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1-Alkyl-2-(*Z*-1,2-diferrocenylvinyl)oxazolinium tetrafluoroborates: synthesis, characterization and nucleophilic ring opening

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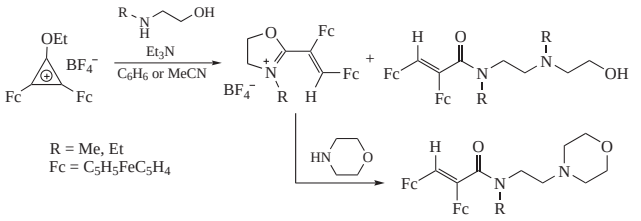
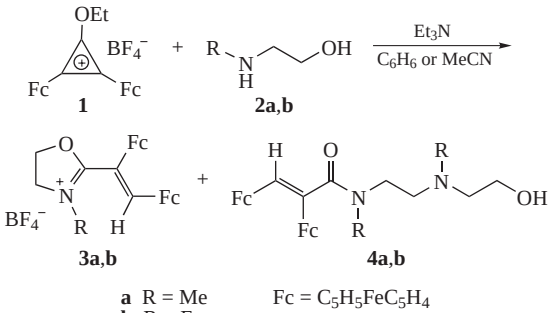
2,3-Diferrocenyl-1-ethoxycyclopropenylium tetrafluoroborate on reaction with 2-(alkylamino)ethanols at ~80–82 °C in the presence of triethylamine gives mixtures of novel 2-(1,2-diferrocenylvinyl)oxazolinium salts and 3,6-diaza-(*E*-2,3-diferrocenyl)acryloyl-3,6-dialkylheptanols. The oxazolidinium salts undergo heterocyclic ring-opening in the presence of N-nucleophiles to afford 2,3-diferrocenylacrylamide derivatives.



Development of new methods for the synthesis of heterocycles with a conjugated system of double bonds and several heteroatoms in the cycle is of interest for producing novel iron-containing compounds, which are an important category of materials.[1,2] The use of the 2,3-diferrocenylcyclopropenylium salts and bis-1,3- or bis-1,4-heteronucleophiles as reactants can provide heterocyclic compounds containing both ferrocene fragments and conjugated multiple bonds with several heteroatoms in the cycles.[3–10] The mutual influence of these components in the molecules should impart a number of specific properties to the compounds, and these properties would have a practical value for synthetic and theoretical organic chemistry, electrochemistry, polymer chemistry, supramolecular chemistry, biology, medicine, *etc*.

Little information concerning the synthesis and chemistry of ferrocene 4,5-dihydrooxazoles is available. To date, only the preparation of 2-ferrocenyloxazolines is described[11] together with some of their chemical properties. Meantime, it is known that 4,5-dihydrooxazoles and their N–H and N–R oxazolinium salts find applications for the preparation of α-amino acids, carboxylic acids, carboxamides, products of polymerization useful as pharmaceutical compounds, corrosion inhibitors, building blocks and auxiliaries in organic synthesis.[12]

Here we study the reactions of 2,3-diferrocenyl-1-ethoxycyclopropenylium tetrafluoroborate **1**[13] with *N*-methylamino- and *N*-ethylaminoethanols **2a** and **2b** with the purpose of the preparation of *N*-alkyl-2-(*Z*-1,2-diferrocenylvinyl)oxazolinium tetrafluoroborates. Hitherto, no reactions of this type have been documented. We found that cyclopropenylium **1** reacts with amino alcohols **2a**,**b** upon boiling in benzene or acetonitrile in the presence of Et_3N to form a mixture of two products (Scheme 1),† whose yields depend on the molar excess of reactants **1** and **2a**,**b**, temperature, and duration of the reaction (Table 1). Products obtained with a twofold molar excess of amino alcohols **2a**,**b** were separated using Al_2O_3 (activity grade III) column chromatography. As a result, 1-alkyl-2-(*cis*-1,2-diferrocenylvinyl)-oxazolinium tetrafluoroborates **3a**,**b** (~30%) and 3,6-diaza-6-[(*E*-2,3-diferrocenyl)acryloyl]-3-alkylheptanols **4a**,**b** (~40%) were isolated.



