Tris(1,10-phenanthroline)iron(II) Complexes. Influence of 4,7-Donor Substitution on the Redox Potential [1]

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Several new 4,7-donor substituted 1,10-phenanthrolines were synthesized and the corresponding tris(1,10-phenanthroline)iron(II) complexes were studied by cyclic voltammetry. All iron(II) complexes showed fully reversible waves at scan rates between 50 and 500 mV/s. For some redox systems the kinetics in their reaction with chlorine was studied. Complexes **7k** and **7l** significantly extend the potential range of tris(1,10-phenanthroline)iron(II) complexes.

Our search for redox active sensoric materials and our continued interest in developing new reactions [2] by applying electron transfer concepts has emphasized the necessity to prepare a series of structurally related, stable one-electron redox systems that exhibit a broad variation in their potentials. In particular for the rational development of oxygen and chlorine sensors based on one-electron oxidation/reduction processes, redox systems ($M^{n+}/M^{(n+1)+}$) with neatly spaced potentials are highly desirable.

To some extent, triaryl amines and their cation radicals fulfill the desired criteria, since by variation of the substituent pattern in the aromatic rings, a whole series of redox systems was synthesized by Steckhan that cover the wide potential range from 0.51–1.72 V vs. SCE [3]. Unfortunately, the triarylamine/triarylamine cation radical redox systems display three decisive disadvantages for their use as sensoric materials: (1) not all the cation radical salts prove to be sufficiently stable [4], especially in the presence of nucleophiles [4, 5], (2) the oxidized form reacts readily with radicals [6], and (3) the reduced form is highly insoluble in water, which would be the solvent of

choice. As an alternative we have decided to investigate Fe(II)/Fe(III)-tris(1,10-phenanthroline) redox systems, since (1) these are much more stable towards nucleophilic attack [7], (2) they are much slower in their reaction with radicals [8], (3) the Fe(II) complexes can readily be analyzed by their strong absorbance around 500 nm [7] and (4) they are water soluble if a proper counter ion is chosen [7]. In order to speed up the response time in chlorine/oxygen sensors, stable systems with relatively low potential (<0.5 V vs. SCE) are needed.

Despite the fact that substituted iron(II)-1,10-phenanthrolines (ferroins) have been playing an important role in analytical chemistry [7] and that ruthenium(II)-1,10-phenanthrolines have attracted wide interest due to their potential for solar energy conversion [9, 10], relatively little effort has been undertaken to influence the electronic situation of the complex by variation of the substituents. A straightforward reason for this neglect is the difficulty to synthesize the corresponding substituted 1,10-phenanthrolines by a simple strategy.

For a moderate number of examples, a variation of the redox potential of tris(1,10-phenanthroline)iron(II) complexes has been observed when the electron density in the 1,10-phenanthroline ligands was changed [8, 11]. However, only a very narrow range of potentials (0.4–0.9 V vs. ferrocene) was measured in acetonitrile [8, 11]. According to a simple VB description the strongest influence on the electron density of the N-donor atoms should be exerted by substituents in the positions 2, 4, 7 and 9. But since substitution in 2- and/or 9-positions does hinder complex formation with tran-

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sition metals by steric effects, in many cases the corresponding tris(1,10-phenanthroline)iron(II) complexes are not formed any more [8]. Therefore, to alter the electronic properties of tris(1,10-phenanthroline)iron(II) complexes, substitution in 4- and 7-position with electron donating substituents seemed to be the method of choice. Interestingly, only a limited number of 4,7-disubstituted 1,10-phenanthrolines ($R = -OMe$ [12], $-OPh$ [12], $-NH_2$ [12, 13], $-NHR''$ [13–17]) is known in the literature. But the effect of 4,7-substitution on the oxidation potential of corresponding iron(II)-tris-chelates was not studied in the amino cases. Herein, we report on the synthesis of some new aryloxy- and alkylamino substituted 1,10-phenanthrolines **1** and describe the effect of the substitution on the oxidation potentials of the corresponding iron(II)tris-chelates.

