Ferrocene-containing [2]- and [3]rotaxanes. Preparation *via* an end-capping cross-metathesis reaction and electrochemical properties

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Cross-metathesis reactions of terminal olefins with acrylic esters catalyzed by a Ru–carbene complex ($(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$, H_2IMes = *N,N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) were applied to the end-capping of [2]pseudorotaxanes composed of dibenzo[24]crown-8 (DB24C8) and ferrocenylmethylammonium derivatives as the macrocyclic and axle components. A [3]rotaxane consisting of two DB24C8s and an axle molecule having ferrocenyl groups at both ends was obtained from the cross-metathesis reaction of two [2]pseudorotaxanes with $Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$. Cyclic voltammograms of the ferrocene-containing rotaxanes show reversible redox reactions whose potentials vary depending on the presence or absence of cationic dialkylammonium groups in the vicinity of the ferrocene units.

Introduction

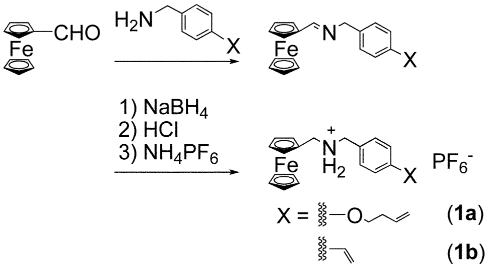
Rotaxane[1,2] is a mechanically interlocked supramolecule composed of macrocyclic molecules threaded by a linear molecule having bulky end groups. Pseudorotaxanes composed of dibenzo[24]crown-8 (DB24C8) and dialkylammonium salt have often been used as a precursor of the rotaxane due to its high stability owing to N–H · · · O and C–H · · · O attractive interactions between the linear and cyclic components.[3] Various reactions, such as cycloaddition of azide,[4] addition of isocyanates with amines[5] and with alcohol,[6] Wittig reactions,[7] disulfide formation,[8] ester formation,[9] and acid anhydride formation,[10] introduce a bulky group at the end of the axle molecule of the pseudorotaxanes to fix the interlocked structure. Olefin metathesis reactions were also used for the synthesis of rotaxanes[11–13] and related supramolecules[14–16] because of efficient C=C bond formation under mild conditions. Recent progress in the type of catalyst used in the metathesis reactions has enabled selective cross-metathesis reactions of terminal alkenes with alkyl acrylates or styrene.[17,18]

Recently, we reported that electrochemical oxidation of a solution containing ferrocenylmethylamine derivatives and dibenzo[24]crown-8 (DB24C8) in the presence of 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH) formed [2]pseudorotaxane *via* formal protonation of the secondary amine group.[19] Introduction of a redox active ferrocene unit to a component of the supramolecule is of significant importance because these supramolecules are potentially applicable to the stimulus responsive molecular materials that change optical or chemical properties upon electrochemical reaction.[20–22] A suitable end-capping reaction would convert the pseudorotaxanes having a ferrocenyl group into the corresponding rotaxanes.

In this paper, we report the synthesis of new [2]rotaxanes *via* the end-capping of [2]pseudorotaxane by cross-metathesis reactions using a Ru catalyst ($(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$, H_2IMes = *N,N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene). Synthesis of [3]rotaxane by a similar procedure and the electrochemical properties of these rotaxanes are also described. Part of this work has been reported in a preliminarily form.[23]

Results and discussion

Scheme 1 summarizes the preparative procedure for the ammonium salts which are employed as precursors of the axle components of the rotaxane in this study. The dehydration reaction of ferrocenecarboxaldehyde with *p*-butenoxybenzylamine forms $FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ ($Fc = Fe(C_5H_4)(C_5H_5)$). Fig. 1 depicts the molecular structure of $FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ determined by X-ray crystallography. Cyclopentadienyl ligands are in the eclipsed positions. Reduction of the product with $NaBH_4$, followed by hydrolysis with HCl and exchange of the counter anion, yields the PF_6 salt $[FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CH_2](PF_6)$ (**1a**). Analogous reactions of *p*-vinylbenzylamine yield **1b**. These compounds were



Scheme 1

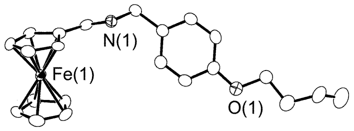


Fig. 1 ORTEP plot of $FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ with 30% probability. Hydrogen atoms were omitted for simplicity.