Scheme 1

Table 1 Reactions of 2,3-diferrocenyl-1-ethoxycyclopropenylium tetrafluoroborate **1** with (2-alkylamino)ethanols **2a**,**b** at 80 °C.

Reactant **2**	Molar ratio **1**:**2**	Solvent	*t*/h	Yield of **3**[a] (%)	Yield of **4**[a] (%)
2a	1:2	C_6H_6	6	28 (30)	35 (44)
2b	1:2	C_6H_6	6	32 (32)	40 (43)
2a	1:2	MeCN	6	23 (31)	34 (45)
2b	1:2	MeCN	8	28 (33)	39 (44)
2a	1:1	MeCN	8	62 (71)	4 (8)
2b	1:1	MeCN	6	57 (74)	3 (10)
2a	1:3	C_6H_6	6	5 (5)	58 (77)
2b	1:3	C_6H_6	6	5 (7)	61 (80)

[a]The yields upon 12 h of processing are given in parentheses.

Treatment of salt **1** (1 mmol) with amino alcohols **2a**,**b** (1 mmol) led to salts **3a**,**b** (yields 71–74%) and compounds

† *Reaction between 2,3-diferrocenyl-1-ethoxycyclopropenylium tetrafluoroborate* **1** *and 2-(alkylamino)ethanols* **2a**,**b**. (A) 2-(Alkylamino)-ethanol **2a** or **2b** (6 mmol) and Et_3N (1.0 ml) were added with stirring to the solution of diferrocenylcyclopropenylium tetrafluoroborate **1** (3 mmol) in dry benzene or acetonitrile (70 ml). After stirring for 6–12 h at ~80 °C, the volatiles were removed *in vacuo*; the residue was chromatographed on a column with Al_2O_3 (activity III) (hexane–diethyl ether, 3:1) to afford the reaction products **3a**,**b** (30–32%) and **4a**,**b** (43–44%), respectively.

(B) Following the general procedure, reaction of **1b** (1 mmol) in MeCN (30 ml, 80 °C, 6–12 h) in the presence of Et_3N (0.3 ml) with amino alcohols **2a**,**b** (1 mmol) afforded compounds **3a** (62–71%) or **3b** (67–74%) and **4a**,**b** (3–10%).

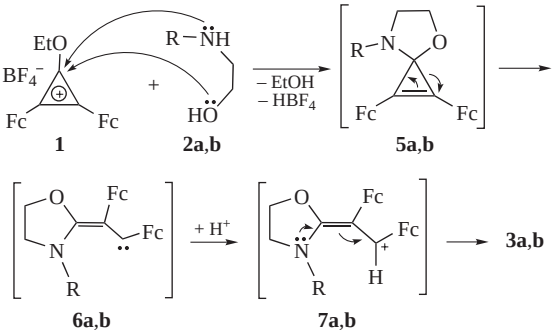
(C) Reaction of **1b** (1 mmol) in dry benzene (30 ml, 80 °C, 6–12 h) in the presence of Et_3N (0.3 ml) with amino alcohols **2a**,**b** (3 mmol) afforded compounds **3a**,**b** (5–7%) and **4a** (58–77%), **4b** (61–80%).

4a,**b** (yields 8–10%), whereas the reaction of salt **1** with a three-fold molar excess of amino alcohols **2a**,**b** afforded preferentially compounds **4a**,**b** (yields 77–80%) (Table 1).

