Journal of Organometallic Chemistry 660 (2002) 78–84

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Preparation, properties, and reactions of metal-containing heterocycles[1]

Part CVIII. A novel generation of rigid, nanoscaled 1,1′-ferrocenediyl-bridged bis(pyridine), bis(bipyridine), and bis(phenanthroline) ligands

Ekkehard Lindner *, Ruifa Zong, Klaus Eichele, Markus Ströbele

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received 23 May 2002; received in revised form 24 June 2002; accepted 5 July 2002

Abstract

Four novel, rigid, and conjugated 1,1′-ferrocenediyl-bridged, bis(pyridine), bis(bipyridine), and bis(phenanthroline) ligands **2** and **5**–**7** have been synthesized by palladium promoted C–C coupling reactions and characterized by ^{1}H-, ^{13}C{^{1}H}-NMR, FT-IR, and mass spectroscopy as well as by elemental analyses. Ligand **2** was prepared from 5-ethynyl-2,2′-bipyridine and 1,1′-diiodoferrocene, while compounds **5**–**7** were readily accessible by reactions between pre-constructed ferrocene **4** and 4-bromopyridine, 5-bromo-2,2′-bipyridine, and 3-bromo-1,10-phenanthroline, respectively. Treatment of 1,1′-diiodoferrocene with 1-ethynyl-4-triisopropylsilyl ethynyl-2,5-dipropoxybenzene resulted in the formation of the ferrocene derivative **3**. Via a Si–C bond cleavage in **3** in the presence of tetra-*n*-butylammonium fluoride in THF the intermediate **4** was obtained. Ligand $\mathbf{1}\cdot 0.5H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.2711(10)$, $b = 13.3346(12)$, $c = 14.0879(14)$ Å, $\alpha = 105.007(12)$, $\beta = 105.179(11)$, $\gamma = 105.218(10)^\circ$, $V = 1845.7$ Å^3, $Z = 2$, $R = 0.0640$, and $wR_2 = 0.1292$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bis(pyridines); Bis(2,2′-bipyridines); Bis(1,10-phenanthrolines); 1,1′-Ferrocene; C–C coupling reactions; X-ray structure

---

1. Introduction

Due to the potential application in material sciences as molecular devices and electronic sensors the incorporation of redox active metallocenes in supramolecular structures encounters increasing interest in recent years. Systems of this type open the possibility to study electronic communication between metal-based centers [2–9]. Basically there is a distinction between two different effects, namely through bond and through space, or through solvents in solution. The former is more effective than the latter [10] and the redox properties can be easily controlled [11,12]. Several factors such as host–guest interactions [13], the nature of connectors between the metal centers [14–16], structural rearrangements [16], orbital alignments [17], orbital orderings [18], and in particular the distance between the metals [14,19] are influencing the degree of electronic communication. Therefore, it is important to construct molecules which guarantee to keep the metals well separated from each other to rule out through space electronic communication. Furthermore, it was demonstrated that the degree of conjugation within the molecular backbone between the transition metals also plays an important role [20]. In this investigation we report on the synthesis of hitherto unknown conjugated rigid ligand systems which are able to function as valuable precursors for the access to macrocycles with the potential to show electronic communication. Building blocks for the construction of these ligands are ferrocene, pyridine and its derivatives bipyridine, and phenanthroline, 1,4-diethynylbenzene, or acetylene.

---

* Corresponding author. Tel.: +49-7071-2972039; fax: +49-7071-295306

E-mail address: ekkehard.lindner@uni-tuebingen.de (E. Lindner).

[1] Part CVII, see Ref. [1].

PII: S0022-328X(02)01774-6

2. Results and discussion

2.1. Design of the polydentate ligands **1** [21,22], **2**, and **5**–**7**

Pyridine and its derivatives 2,2′-bipyridine and 1,10-phenanthroline functionalized at positions 4 [23], 5 or 5,5′ [24,25], and 3 or 3,8 [26], respectively, have attracted great attention. Because of their structural characteristics they are employed in the investigation of molecular wires. 5- and 3-Ethynyl substituted 2,2′-bipyridine [24,27] and 1,10-phenanthroline [28,29], respectively, are important building blocks for the synthesis of materials applied in molecular electronics, because the acetylene moiety is connected to the electron rich positions of the aromatic amines. Such a unit is expected to favor through bond electronic communication. Due to mainly synthetic difficulties, only rather limited experiments have been carried out with these promising pyridine derivatives. Incorporation of these building blocks into the ligands **1**, **2**, and **5**–**7** will make the side chains of the subunits linear and the ferrocene based ligands symmetric. Here we present the first examples of ligand systems in which a 1,1′-ferrocenediyl unit is connected to 2,2′-bipyridine and 1,10-phenanthroline at position 5 and 3, respectively, via conjugated linkers. The introduction of propoxy substituents into the *para*-position of the phenylene bridges solves the problem of low solubility.

