1.238(3)	C(23)-N(2)-C(25)	105.9(2)
N(1)-C(19)	1.336(4)	C(23)-N(2)-C(22)	127.1(3)
N(1)-C(20)	1.454(3)	C(25)-N(2)-C(22)	126.8(3)
N(2)-C(23)	1.341(3)	C(23)-N(3)-C(24)	104.5(2)
N(2)-C(25)	1.362(4)	C(12)-C(11)-C(1)	127.5(3)
N(2)-C(22)	1.461(4)	C(12)-C(11)-Cl(1)	120.0(2)
N(3)-C(23)	1.303(3)	C(1)-C(11)-Cl(1)	112.4(2)
N(3)-C(24)	1.361(4)	N(3)-C(23)-N(2)	112.7(2)
C(11)-C(12)	1.316(4)	C(25)-C(24)-N(3)	110.6(3)
C(12)-C(13)	1.469(4)	C(24)-C(25)-N(2)	106.3(3)
Fe(1)-Pl(C1-C5)	1.639(2)	Fe(1)-Pl(C6-C10)	1.646(2)