The structures of the products were established on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. According to ^{1}H NMR spectra, all compounds (**3a**,**b** and **4a**,**b**) were obtained in the form of one geometric isomer with *cis*-oriented ferrocene substituents at the double bond.†

The supposed mechanism of the formation of salts **3a**,**b** is outlined in Scheme 2, where amino alcohol attacks the C(1) carbon atom of the cyclopropenylium cations twice with the formation of intermediate spirane oxazolidiniums **5a**,**b**. The latter undergo three-carbon ring opening into intermediate vinylcarbenes **6a**,**b** and allylic carbocations **7a**,**b**, and finally give oxazolinium derivatives **3a**,**b**.

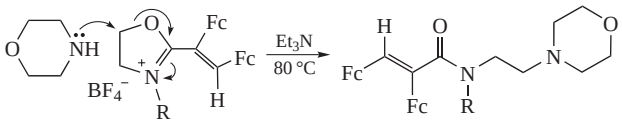
The formation of compounds with linear structures **4a**,**b** in the reactions of salt **1** with N-nucleophiles **2a**,**b** proceeds, in our opinion, *via* the opening of the five-membered ring in primary products **3a**,**b**, which occurs as a nucleophilic attack of nitrogen



Scheme 2

atom of amino alcohols **2a**,**b** at the C(5) atom of the oxazolinium salts. This suggestion has been confirmed in the studies of the chemical behavior of tetrafluoroborates **3a**,**b** upon the action of other nucleophiles, as for instance, of morpholine **2c**.

In fact, the treatment of *N*-alkyloxazolinium salt **3a**,**b** with morpholine under similar conditions results in (*E*)-*N*-alkyl-*N*-(2-morpholinoethyl)-2,3-diferrocenylacrylamides **8a**,**b** in 70–73% yields (Scheme 3).‡



Scheme 3

*2-(*Z*-2,3-Diferrocenylvinyl)-3-methyl-4,5-dihydrooxazol-3-ium tetrafluoroborate* **3a**: red powder, mp 191–192 °C. IR (KBr, ν/cm^{-1}): 469, 484, 727, 776, 815, 835, 899, 935, 1001, 1027, 1040, 1049, 1107, 1147, 1190, 1214, 1253, 1331, 1353, 1387, 1412, 1442, 1474, 1604, 1700, 1788, 2025, 2225, 2821, 2891, 2961, 3087, 3327. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.21 (s, 3H, Me), 2.68 (t, 2H, CH_2, *J* 5.7 Hz), 3.86 (s, 5H, C_5H_5), 4.11 (s, 5H, C_5H_5), 3.98 (m, 3H, C_5H_4), 4.08 (m, 2H, C_5H_4), 4.24 (m, 3H, C_5H_4), 4.32 (t, 2H, CH_2, *J* 5.7 Hz), 7.67 (s, 1H, CH=). MS (EI, 70 eV), *m*/*z*: 101, 465, 466 $[M]^+$.

*2-(*Z*-2,3-Diferrocenylvinyl)-3-ethyl-4,5-dihydrooxazol-3-ium tetrafluoroborate* **3b**: red powder, mp 109–110 °C. IR (KBr, ν/cm^{-1}): 469, 480, 727, 777, 814, 899, 1000, 1026, 1040, 1049, 1106, 1146, 1189, 1214, 1253, 1330, 1386, 1411, 1443, 1474, 1605, 1633, 1699, 1787, 2050, 2240, 2821, 2866, 2891, 2961, 3088, 3327. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19 (t, 3H, Me, *J* 7.2 Hz), 2.79 (q, 2H, CH_2, *J* 7.2 Hz), 3.07 (t, 2H, CH_2, *J* 5.7 Hz), 4.05 (s, 5H, C_5H_5), 4.07 (s, 5H, C_5H_5), 4.22 (m, 2H, C_5H_4), 4.24 (m, 4H, C_5H_4), 4.41 (t, 2H, CH_2, *J* 5.7 Hz), 4.45 (m, 2H, C_5H_4), 7.29 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.47 (Me), 44.08, 48.30, 64.23 (3CH_2), 69.28, 69.47 (2C_5H_5), 67.96, 69.64, 70.60, 70.62 (2C_5H_4), 79.54, 79.72 (2C_{ipso}Fc), 137.06 (CH=), 126.45, 167.71 (2C). Found (%): C, 55.89; H, 4.67; N, 2.26. Calc. for $C_{27}H_{28}BF_4Fe_2NO$ (%): C, 55.81; H, 4.86; N, 2.41.