There are two general pathways to obtain 4,7-donor substituted 1,10-phenanthrolines **1**: (1) the *de novo* synthesis of the 1,10-phenanthroline system from diaminobenzenes and appropriately substituted C_3 -units or (2) the modification of an already existing 1,10-phenanthroline, for instance by substitution. For the latter method, a key compound is 4,7-dichloro-1,10-phenanthroline (**1c**) [15, 16] which itself is accessible *via* route (1). In a five step synthesis, **1c** can be synthesized from 1,2-diaminobenzene (**2**) and diethyl ethoxymethylenemalonate (**3**) [15, 16]. An analogous route gives the 4,7-dibromosubstituted 1,10-phenanthroline **1d** [18]. The chlorine atoms in compound **1c** can be replaced *via* nucleophilic substitution by a variety of other substituents, like alkoxy, aryloxy and amino groups. Table I lists all 4,7-disubstituted 1,10-phenanthrolines **1** synthesized in this work and the 1H NMR signals of the 1,10-phenanthroline moiety. The 1H NMR and all other analytical data support the assignment of 4,7-substituted 1,10-phenanthrolines **1**.

Using the new 1,10-phenanthrolines **1** listed in Table I, we have synthesized the corresponding iron(II) complexes using a modification of a literature procedure [11]. Thus, a solution of the 1,10-

phenanthrolines **1f–1l** in acetonitrile/water was reacted with $FeSO_4 \cdot 7 H_2O$ and from the intensely red-colored solutions the red salts were precipitated by addition of ammonium hexafluorophosphate. The complexes were identified by their characteristic, strong UV absorbance between

Table I. 4,7-Disubstituted 1,10-phenanthrolines **1**.

1	R	Yield (%)	Synthesized from	¹ H NMR (250 MHz, CDCl ₃)		
				d, 2H (<i>J</i> in Hz) 3-H, 8-H	s, 2H 5-H, 6-H	d, 2H (<i>J</i> in Hz) 2-H, 9-H
1a	H	—	Commercially available	—	—	—
1b	Me	4	2 [19]	7.49 (5)	8.06	9.08 (5)
1c	Cl	31	2 [16]	7.77 (4.5)	8.35	9.09 (4.5)
1d	Br	10	2 [18]	7.94 (4.5)	8.27	8.93 (4.5)
1e	OMe	76	1c [12]	7.0 (4.5)	8.2	9.0 (4.5)
1f	OC ₆ H ₅	55	1c [12]	6.85 (6)	8.39	8.94 (6)
1g	O- <i>p</i> -C ₆ H ₄ Me	73	1c	6.80 (5.3)	8.38	8.93 (5.3)
1h	O- <i>p</i> -C ₆ H ₄ <i>t</i> Bu	85	1c	6.84 (5)	8.38	8.92 (5)
1i	O- <i>p</i> -C ₆ H ₄ OMe	70	1c	6.79 (5.3)	8.41	8.93 (5.3)
1j	O-(1-naphthyl)	40	1c	6.82 (4.5)	8.74	9.10 (4.5)
1k	NH(CH ₂) ₃ NH ₂	72	1c	6.66 (6.0)	8.00	8.54 (6.0) ^a
1l	NEt ₂	16	1c	7.02 (7.2)	7.83	9.02 (7.2)

^a In CD₃CD₂OD.

490–495 nm and by the ¹H NMR spectra. Unfortunately, according to elemental analysis the iron(II) complexes prepared by this precipitation strategy always contained small amounts of the iron(III) tris-chelates (presumably by air oxidation). The presence of small amounts of paramagnetic Fe(III) complexes may also be inferred from the broadening of the ¹H NMR signals. Since iron(III) impurities do not cause problems in the cyclic voltammetry study all new systems were prepared by the ammonium hexafluorophosphate precipitation route. The red complexes **7k** and **7l** proved to be extremely air-sensitive, but they could be handled in the presence of an added reductant, like hydroxylamine or hydrazine. Likewise, the oxidized form of **7l** (green) could be reduced to the red iron(II) state by careful addition of a hydrazine solution in acetonitrile and reoxidized by Ce(IV).

