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Ferrocene substituted nitronyl nitroxide and imino nitroxide radicals. Synthesis, X-ray structure and magnetic properties

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Abstract

The synthesis, X-ray structure and magnetic properties of two new ferrocene substituted nitroxide monoradicals are described. The magnetic susceptibility data was nicely fitted in both cases to the Curie–Weiss law yielding the Weiss constants of $\theta = -1.8$ and -1.1 K for radicals **1** and **2**, respectively. This result evidenced the presence of very weak antiferromagnetic intermolecular interactions between neighbor molecules. Moreover, the X-ray structure of the key precursor 2,3-bis(hydroxyamino-)-2,3-dimethylbutane (**3**) is also included. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnetochemistry; Organic radical; Ferrocene; Crystal structures

1. Introduction

Paramagnetic building blocks like Ullman's nitronyl and imino nitroxide have attracted considerable interest in the field of molecular magnetism [1]. Since the discovery of ferromagnetism at a critical temperature $T_c = 0.6$ K in the β-phase of the (*p*-nitrophenyl) nitronyl nitroxide [2], ferromagnetic order has been observed in other nitroxide compounds [3] being the highest critical temperature known to date of $T_c = 1.48$ K corresponding to a diazaadamantane dinitroxide. To explore new supramolecular magnetic materials based on the self-assembly of nitroxide radicals, we reported a novel family of monoradical and biradical compounds consisting of purely organic α-nitronyl nitroxide radicals connected to different metallocenylene bridges (see Chart 1) [4].

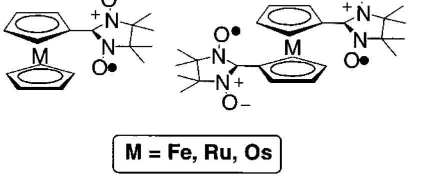

Chart 1.

In both cases, the study of the magnetic properties in the solid state revealed the existence of weak antiferromagnetic interactions between neighbor molecules. Such interactions were promoted by the presence of weak intermolecular C–H···O hydrogen bonds as shown by crystal data. Moreover, these studies showed that metallocene units act as effective magnetic couplers that transmit the magnetic interactions through their skeletons. Nevertheless, the small spin density located on the metallocene units of these systems and the presence of intramolecular hydrogen bonds, which determines the existence of a direct intramolecular through-space magnetic interaction, lead to the appearance of an effective antiferromagnetic interaction between the two α-nitronyl nitroxide radical units that is very sensitive to the molecular conformation [5].

Here we report the synthesis and magnetic characterization of two new ferrocene-substituted α-nitronyl nitroxide monoradicals, the 2-(1-formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-

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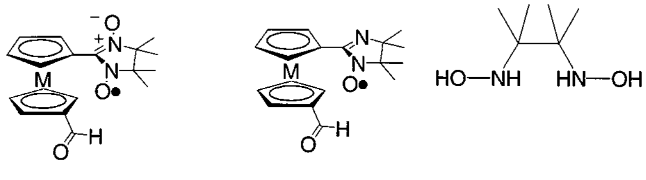


1 2 3

Chart 2.

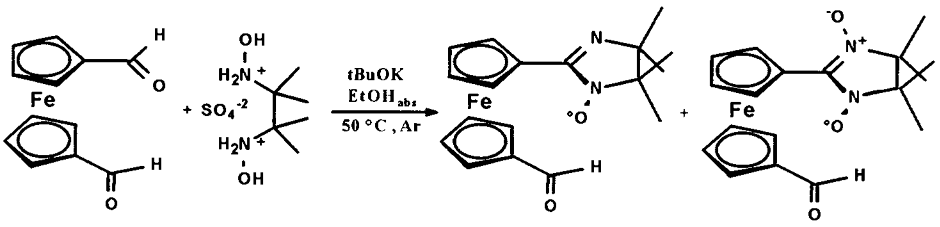
oxid-1-yl-oxyl radical (**1**) and the 2-(1-formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-yl-oxyl radical (**2**) (Chart 2).

The objective is to study the influence of the formyl group, which may be involved in the formation of hydrogen-bonds, in the supramolecular array of the open-shell units and therefore, its influence in the resulting magnetic properties. Moreover, the X-ray structure and NMR characterization of the precursor 2,3-bis(hydroxyamino-)-2,3-dimethylbutane (**3**) which has remained elusive for years, is also described and discussed here. This compound is a key intermediate—normally in the form of sulphate—in the synthesis of all the members of this family of free radicals (vide infra) [6,7].