*6-[(*E*-2,3-Diferrocenyl)acryloyl]-3-methyl-3,6-diazaheptanol* **4a**: orange powder, mp 98–99 °C. IR (KBr, ν/cm^{-1}): 466, 619, 645, 745, 803, 814, 874, 1000, 1025, 1036, 1106, 1161, 1249, 1294, 1312, 1333, 1407, 1448, 1461, 1499, 1572, 1595, 1622, 1769, 2050, 2190, 2240, 2776, 2800, 2875, 2936, 3091, 3415. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, Me), 2.61 (br.s, 1H, OH), 2.68 (t, 2H, CH_2, *J* 5.1 Hz), 2.77 (t, 2H, CH_2, *J* 6.3 Hz), 3.20 (s, 3H, Me), 3.66 (m, 4H, 2CH_2), 4.09 (s, 5H, C_5H_5), 4.12 (s, 5H, C_5H_5), 4.17 (m, 3H, C_5H_4), 4.23 (m, 4H, C_5H_4), 4.37 (m, 1H, C_5H_4), 6.25 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 37.78, 44.80 (2Me), 42.26, 54.86, 58.76, 59.23 (4CH_2), 69.11, 69.20 (2C_5H_5), 68.13, 68.71, 69.21, 69.65 (2C_5H_4), 80.22 (2C_{ipso}Fc), 127.28 (CH=), 131.17 (C), 171.53 (C=O). MS (EI, 70 eV), *m*/*z*: 554 $[M]^+$. Found (%): C, 62.65; H, 6.21; N, 5.09. Calc. for $C_{29}H_{34}Fe_2N_2O_2$ (%): C, 62.84; H, 6.18; N, 5.05.

*6-[(*E*-2,3-Diferrocenyl)acryloyl]-3-ethyl-3,6-diazaoctanol* **4b**: orange powder, mp 95–96 °C. IR (KBr, ν/cm^{-1}): 465, 481, 743, 764, 806, 821, 900, 999, 1027, 1041, 1083, 1104, 1163, 1187, 1249, 1296, 1350, 1404, 1456, 1498, 1572, 1594, 1616, 2045, 2100, 2230, 2785, 2842, 2875, 2920, 2942, 3088, 3100, 3188, 3437. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.11 (t, 3H, Me, *J* 7.2 Hz), 1.27 (t, 3H, Me, *J* 6.9 Hz), 2.04 (br.s, 1H, OH), 2.63 (t, 2H, CH_2, *J* 6.9 Hz), 2.69 (m, 4H, 2CH_2, *J* 6.9, 7.2 Hz), 2.74 (t, 2H, CH_2, *J* 6.9 Hz), 3.54 (t, 2H, CH_2, *J* 6.9 Hz), 3.65 (t, 2H, CH_2, *J* 6.9 Hz), 4.08 (s, 5H, C_5H_5), 4.12 (s, 5H, C_5H_5), 4.18 (m, 4H, C_5H_4), 4.22 (m, 4H, C_5H_4), 6.60 (s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.05, 14.40 (2Me), 42.64, 44.51, 48.12, 51.05, 55.53, 58.95 (6CH_2), 69.18, 69.40 (2C_5H_5), 68.25, 68.72, 69.43, 69.74 (2C_5H_4), 80.41, 81.59 (2C_{ipso}Fc), 126.76 (CH=), 132.14 (C), 171.78 (C=O). MS (EI, 70 eV), *m*/*z*: 582 $[M]^+$. Found (%): C, 63.79; H, 6.69; N, 4.73. Calc. for $C_{31}H_{38}Fe_2N_2O_2$ (%): C, 63.93; H, 6.58; N, 4.81.