In cyclic voltammetry investigations (CV), all iron(II)/iron(III) redox couples exhibited clean and completely reversible waves (between 50–500 mV/s) and fulfilled other criteria for complete reversibility: (1) $E_{1/2}$ is independent of the scan rate; (2) the peak current ratio i_{pc}/i_{pa} is unity; (3)

the separation of the cathodic and anodic peaks is 60 ± 5 mV (Table II) and (4) $i_{pa}/v^{1/2}$ is constant.

When the aryloxy substituted iron 1,10-phenanthrolines **7f–i** are compared within the series no major shift of the oxidation potentials was observed reflecting the small range of oxidation potentials of the 1,10-phenanthroline ligands themselves ($\Delta E_{pa} = 0.1$ V). This outcome is surprising when considering that the substituents R at the phenanthroline **1** usually entail a much larger oxidation potential difference when being attached to a methyl group (*e.g.* $\Delta E_{ox} = 0.37$ V for 4-methoxy-

Table II. Cyclic voltammetry data and redox potentials $E_{1/2}$ ^a of tris(1,10-phenanthroline)iron(II)hexafluorophosphates **7**·(PF₆)₂ in acetonitrile and anodic peak potentials E_{pa} for the ligands **1**.

7	Substituent in 4,7-position	$E_{1/2}$ (7) [V]	i_a/i_c ^b	ΔE_p ^c [mV]	E_{pa} (1) ^d [V]
7a	H	0.69	1	57	>2 ^e
7e	OMe	0.38	1	55	1.34
7f	O- <i>p</i> -C ₆ H ₅	0.47	1	60	1.44
7g	O- <i>p</i> -C ₆ H ₄ -Me	0.45	1	60	1.40
7h	O- <i>p</i> -C ₆ H ₄ - <i>t</i> Bu	0.47	1	60	1.44
7i	O- <i>p</i> -C ₆ H ₄ -OMe	0.45	1	60	(1.55) ^f
7j	O-(1-naphthyl)	0.49	1	60	1.41
7k	NH(CH ₂) ₃ NH ₂	-0.23	1	60	^f
7l	NEt ₂	-0.09	1	60	0.71

^a All potentials are referenced to ferrocene which itself has $E_{1/2} = +0.39$ V vs. SCE; ^b ratio of the anodic to cathodic peak current of **7** (accuracy $\pm 5\%$); ^c peak to peak separation of **7**; ^d anodic peak potentials; ^e no anodic peak was detected up to 2 V; ^f a strong coating of the electrode occurred during the anodic sweep.

toluene and 1,4-dimethoxybenzene [20]), but this difference cannot be found in the substituted 1,10-phenanthrolines **1g** and **1i**.

On the other hand, the diamino substituted iron 1,10-phenanthroline complexes **7k** ($E_{1/2} = -0.23$ V vs. ferrocene) and **7l** ($E_{1/2} = -0.09$ V vs. ferrocene) revealed quite pronounced substituent effects on the redox potentials. In the CV investigation both, **7k** and **7l**, exhibited fully reversible waves in acetonitrile, but interestingly, the cyclic voltammogram of **7l** showed, beside the reversible Fe(II)/Fe(III) redox process, a second reversible wave at $E_{1/2} = 0.95$ V vs. ferrocene that was followed by an irreversible one at $E_{pa} = 1.19$ V (see Fig. 1). In the presence of tris(4-bromophenyl)amine as internal reference and at higher scan rates ($\nu = 0.5$ V/s) the wave at 1.19 V exhibited some reversibility ($E_{1/2} = 1.14$ V). A control experiment proved that the ligand **1l** itself, which can be regarded as a vinylogous Wurster type system, was oxidized irreversibly at $E_{pa} = 0.71$ V. Thus, we ascribe the reversible wave at $E_{1/2} = -0.09$ V to an Fe(II)–Fe(III) redox process, while the reversible wave at $E_{1/2} = 0.95$ V and the partially reversible one at $E_{1/2} = 1.14$ V are supposed to correspond to formation of ligand cation radicals. It is noteworthy that the irreversible oxidation wave in **1l** ($E_{pa} = 0.71$ V) becomes reversible in the iron tris-chelate ($E_{1/2} = 0.95$ V), a process not understood at present.