2. Results and discussion

2.1. Synthesis

As outlined in Eq. (1), the synthetic route for preparing radical **1** and **2** is based on two main steps. First, reduction of the 2,3-dimethyl-2,3-dinitrobutane by zinc in the presence of NH_4Cl to give the sulphate monohydrate compound. Second, the condensation reaction of the resulting compound with ferrocene dialdehyde to yield the desired radicals **1** and **2** (see Eq. (1)[1]).



(1)

The synthesis of the sulphate monohydrate was done according to the procedure published by Ovcharenko and Rey [6]. This synthetic procedure is a variation of that previously described by Lamchen and Mittag [7]. The main variation is the use of THF instead of ethanol during the synthesis of the bis-hydroxlamine precursor, fact that has been shown to increase the reaction yield dramatically. In the second step, condensation of the ferrocene aldehyde with an equivalent of the sulphate monohydrate gives a mixture of radicals **1** and **2**. Both radicals were isolated as stable solids after chromatographic purification. In addition, the 1,1′-ferrocenyl nitronyl nitroxide diradical was obtained as a minor side product (7%).

2.2. X-ray structures

Crystallographic data of compounds **1**, **2** and **3** are given in Table 1.

The free base 2,3-bis(hydroxyamino-)2,3-dimethylbutane (**3**) was obtained after treatment of the sulphate monohydrate with NaOH. Single crystals of **3** were obtained by sublimation. The ORTEP plot of compound **3** with disordered hydrogen atoms at N- and O-atoms is shown in Fig. 1. The 1:1 disorder of the H-atoms is found statistically over the 2D sheets builded by staggered molecules.

The crystal packing of the sheets along the crystallographic *a*-axis is shown in Fig. 2 (top). There are four different H-bonds between N to O and O to O atoms. The disordering of the hydrogen atoms is originated by short O(1)–O(1c) contacts as depicted in Fig. 2 (bottom), where a fragment of the sheet with exact disorder positions of the H-atoms is shown.

Compounds **2** and **3** crystallize in the same space groups *C*2/*c* with similar lattice constants (see Table 1). In both compounds, the molecules adopt crystal packing showing staggered orientation of the nitroxide radical and the aldehyde moiety. The formyl–ferrocene nitronyl nitroxide **1** crystallizes in sheet layers oriented along the *c** axis, as shown in Fig. 3. Between the sheet layers only weak H-bonds between N–O groups and the C_5H_5 ligand of the neighboring ferrocene molecules exist (O1···H = 2.696; O2···H = 2.535).

The sheet layers originated by radical **2** are shown in Fig. 4. In this case, since the formyl–ferrocene imino nitroxide **2** contains only one oxygen center, only one sort of H-bonds is present (O1···H = 2.742).

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[1] Condensation of the ferrocene–dialdehyde with the sulphate monohydrate gives a mixture of formyl–ferrocene imino nitroxide **2** and formyl–ferrocene nitronyl nitroxide **1**.

2.3. Solid state magnetic properties

Variable-temperature magnetic susceptibility data for a crystalline sample of complexes **1** and **2** were measured on a SQUID susceptometer over the temperature range of 2–250 K with an applied external field of 1 kG. A plot of χT versus T of radical **1** is depicted in Fig. 5. The effective magnetic moments found at room temperature for radicals **1** and **2** were 0.38 and 0.37 emu K mol^{-1}, respectively. Such values are in excellent agreement with the theoretical effective magnetic moment expected for a simple monoradical (0.37 emu K