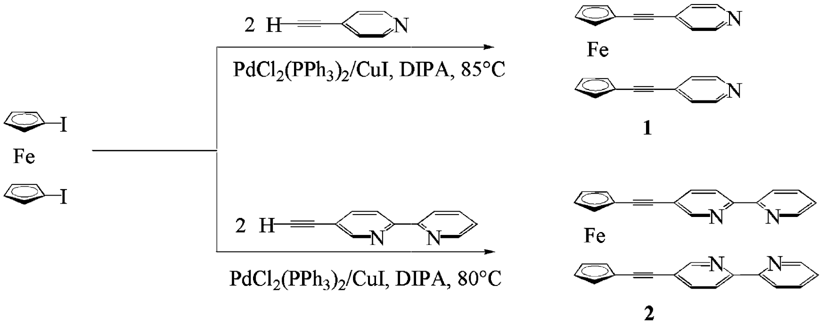
2.2. Synthesis of the ligands **2** and **5**–**7**

All C–C coupling reactions mentioned in Schemes 1–3 were promoted by either $Cl_2Pd(PPh_3)_2/CuI$ or $Pd(PPh_3)_4$ in the presence of organic amines [30]. While ligand **1** has already been described in an earlier paper [21], **2** is accessible in 19% yield by reaction of 1,1′-diiodoferrocene [31] with 5-ethynyl-2,2′-bipyridine [32] in diisopropylamine as a solvent which concomitantly functions as a proton acceptor (Scheme 1). The red bipyridine derivative is thermally and air stable and only slightly soluble in common organic solvents. Its molecular composition was evidenced by an EI mass spectrum.

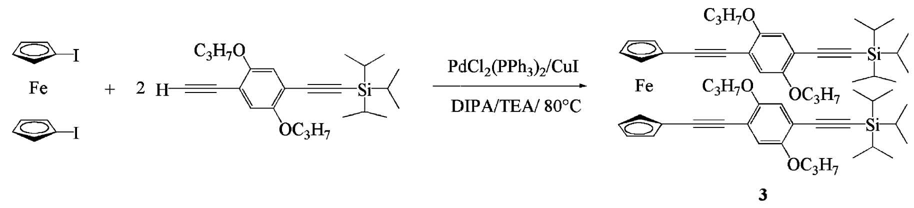
A suitable way for the access of the ligands **5**–**7** is the employment of the pre-constructed 1,1′-ferrocenediylbis(ethynylene) (**4**). As a first step for the preparation of **4** the ferrocene derivative **3** was synthesized in 55% yield by a C–C coupling reaction between 1,1′-diiodoferrocene and 1-ethynyl-4-(triisopropylsilylethynyl)-2,5-dipropoxybenzene [33] in a mixture of THF and diisopropylamine (Scheme 2). The intermediate **3** was characterized by mass and NMR spectroscopy as well as by elemental analyses (see Section 4). In a following reaction the ferrocene derivative **4** was obtained by cleavage of the triisopropylsilyl substituents from **3** in the presence of tetra-*n*-butylammonium fluoride in THF at 20 °C (Scheme 3). No isolation of **4** is necessary and the removal of the protecting group is performed prior to the coupling reaction with 4-bromopyridine, 5-bromo-2,2′-bipyridine, and 3-bromo-1,10-phenanthroline in THF–diisopropylamine. To optimize the yields of **5**–**7** an excess amount of the bromo-*N*-heterocycles was applied. After column chromatography with silica gel and dichloromethane–methanol–THF, compounds **5**–**7** are obtained as orange, air-stable powders in yields between 45 and 52%, which are soluble in chlorinated solvents and THF, but insoluble in acetonitrile, diethyl ether, or saturated hydrocarbons. The molecular compositions of **5**–**7** were confirmed by FD, EI, and FAB mass spectra.

2.3. NMR and IR spectroscopic characterization of **5**–**7**

The polydentate nitrogen ligands **5**–**7** were unequivocally identified by their ^1H- and $^{13}C\{^1H\}$-NMR spectra. Because of the high symmetry of **5**–**7** the protons and carbon atoms in both side chains of the ferrocene unit do not differ in their chemical shifts. Both protons in the phenylenes of **5**–**7** which are unsymmetrically substituted in the *para*-position, give rise to each one singlet at ca. 7 ppm in the ^1H-NMR spectra. The propoxy group is characterized by two triplets resulting from the protons of the α-methyl and γ-methylene functions and a multiplet which is assigned to the



Scheme 1.



Scheme 2.

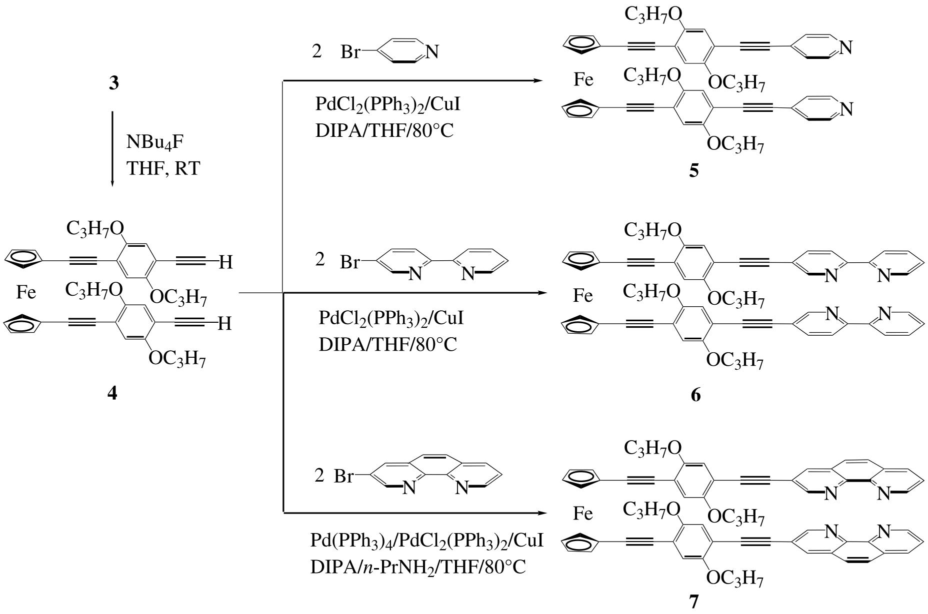
protons of the β-CH_2 unit. In $CDCl_3$ or CD_2Cl_2, the cyclopentadienyl protons in **5**–**7** reveal an AA′XX′ pattern with centers lying between 4.6 and 4.4 ppm. The α-protons in the *N*-heterocycles exhibit the largest chemical shifts at 8.5, 8.8, and 9.2 ppm in the ^{1}H-NMR spectra of **5**, **6**, and **7**, respectively. All other resonances are summarized in Section 4.

