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Syntheses and crystal structures of ferrocenyl derivatives of biphenyl*

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Arylation of ferrocene with substituted biphenyldiazonium tetrafluoroborates afforded 4-bromo-, 4-nitro-, and 4-cyano-4'-ferrocenylbiphenyls. 4-Nitro- and 4-cyano-4'-ferrocenylbiphenyls were studied by X-ray diffraction analysis. In the crystals of 4-nitro-4'-ferrocenylbiphenyl, the molecules are linked *via* stacking π - π interactions.

Key words: arylation, ferrocene, aryldiazonium tetrafluoroborates, biphenylferrocenes, X-ray diffraction analysis.

Earlier,¹ we have reported the synthesis of ferrocenyl derivatives of biphenyl.

Having rigid rod-like structures, biphenyl derivatives can serve as precursors of liquid-crystalline materials. The

introduction of an electron-withdrawing group and an easily polarizable electron-donating group at positions 4 and 4' of

 $\mathsf{Fc} = (\mathsf{C}_5\mathsf{H}_5)\mathsf{Fe}(\mathsf{C}_5\mathsf{H}_4); \mathsf{X} = \mathsf{Br}, \, \mathsf{CN}$

the biphenyl molecule should lead to the asymmetry of the electron density distribution. This may facilitate aggregation of the molecules both through intermolecular dipole-dipole interactions and the formation of intermolecular charge-transfer complexes. The ferrocenyl fragment is a promising donor group in these compounds. In addition to the ability of ferrocenyl derivatives of biphenyl to undergo intermolecular aggregation, these compounds can also exhibit nonlinear optical properties. Besides, the presence of the ferrocenyl group allows the molecule to be involved in reversible redox processes.

Recently,² 4-formyl-4´-ferrocenylbiphenyl derivatives possessing liquid-crystalline properties have been synthesized. However, approaches to the synthesis of ferrocenyl derivatives of biphenyl have been poorly developed. The cross-coupling reactions involving arylboronic $acids^2$ or organomercury compounds³ have received the most study. Unfortunately, the synthesis *via* arylboronic acids by crosscoupling reactions is a rather complicated process, because, first, it involves the preparation of 4-bromophenylferrocene and, second, arylboronic acids are synthesized with the use of organolithium compounds. Syntheses based on organomercury compounds are carried out with the use of toxic diferrocenylmercury. In addition, this approach requires the preliminary synthesis of the corresponding 4-X-4'-Y-biphenyls.

In the case of biphenyl derivatives, the classical method for the synthesis of arylferrocenes involving arylation of ferrocene with diazonium salts was applied only to 4-ferrocenylbiphenyl.⁴

In the present study, we examined the possibility of the preparation of biphenylferrocene derivatives by arylation of ferrocene with salts of substituted biphenyldiazonium, found the optimum reaction conditions, and demonstrated that this approach is highly competitive with known procedures for the synthesis of these compounds.

Results and Discussion

Substituted ferrocenylbiphenyls can be prepared by arylation of ferrocene with aryldiazonium salts. However, these reactions performed with the use of aqueous solu-

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tions of aryldiazonium chlorides gave unsatisfactory results. The arylation products were produced in very low yields and their isolation presented problems due to a high degree of resinification. We found that substituted ferrocenylbiphenyls were readily generated by arylation of ferrocene with aryldiazonium tetrafluoroborates 1a-cisolated in the individual form (Scheme 1). In these reactions, the choice of the solvent is of great importance. The best results were achieved by performing the reactions in an acetic acid—trifluoroacetic acid—dichloroethane mixture.

Scheme 1



 $Fc = (C_5H_5)Fe(C_5H_4); X = Br(a), NO_2(b), CN(c)$

The structures of compounds 2a-c were established by IR and ¹H NMR spectroscopy. Compounds 2b,c were also studied by X-ray diffraction analysis.

The synthesis of arylamines, which are necessary for the preparation of tetrafluoroborates 1a-c, is presented in Scheme 2.

Both arylamines 3a-c and intermediates in their synthesis have been described earlier.⁵⁻⁹ However, procedures published in the literature often give unsatisfactory results. We developed well-reproducible procedures for the synthesis of these compounds.

Diazotization of amines **3a**—**c** was carried out according to a standard procedure (Scheme 3).

We attempted to replace the bromine atom in compound 2a by the SH group according to a procedure described earlier.¹⁰ However, this attempt led only to the formation of sulfide 4 (Scheme 4).