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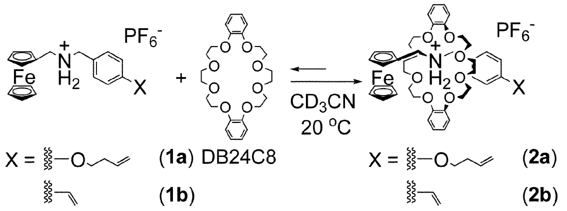
characterized by ^1H and $^{13}C\{^1H\}$ NMR and IR spectrometry as well as elemental analyses.

Dissolution of **1a** and DB24C8 in CD_3CN forms [2]pseudorotaxane **2a** as shown in Scheme 2. Formation of **2a** and **2b** in the solutions was confirmed from electrospray ionization mass spectrometry (ESIMS) which exhibited peaks due to the cationic pseudorotaxanes. Fig. 2(a) and (b) show the ^1H NMR spectra of **1a** and a mixture of **1a** and DB24C8 ($[\mathbf{1a}]_0 = [\mathrm{DB24C8}]_0 = 10$ mM), respectively. The latter spectrum contains the signals of the NCH_2 hydrogens of the pseudorotaxane (δ 4.37, 4.50) at lower magnetic field positions than those of **1a** (δ 4.02, 4.04). The signals of the aromatic hydrogens of the axle molecule of **2a** are observed at higher magnetic field positions (δ 6.55, 7.17) than those of **1a** (δ 6.95, 7.33). The ratios of the free axle molecules and the pseudorotaxane in these solutions were calculated to be **1a**/**2a** = 36/64 and **1b**/**2b** = 43/57 from comparison of the peak areas of the phenylene hydrogen signals at 20 °C.[24–26]



Scheme 2

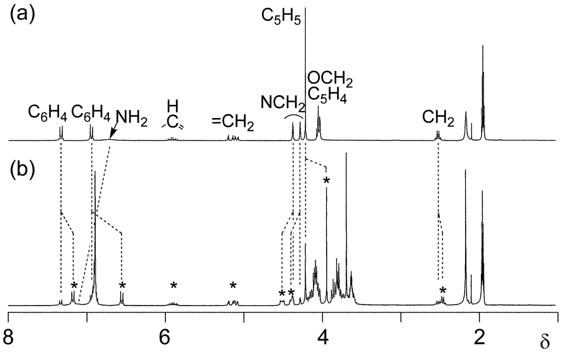


Fig. 2 ^1H NMR spectra of (a) **1a** and (b) **1a** and DB24C8 ($[\mathbf{1a}]_0 = [\mathrm{DB24C8}]_0 = 10$ mM) in CD_3CN. Peaks with an asterisk indicate the signals of the complex of DB24C8 and **1a**.