Table 1
Crystal data and structure refinement for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{18}H_{21}FeN_2O_3$	$C_{18}H_{21}FeN_2O_2$	$C_6H_{16}N_2O_2$
Formula weight	369.22	353.22	148.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
Unit cell dimensions			
a (pm)	1196.0(2)	1188.47(3)	2356.69(7)
b (pm)	1201.7(2)	1225.28(4)	612.9(1)
c (pm)	1262.6(3)	1224.16(3)	1343.5(1)
α (°)	90	90	90
β (°)	110.04(2)	111.539(2)	121.852(6)
γ (°)	90	90	90
V (nm^3)	1.7048(6)	1.65819(8)	1.6483(3)
Z	4	4	8
Temperature (K)	213(2)	223(2)	223(2)
D_{calc} (Mg m^{-3})	1.439	1.415	1.194
Absorption coefficient (mm^{-1})	0.903	0.920	0.089
F (000)	772	740	656
Color, habit	Dark brown prism	Dark red prism	Colorless plate
Crystal size (mm)	$0.58 \times 0.24 \times 0.12$	$0.3 \times 0.16 \times 0.15$	$0.25 \times 0.2 \times 0.07$
θ Range for data collcn (°)	2.64–22.49	2.04–24.48	2.03–21.48
Index ranges	$-1 \le h \le 12$, $-1 \le k \le 12$, $-13 \le l \le 11$	$0 \le h \le 14$, $-14 \le k \le 14$, $-14 \le l \le 13$	$0 \le h \le 25$, $-6 \le k \le 6$, $-14 \le l \le 12$
No. of reflections collected	24593	9533	3151
No. of independent reflections	2119 ($R_{int} = 0.0293$)	2754 ($R_{int} = 0.0318$)	948 ($R_{int} = 0.0444$)
No. of reflections with $I > 2\sigma(I)$	1742	2312	787
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2119/0/222	2638/0/213	907/8/128
Goodness-of-fit on F^2	1.047	1.045	1.106
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0355$, $wR_2 = 0.0869$	$R_1 = 0.0324$, $wR_2 = 0.0747$	$R_1 = 0.0510$, $wR_2 = 0.1250$
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.0948$	$R_1 = 0.0434$, $wR_2 = 0.0798$	$R_1 = 0.0638$, $wR_2 = 0.1464$
Max. difference peak and hole (e nm^{-3})	300 and −274	339 and −232	303 and −173

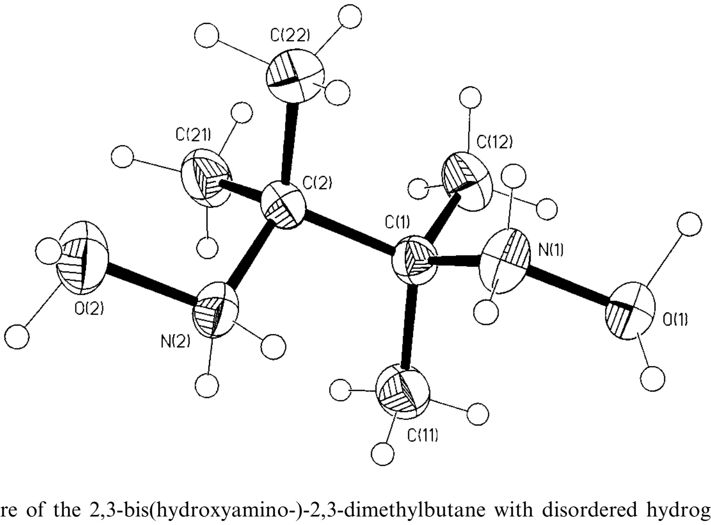

Fig. 1. Molecular structure of the 2,3-bis(hydroxyamino-)-2,3-dimethylbutane with disordered hydrogens at N- and O-atoms.