In order to probe these Fe(II)/Fe(III) complexes as potential materials in gas sensors, we have undertaken a kinetic analysis of the reduction of chlorine using the redox systems **7e**, **7g**, **7j** and **7k**.

The kinetics were followed at 25 °C under pseudo-first order conditions in methylene chloride/ CCl_4 , since in acetonitrile/ CCl_4 or water the reaction was too fast to be monitored by our set-up (Table III). But even in methylene chloride/ CCl_4 , the reaction of **7k** with chlorine was too rapid to be measured. This suggests that 4,7-substitution of the ligand with amino groups should lead to an improvement of the response time of the corresponding iron(II) 1,10-phenanthroline complexes in the reaction with chlorine.

The easily oxidizable **7k** not only has significantly extended the range of oxidation potentials of iron(II)1,10-phenanthrolines **7** but also is much more rapid in its reaction with chlorine. To assess the general potential for their use in sensors, other donor substituted 1,10-phenanthrolines are under current investigation. In addition, mixed-ligand complexes [21] should allow to access the potentials between -0.23 and 0.35 V. Since these structurally related compounds most likely constitute outer-sphere one-electron oxidants they may serve

Fig. 1. Cyclic voltammetry study of 1,10-phenanthroline **1l** (trace a) and complex **7l** (trace b and c) in acetonitrile at a scan rate of 100 mV/s.

Table III. Kinetic data for the reduction of chlorine by the iron(II) complexes **7** (at 25 °C).

7	R	$E_{1/2}$ (7) [V]	solvent	$\tau_{1/2}$ ^a
7e	OMe	0.35	CH ₂ Cl ₂ /CCl ₄	5 min
7g	O- <i>p</i> -C ₆ H ₄ -Me	0.45	CH ₂ Cl ₂ /CCl ₄	64 min
7j	O-(1-naphthyl)	0.49	CH ₂ Cl ₂ /CCl ₄	36 min
7k	NH(CH ₂) ₃ NH ₂	-0.23	CH ₂ Cl ₂ /CCl ₄	upon mixing
7g	O- <i>p</i> -C ₆ H ₄ -Me	0.45	CH ₃ CN/CCl ₄	several s
7j	O-(1-naphthyl)	0.49	CH ₃ CN/CCl ₄	several s

^a Half time for the disappearance of iron(II) complexes **7**.

as important mechanistic probes for testing the involvement of cation radicals in electron transfer reactions [22].

Experimental

General remarks: see [22, 23]. The cyclic voltammograms of all the Fe(II)/Fe(III) couples were measured using a standard three electrode set-up (Pt working at Pt auxiliary electrode, silver wire as reference electrode) hooked up to a Princeton Applied Research Model 362 potentiostat. The experiments were carried out on a 1 mM solution of the iron salt or 1,10-phenanthroline ligand in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials were measured at a scan rate of 100 mV s⁻¹ and are referenced to internal ferrocene for practical reasons. The ferrocene/ferrocenium couple exhibits $E_{1/2} = +0.39$ V vs. SCE under our conditions. The oxidation potentials of **1i** and **7i** were originally measured against internal tris(*p*-bromophenyl)amine, which has $E_{1/2} = 0.70$ V vs. ferrocene. 4,7-Dichloro-1,10-phenanthroline (**1c**) was prepared according to the procedure described by Snyder and Freier [16]. Complexes **7a** and **7e** are described in ref. [4, 11].

4,7-Dimethoxy-1,10-phenanthroline (1e): 0.75 g (32 mmol) of sodium was dissolved in *ca.* 50 ml of dry methanol. Then at room temp. 1.0 g (4.0 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**) was added and the mixture was refluxed for 1 h. The methanol was distilled off, 30 ml of dichloromethane was added, the solution was washed with 30 ml of water and the organic layer was dried with MgSO₄. After evaporation of the solvent, the residue was recrystallized from 50 ml of toluene yielding 0.73 g (76%) of **1e** (23% [12]), m.p. 209 °C (209–210 °C [12]). – IR (KBr): $\nu = 1580, 1560, 1500$ cm⁻¹ (arom.), 1280, 1220, 1025 (C–O). – ¹H NMR (250 MHz, CDCl₃):

$\delta = 4.1$ (s, 6H), 7.0 (d, $J = 4.5$ Hz, 2H), 8.2 (s, 2H), 9.0 (d, $J = 4.5$ Hz, 2H). – MS (70 eV): m/z (%) = 240 (100), 225 (26), 210 (6).