Each ligand is provided with two alkyne moieties as connectors. Hence four different chemical shifts are found in the $^{13}C\{^1H\}$-NMR spectra of **5**–**7** located between 82 and 94 ppm. Six well resolved singlets are observed for the phenylene carbon atoms in the regions 153–154 (*C*–OC_3H_7), 116.4–116.8 (C–H), and 111.7–115.7 ppm (C1 and C4). Three ^{13}C resonances between 73 and 66 ppm in the spectra of the ligands **5**–**7** are attributed to the cyclopentadienyl carbon atoms. In contrast to dialkylsubstituted 1,1′-ferrocenes the *ipso*-C atoms resonate at higher field than the other carbon atoms. The assignment of the carbon atoms was supported by a DEPT-135 experiment, because in the above-mentioned region also the ^{13}C signals of the α-carbon atoms of the propoxy groups can be observed. The ^{13}C part of the *N*-heterocycles in **5**–**7** shows the expected signals for the different carbon atoms and the largest downfield shifts are ascribed to the carbon atoms adjacent to the nitrogen atoms. Carbon atoms next to the alkyne moieties give rise to ^{13}C signals at 131.8 (**5**), 120.6 (**6**), and 119.3 ppm (**7**).

A characteristic absorption in the IR spectra (KBr) of **2**, and **5**–**7** at about 2210 cm^{-1} corresponds to the C≡C stretching vibration of the alkyne functions.

2.4. X-ray crystal structure of ligand 1

Although the preparation of ligand **1** has already been reported [21,22], its structure is still unknown. Ligand **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two crystallographically independent molecules A and B of **1** and a molecule of water, which is hydrogen bonded to N(1) and N(4), with O–N distances of 2.773 and 2.916 Å, respectively. Selected distances and angles are listed in Table 1. An ORTEP plot of A and B with atom labeling is depicted in Fig. 1. The iron ring-centroid distances Fe(1)–Cp(center) and Fe(2)–Cp(center) are 1.66 and 1.67/1.64 Å, respectively. Between the pyridine units the average nitrogen–nitrogen distance was found to be 3.96 Å. While the two cyclopentadienyl rings in A and B are nearly parallel with angles of $\delta = 176.7°$ (ring center–iron–ring center), the resulting dihedral angles (tilt angle α) are found to



Scheme 3.

Table 1
Selected bond lengths (Å) and angles (°) for **1**·0.5H_2O

	Molecule A	Molecule B
Distances		
N(1)–N(2)	3.929(16)	
N(3)–N(4)		4.006(16)
Fe–center Cp(1)	1.66	1.67
Fe–center Cp(2)	1.66	1.64
Center Py(1)–center Py(2)	3.78	3.85
Bond angles		
δ = (Cp–Fe–Cp)	176.7	176.7
Interplanar angles		
α = Cp(1)–Cp(2)	4.04(47)	4.60(85)
Py(1)–Py(2)	5.16(47)	15.85(49)
Cp–Py	5.60(49)	17.12(63)
	5.89(46)	29.20(49)
Torsion angles		
C(6)–Cp(1)–Cp(2)–C(18)	−0.3	
C(30)–Cp(1)–Cp(2)–C(42)		−0.8
C(8)–C(1)–C(13)–C(20)	−3.4	
C(32)–C(25)–C(37)–C(45)		1.3
Centers Py(1)–Cp(1)–Cp(2)–Py(2)	−3.4	0.3

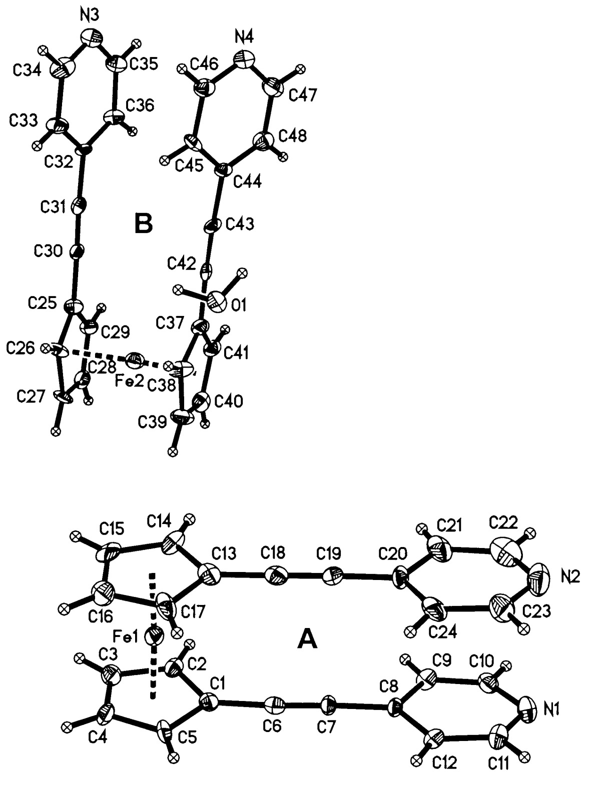


Fig. 1. ORTEP plot of the two independent molecules A and B of **1** and of the water molecule, indicating the numbering scheme. In this projection the water molecule is located nearly above molecule B. Probabilities are drawn at the 20% level.