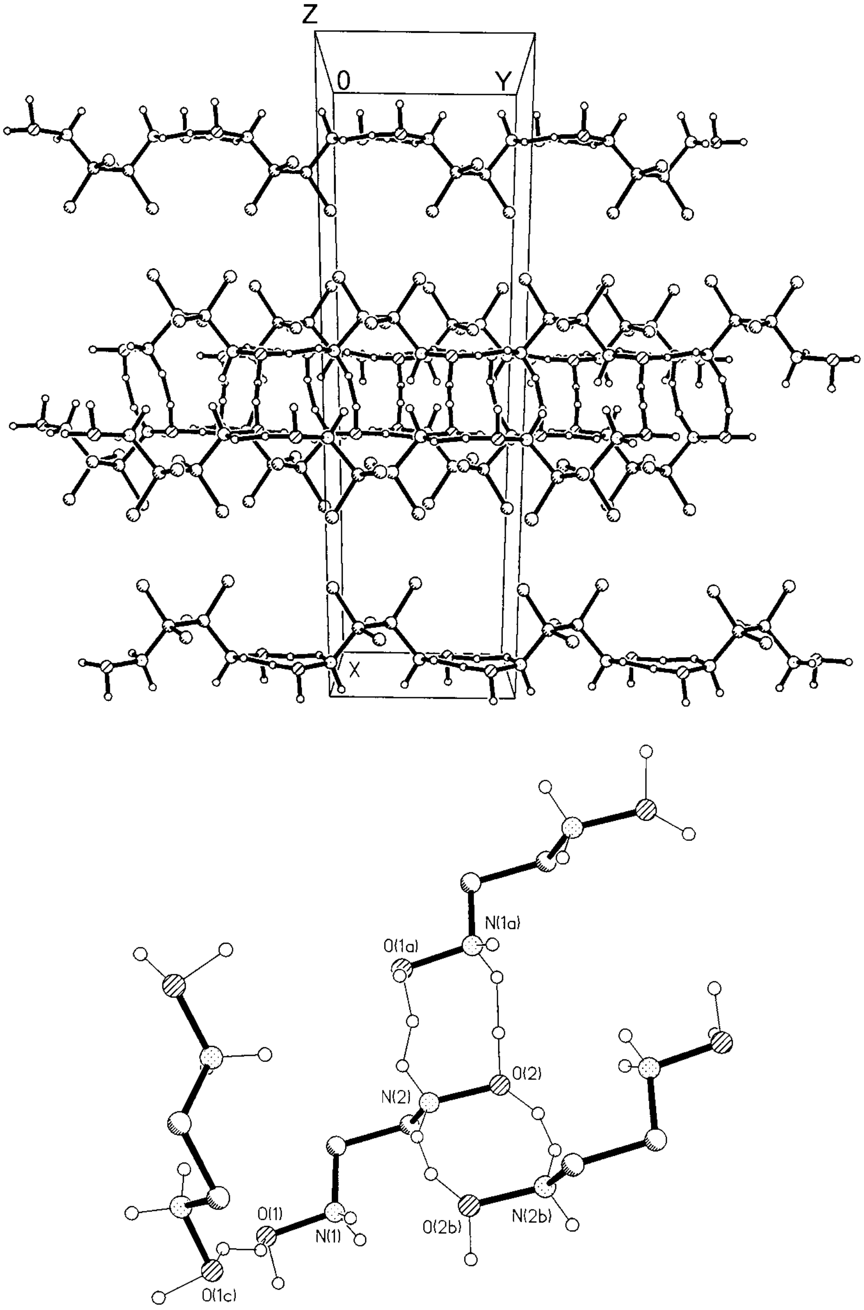

Fig. 2. The packing of the sheets along the crystallographic *a*-axis of compound **3** (top). A fragment of the sheet with exact disorder positions of the H-atoms of compound **3** is shown (bottom).

mol^{-1}). Afterwards, in both cases, the effective magnetic moment remains constant down to 10–15 K whereupon a small downward deviation is observed. This fact indicates the existence of very weak antiferromagnetic intermolecular interactions.

The magnetic susceptibility data was nicely fitted in both cases to the Curie–Weiss law yielding the Weiss constants of $\theta = -1.8$ and -1.1 K for radicals **1** and **2**, respectively. A plausible explanation of the weak magnetic exchange interactions can be rationalised by analysing the overlap of atomic orbitals belonging to atoms with large spin densities. Indeed, in the crystal packing of radicals **1** and **2** molecules are aligned with the N–O groups facing perpendicularly one to each other. Such packing results in large distances (> 5 Å) between the interacting N–O groups where most of the spin density is localised, justifying the weakness of the observed magnetic interaction.

Similar results were previously observed for a related family metallocene-substituted α-nitronyl aminoxyl monoradicals, which in solid state exhibited quasi-para-

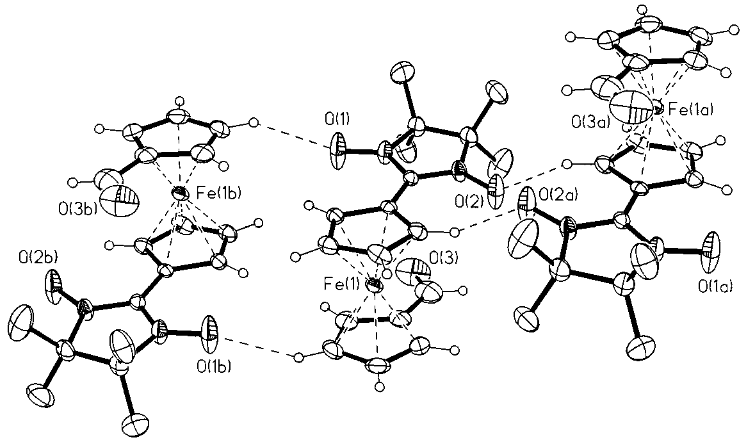

Fig. 3. Sheet layers of formyl–ferrocene nitronyl nitroxide **1** with two kind of H-bonds between the N–O groups and the C_5H_5-ligand.