Under the above-described conditions, the reaction ended in the formation of sulfide even in the presence of a substantial excess of sodium ethylthiolate.

The molecular and crystal structures of ferrocenylbiphenyls **2b** and **2c** were established by X-ray diffraction analysis.

The molecular structures of compounds **2b** and **2c** are shown in Figs. 1 and 2, respectively. The principal bond lengths and bond angles are listed in Tables 1 and 2, respectively.





3a (88%) **3b** (63%) **3c** (83%)

 $X = Br(a), NO_2(b), CN(c)$

Reagents and conditions: *i*. 1) CuCN, DMF, 153 °C; 2) FeCl₃, HCl; *ii*. SnCl₂, HCl, and EtOH or NaSH and MeOH.

Scheme 3



 $X = Br(a), NO_2(b), CN(c)$

Scheme 4





Fig. 1. Structure of one of the crystallographically independent molecules (A) in the crystal of compound 2b.



Fig. 2. Molecular structure of compound 2c.

The crystal structure of 2b contains two cystallographically independent 4-nitro-4'-ferrocenylbiphenyl molecules (A and B, see Fig. 1), which differ by the conformation of the Cp–Fe–Cp' ferrocenyl fragment (Cp and Cp' are unsubstituted and substituted cyclopentadienyl rings, respectively). In the molecule A, the cyclopentadienyl rings are in an eclipsed conformation $(C(10)-Cnt^{1}-Cnt^{2}-C(5))$ pseudotorsion angle is 0.7°, where Cnt^1 and Cnt^2 are the centroids of the Cp' and Cp rings, respectively). In the molecule B, the corresponding C(10')-Cnt¹-Cnt²-C(5') angle is 30.1°, which indicates that the cyclopentadienyl rings are in a skewed conformation (ideal angle characterizing this conformation is 36°). The Cp and Cp' rings are coplanar (angles between the planes of the rings are 0.2° and 2.6° in the molecules A and B, respectively). In both molecules, the $Cp'-Ar^1-Ar^2-NO_2$ fragments (Ar = C₆H₄) have identical structures, all rings of the fragment being noncoplanar. The dihedral angles between the planes of Cp' and Ar^1 , Ar^1 and Ar^2 , and Ar^2 and NO_2 are 7.2(3)°, $23.7(2)^{\circ}$, and $5.1(5)^{\circ}$ in the molecule A and $10.7(3)^{\circ}$,

21.7(2)°, and 7.4(5)° in the molecule B, respectively. The Ar^1 — Ar^2 — NO_2 fragment is slightly bent from the Cp' ring toward the unsubstituted Cp ring. The C(11)...C(14)...C(17)...C(20)...N(1) line forms angles of 2.7° (in the molecule A) and 4.1° (in the molecule B) with the plane of the Cp' ring. The molecules A and B (except for the unsubstituted cyclopentadienyl rings) are related by a center of a pseudosymmetry.

In the crystal of 4-cyano-4'-ferrocenylbiphenyl (**2c**), the rings of the Cp'-Ar¹-Ar² fragment are also noncoplanar. The dihedral angles between the Cp' and Ar¹ planes and the Ar¹ and Ar² planes are 9.9(1)° and 42.39(7)°, respectively. The Cp rings are in a nearly eclipsed conformation with the C(10)-Cnt¹-Cnt²-C(5) pseudotorsion angle of 7.9°.

In molecules **2b** and **2c**, all aromatic rings are planar (average deviations are in the ranges of 0.001-0.003 and 0.002-0.007 Å for the Cp and phenyl rings, respectively).

The bond lengths in **2b** and **2c** are close to standard values. The average C–C bond lengths in the phenyl and Cp rings are 1.39 and 1.42 Å, respectively. The Fe–C