4,7-Bis(4-methylphenoxy)-1,10-phenanthroline (1g): In a flask fitted with a drying tube, 2.00 g (8.00 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**), 11.80 g (110.0 mmol) of *p*-methylphenol and 2.25 g (40.0 mmol) of powdered KOH were stirred at 130 °C for 22 h. The dark brown reaction product was dissolved in 100 ml of 30% KOH and extracted six times with 50 ml of dichloromethane. The combined organic layer was washed twice with 50 ml of 2 N NaOH and twice with 60 ml of water. After drying with MgSO₄, the solvent was evaporated, and the brown solid residue was recrystallized first from aqueous ethanol, then from methylene chloride yielding 2.30 g (73%) of **1g**, m.p. 256–257 °C. – IR (KBr): $\nu = 3050$ cm⁻¹, 1613, 1586, 1557, 1491 (arom.), 1273, 1231, 1202, 1023 (C–O), 916, 839 (arom.). – ¹H NMR (250 MHz, CDCl₃): $\delta = 2.40$ (s, 6H), 6.80 (d, $J = 5.3$ Hz, 2H), 7.10 (m, 4H), 7.27 (m, 4H), 8.38 (s, 2H), 8.93 (d, $J = 5.3$ Hz, 2H). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.9$ (C-7', C-7''), 107.0 (C-3, C-8), 119.5 (C-5, C-6), 120.8 (C-2', C-6', C-2'', C-6''), 121.3 (C-4a, C-6a), 130.8 (C-3', C-5', C-3'', C-5''), 135.5 (C-4', C-4''), 147.4 (C-1a, C-10a), 151.0 (C-2, C-9), 152.1 (C-1', C-1''), 162.2 (C-4, C-7). – MS (70 eV): m/z (%) = 392 (100), 377 (15), 285 (11), 270 (5), 195 (10), 91 (17), 84 (7), 65 (18).

C₂₆H₂₀N₂O₂

Calcd 392.1518,
Found 392.1525.

C₂₆H₂₀N₂O₂ · 1/4 H₂O (396.6)

Calcd C 78.74 H 5.21 N 7.06,
Found C 78.64 H 5.08 N 7.05.

4,7-Bis[4-(1,1-dimethylethyl)-phenoxy]-1,10-phenanthroline (1h): 4.10 g (16.5 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**), 33.0 g (220 mmol) of 4-*tert*-butylphenol and 4.5 g (80 mmol) of powdered KOH were melted at 130 °C and stirred for 11 h. At room temp. the product was dissolved in 30% KOH and extracted with dichloromethane (3 times 80 ml). After washing the combined organic layers with 80 ml of 2 N NaOH and 80 ml of water and drying with MgSO₄, the solvent was evaporated. The residue was recrystallized from ethanol yielding 6.67 g (85%) of **1h**, m.p. 233 °C. – IR (KBr): $\nu = 2945$ cm⁻¹, 1581, 1553, 1490 (arom.), 1228 (C–O). – ¹H NMR (250 MHz, CDCl₃): $\delta = 1.37$ (s, 18H), 6.84 (d, $J = 5$ Hz, 2H), 7.14 (d, $J = 9$ Hz, 4H), 7.49 (d, $J = 9$ Hz, 4H), 8.38 (s, 2H), 8.92 (d, $J = 5$ Hz, 2H). – MS (70 eV): m/z (%) = 476 (88), 461 (100), 405 (23).

C₃₂H₃₂N₂O₂ (322.45)

Calcd	C 80.64	H 6.76	N 5.87,
Found	C 80.45	H 6.70	N 5.84.