‡ *Reactions of 2-(*Z*-2,3-diferrocenylvinyl)-3-alkyl-4,5-dihydrooxazol-3-ium salts* **3a**,**b** *with morpholine*. A mixture of compound **3a** or **3b** (1 mmol), benzene (50 ml), Et_3N (1 ml) and morpholine (1 ml) was stirred for 5 h at 80 °C. The solvents were evaporated *in vacuo* and the residues were chromatographed on a column with Al_2O_3 (hexane–diethyl ether, 3 : 1) to afford products **8a** or **8b**, respectively.

*(*E*)-N-Methyl-*N*-(2-morpholinoethyl)-2,3-diferrocenylacrylamide* **8a**: orange powder, yield 0.4 g (70%), mp 125–126 °C. IR (KBr, ν/cm^{-1}): 477, 645, 727, 766, 815, 854, 912, 923, 1001, 1037, 1069, 1105, 1116, 1144, 1257, 1298, 1356, 1397, 1455, 1487, 1629, 1680, 1709, 2807, 2852, 2918, 2953, 3092. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.60 (m, 4H, CH_2), 2.70 (t, 2H, CH_2, *J* 6.0 Hz), 3.20 (s, 3H, Me), 3.69 (t, 2H, CH_2, *J* 6.0 Hz), 3.77 (m, 4H, 2CH_2), 4.09 (s, 5H, C_5H_5), 4.13 (s, 5H, C_5H_5), 4.19 (m, 2H, C_5H_4), 4.25 (m, 4H, C_5H_4), 4.44 (m, 2H, C_5H_4), 6.26 (s, 1H, CH=). ^{13}C NMR (75 MHz, C_6D_6) δ: 37.29 (Me), 43.14, 56.31 (2CH_2), 54.05 (2CH_2), 67.14 (2CH_2), 69.48, 69.83 (2C_5H_5), 68.50, 69.02, 69.71, 70.00 (2C_5H_4), 81.09, 81.14 (2C_{ipso}Fc), 126.35 (CH=), 132.74 (C), 171.03 (C=O). MS (EI, 70 eV), *m*/*z*: 566 $[M]^+$. Found (%): C, 63.42; H, 6.14; N, 5.07. Calc. for $C_{30}H_{34}Fe_2N_2O_2$ (%): C, 63.64; H, 6.05; N, 4.94.

*(*E*)-N-Ethyl-*N*-(2-morpholinoethyl)-2,3-diferrocenylacrylamide* **8b**: orange powder, yield 0.43 g (73%), mp 104–105 °C. IR (KBr, ν/cm^{-1}): 471, 617, 651, 732, 766, 787, 805, 822, 875, 922, 1005, 1024, 1113, 1141, 1243, 1269, 1289, 1343, 1355, 1422, 1437, 1457, 1468, 1554, 1617, 1703, 1773, 2754, 2800, 2818, 2942, 2957, 3094. ^{1}H NMR (300 MHz, C_6D_6) δ: 0.99 (t, 3H, Me, *J* 7.5 Hz), 2.20 (m, 2H, CH_2), 2.33 (m, 4H, 2CH_2), 2.52 (m, 2H, CH_2), 3.55 (m, 2H, CH_2), 3.66 (m, 4H, 2CH_2), 3.96 (s, 5H, C_5H_5), 4.24 (s, 5H, C_5H_5), 4.01 (m, 3H, C_5H_4), 4.09 (m, 2H, C_5H_4), 4.25 (m, 3H, C_5H_4), 6.42 (s, 1H, CH=). ^{13}C NMR (75 MHz, C_6D_6) δ: 13.76 (Me), 39.68, 43.33 (2CH_2), 53.96 (2CH_2), 56.43 (CH_2), 66.84 (2CH_2), 69.18, 69.72 (2C_5H_5), 68.21, 68.59, 69.23, 79.74 (2C_5H_4), 80.63, 81.35 (2C_{ipso}Fc), 125.13 (CH=), 133.67 (C), 170.0 (C=O). MS (EI, 70 eV), *m*/*z*: 580 $[M]^+$. Found (%): C, 64.29; H, 6.02; N, 4.63. Calc. for $C_{31}H_{36}Fe_2N_2O_2$ (%): C, 64.16; H, 6.15; N, 4.82.