Table 1. Selected bond lengths in compounds 2b,c

Bond	d/Å			
	2	b	2c	
	Molecule A	Molecule B		
C(1)–C(2)	1.419(7)	1.417(6)	1.418(3)	
C(2) - C(3)	1.394(7)	1.419(7)	1.419(2)	
C(3) - C(4)	1.409(7)	1.406(7)	1.415(3)	
C(4) - C(5)	1.406(7)	1.409(7)	1.419(3)	
C(5) - C(1)	1.395(7)	1.383(7)	1.428(3)	
C(6) - C(7)	1.418(6)	1.413(6)	1.427(3)	
C(7) - C(8)	1.408(6)	1.413(6)	1.422(2)	
C(8) - C(9)	1.436(6)	1.412(6)	1.421(3)	
C(9)-C(10)	1.427(5)	1.432(5)	1.438(2)	
C(10)-C(6)	1.423(5)	1.433(5)	1.439(2)	
C(10)-C(11)	1.473(5)	1.465(5)	1.468(2)	
C(11)–C(12)	1.396(5)	1.400(5)	1.401(2)	
C(12)-C(13)	1.376(6)	1.385(6)	1.385(2)	
C(13)-C(14)	1.394(5)	1.383(5)	1.404(2)	
C(14)-C(15)	1.399(5)	1.408(5)	1.402(2)	
C(15)-C(16)	1.382(6)	1.368(5)	1.389(2)	
C(16)-C(11)	1.387(5)	1.395(5)	1.399(2)	
C(14)-C(17)	1.479(5)	1.487(5)	1.475(2)	
C(17)-C(18)	1.405(5)	1.400(5)	1.403(2)	
C(18)-C(19)	1.378(6)	1.370(6)	1.382(3)	
C(19)-C(20)	1.379(6)	1.378(5)	1.398(3)	
C(20)-C(21)	1.384(6)	1.377(6)	1.396(3)	
C(21)-C(22)	1.367(6)	1.379(6)	1.383(3)	
C(22)-C(17)	1.402(5)	1.398(5)	1.398(2)	
C(20)-N(1)	1.470(5)	1.464(5)	_	
N(1)-O(1)	1.223(5)	1.221(5)	_	
N(1)-O(2)	1.225(5)	1.232(5)	_	
C(20)-C(23)	_ `	_	1.438(3)	
C(23)-N(1)	—	—	1.143(2)	

distance in the ferrocenyl fragment is 2.04 Å. The average N–O and C–N (Ar^2 – NO_2) bond lengths are 1.225 and 1.467 Å, respectively.

Table 2. Selected bond angles in compounds 2b,c

Angle	ω/deg			
	2b		2c	
	Molecule B	Molecule B		
O(2)-N(1)-O(1)	123.9(4)	123.8(4)	_	
O(1) - N(1) - C(20)	118.4(4)	118.2(4)	_	
C(21) - C(20) - N(1)	119.5(4)	119.6(3)	_	
C(9) - C(10) - C(11)	126.7(4)	126.0(3)	126.74(15)	
C(15) - C(14) - C(17)	120.6(3)	120.3(3)	121.58(16)	
C(15) - C(16) - C(11)	121.4(4)	122.3(3)	121.33(16)	
C(19) - C(18) - C(17)	121.8(4)	121.8(4)	120.97(17)	
C(16) - C(11) - C(10)	120.3(3)	121.2(3)	121.21(15)	
C(18) - C(17) - C(14)	120.6(3)	120.8(3)	121.52(16)	
C(19) - C(20) - C(23)		_	120.28(16)	
C(20)-C(23)-N(1)	_	_	179.5(2)	

Analysis of the crystal packing of the 4-nitro-4'ferrocenylbiphenyl molecules (Fig. 3) showed that the molecules A and B are linked in the centrosymmetrical A...A and B...B dimers in a head-to-tail fashion. The intermolecular distances between the parallel overlapping phenyl rings (3.323(5) and 3.256(5) Å in the A...A and B...B dimers, respectively) are shorter than the values expected for the van der Waals contacts. In the dimers, the shortest C(17)...C(21A) (C(21)...C(17A)) and C(17')...C(21B) (C(21')...C(17B)) intermolecular con-



Fig. 3. Centrosymmetrical A...A dimer. (The molecules B are linked in the B...B dimers with a similar structure.)



Fig. 4. Fragment of the molecular packing in the crystal of compound 2b.



Fig. 5. Fragment of the molecular packing in the crystal of compound 2c. Weak C...C and C...N contacts are indicated by dashed lines.

tacts are 3.337(5) and 3.268(5) Å, respectively. The shortened C...C contacts in the crystal structure of **2b** are indicative of the presence of specific stacking π - π interactions between the molecules with the resulting formation of dimers.

In the A...A dimer, the molecules related by a center of symmetry are linked *via* the C_{Ar} —H...O contacts (shown by dashed lines in Fig. 4; H(5A)...O(2A) is 2.55 Å, the C(5)H(5A)O(2A) angle is 164°), which can be assigned to weak hydrogen bonds. In the B...B dimer, the corresponding H(5'A)...O(2'B) distance is larger (2.73 Å) due to rotation of the Cp ring. This rotation leads also to a shortening of the H(4'A)...O(1'B) distance (2.70 Å) compared to the H(1A)...O(1A) distance (3.74 Å) in the A...A dimer. The second oxygen atom of each molecule in the A...A dimer forms the O(1A)...H(9'A) contact (2.48 Å; C(9')H(9'A)O(1A), 169°) with one of the molecules of the B...B dimer. As a result, the A...A and B...B dimers are linked in ribbons *via* weak H...O bonds (see Fig. 4).