4,7-Bis(4-methoxyphenoxy)-1,10-phenanthroline (1i): In a flask fitted with a drying tube, 1.70 g (6.7 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**), 11.50 g (92.0 mmol) of 4-hydroxyanisole and 1.90 g (33.5 mmol) of powdered KOH were stirred at 110 °C for 21 h. After work-up analogous to **1g**, the resulting slightly brown solid was recrystallized first from toluene, then from methylene chloride yielding 2.00 g (70%) of **1i**, m.p. 250–251 °C. – IR (KBr): $\nu = 3056\text{ cm}^{-1}$ (arom.), 2831 (OCH₃), 1611, 1586, 1558, 1491 (arom.), 1277, 1231, 1201, 1042 (C–O), 916, 843 (arom.). – ¹H NMR (250 MHz, CDCl₃): $\delta = 3.87$ (s, 6H), 6.79 (d, $J = 5.3$ Hz, 2H), 7.02 (m, 4H), 7.18 (m, 4H), 8.41 (s, 2H), 8.93 (d, $J = 5.3$ Hz, 2H). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 55.7$ (C-7', C-7''), 106.6 (C-3, C-8), 115.4 (C-3', C-5', C-3'', C-5''), 120.0 (C-5, C-6), 121.2 (C-4a, C-6a), 122.2 (C-2', C-6', C-2'', C-6''), 147.1 (C-1a, C-10a), 147.6 (C-1', C-1''), 151.0 (C-2, C-9), 157.4 (C-4', C-4''), 162.6 (C-4, C-7). – MS (70 eV): m/z (%): 424 (100), 301 (18), 285 (6), 212 (8), 178 (23).

C₂₆H₂₀N₂O₄

Calcd	424.1413,
Found	424.1423.

C₂₆H₂₀N₂O₄ · 1/4 H₂O (429.0)

Calcd	C 72.80	H 4.82	N 6.53,
Found	C 72.63	H 4.65	N 6.58.

4,7-Bis(1-naphthoxy)-1,10-phenanthroline (1j): In a flask fitted with a drying tube, 2.00 g (8.0 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**), 15.8 g (110 mmol) of 1-naphthol and 2.25 g (40.0 mmol) of powdered KOH were stirred at 125 °C for 7.5 h. The dark brown product as dissolved in 150 ml of 30% KOH, and extracted with dichloromethane for 5 d. The dark green organic layer was washed three times with 60 ml of 30% KOH, three times with 100 ml of 2 N NaOH, and twice with 100 ml of water. After drying with MgSO₄ and evaporation of the solvent, the residue was recrystallized from aqueous ethanol, yielding 1.5 g (40%) of **1j**, m.p. 203 °C. – IR (KBr): $\nu = 3046\text{ cm}^{-1}$, 1591, 1559, 1499 (arom.), 1265, 1239 (C–O), 921, 841, 813 (arom.). – ¹H NMR (250 MHz, CDCl₃): $\delta = 6.82$ (d, 2H, $J = 4.5$ Hz), 7.39 (dd, 2H, $J_1 = 6.75$ Hz, $J_2 \leq 1.0$ Hz), 7.49 (m, 4H), 7.59 (dt, 4H, $J_t = 9.0$ Hz, $J_d \leq 1.0$ Hz), 7.87 (d, 2H, $J = 9.0$ Hz), 7.91 (d, 2H, $J = 9.0$ Hz), 8.00 (d, 2H, $J = 9.0$ Hz), 8.74 (s, 2H), 9.10 (d, 2H, $J = 4.5$ Hz). – ¹³C NMR (100 MHz, CDCl₃): $\delta = 107.43$ (C-3, C-8), 117.15 (C-2', C-2''), 119.84 (C-5, C-6), 121.34 (C-4a,

C-6a), 121.60, 125.87, 125.95, 126.14, 126.89, 127.09, 128.33, 135.37 (C-10', C-10''), 147.36 (C-1a, C-10a), 150.23 (C-1', C-1''), 151.30 (C-2, C-9), 162.43 (C-4, C-7). – MS (70 eV): m/z (%) = 464 (100), 335 (9), 321 (9), 232 (6), 195 (6), 127 (37), 115 (18), 77 (8).