Slow addition of Et_2O to a CH_2Cl_2 solution of **1b** and DB24C8 causes separation of [2]pseudorotaxane **2b** as single crystals. Fig. 3 shows the molecular structure of **2b** obtained by X-ray crystallography. The NH_2 and CH_2 groups of the axle component show short contacts with the oxygen atoms of DB24C8 (N(1)–H(1) ··· O(4), 2.18 Å and C(10)–H(13) ··· O(6), 2.35 Å), indicating that hydrogen bonds between them stabilize the interlocked structure. A C–H ··· π attractive interaction is also observed between a cyclopentadienyl hydrogen and the aromatic plane of DB24C8; the distance between a cyclopentadienyl hydrogen and the centroid of the aromatic ring of DB24C8 is 3.07 Å. An aromatic plane of DB24C8 in **2b** is close to the olefinic carbons with a distance of 4.14(2) Å between C(24) and C(2). The dihedral angle of the aryl ring of **2b** and one of the catechol rings is 162°, while Stoddart reported that the 1 : 1 complex of DB24C8 and the dibenzylammonium cation[3b,25] possess co-conformation[27] where one of the aryl rings in the axle is oriented almost parallel to one of the catechol rings on the DB24C8. The IR spectrum of **2b** shows peaks due to asymmetric and symmetric stretching vibrations of the NH_2 group at 3156 and 3085 cm⁻¹, which is observed at lower wavenumber than those of **1b** (3235, 3260 cm⁻¹) due to N–H ··· O hydrogen bonds between the axle molecule and DB24C8 in **2b**.

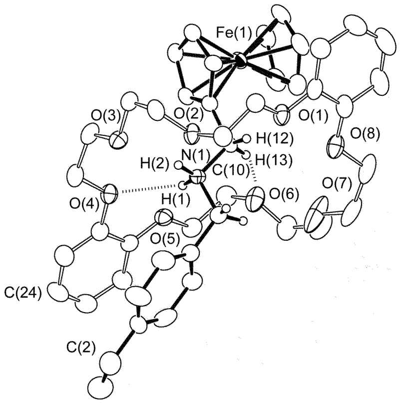
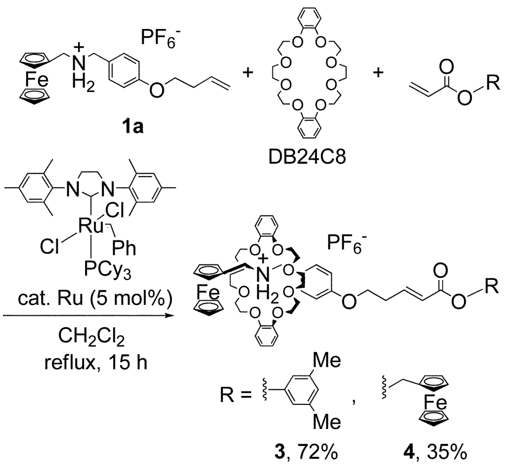


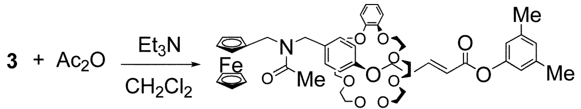
Fig. 3 ORTEP plot of pseudorotaxane **2b** with 30% probability. Some of the hydrogen atoms and PF_6^- were omitted for simplicity.

A cross-metathesis reaction of 3,5-dimethylphenyl acrylate (0.20 mmol) with **1a** (0.10 mmol) in the presence of DB24C8 (0.12 mmol) using a Ru catalyst[17] affords [2]rotaxane **3** in 72% isolated yield (Scheme 3). The ^1H NMR spectrum, showing a large coupling constant of vinylene hydrogens (J = 15 Hz), indicates a *trans* configuration of the C=C bond, similar to the products of the other cross-metathesis reactions.[18] Analogous reaction using ferrocenylmethyl acrylate yields rotaxane **4** having ferrocenyl groups at both ends of the axle molecule. The IR spectra of these compounds show peaks due to N–H vibrations (3162, 3073 cm⁻¹ for **3** and 3166, 3092 cm⁻¹ for **4**) at similar positions to **2b**. The reaction of 3,5-dimethylphenyl acrylate with **1b** in the presence of DB24C8 does not form the corresponding [2]rotaxane. Low yields of the cross-metathesis reaction of **2b** may be ascribed to steric hindrance by DB24C8 or low reactivity of the vinyl group attached to the aromatic ring. Acetylation of the