be 4.04(47) and 4.60(85)°. The dihedral angles between the pyridine rings in A and B show values of 5.16(47) and 15.85(49)°, respectively. The pyridine ring centers of **1** are separated by distances of 3.78 (molecule A) and 3.85 Å (molecule B). A significant deviation from coplanarity is observed, as revealed by tilt angles of 5.89(46)/5.60(49) (A) and 17.12(63)/29.20(49)° (B) between the cyclopentadienyl ring and the pyridines. The torsion angles of −3.4 and 1.30° defined by C(8)–C(1)–C(13)–C(20) and C(32)–C(25)–C(37)–C(44), indicate a nearly eclipsed structure of **1** in the solid state. It is of interest that the two side chains of **1** point roughly to the same direction, which is similar to our previous observation in the crystal structure of 1,1′-bis(3-pyridylethynyl)ferrocene [21]. This is attributed either to π–π interactions between the two side chains [34] or to crystal packing forces. Crystal data and structure refinement are given in Table 2.

3. Conclusion

In order to connect two *N*-heterocycles with two cyclopentadienyl rings of a 1,1′-ferrocene entity with acetylene or *para*-phenylene ethynylene linkers, two synthetic strategies have been developed and discussed. The first one is featured by pre-constructed terminal

Table 2
Crystal data and structure refinement for **1**·0.5H_2O

Empirical formula	$C_{48}H_{34}Fe_2N_4O$
Formula weight	794.49
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.2711(10)
b (Å)	13.3346(12)
c (Å)	14.0879(14)
α (°)	105.007(12)
β (°)	105.179(11)
γ (°)	105.218(10)
V (Å^3)	1845.7(3)
Z	2
D_{calc} (g cm^{-3})	1.430
Absorption coefficient (mm^{-1})	0.830
F(000)	820
Crystal size (mm^3)	0.46 × 0.22 × 0.02
θ Range for data collection (°)	2.11–24.94
Limiting indices	$-13 \le h \le 13$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflections collected	8518
Unique reflections	3535 [$R_{int} = 0.0966$]
Completeness to $\theta = 24.94$	54.7%
Refinement methods	Full-matrix least-square on F^2
Data/restraints/parameters	3535/0/504
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0640$, $wR_2 = 0.1292$
R indices (all data)	$R_1 = 0.1609$, $wR_2 = 0.1617$
Goodness-of-fit on F^2	0.791
Largest difference peak and hole (e Å^{-3})	0.980 and −0.373

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|$. $wR_2 = [\Sigma\ [w(F_o^2 - F_c^2)^2]/\Sigma\ [w(F_o^2)^2]]^{0.5}$.

ethynyl-*N*-heterocycles, while the second one refers to the pre-organized 1,1′-ferrocenediylbis(acetylene) derivative **4**. Both of the approaches have been successively applied for the synthesis of the ligands **2** and **5**–**7**, respectively. The parallel arrangement of the side chains in the crystal structure of **1** is expected to play a role in the formation of transition metal complexes. The complexation of the nitrogen functionalized bidentate and tetradentate ligands and electronic communication of their complexes are under investigation.

4. Experimental

4.1. General procedures

All reactions and manipulations were carried out under an atmosphere of Ar by use of standard Schlenk techniques except otherwise noted. Amines were dried by NaOH or CaH_2 and distilled, degassed, and stored under Ar. THF was distilled from sodium benzophenone ketyl prior to use. Column chromatography (30 × 5 cm) was conducted using either activated silica gel, 0.063–0.200 mm (Merck), or neutral Al_2O_3 (Merck) as reported in the specific sections describing the synthesis of the compounds. IR data were obtained with a Bruker IFS 48 FT-IR spectrometer. EI mass spectra were taken on a Finnigan MAT TSQ 70 (200 °C) instrument while FD and FAB mass spectra were recorded on a Finnigan MAT 711A (8 kV) instrument, modified by AMD. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded at 25 °C on a Bruker DRX 250 spectrometer operating at 250.13 and 62.90 MHz, respectively. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively, which are reported relative to Me_4Si. Elemental analyses were carried out with an Elementar Vario EL analyzer.

1,1′-Diiodoferrocene [31], 5-bromo-2,2′-bipyridine [35], 5-ethynyl-2,2′-bipyrdine [32], and 3-bromo-1,10-phenanthroline [26] were synthesized according to literature methods. A highly selective method similar to a recent publication is applied for the preparation of 1-ethynyl-4-triisopropylsilylethynyl-2,5-dipropoxybenzene [33], which was purified by column chromatography with neutral Al_2O_3 and 0–1% Et_2O in *n*-C_6H_{14}.