In the crystal of 4-cyano-4'-ferrocenylbiphenyl (**2c**), the molecules are packed in a radically different fashion. These molecules form parallel layers within which they are arranged in a ladder-like mode (Fig. 5). In each layer, the molecules are linked by shortened C...C and C...N contacts, *viz.*, C(19f)–C(3), C(21d)–C(11), C(22d)–C(10), C(3a)–N(1), and C(2a)–N(1) (3.474(3), 3.406(3), 3.404(3), 3.382(3), and 3.386(3) Å, respectively).

Experimental

The reactions were carried out with the use of biphenyl and 4,4'-dinitrobiphenyl of high-purity grade, 4-bromobiphenyl (98% purity) purchased from Lancaster, sodium hydrosulfide monohydrate (90% purity), and copper(1) cyanide purchased from Riedel—deHaën.

Dimethylformamide of high-purity grade was kept over calcium hydride and distilled *in vacuo*. Hexamethylphosphoramide (high-purity grade) was kept over zeolite calcinated *in vacuo* and distilled over sodium under reduced pressure. Sodium ethylthiolate was prepared according to a known procedure.¹⁰

The resulting compounds were purified by column chromatography on aluminum oxide (Brockmann activity II). Thinlayer chromatography was carried out on Silufol UV-254 plates.

The ¹H NMR spectra were measured on a Varian VXR-400 spectrometer (400 MHz) using CDCl₃ as the solvent. The IR spectra were recorded on a UR-20 spectrometer in Nujol mulls.

4-Nitrobiphenyl. Glacial acetic acid (60 mL) and 75% HNO₃ (35 mL, density 1.44 g cm⁻³; 0.6 mol) were added to biphenyl (44 g, 0.286 mol). The reaction mixture was refluxed for 2.5 h and then cooled to ~20 °C. The precipitate that formed was filtered off, washed with warm water, and dried in air. The product was recrystallized from glacial acetic acid (50 mL). 4-Nitrobiphenyl was obtained in a yield of 29.1 g, m.p. 105–112 °C. After repeated recrystallization from glacial acetic acid (50 mL), 4-nitrobiphenyl was obtained in a yield of 25.6 g (45%), m.p. 109–113 °C (*cf.* lit. data⁵: m.p. 112–113 °C).

4-Bromo-4'-nitrobiphenyl. *A*. Furning nitric acid was prepared by distillation of concentrated HNO_3 with concentrated H_2SO_4 . The fraction with b.p. 82–85 °C was collected.

Fuming nitric acid (23 mL, 35 g, 0.56 mol) was added to a solution of 4-bromobiphenyl (43.10 g, 0.185 mol) in glacial acetic acid (70 mL). The reaction mixture was refluxed for 3 h and cooled to 45 °C in air and then to 20 °C (but not lower) with stirring using cold water. The crystalline precipitate that formed was filtered off and washed with glacial acetic acid (2×20 mL) and water until it became neutral. After drying in air, 4-bromo-4'-nitrobiphenyl was obtained in a yield of 25.66 g (50%), m.p. 170–172 °C (*cf.* lit. data⁶: m.p. 175–176 °C).

B. Chloroform (60 mL), bromine (6.5 mL, 20.15 g, 0.13 mol), and powdered iron (0.73 g, (0.013 mol) were added to 4-nitrobiphenyl (19.90 g, 0.10 mol). The reaction mixture was carefully heated until the vigorous reaction started, refluxed for 3 h, and then cooled to ~ 20 °C. Then an aqueous solution of sodium sulfite was added and the resulting mixture was stirred to remove an excess of bromine. The precipitate of the product, which is gray-brown in color due to the presence of impurities, was filtered off, washed with water, and dried in air. Crude 4-bromo-4'-nitrobiphenyl was obtained in a yield of 16.90 g. An additional portion of the product (2.45 g) was obtained after evaporation of the chloroform solution (from the filtrate) and recrystallization of the residue from acetic acid with activated carbon. Both portions of 4-bromo-4'-nitrobiphenyl were extracted in a Soxlet apparatus with light petroleum to obtain 4-bromo-4'-nitrobiphenyl in a yield of 17.50 g (63%) as yellowish crystals, m.p. 174-176 °C.