magnetic behaviors with intermolecular magnetic exchange contacts with J/k values ranging from -0.8 to -3 K.

3. Conclusions

Two new ferrocene substituted nitroxide radicals have been generated and isolated as stable radicals. The magnetic susceptibility measurements for the isolated radicals have showed the presence of very weak antiferromagnetic intermolecular interactions, which can be rationalized by analyzing the overlap of atomic orbitals belonging to atoms with large spin densities.

4. Experimental

4.1. General procedures

Compound **3** was obtained as described previously [6]. UV–vis and near-IR were recorded using a Varian Cary 05E spectrophotometer. The ^{1}H-NMR spectra were recorded with Bruker FT80 spectrophotometer (^{1}H-NMR 80 MHz). DC magnetic susceptibility data from 2 to 250 K, in a magnetic field of 1 T, were collected using a Quantum Design MPMS superconducting SQUID susceptometer and using microcrystalline sample (60–70 mg) of the radicals. Background correction data were collected from magnetic susceptibility measurements on the empty holder capsules. Diamagnetic corrections, estimated from the Pascal constants, were applied to all data for determination of the molar paramagnetic susceptibilities of the compounds.

4.2. X-ray crystallographic data

For compound **1** a Bruker P4 diffractometer with graphite-monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å) was used for data collection. Intensities were measured via ω-scans and corrected for Lorentz and polarization effects. Compounds **2** and **3** were measured on a Nonius Kappa CCD area-detector diffractometer ($l = 0.71073$ Å) with the CCD detector placed 36 mm from the crystal via a mixture of 2° ϕ

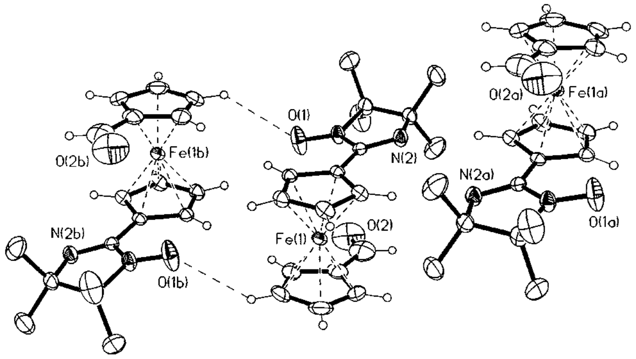

Fig. 4. Structure of formyl–ferrocene imino nitroxide **2** with H-bonds.

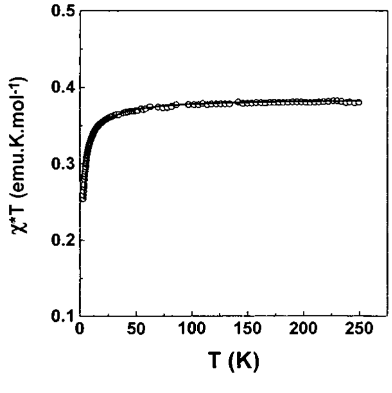

Fig. 5. Temperature dependence of the magnetic susceptibilities for radical **1** in the form χT vs. T. The solid line was calculated with Curie–Weiss equation and the parameters given in the text.

and ω-cans. The raw data were processed with the program DENZO-SMN [8] to obtain conventional data. The structures were solved by direct methods (SHELXS-86) [9] and refined by full-matrix least-squares against F^2 (SHELXL-93).[10] The function minimised was $\Sigma[\omega(F_o^2 - F_c^2)^2]$ with the weight defined as $\omega^{-1} = [2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by different Fourier methods, but in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 times and 1.5 (for the methyl group) higher then U_{eq} of the attached carbon atoms. In compound **1**, the hydrogen atoms at O(1), O(2), N(1) and N(2) were disordered in ration 1:1 in two positions. Each of these hydrogen atoms were refined isotropically with restrained bond distances to the attached nitrogen and oxygen atoms.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see Section 5).