*4.2. Preparation of the intermediates **3** and **4** and of the ligands **2**, **5**–**7***

*4.2.1. Synthesis of 1,1′-bis(2,2′-bipyridine-5-yl-ethynyl)ferrocene (**2**)*

To a solution of 1,1′-diiodoferrocene (440 mg, 1.0 mmol) and 5-ethynyl-2,2′-bipyridine (400 mg, 2.2 mmol) in diisopropylamine (20 ml), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and CuI (19 mg, 0.1 mmol) were added. The mixture was refluxed at 80 °C for 2 days. Then the solvents were removed in vacuo and the residue was treated with 100 ml of a 1:1 mixture of water and $CHCl_3$. The organic extract was dried over $MgSO_4$. Column chromatography was conducted with silica gel and 0–5% MeOH in CH_2Cl_2. Yield: 105 mg (19%), air stable, red powder, m.p. >260 °C (dec.). ^{1}H-NMR (CD_2Cl_2): $\delta = 8.53$ (d, $^4J_{HH} = 2.1$ Hz, 2H, H-6), 8.50 (ddd, $^3J_{HH} = 4.8$, $^4J_{HH} = 1.7$, $^5J_{HH} = 0.7$ Hz, 2H, H-6′), 8.20 (ddd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.0$, $^5J_{HH} = 1.0$ Hz, 2H, H-3′), 8.18 (d, $^3J_{HH} = 8.2$ Hz, 2H, H-3), 7.69 (dd, $^3J_{HH} = 8.2$, $^4J_{HH} = 2.1$ Hz, 2H, H-4), 7.55 (ddd, $^3J_{HH} = 7.7$, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.7$ Hz, 2H, H-4′), 7.12 (ddd, $^3J_{HH} = 7.5$, $^4J_{HH} = 4.8$, $^5J_{HH} = 1.2$ Hz, 2H, H-5′), 4.62 (m [36], 4H, C_4H_4C), 4.40 (m [37], 4H, C_4H_4C). EI-MS (70 eV, 200 °C): *m*/*z* 542.0 [M^+], 241.9 [$(M-Fe)/2]^+$. IR (KBr, cm^{-1}): $\nu(C{\equiv}C) = 2207$. Anal. Found: C, 73.99; H, 3.83; N, 10.18. Calc. for $C_{34}H_{22}FeN_4 \cdot 0.1CH_2Cl_2$ (550.91): C, 74.34; H, 4.06; N, 10.17%.

*4.2.2. 1,1′-Bis{[2,5-dipropoxy-4-(triisopropylsilylethynyl)phenyl]ethynyl}ferrocene (**3**)*

To a solution of 1,1′-diiodoferrocene (642 mg, 1.47 mmol) and 1-ethynyl-4-(triisopropylsilyl)ethynyl-2,5-dipropoxybenzene (1245 mg, 3.1 mmol) in a mixture of Et_3N–diisopropylamine (50/20 ml), $Pd(PPh_3)_2Cl_2$ (102 mg, 0.15 mmol) and CuI (108 mg, 0.57 mmol) were added. The mixture was refluxed at 80 °C for 2 days followed by removal of the solvents under vacuum. The residue was extracted with Et_2O (4 × 100 ml) and the organic layer was dried over $MgSO_4$. After removal of the solvent by a rotation evaporator, the residue was subjected to column chromatography (Al_2O_3, 0–5% Et_2O in *n*-C_6H_{14}). The desired ferrocene derivative **3** was isolated in the third fraction. Yield: 798 mg (55%), orange, air-stable powder, m.p. 149 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 6.92$ (s, 2H, C_6H_2), 6.88 (s, 2H, C_6H_2), 4.57 (m [36], 4H, C_4H_4C), 4.35 (m [37], 4H, C_4H_4C), 3.96 (t, $^3J_{HH} = 6.4$ Hz, 4H, $OCH_2CH_2CH_3$), 3.85 (t, $^3J_{HH} = 6.4$ Hz, 4H, $OCH_2CH_2CH_3$), 1.85 (m, 8H, $OCH_2CH_2CH_3$), 1.15 (s, 42H, SiC_9H_{21}), 1.03 (m, 12H, $OCH_2CH_2CH_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 154.29$, 153.15 (C-2 and C-5, C_6H_2), 117.52, 116.19 (C-3 and C-6, C_6H_2), 114.59, 113.35 (C-1 and C-4, C_6H_2), 103.06, 96.00 ($C{\equiv}C$–SiC_9H_{21}), 92.87, 82.69 ($C{\equiv}C$–C_5H_4), 73.00 (C_4H_4C), 71.44 (C_4H_4C), 71.05, 70.60 ($OCH_2CH_2CH_3$), 66.64 (C_4H_4C), 22.74, 22.61 ($OCH_2CH_2CH_3$), 18.64, 11.30 (SiC_9H_{21}), 10.62, 10.57 ($OCH_2CH_2CH_3$). EI-MS (70 eV, 200 °C): *m*/*z* 978.5 [M^+]. IR (KBr, cm^{-1}): $\nu(C{\equiv}C) = 2150$. Anal. Found: C, 73.50; H, 7.94. Calc. for $C_{60}H_{82}FeO_4Si_2$ (979.32): C, 73.59; H, 8.44%.

*4.2.3. General procedure for the preparation of the ligands **5**–**7***

To a solution of **3** (980 mg, 1.0 mmol) in THF (50 ml) two equivalents of tetra-*n*-butylammonium fluoride

(520 mg, 2.0 mmol) were added at 20 °C. The solution was stirred for 2 h at the same temperature. Then a 50% excess of 4-bromopyrydine hydrochloride, 5-bromo-2,2′-bipyridine, and 3-bromo-1,10-phenanthroline, respectively, diisopropylamine (20 ml) (and in the case of phenanthroline also 20 ml of *n*-propylamine) as well as $Pd(PPh_3)Cl_2$ (35 mg, 0.05 mmol) and CuI (20 mg, 0.1 mmol) were added. In the case of phenanthroline additional $Pd(PPh_3)_4$ was used as a catalyst. The oil-bath temperature was controlled at 80 °C, and the mixture was stirred for 2 days. After cooling down to room temperature (r.t.), the solvents were removed under vacuum and a concd. aq. NH_4Cl solution (50 ml) was added. The residue was extracted at least four times, each with 50 ml of CH_2Cl_2. The organic extract was washed with 200 ml of an aq. NaCl solution and finally it was dried over $MgSO_4$. After removal of the solvents, the residue was ready for column chromatography using silica gel and CH_2Cl_2. The product was eluted by a solvent mixture of MeOH (0–5%), THF (10–50%), and CH_2Cl_2. Recrystallization from CH_2Cl_2 and *n*-pentane gave spectroscopically pure products.