Scheme 3

ammonium group of **3** according to Takata's method[28] forms a neutral rotaxane **5** in 91% yield, as shown in Scheme 4. The IR peak of **5** at 1728 cm^{-1} is assigned to vibration of the C=O bond in the amide group. The ^{1}H NMR spectrum of **5** shows the signal of the vinylene hydrogens (δ 6.38, 7.71) at lower magnetic field positions than those of the corresponding signals of **3** (δ 6.13, 7.18). Reaction of **1a**, DB24C8 and $Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$ (see Fig. 4) ([**1a**] = 0.10 mmol, [DB24C8] = 0.14 mmol, [$Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$] = 0.05 mmol) forms [3]rotaxane **6**, having one ferrocenylene and two ferrocenyl groups in the axle component, in 50% yield (Scheme 5). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **6** in $CDCl_3$ indicate a symmetrical molecular structure.



5, 91%

Scheme 4

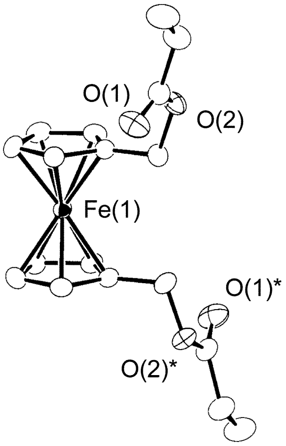


Fig. 4 ORTEP plot of $Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$ with 30% probability. Hydrogen atoms were omitted for clarity. Fe(1) lies on a crystallographic two fold axis. The asterisk in the atom labels indicates that these atoms are at equivalent positions (−*x*, *y*, 1/2 − *z*).

Table 1 Electrochemical data for ferrocene compounds[a]

Compound	E_{pa}/V	E_{pc}/V	$E_{1/2}$ (Δ*E*)/V
1a	0.52	0.42	0.47 (0.10)
3	0.50	0.43	0.47 (0.07)
4[b]	0.38, 0.49	0.34, 0.43	—
5	0.39	0.31	0.35 (0.08)
6	0.51[c]	0.45[c]	—
$Fe(C_5H_5)(C_5H_4CH_2OCOCH{=}CH_2)$	0.40	0.33	0.37 (0.07)
$Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$	0.51	0.45	0.48 (0.06)
Ferrocene	0.32	0.25	0.29 (0.07)

[a] Electrochemical potentials are obtained by cyclic voltammetry in MeCN containing $^nBu_4NPF_6$ as the electrolyte. Potentials are referenced to Ag^+/Ag. Sweep rate: 0.10 V s^{-1}. [b] Two step redox behavior. [c] Redox peaks of the Fe centers in the molecule are overlapped (see text).

The ferrocene-containing rotaxanes undergo reversible electrochemical oxidation and reduction. Electrochemical data for the compounds taken from the cyclic voltammograms are summarized in Table 1. Fig. 5(a) shows the cyclic voltammogram of **3** in a MeCN solution of $^nBu_4NPF_6$ (0.10 M) with scan rate 0.10 V s^{-1}. A reversible redox peak pair of Fe(III)/Fe(II) of the ferrocenyl group is observed at $E_{1/2}$ = 0.47 V (*vs.* Ag^+/Ag) which is similar to **1a**. The peak separation of **3**, Δ*E* = E_{pa} − E_{pc} = 0.07 V, however, is smaller than that of **1a** (Δ*E* = 0.10 V). The cyclic