4-Cyano-4'-nitrobiphenyl. A mixture of 4-bromo-4'-nitrobiphenyl (7.55 g, 0.027 mol), copper(1) cyanide (3.95 g, 0.044 mol), and DMF (35 mL) was refluxed with stirring under an argon atmosphere for 8 h. After refluxing for ~2 h, a brown solution containing a small amount of a precipitate was obtained. The warm reaction mixture (~50 °C) was poured into a solution of iron(111) chloride hexahydrate (23 g) in water (300 mL) and then 36% hydrochloric acid (10 mL) and chloroform (220 mL) were added. The resulting mixture was stirred at 40–50 °C for 30 min. The organic layer was separated, washed with water, dried with sodium sulfate, and filtered through a 6-cm layer of aluminum oxide. The solvent was distilled off on a rotary evaporator and 4-cyano-4'-nitrobiphenyl was obtained in a yield of 3.9 g (63%), m.p. 196–200 °C (*cf.* lit. data⁷: m.p. 199.5–200 °C).

4-Amino-4'-bromobiphenyl (3a). A solution of tin(II) chloride dihydrate (54.0 g, 0.240 mol) in concentrated hydrochloric acid (60 mL) was added to a solution of 4-bromo-4'-nitrobiphenyl (15.0 g, 0.054 mol) in ethanol (120 mL). The reaction mixture was refluxed with stirring on a water bath for 2 h. Then the reaction solution was cooled and diluted with a threefold volume of water. The precipitate of the salt of amine that formed was filtered off and a solution of potassium hydroxide (50 g) in water (80 mL) was added. The reaction mixture was stirred for 5 h, water (100 mL) was added, and a precipitate of the amine was filtered off. The precipitate was washed with water until it became neutral and dried in air. 4-Amino-4'-bromobiphenyl was obtained in a yield of 11.74 g (88%) as a white powder, m.p. 142–144 °C (*cf.* lit. data⁸: m.p. 143–144 °C).

4-Amino-4'-nitrobiphenyl (3b). The synthesis was carried out according to a modified procedure described earlier.⁹ A solution of 90% sodium hydrosulfide monohydrate (4.1 g, 0.050 mol) in

methanol (100 mL) was added dropwise with stirring to a boiling mixture of 4,4'-dinitrobiphenyl (9.00 g, 0.037 mol), toluene (50 mL), and methanol (200 mL) during 30 min. The reaction mixture was refluxed with stirring for 3.5 h, a yellow precipitate was separated, and the remaining red-orange solution was concentrated on a rotary evaporator. The product was obtained as an orange powder in a yield of 5.69 g. After recrystallization from ethanol (300 mL), 4-amino-4'-nitrobiphenyl was obtained in a yield of 4.90 g (63%) as orange crystals, m.p. 191–201 °C (*cf.* lit. data⁹: m.p. 201–203 °C).

4-Amino-4'-cyanobiphenyl (3c). A solution of 90% sodium hydrosulfide monohydrate (1.90 g, 0.023 mol) in water (15 mL) was added dropwise with stirring to a boiling suspension of 4-nitro-4'-cyanobiphenyl (2.70 g, 0.012 mol) in methanol (110 mL) during 15 min. The reaction mixture was refluxed with stirring for 6 h, during which 4'-cyano-4-nitrobiphenyl was completely dissolved. The methanolic solution was concentrated on a rotary evaporator and the residue was treated with water (150 mL). The precipitate of the amine that formed was filtered off, washed on a filter with water (4×25 mL), and dried in air. The product was purified by chromatography on a column (*l* 20 cm, *d* 2.5 cm) with aluminum oxide. 4-Amino-4'-cyanobiphenyl was eluted with chloroform in a yield of 1.95 g (83%), m.p. 180–184 °C (*cf.* lit. data⁷: m.p. 182–184 °C).