*4.2.3.1. 1,1′-Bis{[4-(4-pyridylethynyl)-2,5-dipropoxyphenyl]ethynyl}ferrocene (**5**).* Initial weight: 4-bromopyridiniumchloride (580 mg, 3.0 mmol). Yield: 427 mg (52%), orange powder, m.p. 161 °C. ^1H-NMR ($CDCl_3$): $\delta = 8.50$ (d, $^3J_{HH} = 5.0$ Hz, 4H, H-α, C_5H_4N), 7.34 (d, $^3J_{HH} = 5.0$ Hz, 4H, H-β, C_5H_4N), 6.96 (s, 2H, C_6H_2), 6.91 (s, 2H, C_6H_2), 4.57 (m [36], 4H, C_4H_4C), 4.36 (m [37], 4H, C_4H_4C), 3.95 (t, $^3J_{HH} = 6.1$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 3.91 (t, $^3J_{HH} = 6.4$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.86 (m, 8H, $OCH_2C\mathit{H}_2CH_3$), 1.10 (m, 12H, $OCH_2CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 153.90$, 153.28 (C-2 and C-5, C_6H_2), 149.66 (C-α, C_5H_4N), 131.57 (C-γ, C_5H_4N), 125.27 (C-β, C_5H_4N), 116.81, 116.50 (C-3 and C-6, C_6H_2), 115.74, 111.70 (C-1 and C-4, C_6H_2), 93.58, 91.60, 90.77, 82.61 ($\mathit{C}{\equiv}\mathit{C}-C_6H_2-\mathit{C}{\equiv}\mathit{C}$), 72.93 ($\mathit{C}_4H_4C$), 71.50 ($\mathit{C}_4H_4C$), 70.94, 70.79 ($O\mathit{C}H_2CH_2CH_3$), 66.62 ($C_4H_4\mathit{C}$), 22.67, 22.62 ($OCH_2\mathit{C}H_2CH_3$), 10.60, 10.50 ($OCH_2CH_2\mathit{C}H_3$). FD-MS (30 °C): *m*/*z* (%) 817.6 (7), 818.6 (4), 819.6 (100), 820.6 (60), 821.6 (21), 822.6 (5) [M^+]. IR (KBr, cm^{-1}): *ν*(C≡C) = 2213. Anal. Found: C, 75.85; H, 5.41; N, 3.28. Calc. for $C_{52}H_{48}FeN_2O_4$ (820.80): C, 76.09; H, 5.89; N, 3.41%.

*4.2.3.2. 1,1′-Bis{[4-(2,2′-bipyridine-5-ylethynyl)-2,5-dipropoxy-phenyl]ethynyl}ferrocene (**6**).* Initial weight: 5-bromo-2,2′-bipyridine (700 mg, 3.0 mmol). Yield: 440 mg (45%), orange powder, m.p. 165 °C. ^1H-NMR ($CDCl_3$): $\delta = 8.80$ (dd, $^4J_{HH} = 2.2$, $^5J_{HH} = 0.8$ Hz, 2H, H-6), 8.67 (ddd, $^3J_{HH} = 4.7$, $^4J_{HH} = 1.7$, $^5J_{HH} = 0.9$ Hz 2H, H-6′), 8.40 (ddd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.0$, $^5J_{HH} = 1.0$ Hz 2H, H-3′), 8.37 (dd, $^3J_{HH} = 8.2$, $^5J_{HH} = 0.8$ Hz, 2H, H-3), 7.92 (dd, $^3J_{HH} = 8.2$, $^4J_{HH} = 2.2$ Hz, 2H, H-4), 7.80 (ddd, $^3J_{HH} = 7.8$, $^3J_{HH} = 7.8$, $^4J_{HH} = 1.7$ Hz, 2H, H-4′), 7.30 (ddd, $^3J_{HH} = 7.5$, $^3J_{HH} = 4.8$, $^4J_{HH} = 1.1$ Hz, 2H, H-5′ in $C_{10}H_7N_2$), 6.99 (s, 2H, C_6H_2), 6.93 (s, 2H, C_6H_2), 4.59 (m [36], 4H, C_4H_4C), 4.37 (m [37], 4H, C_4H_4C); 3.99 (t, $^3J_{HH} = 6.44$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 3.94 (t, $^3J_{HH} = 6.44$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.88 (m, 8H, $OCH_2C\mathit{H}_2CH_3$), 1.13 (t, $^3J_{HH} = 7.38$ Hz, 6H, $OCH_2CH_2C\mathit{H}_3$), 1.11 (t, $^3J_{HH} = 7.38$ Hz, 6H, $OCH_2CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 155.43$, 154.57 (C-2 and C-2′, $C_{10}H_7N_2$), 153.73, 153.38 (C-2 and C-5, C_6H_2), 151.52, 149.22 (C-6 and C-6′, $C_{10}H_7N_2$), 139.09, 136.90 (C-4 and C-4′, $C_{10}H_7N_2$), 123.82, 121.26 (C-3 and C-3′, $C_{10}H_7N_2$), 120.58 (C-5, $C_{10}H_7N_2$), 120.30 (C-5′, $C_{10}H_7N_2$), 116.70, 116.59 (C-3 and C-6, C_6H_2), 115.23, 112.40 (C-1 and C-4, C_6H_2), 93.33, 91.47, 90.35, 82.76 ($\mathit{C}{\equiv}\mathit{C}-C_6H_2-\mathit{C}{\equiv}\mathit{C}$), 72.93, 71.52 ($\mathit{C}_4H_4C$), 70.99, 70.90 ($O\mathit{C}H_2CH_2CH_3$), 66.77 ($C_4H_4\mathit{C}$), 22.74 ($OCH_2\mathit{C}H_2CH_3$), 10.67, 10.59 ($OCH_2CH_2\mathit{C}H_3$). EI-MS (70 eV, 200 °C): *m*/*z* 974.3 [M^+], 460.1 [$(M-Fe)/2+1]^+$. IR (KBr, cm^{-1}): *ν*(C≡C) = 2216. Anal. Found: C, 76.01; H, 5.94; N, 5.20. Calc. for $C_{62}H_{54}FeN_4O_4$ (974.98): C, 76.38; H, 5.58; N, 5.75%.

