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Ferrocene-bridged Bis(2,2′-Bipyridines) - New Tweezer-type Ligands for Transition Metal Ions

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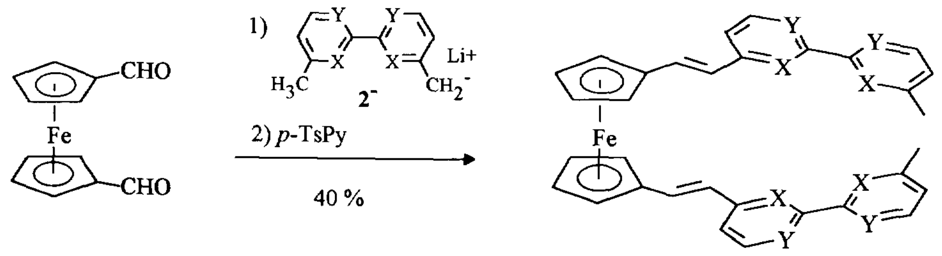
Abstract: Ferrocene-bridged bis(2,2′-bipyridines) **3** were synthesized from ferrocene-1,1′-dicarbaldehyde (**1**) and dimethyl-2,2′-bipyridines (**2**) *via* a two step condensation reaction. **3a** and **3b** can serve as tetradentate ligands for transition metal ions, whereby the silver(I) complex of **3a** shows a restricted mobility on NMR time scale at room temperature.

Molecular structures that contain two or more different coordinated metal ions are involved in many important biological and catalytic processes[1]. The distance between the metal centers and their orientation is important for the function of these molecular devices[2]. Electronic interactions have been studied on various bimetallic model compounds[3], whereby ferrocenes[4] are frequently employed due to their good synthetic availability and well known redox chemistry. In this paper we describe the synthesis of ferrocenyl-bis(vinylmethyl-2,2′-bipyridines) and their ability to act as molecular tweezers for transition metal ions[5].

Ferrocene-1,1′-dicarbaldehyde (**1**)[6] was treated with two equivalents of the monoanion **2a**$^-$, readily obtained by deprotonation of 6,6′-dimethyl-2,2′-bipyridine (**2a**) with 1.2 equiv. LDA at room temp., to give the corresponding dialcohol as a mixture of diastereomers. Subsequent treatment with pyridinium-*para*-tolylsulfonate (*p*-TsPy) in toluene at 110°C gave exclusively the *trans*-elimination product **3a** in 40% overall isolated yield. The isomeric 4,4′-compound **3b** was synthesized from 4,4′-dimethyl-2,2′-bipyridine (**2b**) by the same procedure[7].

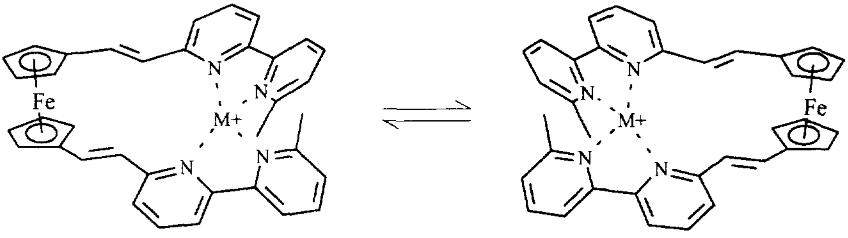


1

a: X = N; Y = CH
b: X = CH; Y = N

3

Silver(I) complexes were obtained from **3a** and **3b** upon treatment of the ligands with Ag(ClO$_4$) in acetonitrile. The FAB- and electrospray (ESI) mass spectra clearly show their 1:1 stoichiometries, while the signals of helical, dimeric silver complexes could only be detected in traces. A simple twist motion of the bipyridine ligands leads to the racemization of the C_2 symmetric complexes. The unstructured, broad NMR signals of **3a•AgClO$_4$** indicate that this process is slow on the NMR time scale at room temp. due to the conformational restrictions of the vinyl-ferrocene bridge and the steric repulsion of the 6′-methyl substituents. By heating the sample to + 90°C the interconversion is accelerated leading to well resolved resonances of **3a•AgClO$_4$**. Cooling of the sample slows down the process, however, the decreasing solubility restricts the experiment to - 30°C.[8]