4'-Nitro-4-biphenyldiazonium tetrafluoroborate (1b). Hydrochloric acid (36%; 15 mL) was added to a suspension of 4-amino-4'-nitrobiphenyl (3.83 g, 0.018 mol) in water (120 mL). The reaction mixture was cooled with ice to 2 °C and then a solution of sodium nitrite (1.44 g, 0.021 mol) in water (16 mL) was added dropwise with stirring during 15 min. The reaction mixture was stirred at 2-4 °C for 30 min and then a solution of ammonium tetrafluoroborate (2.20 g, 0.021 mol) in water (15 mL) was added, after which the reaction mixture turned pale-pink and solidified. Then the mixture was kept with periodic stirring at 3-4 °C for 40 min. The precipitate that formed was filtered off, washed on a filter with cold water (2×35 mL) and ether (2×30 mL), and dried in air. 4'-Nitro-4-biphenyldiazonium tetrafluoroborate was obtained as a pale-pink powder (t.decomp. >125-127 °C) in a yield of 4.90 g (87%). The precipitation with diethyl ether from a solution in acetonitrile afforded pure 4'-nitro-4-biphenyldiazonium tetrafluoroborate. Found (%): C, 46.03; H, 2.42; N, 13.54. C₁₂H₈BF₄N₃O₂. Calculated (%): C, 46.05; H, 2.58; N 1342

4'-**Bromo-4-biphenyldiazonium tetrafluoroborate (1a).** The synthesis was carried out analogously to the synthesis of 4'-nitro-4-biphenyldiazonium tetrafluoroborate. 4'-Bromo-4-biphenyldiazonium tetrafluoroborate was prepared from 4-amino-4'bromobiphenyl (6.0 g) in a yield of 7.37 g (88%) as a yellow powder, t.decomp. >128 °C. Pure 4'-bromo-4-biphenyldiazonium tetrafluoroborate was obtained by precipitation with diethyl ether from a solution in acetonitrile. Found (%): C, 41.29; H, 2.09; N, 7.87. C₁₂H₈BBrF₄N₂. Calculated (%): C, 41.55; H, 2.32; N, 8.07.

4'-Cyano-4-biphenyldiazonium tetrafluoroborate (1c). The synthesis was carried out analogously to the synthesis of 4'-nitro-4-biphenyldiazonium tetrafluoroborate. 4'-Cyano-4-biphenyldiazonium tetrafluoroborate was prepared from 4-amino-4'cyanobiphenyl (2.91 g) in a yield of 3.75 g (85%) as a yellow powder, t.decomp. >129–131 °C. Pure 4'-cyano-4-biphenyldiazonium tetrafluoroborate was obtained by precipitation with diethyl ether from a solution in acetonitrile. Found (%): C, 53.34; H, 2.57; N, 14.09. $C_{13}H_8BF_4N_3$. Calculated (%): C, 53.29; H, 2.75; N, 14.34.

4-Bromo-4´-ferrocenylbiphenyl (2a). 4´-Bromo-4-biphenyldiazonium tetrafluoroborate (9.09 g, 0.026 mol) was added portionwise with stirring to a solution of ferrocene (8.37 g, 0.045 mol) in a mixture of 1,2-dichloroethane (50 mL), glacial acetic acid (200 mL), and trifluoroacetic acid (15 mL). The diazonium salt was added at ~20 °C during 1 h, after which the reaction mixture was stirred for 4 h and kept at ~20 °C for 12 h. Then water (350 mL) and chloroform (150 mL) were added. The organic layer was separated and the aqueous layer was extracted with chloroform (50 mL). The combined organic phases were washed with a solution of ascorbic acid and water until the reaction mixture became neutral, dried with sodium sulfate, and filtered. The solvent was removed on a rotary evaporator. The residue (~12 g) was chromatographed on a column (l 50 cm, d 2.5 cm) with aluminum oxide. A mixture of ferrocene and 4-bromobiphenyl was eluted with light petroleum, after which virtually pure 4-bromo-4'-ferrocenylbiphenyl was eluted with a 1:3 benzene—light petroleum mixture in a yield of 1.16 g (first portion) and then 4-bromo-4'-ferrocenylbiphenyl weakly contaminated with an impurity (second portion) was eluted with benzene in a yield of 3.40 g. Repeated chromatography of the first portion on a column (l 15 cm, d 2.5 cm) with aluminum oxide afforded 4-bromo-4'-ferrocenylbiphenyl in a yield of 0.93 g as orange pearly platelet-like crystals, m.p. 202-204 °C. The second portion of the product was chromatographed three times on a column (l 20 cm, d 2.5 cm) to obtain 4-bromo-4'ferrocenylbiphenyl in a yield of 2.60 g, m.p. 202-204 °C. The total yield of 4-bromo-4'-ferrocenylbiphenyl was 3.53 g (32%). Found (%): C, 63.37; H, 4.11; Br, 19.04. C₂₂H₁₇BrFe. Calculated (%): C, 63.35; H, 4.11; Br, 19.16. ¹H NMR, δ: 4.05 (s, 5 H, C₅H₅); 4.33 (m, 2 H, C(7)H, C(8)H); 4.66 (m, 2 H, C(6)H, C(9)H); 7.45–7.54 (m, 8 H, Ar).