*4.2.3.3. 1,1′-Bis{[4-(1,10-phenanthroline-3-yl-ethynyl)-2,5-dipropoxy-phenyl]ethynyl}ferrocene (**7**).* Initial weights: 3-bromo-1,10-phenanthroline (780 mg, 3.0 mmol), $Pd(PPh_3)_4$ (140 mg, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), and CuI (15 mg, 0.08 mmol). Prior to chromatography the copper complex was extracted with a 2% solution of KCN in water (100 ml). Recrystallization was carried out with $CHCl_3$ and *n*-C_6H_{14}. Yield: 521 mg (51%), orange powder, m.p. 172 °C. ^1H-NMR (CD_2Cl_2): $\delta = 9.13$ (d, $^4J_{HH} = 2.0$ Hz, 2H, H-2, $C_{12}H_7N_2$), 9.04 (dd, $^3J_{HH} = 4.3$, $^4J_{HH} = 1.7$ Hz, 2H, H-9, $C_{12}H_7N_2$), 8.10 (d, $^4J_{HH} = 2.0$ Hz, 2H, H-4, $C_{12}H_7N_2$), 8.01 (dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.7$ Hz, 2H, H-7, $C_{12}H_7N_2$), 7.53 (dd, $^3J_{HH} = 8.0$, $^3J_{HH} = 4.3$ Hz, 2H, H-8, $C_{12}H_7N_2$), 7.47 (s, 4H, H-5 and H-6, $C_{12}H_7N_2$), 6.96 (s, 2H, H-3 or 6, C_6H_2), 6.81 (s, 2H, H-3 or 6, C_6H_2), 4.58 (m [36], 4H, C_4H_4C), 4.38 (m [37], 4H, C_4H_4C), 3.96 (t, $^3J_{HH} = 6.4$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 3.93 (t, $^3J_{HH} = 6.4$ Hz, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.91 (m, 8H, $OCH_2C\mathit{H}_2CH_3$), 1.19 (t, $^3J_{HH} = 7.4$ Hz, 6H, $OCH_2CH_2C\mathit{H}_3$), 1.15 (t, $^3J_{HH} = 7.5$ Hz, 6H, $OCH_2CH_2C\mathit{H}_3$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 154.05$, 153.44 (C-2 and C-5 in C_6H_2), 151.85 (C-2), 150.38 (C-9), 145.93 (C-1a), 144.48 (C-10a), 137.44 (C-4), 135.92 (C-7), 128.94 (C-6a), 127.80 (C-4a), 127.16, 126.07 (C-5 and C-6), 123.12 (C-8), 119.96 (C-3, $C_{12}H_7N_2$), 116.97, 116.38 (C-3 and C-6, C_6H_2), 115.68, 112.37 (C-1 and C-4, C_6H_2), 92.73, 91.72, 90.87, 83.89 ($\mathit{C}{\equiv}\mathit{C}-C_6H_2-\mathit{C}{\equiv}\mathit{C}$), 72.91 ($\mathit{C}_4H_4C$), 71.24 ($O\mathit{C}H_2CH_2CH_3$), 71.05 ($\mathit{C}_4H_4C$), 71.02 ($O\mathit{C}H_2CH_2CH_3$), 68.18 ($C_4H_4\mathit{C}$), 23.10 ($OCH_2\mathit{C}H_2CH_3$), 23.07 ($OCH_2\mathit{C}H_2CH_3$), 10.77 ($OCH_2CH_2\mathit{C}H_3$), 10.75 ($OCH_2CH_2\mathit{C}H_3$). FAB-MS

(NBA, 50 °C): *m*/*z* 1023.1 [M^+]. IR (KBr, cm^{-1}): ν(C≡C) = 2202. Anal. Found: C, 73.46; H, 5.45; N, 5.19. Calc. for $C_{66}H_{54}FeN_4O_4 \cdot 0.5CHCl_3$ (1082.71): C, 73.72; H, 5.07; N, 5.18%.