Λ-3a•M$^+$ X$^-$ Δ-3a•M$^+$ X$^-$

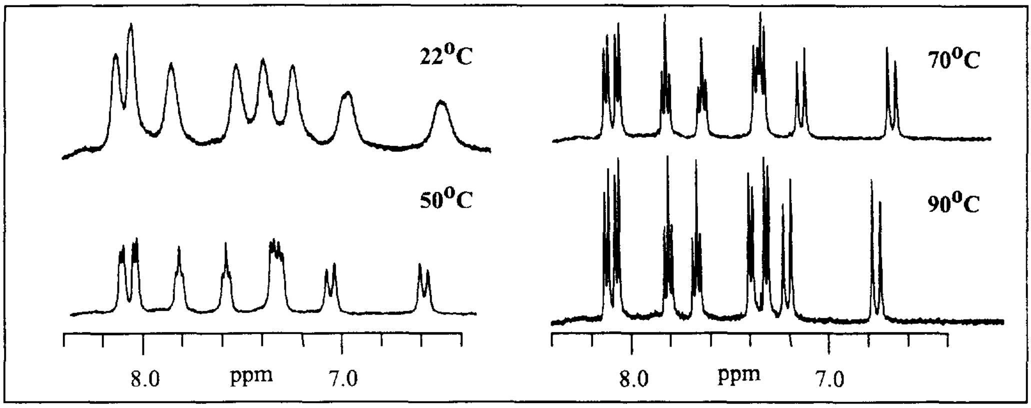


Fig. 1: Aromatic region of the ^{1}H-NMR spectra of **3a•AgClO$_4$** at different temperatures in DMSO-[D$_6$].[9]

By treatment of **3a** with Cu(CH$_3$CN)$_4$PF$_6$ in acetonitrile the dark red complex **3a•CuPF$_6$** was obtained[10]. The monomeric structure of the coordination compound was confirmed by ESI-MS and NMR. The stronger coordination of the copper ion to the bipyridine units restricts the facile twist motion observed for the analogous silver complex at room temp. Therefore a well resolved ^{1}H NMR spectrum of **3a•CuPF$_6$** is recorded at ambient temperature[11].

The redox potentials of the new ligands and their coordination compounds were investigated by cyclic voltammetry. The substitution of the central ferrocene unit in **3a** and **3b** induces only a small variation in the redox potential compared to the parent system. With the coordination of a Ag(I) ion the Fe^{2+}/Fe^{3+} redox potential becomes more positive. The electron transfer is still a quasi reversible process if the potential range is restricted to the ferrocene redox wave. However, by extending the potential scan range irreversible processes are observed[12].

Table 1. Electrochemical Data for Ligands and Complexes.

	3a	**3b**	**3a•AgClO$_4$**	**3b•AgClO$_4$**	**3a•CuPF$_6$**
E^f [mV][a]	+ 37	+ 49	+ 81	+ 95	+52

[a] Values quoted were at 100 mV/s in 3 x 10^{-3} M solutions of the compounds in 0.1 M $Bu_4N\ PF_6$ - CH_3CN at 25°C *vs* ferrocene/ferrocenium. Formal potential $E^f = 1/2(E_{p,c} + E_{p,a})$. $E_{p,c}$ = cathodic peak potential; $E_{p,a}$ = anodic peak potential.