C₃₂H₂₀N₂O₂ (464.0)

Calcd	C 82.75	H 4.32	N 6.03,
Found	C 82.90	H 4.33	N 6.10.

4,7-Bis(3-aminopropylamino)-1,10-phenanthroline (1k): 0.40 g (1.6 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**) and 4.7 g (63 mmol) of 1,3-diaminopropane were stirred for 3.5 h at 140–150 °C. The beige-colored product was filtered off, washed several times with chloroform and dried *in vacuo*, yielding 0.38 g of **1k** (72%), m.p. 117–136 °C (decomposition). – IR (KBr): $\nu = 2920\text{ cm}^{-1}$, 1580, 1420, 1320. – ¹H NMR (250 MHz, CD₃CD₂OD): $\delta = 1.91$ (quint., $J = 7.2$ Hz, 4H), 2.81 (t, $J = 7.2$ Hz, 4H), 3.42 (t, $J = 7.2$ Hz, 4H), 5.29 (br. s, H₂O/OH and NH/NH₂), 6.66 (d, $J = 6.0$ Hz, 2H), 8.00 (s, 2H), 8.54 (d, $J = 6.0$ Hz, 2H). – MS (70 eV): m/z (%) = 324 (45), 294 (78), 280 (100), 235 (41), 223 (44).

C₁₈H₂₄N₆

Calcd	324.2062,
Found	324.2057.

C₁₈H₂₄N₆ · H₂O (342.45)

Calcd	C 63.14	H 7.65	N 24.54,
Found	C 62.83	H 6.98	N 23.97.

4,7-Bis(diethylamino)-1,10-phenanthroline (1l): 2.5 g (9.4 mmol) of 4,7-dichloro-1,10-phenanthroline (**1c**) and 100 ml of diethylamine were shaken in an autoclave at 120 °C for 20 h. At room temp. the volatiles were evaporated *in vacuo*, the residue was dissolved in 200 ml of dichloromethane and washed twice with 60 ml of 2 N NaOH and twice with 50 ml of water. After drying with MgSO₄, the solvent was evaporated and the residue was recrystallized from acetone, yielding 0.5 g (16%) of **1l**, m.p. 131 °C. – IR (KBr): $\nu = 1594\text{ cm}^{-1}$, 1555, 1500 (arom.). – ¹H NMR (250 MHz, CDCl₃): $\delta = 1.33$ (t, $J = 7.2$ Hz, 12H), 3.61 (q, $J = 7.2$ Hz, 8H), 7.02 (d, $J = 7.2$ Hz, 2H), 7.83 (s, 2H), 9.02 (d, $J = 7.2$ Hz, 2H). – MS (70 eV): m/z (%) = 322 (84), 307 (100), 278 (68).

C₂₀H₂₆N₄ (322.45)

Calcd	C 74.49	H 8.12	N 17.37,
Found	C 74.22	H 8.07	N 17.32.

General procedure for the preparation of the tris-(4,7-disubstituted-1,10-phenanthroline)iron(II)-hexafluorophosphates (7)

1.28 mmol of a 4,7-disubstituted-1,10-phenanthroline **1** was added to a solution of 0.55 mmol

of iron(II)-sulfateheptahydrate in 10 ml of distilled water, and the red suspension was sonicated with ultrasound for 30 min at 60 °C. Addition of 5 ml of acetonitrile gave a deep-red, clear solution, from which **7** precipitated after addition of 1.00 mmol of ammoniumhexafluorophosphate. The red solid was filtered off, washed with 80 ml of distilled water and dried at 120 °C *in vacuo*.

Tris-(4,7-diphenoxy-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7f**): Yield: 95%. – IR (KBr): $\nu = 3055\text{ cm}^{-1}$, 1617, 1607, 1575, 1414, 1290, 1236, 1207, 926, 835. – UV (CH₃CN): $\lambda_{\text{max}} = 490\text{ nm}$. – ¹H NMR (250 MHz, CDCl₃): $\delta = 6.98$ (br. s, 6H), 7.24 (br. m, 18H), 7.46 (br. s, 12H), 7.67 (br. s, 6H), 8.50 (br. s, 6H).