4-Nitro-4´-ferrocenylbiphenyl (2b). 4´-Nitro-4-biphenyldiazonium tetrafluoroborate (4.4 g, 0.014 mol) was added portionwise with stirring to a solution of ferrocene (3.9 g, 0.021 mol) in a mixture of 1,2-dichloroethane (17 mL), glacial acetic acid (110 mL), and trifluoroacetic acid (24 mL) at ~20 °C during 30 min. The reaction mixture was stirred at ~20 °C for 6 h. The mixture gradually turned dark-cherry and a cherrycolored precipitate formed. Then the reaction mixture was kept without stirring at 4 °C for 18 h, after which water (200 mL) and chloroform (150 mL) were added. The organic laver was separated and the aqueous laver was extracted with chloroform (150 mL). The combined organic solutions were washed with water until the mixture became neutral, dried with sodium sulfate, and filtered. The solvent was removed on a rotary evaporator. The crude product, which was obtained as a dark-red powder in a yield of 5.5 g, was divided into two equal portions. Each portion was chromatographed on a column (l 20 cm, d 2.9 cm) with aluminum oxide. Ferrocene was eluted with light petroleum. Three fractions, viz., 4-nitrobiphenyl, 4-nitro-4'-ferrocenylbiphenyl with a small impurity of 4-nitrobiphenyl, and pure 4-nitro-4'-ferrocenylbiphenyl, were eluted with a 1:2light petroleum-chloroform mixture. 4-Nitrobiphenvl was extracted from the second fraction with two portions of boiling light petroleum (2×10 mL). From two portions, 4-nitro-4'ferrocenylbiphenyl was obtained in a yield of 2.2 g (41%) as

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cherry-red crystals, m.p. 230–233 °C (decomp.). Found (%): C, 68.86; H, 4.47; N, 3.72. $C_{22}H_{17}FeNO_2$. Calculated (%): C, 68.95; H, 4.47; N, 3.65. ¹H NMR, δ : 4.05 (s, 5 H, C_5H_5); 4.36 (m, 2 H, C(7)H, C(8)H); 4.69 (m, 2 H, C(6)H, C(9)H); 7.56 (m, 4 H, Ar); 7.74 (m, 2 H, Ar); 8.28 (m, 2 H, Ar). IR, v/cm⁻¹: 1340 (NO₂); 1520 (NO₂).

4-Cyano-4´-ferrocenylbiphenyl (2c). 4´-Cyano-4-biphenyldiazonium tetrafluoroborate (2.3 g, 0.0078 mol) was added portionwise with stirring to a solution of ferrocene (2.18 g, 0.0117 mol) in a mixture of 1,2-dichloroethane (10 mL), glacial acetic acid (62 mL), and trifluoroacetic acid (10 mL) at ~20 °C for 15 min. The reaction mixture was stirred for 5 h and then kept without stirring at ~20 °C for 12 h, after which water (200 mL) and chloroform (100 mL) were added. The aqueous layer was separated and extracted with chloroform (50 and 30 mL). The combined organic extracts were washed with water $(3 \times 100 \text{ mL})$ and dried with magnesium sulfate. The chloroform was distilled off on a rotary evaporator and the crude product was obtained in a yield of 2.3 g. The product was chromatographed on a column (l 24 cm, d 2.5 cm) with aluminum oxide. Ferrocene was eluted with light petroleum and then 4-cyano-4'-ferrocenylbiphenyl was eluted with a 1 : 5 light petroleum-benzene mixture in a yield of 1.17 g (41%), m.p. 189-196 °C. The product was treated with boiling light petroleum (2×15 mL) and 4-cyano-4'-ferrocenylbiphenyl was obtained in a yield of 0.94 g (33%), m.p. 195–198 °C. Found (%): C, 75.93; H, 4.75; N, 3.78. C₂₃H₁₇FeN. Calculated (%): C, 76.05; H, 4.72; N, 3.86. ¹H NMR, δ: 4.06 (s, 5 H, C₅H₅); 4.36 (m, 2 H, C(7)H, C(8)H); 4.69 (m, 2 H, C(6)H, C(9)H); 7.53-7.71 (m, 8 H, Ar). IR, v/cm⁻¹: 2238 (CN).