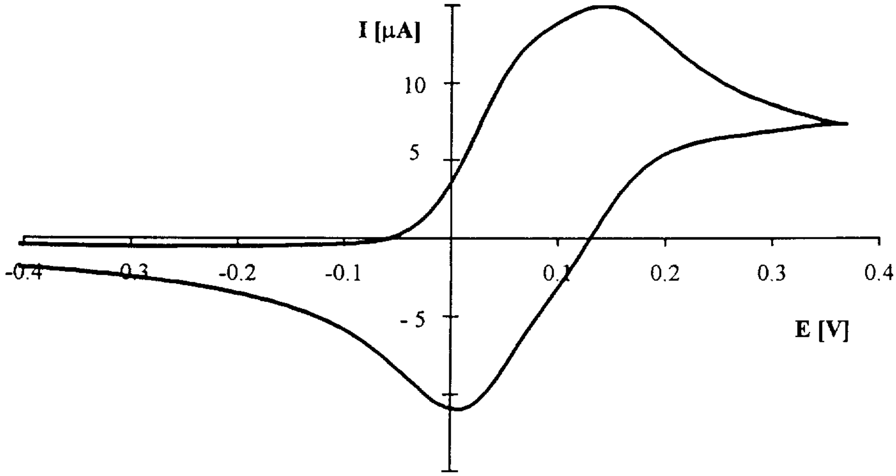


Fig. 2. Cyclic voltammogram for a solution containing 3 x 10^{-3} M **3a•AgClO$_4$** in 0.1 M $Bu_4N\ PF_6$ - CH_3CN, 0.1 V/s, 25°C, E *vs* ferrocene/ferrocenium.

In addition to previous reports[13] we have demonstrated the use of ferrocene as a spacer unit in the design of multidentate coordination compounds. Due to the small rotational barrier ferrocenes can act as atomic ball bearings that allow the coordinating residues to rotate out to reduce steric hindrance but readily return for complexation.

EXPERIMENTAL

^1H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra at 100 MHz. Mass spectra: EI 70 eV ionizing voltage; FAB matrix NBA; electrospray mass spectra (ESI) solvent CH_3CN. THF used in the reactions was dried by distillation from metallic potassium and benzophenone; acetonitrile was distilled from CaH_2, toluene was distilled from metallic sodium. Ferrocene-1,1′-dicarbaldehyde[6], 6,6′-dimethyl-2,2′-bipyridine[14] and 4,4′-dimethyl-2,2′-bipyridine[14] were prepared according to literature procedures.

Ferrocene-1,1′-di(6-vinyl-6′-methyl-2,2′-bipyridine) (3a). To a solution of 921 mg (5 mmol) 6,6′-dimethyl-2,2′-bipyridine in 40 ml THF at -78°C were added 5.5 mmol freshly prepared LDA in 20 ml THF and the dark blue mixture was stirred for 0.5 h at -78°C and 2 h at 0°C. 580 mg (2.4 mmol) **1** were added and the mixture was stirred for additional 4 h, quenched with 10 ml sat. NH_4Cl, diluted with 50 ml CH_2Cl_2, washed with water (3 x 50 ml), dried over $MgSO_4$ and evaporated *in vacuo*. The solid residue was dissolved in 50 ml toluene, 70 mg (0.27 mmol) pyridinium-4-tosylate were added and the mixture was refluxed for 45 min. The reaction mixture was diluted with 100 ml CH_2Cl_2 washed with water, dried over $MgSO_4$ and evaporated *in vacuo*. Column chromatography (CC) on silica gel [$CH_2Cl_2/CH_3OH/NH_3$(32 % in water) 100:2:0.5] and recrystallization from cyclohexane yielded 580 mg (42 %) **3a** (R_f = 0.51), as red crystals, m. p. 188°C. ^1H NMR ($CDCl_3$) δ 2.63 (6 H, s), 4.33 (4 H, m), 4.54 (4 H, m), 6.74 (2 H, d, ^3J = 15.9 Hz), 7.03 (2 H, d, ^3J = 7.1 Hz), 7.12 (2 H, d, ^3J = 7.6 Hz), 7.31 (2 H, d, ^3J = 15.9 Hz), 7.46 (2 H, dd, ^3J = 7.7 Hz), 7.62 (2 H, dd, ^3J = 7.7 Hz), 8.10 (2 H, d, ^3J = 7.1 Hz), 8.19 (2 H, d, ^3J = 7.8 Hz); ^1H NMR (DMSO-[D_6]) δ 2.38 (6 H, s), 4.38 (4 H, m), 4.66 (4 H, m), 6.74 (2 H, d, ^3J = 16.0 Hz), 7.14 (2 H, d, ^3J = 7.7 Hz), 7.21 (2 H, d, ^3J = 7.7 Hz), 7.27 (2 H, d, ^3J = 16.0 Hz), 7.50 (2 H, dd, ^3J = 7.7 Hz), 7.67 (2 H, dd, ^3J = 7.7 Hz), 7.97 (2 H, d, ^3J = 7.6 Hz), 8.06 (2 H, d, ^3J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 24.65, 68.59, 70.45, 83.39, 118.14, 118.53, 120.55, 122.97, 126.74, 130.41, 136.82, 136.94, 155.10, 155.74, 155.76, 157.59; MS (EI, 70 eV) *m/z* 574 (26, M^+), 315 (100); IR (KBr): υ = 1635 cm^{-1}, 1574, 1564, 1459, 819; UV-VIS (CH_3CN): λ_{max} (lg ε): 198 nm (4.842), 240 (4.479), 284 (4.548); HRMS $C_{36}H_{30}FeN_4$: calcd. 574.1820; found 574.1820; $C_{36}H_{30}FeN_4$: calcd. C 75.24 H 5.27 N 9.76 ; found C 75.18 H 5.22 N 9.45.