*Reactions of 2-(*Z*-2,3-diferrocenylvinyl)-3-alkyl-4,5-dihydrooxazol-3-ium salts with 2-(alkylamino)ethanols and morpholine*. This was carried out analogously using **3a** or **3b** (1 mmol), amino ethanols **2a** or **2b**, or morpholine (1 ml), Et_3N (1 ml) and benzene (50 ml). The reaction mixtures were worked up as described above, subsequent chromatography on Al_2O_3 (hexane–diethyl ether, 4 : 1) gave compounds **4a** (78%), **4b** (82%), **8a** (72%), **8b** (76%).

X-ray diffraction analysis of single crystals of compounds **4a** and **8b** obtained by crystallization from CH_2Cl_2 confirms their structures (Figures 1 and 2).§

In conclusion, the opening of the five-membered ring in *N*-alkyloxazolinium cations **3a**,**b** as a result of the nucleophilic attack on the carbon atom C(5) of the heterocyclic system has been described for the first time. This feature should be of general nature, pertaining to all compounds of a similar structure; thus, they can be used in organic synthesis of the macromolecules as six-atom building blocks.

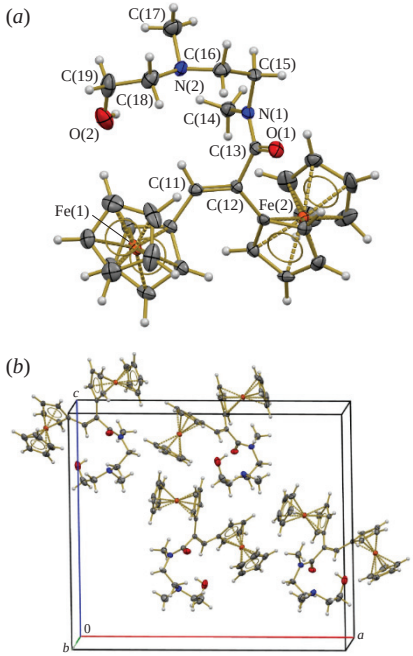


Figure 1 (*a*) Crystal structure and (*b*) crystal packing of compound **4a**. Selected bond lengths (Å) and angles (°): C(11)–C(12) 1.346(5), C(12)–C(13) 1.500(5), C(13)–O(1) 1.246(5), C(13)–N(1) 1.340(5), C(14)–N(1) 1.460(5), C(15)–N(1) 1.468(5), C(16)–N(2) 1.462(5), C(17)–N(2) 1.462(6), C(18)–N(2) 1.461(6), C(18)–C(19) 1.499(7), C(19)–O(2) 1.409(6); C(11)–C(12)–C(13) 116.1(3), O(1)–C(13)–N(1) 121.5(4), O(1)–C(13)–C(12) 118.8(4), N(1)–C(13)–C(12) 119.6(3), N(1)–C(15)–C(16) 110.5(3), N(2)–C(16)–C(15) 112.0(4), N(2)–C(18)–C(19) 114.4(4), O(2)–C(19)–C(18) 114.7(4), C(13)–N(1)–C(14) 124.3(3), C(14)–N(1)–C(15) 117.4(3), C(13)–N(1)–C(15) 117.6(3), C(18)–N(2)–C(16) 110.6(3), C(18)–N(2)–C(17) 110.6(3), C(16)–N(2)–C(17) 110.1(4).