4-Ethylthio-4´-ferrocenylbiphenyl (4). Sodium ethylthiolate (0.25 g, 2.98 mmol) and anhydrous hexamethylphosphoramide (15 mL) were added to 4-bromo-4'-ferrocenylbiphenyl (0.40 g, 0.96 mmol). The reaction mixture was stirred under argon at 95 °C for 2.5 h until 4-bromo-4'-ferrocenylbiphenyl was completely consumed (TLC control). After cooling to ~20 °C, the reaction mixture was poured into a mixture of 36% hydrochloric acid (7 mL) and water (100 mL). The aqueous phase was extracted with diethyl ether (100 mL). The organic layer was separated, dried with magnesium sulfate, and filtered. The ether was removed in vacuo. The residue was chromatographed on a column (16.5 cm, d 2.5 cm) with aluminum oxide. 4-Ethylthio-4'ferrocenylbiphenyl was eluted with a 1:4 benzene-light petroleum mixture in a vield of 0.25 g (66%). After recrystallization from light petroleum, 4-ethvlthio-4'-ferrocenvlbiphenvl was obtained as orange crystals in a vield of 0.23 g (61%). m.p. 174-176 °C. Found (%): C, 72.56; H, 5.58; Fe, 14.11. C₂₄H₂₂FeS. Calculated (%): C, 72.37; H, 5.57; Fe, 14.02. ¹H NMR, δ : 1.35 (t, 3 H, Me, ³*J* = 7.2 Hz); 2.99 (q, 2 H, CH₂S, ${}^{3}J = 7.2$ Hz); 4.06 (s, 5 H, C₅H₅); 4.33 (m, 2 H, C(7)H, C(8)H); 4.67 (m, 2 H, C(6)H, C(9)H); 7.38-7.56 (m, 8 H, Ar).

X-ray diffraction study. Crystals of 4-nitro-4'-ferrocenylbiphenyl (**2b**) and 4-cyano-4'-ferrocenylbiphenyl (**2c**) suitable for X-ray diffraction analysis were grown by the gradual addition of light petroleum to solutions of **2b** and **2c** in benzene. X-ray diffraction data for compounds **2b** and **2c** were collected on a four-circle automated Syntex-P2₁ diffractometer and a SMART Bruker diffractometer (graphite monochromator, λ (Mo-K α) = 0.71073 Å) at 168 and 100 K, respectively. The crystallographic data are given in Table 3.

Table 3. Crystallographic data and details of X-ray diffraction study of compounds 2b and 2c

Parameters	2b	2c		
Molecular formula	C ₂₂ H ₁₇ FeNO ₂	C ₂₃ H ₁₇ FeN		
Molecular weight	383.22	363.23		
Crystal system	Monoclinic	Triclinic		
Space group	$P2_1/c$	$P\overline{1}$		
T/K	168(2)	100(2)		
Z	8	2		
a/Å	10.700(2)	7.6572(11)		
b/Å	30.986(6)	9.3248(3)		
c/Å	10.145(2)	12.6740(18)		
α/deg	90	74.468(2)		
β/deg	98.64(3)	74.446(3)		
γ/deg	90	87.711(3)		
$V/Å^3$	3325.6(11)	839.5(2)		
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.531	1.437		
Absorption coefficient, μ/mm^{-1}	0.923	0.902		
<i>F</i> (000)	1584	376		
Scan mode	$\theta/2\theta$	ω		
θ Scan range/deg	2-26	2-30		
Number of measured	6890	7861		
reflections				
Number of independent reflections	6513	4647		
R	0 1504	0.0207		
Number of refinable	469	294		
parameters	,	_, .		
GOOF	1.050	0.961		
Number of reflections with $I \ge 2\sigma(I)$	4270	3730		
Final <i>R</i> factors				
(for reflections with $I \ge 2\sigma(I)$):				
R_1	0.0568	0.0368		
wR_2	0.1282	0.0852		
R factors for all reflections:				
R_1	0.1223	0.0507		
wR_2	0.1509	0.0906		
Residual electron	-1.225/0.441	-0.349/0.548		
density/e \cdot Å ⁻³	,			
$(u_{\rm min}/u_{\rm max})$				

The structures of **2b** and **2c** were solved by direct methods and refined isotropically by the full-matrix least-squares method. The X-ray data for compound **2c** were processes with the use of the SAINT program.¹¹ The absorption correction was applied using the SADABS program.¹² The final refinement was carried out by the full-matrix least-squares method with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. All calculations were carried out with the use of the SHELXTL program package¹³ on IBM PC.

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