Ferrocene-1,1′-di(4-vinyl-4′-methyl-2,2′-bipyridine) (3b). 404 mg (2.2 mmol) 4,4′-Dimethyl-2,2′-bipyridine, 2.4 mmol LDA and 260 mg (1.1 mmol) **1** were treated and worked up as described for **3a**. CC of the crude product on silica gel [$CH_2Cl_2/CH_3OH/NH_3$(32 % in water) 100:2:0.5] and recrystallization from heptane/chloroform 10:1 yielded 243 mg (38 %) **3b** (R_f = 0.52), as red plates, m. p. 202°C. ^1H NMR ($CDCl_3$) δ 2.41 (6 H, s); 4.33 (4 H, m), 4.46 (4 H, m), 6.52 (2 H, d, ^3J = 16.1 Hz), 6.96 (2 H, d, ^3J = 5.0 Hz), 6.98 (2 H, d, ^3J = 16.1 Hz), 7.08 (2 H, d, ^3J = 4.0 Hz), 8.13 (2 H, s), 8.21 (2 H, s), 8.30 (2 H, d, ^3J = 5.0 Hz), 8.45 (2 H, d, ^3J = 4.0 Hz); ^1H NMR (DMSO-[D_6]) δ 2.38 (6 H, s); 4.40 (4 H, m), 4.66 (4 H, m), 6.62 (2 H, d, ^3J = 16.3 Hz), 6.97 (2 H, d, ^3J = 16.3 Hz), 7.10 (2 H, d, ^3J = 5.2 Hz), 7.16 (2 H, d, ^3J = 4.0 Hz), 7.99 (2 H, s), 8.07 (2 H, s), 8.18 (2 H, d, ^3J = 5.2 Hz), 8.35 (2 H, d, ^3J = 4.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.17, 68.47, 70.77, 82.91, 117.10, 119.95, 121.89, 124.31, 124.51, 130.72, 145.60, 147.85, 148.70, 149.25, 155.79, 156.19; MS (EI) *m/z* 574 (3, M^+), 315 (100); IR (KBr): υ = 1634 cm^{-1}, 1564, 1459, 959, 784; UV-VIS (CH_3CN): λ_{max} (lg ε): 196 nm (4.837), 242 (4.546), 282 (4.614); HRMS $C_{36}H_{30}FeN_4$: calcd. 574.1820; found 574.1820.

Ferrocene-1,1′-di(6-vinyl-6′-methyl-2,2′-bipyridine)-silver(I)-perchlorate (3a•$AgClO_4$). A suspension of 50 mg (0.087 mmol) **3a** and 18 mg (0.087 mmol) $AgClO_4$ in 5 ml acetonitrile was stirred for 12 h in the dark. The reaction mixture was added dropwise to 150 ml ether, the precipitate collected by filtration, washed with ether and dried *in vacuo* to yield 57 mg (84%) **3a•AgClO$_4$** (R_f = 0.42; CH_2Cl_2/CH_3OH 9:1), as red crystals, m. p. = 114 °C. ^{1}H NMR (DMSO-[D$_6$], 90°C) δ 2.44 (6 H, s); 4.29 (8 H, s), 6.75 (2 H, d, ^3J = 16.0 Hz), 7.20 (2 H, d, ^3J = 15.9 Hz), 7.31 (2 H, d, ^3J = 7.6 Hz), 7.39 (2 H, d, ^3J = 7.8 Hz), 7.66 (2 H, d, ^3J = 7.8 Hz), 8.80 (2 H, d, ^3J = 7.7 Hz), 8.06 (2 H, d, ^3J = 7.7 Hz), 8.11 (2 H, d, ^3J = 7.9 Hz); MS (FAB$^+$, NBA) *m/z* 681 (34, M$^+$), 315 (100), IR (KBr): υ = 1628 cm^{-1}, 1588, 1470, 786, 784; UV-VIS (CH_3CN): λ_{max} (lg ε): 200 nm (4.851), 244 (4.563), 286 (4.514), 316 (4.573); $C_{36}H_{30}FeN_4AgClO_4$: calcd. C 55.31 H 3.83 N 7.17; found C 54.91 H 3.89 N 6.98.