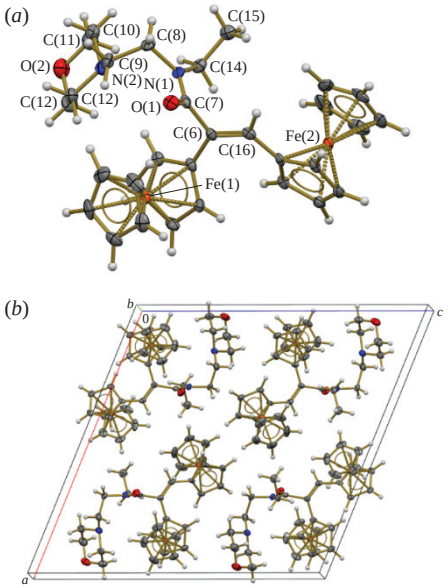


Figure 2 (*a*) Crystal structure and (*b*) crystal packing of compound **8b**. Selected bond lengths (Å) and angles (°): C(6)–C(16) 1.339(4), C(6)–C(7) 1.513(4), C(7)–O(1) 1.229(3), C(7)–N(1) 1.340(5), C(14)–N(1) 1.348(4), C(8)–N(1) 1.465(4), C(9)–N(2) 1.465(4), C(10)–N(2) 1.460(4); C(16)–C(6)–C(7) 118.3(2), O(1)–C(7)–N(1) 121.7(3), O(1)–C(7)–C(6) 120.9(3), N(1)–C(7)–C(6) 117.3(2), N(1)–C(8)–C(9) 111.1(2), N(2)–C(10)–C(11) 109.8(3), C(7)–N(1)–C(8) 118.0(2), C(14)–N(1)–C(7) 124.7(2), C(10)–N(2)–C(9) 112.3(2).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.007.

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§ *Crystal data for* **4a**. Crystals of $C_{29}H_{34}Fe_2N_2O_2$ (M = 554.28), are orthorhombic, space group $Pca2_1$, at 130(2) K: a = 21.8387(11), b = = 6.0311(3) and c = 19.0490(8) Å, V = 2509.0(2) Å^3, Z = 4, d_{calc} = = 1.467 g cm^{-3}, λ(MoKα) = 0.71073 Å, F(000) = 1160, μ = 1.186 mm^{-1}, index ranges –30 ⩽ h ⩽ 27, –8 ⩽ k ⩽ 8, –24 ⩽ l ⩽ 26, scan range 3.505 ⩽ θ ⩽ 29.551°, 6287 independent reflections, R_{int} = 0.0594, 26278 total reflections, 321 refinable parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0387, wR_2 = 0.0681; R indices (all data): R_1 = 0.0560, wR_2 = = 0.0763; goodness-of-fit on F^2 1.053, largest difference peak and hole 0.466/–0.352 eÅ^{-3}.

Crystal data for **8b**. Crystals of $C_{31}H_{36}Fe_2N_2O_2$ (M = 580.32), are monoclinic, space group $P2_1/c$, at 130(2) K: a = 19.5186(16), b = 7.3492(5) and c = 19.7752(18) Å, β = 112.066(9)°, V = 2628.9(4) Å^3, Z = 4, d_{calc} = = 1.466 g cm^{-3}, λ(MoKα) = 0.71073 Å, F(000) = 1216, μ = 1.186 mm^{-1}, index ranges –24 ⩽ h ⩽ 26, –10 ⩽ k ⩽ 7, –24 ⩽ l ⩽ 23, scan range 3.466 ⩽ θ ⩽ 29.579°, 6245 independent reflections, R_{int} = 0.0498, 15151 total reflections, 335 refinable parameters, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0487, wR_2 = 0.0881; R indices (all data): R_1 = 0.0869, wR_2 = 0.1077; goodness-of-fit on F^2 1.076, largest difference peak and hole 0.459/–0.576 eÅ^{-3}.

The unit cell parameters and the X-ray diffraction intensities were recorded on a Gemini (detector Atlas CCD, Cryojet N2) diffractometer. The structures were solved by the direct method (SHELXS-97[14]) and refined using full-matrix least-squares on F^2.

CCDC 1474953 and 1474954 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.