Tris-(4,7-bis(4-methylphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7g**): Yield: 97%. – IR (KBr): $\nu = 3025\text{ cm}^{-1}$, 2915, 1627, 1600, 1576, 1496, 1414, 1290, 1236, 1207, 926, 850. – UV (CH₃CN): $\lambda_{\text{max}} = 492\text{ nm}$. – ¹H NMR (250 MHz, CDCl₃): $\delta = 2.34$ (br. s, 18H), 6.95 (br. s, 6H), 7.07 (br. m, 12H), 7.24 (br. m, 12H), 7.60 (br. s, 6H), 8.46 (br. s, 6H).

Tris-(4,7-bis(4-(1,1-dimethylethyl)-phenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7h**): Yield: 96%. – IR (KBr): $\nu = 3085\text{ cm}^{-1}$, 2950, 2860, 1630, 1576, 1495, 1415, 1250, 1237, 1216, 926, 850. – UV (CH₃CN): $\lambda_{\text{max}} = 495\text{ nm}$. – ¹H NMR (250 MHz, CDCl₃): $\delta = 1.30$ (br. s, 54H), 6.98 (br. s, 6H), 7.12 (br. s, 12H), 7.44 (br. s, 12H), 7.64 (br. s, 6H), 8.46 (br. s, 6H).

Tris-(4,7-bis(4-methoxyphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7i**): Yield: 97%. – IR (KBr): $\nu = 3075\text{ cm}^{-1}$, 2985, 2935, 2825, 1625, 1607, 1575, 1492, 1410, 1288, 1251, 1233, 1205, 1035, 924, 845. – UV (CH₃CN): $\lambda_{\text{max}} = 490\text{ nm}$. – ¹H NMR (250 MHz, CDCl₃): $\delta = 3.80$ (br. s, 18H), 6.94 (br. s, 18H), 7.12 (br. s, 12H), 7.62 (br. s, 6H), 8.48 (br. s, 6H).

Tris-(4,7-bis(1-naphthoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7j**): Yield: 77%. – IR (KBr): $\nu = 3045\text{ cm}^{-1}$, 1625, 1600, 1573, 1413, 1392, 1285, 1265, 1235, 923, 845. – UV (CH₃CN): $\lambda_{\text{max}} = 495\text{ nm}$. – ¹H NMR (250 MHz, CDCl₃): $\delta = 6.96$ (br. s, 6H), 7.48 (br. m, 24H), 7.86 (br. m, 24H), 8.72 (br. s, 6H).

Tris-(4,7-bis(3-aminopropylamino)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7k**): Yield: 75%. – IR (KBr): $\nu = 3434$ and 3384 (NH, NH₂) cm^{-1} , 2909, 2829, 1614, 1569, 1559, 1429, 1383, 1339, 1309, 1237, 1144, 1124, 1113, 1091, 729, 639, 630. – UV (CH₃CN): $\lambda_{\text{max}} = 505$ and 524 nm (broad). – ¹H NMR (250 MHz, CD₃OD): $\delta = 2.03$ (br. m, 12H), 3.07 (br. m, 12H), 3.48 (br. m, 12H), 6.75 (br. s, 6H), 7.30 (br. m, 6H), 8.15 (br. m, 6H).

Tris-(4,7-bis(diethylamino)-1,10-phenanthroline)iron(II)-hexafluorophosphate (**7l**) was only prepared *in situ* in the presence of hydrazine to avoid air oxidation.

Kinetic measurements

One chamber of a tandem cuvette was filled with 1.20 ml of a $2 \cdot 10^{-4}\text{ M}$ solution of **7** (either in acetonitrile or methylene chloride) and the other chamber was filled with an equal amount of a chlorine solution (2.3 M) in CCl₄ [24]. After mixing, the absorbance was followed at λ_{max} of the iron(II)-1,10-phenanthroline for at least 3 half times and showed pseudo-first order behavior.

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