4.3. Synthesis and characterization data

4.3.1. Synthesis and characterization of 2,3-bis(hydroxyamino-)-2,3-dimethylbutane (3)

The synthesis of hydrocarbon **3** was carried out following the previously reported procedures [6,7]. ^{1}H-NMR data: CH_3: 1.12 ppm ($CDCl_3$); 1.12 ppm (MeOH-*d*$_4$), 0.98 ppm (DMSO-*d*$_6$); NH: 5.37 ppm (DMSO-d$_6$); OH: 4.5–6.5 ppm ($CDCl_3$); 4.9–5.2 (MeOH-*d*$_4$), 6.94 (DMSO-*d*$_6$). ^{13}C-NMR data: CH_3: 20.7 ppm ($CDCl_3$); 21.2 ppm (MeOH-*d*$_4$), 20.8 ppm (DMSO-*d*$_6$); C_{quart}: 62.7 ppm ($CDCl_3$); 63.6 ppm (MeOH-*d*$_4$), 61.5 ppm (DMSO-*d*$_6$).

4.3.2. Synthesis of 2-(1-formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxid-1-yl-oxyl radical (1) and 2-(1-Formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-yl-oxyl radical (2)

N,*N*-Dihydroxy-2,3-diamino-2,3-dimethylbutane monosulphate mono-hydrate (2.24 g, 9.09 mmol, 2.2 equivalents) and *tert*-BuOK (2.06 g, 18,4 mmol, 4.4 equivalents) were suspended in a Schlenk flask under argon in ca. 20 ml EtOH(abs), exposed to ultrasound for 10 min in an ultrasonic bath (Bandelin Sonorex TK 30) and agitated for 30 min at 50 °C. Subsequently, fine-powdered ferrocene-dialdehyde (1.00 g, 4.13 mmol) was added and the suspension was again exposed to ultrasound for 15 min and vigorously stirred for 2 h at 50 °C. The reaction mixture was filtered over paper and restricted at the rotavapor. The residue was redisolved in ca. 20 ml toluene mixed with PbO_2 (6 g, 25.1 mmol, 6.0 equivalents) and agitated intensively for further 2 h. The dark-green reaction solution is filtered over paper, absorbed on ca. 5 g SiO_2 and evaporated. Separation of radicals **1** and **2** was done by chromatography over SiO_2 using Et_2O as eluent.

*4.3.2.1. 2-(1-Formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxid-1-yl-oxyl radical (**1**).* Yield: 375 mg (28.0%) dark-green crystals; R_f: 0.32 (SiO_2/Et_2O); m.p.: 138–140 °C (Et_2O/*n*-hexane). IR (KBr), cm^{-1}: 3133 w, 3110 w, 3091 w, 2984 m, 2930 w, 2828 w, 2763 w, 1678vs (C=O), 1553 m (C=N), 1452 m, 1387 vs, 1373 vs (N–O), 1242 s, 1202 s, 1032 m-s, 838 m, 742 m, 540 s. MS (EI 30 eV, 150 °C) (*m*/*e*, % Int.): 369 (87) [M^+], 353 (9) [$M^+ - O$], 255 (100), 239 (83) OCH–Fec–CN, 211 (53).

*4.3.2.2. 2-(1-Formylferrocen-1-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-yl-oxyl radical (**2**).* Yield: 250 mg (19.5%) orange–brown crystals; R_f: 0.42 (SiO_2/Et_2O); m.p.: 117–118 °C (Et_2O/*n*-hexane) IR (KBr), cm^{-1}: 3141 w, 3116 w, 3093 w, 2983 m, 2929 w, 2865 w, 2763 w, 1687 vs, 1582 s, 1452 s, 1389 m, 1373 s, 1290 m, 1242 s, 1034 s, 837 s, 742 s, 528 s. MS (EI 40eV, 100 °C), *m*/*e* (% Int.):353 (25) [M^+], 338 (4) [$M^+ - CH_3$], 239 (100) OCH–Fc–CN, 211(54); 120 (38) Fe–Cp, 83 (41), 56 (32).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 162501 for compound **1**, 162502 for compound **2** and 162503 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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