Ferrocene-1,1'-di(4-vinyl-4'-methyl-2,2'-bipyridine)-silver(I)-perchlorate (3b•AgClO$_4$). A suspension of 45 mg (0.078 mmol) **3b** and 16 mg (0.078 mmol) $AgClO_4$ in 5 ml acetonitrile was stirred for 24 h in the dark. The product was isolated as described above to yield 59 mg (97%) **3b•AgClO$_4$** (R_f = 0.26; CH_2Cl_2/CH_3OH 9:1), as red microcristals, m. p. > 320°C. ^{1}H NMR (DMSO-[D$_6$]) δ 2.42 (6 H, s), 4.56 (4 H, m), 4.71 (4 H, m), 6.51 (2 H, d, ^3J = 16.2 Hz), 6.89 (2 H, d, ^3J = 16.2 Hz), 7.20 (2 H, d, ^3J = 5.1 Hz), 7.27 (2 H, d, ^3J = 5.0 Hz), 7.99 (2 H, s), 8.03 (2 H, s), 8.24 (2 H, d, ^3J = 5.1 Hz), 8.28 (2 H, d, ^3J = 5.0 Hz); ^{13}C NMR (DMSO-[D$_6$]) δ 20.90, 68.42, 70.90, 83.10, 118.37, 121.50, 123.23, 125.95, 132.29, 147.64, 149.73, 149.99, 150.49, 150.75; MS (FAB$^+$, NBA) *m/z* 681 (46, M$^+$), 154 (100); IR (KBr): υ = 1630 cm^{-1}, 1600, 1482, 823, 622; UV-VIS (CH_3CN): λ_{max} (lg ε): 252 nm (4.515), 300 (4.617), 444 (3.654).

Ferrocene-1,1'-di(6-vinyl-6'-methyl-2,2'-bipyridine)-copper(I)-hexafluorophosphate (3a•CuPF$_6$). A suspension of 30 mg (0.052 mmol) **3a** and 25 mg (0.067 mmol) $Cu(CH_3CN)_4PF_6$ in 5 ml acetonitrile was stirred for 12 h in the dark. The solvent was removed *in vacuo* and the residue chromatographed on silica gel [$CH_2Cl_2/CH_3OH/NH_3$(32 % in water) 100:2:0.5] to yield 33 mg (82 %) **3a•CuPF$_6$**, as a red solid, m. p. 120°C. ^{1}H NMR (DMSO-[D$_6$], 400 MHz) δ 2.27 (6 H, s), 4.10 (4 H, m), 4.20 (4 H, m), 5.86 (2 H, d, ^3J = 15.9 Hz), 6.64 (2 H, d, ^3J = 16.0 Hz), 7.47 (2 H, d, ^3J = 8.2 Hz), 7.59 (2 H, d, ^3J = 7.9 Hz), 8.00 (2 H, m), 8.06 (2 H, m), 8.37 (2 H, d, ^3J = 7.7 Hz), 8.45 (2 H, d, ^3J = 7.0 Hz); MS (ESI) *m/z* 637 (100, M$^+$); $C_{36}H_{30}FeN_4CuPF_6$: calcd. C 55.22 H 3.86 N 7.16; found C 54.82 H 3.65 N 6.92.

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11. A separation of the signals of both enantiomers could not be induced by the addition of a chiral shift reagent.
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