4.3. *Crystallographic analysis*

Single crystals of compound **1** suitable for an X-ray structure determination were obtained by slow evaporation of a CH_2Cl_2 and MeOH (commercial product, containing somewhat water) solution (1:1) at r.t. A red crystal was transferred to a glass capillary and measured on a Stoe IPDS diffractometer, using graphite-monochromated Mo–K_α radiation. The structure was solved by direct methods with SHELXS [38] and refined by least-squares methods based on F^2 using SHELXL-97 [39]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions, except for the hydrogen atoms of the water molecule. They were located in the difference electron density map and refined isotropically.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 185968 for ligand **1**. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The Degussa AG is thanked for supplying starting materials. Dipl.-Chem. H.-P. Jing, Institut für Anorganische Chemie, Universität Tübingen, is thanked for his help in checking the quality of the single crystal used in this research.

References

[1] E. Lindner, C. Ayasse, K. Eichele, M. Steimann, Organometallics, in press.
[2] J. Moutet, E. Saint-Aman, G. Royal, S. Tingry, R. Ziessel, Eur. J. Inorg. Chem. (2002) 692.
[3] A. Ion, J. Moutet, E. Saint-Aman, G. Royal, S. Tingry, J. Pecaut, S. Menage, R. Ziessel, Inorg. Chem. 40 (2001) 3632.
[4] M. Buda, J. Moutet, E. Saint-Aman, A. De Cian, J. Fischer, R. Ziessel, Inorg. Chem. 37 (1998) 4146.
[5] N. Sachsinger, C.D. Hall, J. Organomet. Chem. 531 (1997) 61.
[6] C.D. Hall, T. Truong, S.C. Nyburg, J. Organomet. Chem. 547 (1997) 281.
[7] B. König, M. Nimtz, H. Zieg, Tetrahedron 51 (1995) 6267.
[8] I.R. Butler, Organometallics 11 (1992) 74.
[9] I.R. Butler, J.L. Roustan, Can. J. Chem. 68 (1990) 2212.
[10] M. Schmittel, H. Ammon, C. Wöhrle, Chem. Ber. 128 (1995) 845.
[11] J.D. Carr, S.J. Coles, M.B. Hursthouse, M.E. Light, E.L. Munro, J.H.R. Tucker, J. Westwood, Organometallics 19 (2000) 3312.
[12] J. Alvarez, A.E. Kaifer, Organometallics 18 (1999) 5733.
[13] Y. Wang, S. Mendoza, A.E. Kaifer, Inorg. Chem. 37 (1998) 317.
[14] K.R. Justin Thomas, J.T. Lin, Y.S. Wen, Organometallics 19 (2000) 1008.
[15] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometllics 16 (1997) 184.
[16] D. Osella, L. Milone, C. Nervi, M. Ravera, J. Organomet. Chem. 488 (1995) 1.
[17] J.V. Ortega, B. Hong, S. Ghosal, J.C. Hemminger, B. Breedlove, C.P. Kubiak, Inorg. Chem. 38 (1999) 5102.
[18] J.P. Strachan, S. Gentemann, J. Seth, W.A. Kalsbeck, J.S. Lindsey, Dewey Holten, D.F. Bocian, J. Am. Chem. Soc. 119 (1997) 11191.
[19] M. Brady, W.Q. Weng, J.A. Gladysz, J. Chem. Soc. Chem. Commun. (1994) 2655.
[20] J. Seth, V. Palaniappan, R.W. Wagner, T.E. Johnson, J.S. Lindsey, D.F. Bocian, J. Am. Chem. Soc. 118 (1996) 11194.
[21] E. Lindner, R.F. Zong, K. Eichele, Phosphorus Sulfur Silicon 169 (2001) 219.
[22] W.M. Xue, F.E. Kühn, E. Herdtweck, Q.C. Li, Eur. J. Inorg. Chem. (2001) 213.
[23] C.J. Kuehl, S.D. Huang, P.J. Stang, J. Am. Chem. Soc. 123 (2001) 9634.
[24] A. Khatyr, R. Ziessel, J. Org. Chem. 65 (2000) 7814.
[25] P.F.H. Schwab, F. Fleischer, J. Michl, J. Org. Chem. 67 (2002) 443.
[26] D. Tzalis, Y. Tor, S. Failla, J.S. Siegel, Tetrahedron Lett. 36 (1995) 3489.
[27] J. Polin, E. Schmohel, V. Balzani, Synthesis 3 (1998) 321.
[28] M. Schmittel, C. Michel, A. Wiegrefe, V. Kalsani, Synthesis 10 (2001) 1561.
[29] P.J. Connors, D. Tzalis, Jr., A.L. Dunnick, Y. Tor, Inorg. Chem. 37 (1998) 1121.
[30] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 50 (1975) 4467.
[31] R.F. Kovar, M.D. Rausch, H. Rosenberg, Organomet. Chem. Synth. 1 (1970/1971) 173.
[32] V. Grosshenny, F.M. Romero, R. Ziessel, J. Org. Chem. 62 (1997) 1491.
[33] S. Höger, K. Bonrad, A. Mourran, U. Beginn, M. Möller, J. Am. Chem. Soc. 123 (2001) 5651.
[34] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovsii, A.G. Majouga, N.V. Zyk, M. Schröder, Coord. Chem. Rev. 222 (2001) 155.
[35] Y. Uchida, R. Kajita, Y. Kawasaki, S. Oae, Tetrahydron Lett. 36 (1995) 4077.
[36] m: Low field part of an AA′XX′ pattern, $N = |^3J_{HH} + ^5J_{HH}|$.
[37] m: High field part of an AA′XX′ pattern, $N = |^3J_{HH} + ^5J_{HH}|$.
[38] G.M. Sheldrick, Acta Crystallogr. Sect. A 51 (1995) 33.
[39] G.M. Sheldrick, SHELXTL V5.03, University of Göttingen, Germany, 1995.