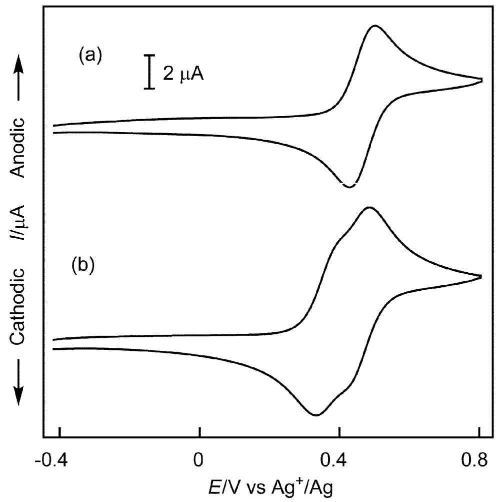
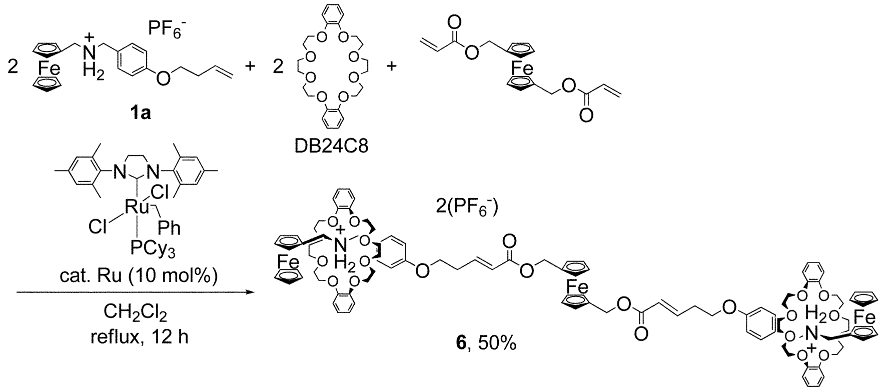


Fig. 5 Cyclic voltammograms of (a) **3** and (b) **4** in MeCN (1.0 mM) containing 0.10 M $^nBu_4NPF_6$.



Scheme 5

voltammogram of **4** shows two reversible waves (Fig. 5(b)). The peaks at higher potentials ($E_{pa} = 0.49$ V, $E_{pc} = 0.43$ V) are assigned to the ferrocene unit close to the ammonium group. The neutral rotaxane **5** shows a redox wave at a lower potential ($E_{1/2} = 0.35$ V) than that of the cationic rotaxanes, **3**, **4**, and **6**.[29] **6** shows an apparent reversible redox due to overlapping of peaks of three Fe centers. A linear relationship is observed between the peak currents I_{pa} and I_{pc} and square root of scan rate below 0.25 V s^{-1} (Fig. 6). Increase of the scan rate above 0.25 V s^{-1} causes quasi-reversible behavior of the redox reactions.[30]

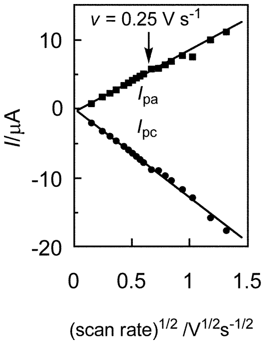


Fig. 6 Scan rate dependence of I_{pa} and I_{pc} of the cyclic voltammograms of **3** in MeCN (1.0 mM) containing 0.10 M $^{n}Bu_4NPF_6$.

In summary, we have succeeded in employing Ru-catalyzed cross-metathesis reactions of the terminal olefins (with acrylate as the end-cap) of [2]pseudorotaxane to afford the rotaxane. The electrochemical properties of the rotaxane with ferrocenyl groups in the axle component are similar to that of the precursor without the interlocked structure.

Experimental

General

Dried solvents were purchased from Kanto Chemical Co., Inc. *p*-Butenoxybenzylamine,[15] *p*-vinylbenzylamine,[31] 3,5-dimethylphenyl acrylate,[32] ferrocenylmethyl acrylate,[33] and ferrocene dimethanol[34] were prepared by the literature method. Other chemicals were commercially available. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, ^{13}C{^{1}H}–^{1}H COSY) were recorded on Varian MERCURY300 and JEOL EX-400 spectrometers. Chemical shifts were referenced with respect to $CHCl_3$ (δ 7.24), CD_2HCN (δ 1.93) for ^{1}H and $CDCl_3$ (δ 77.0), CD_3CN (δ 1.30) for ^{13}C as internal standards. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Cyclic voltammograms (CV) were measured in CH_3CN solution containing 0.10 M $^{n}Bu_4NPF_6$ using an ALS Electrochemical Analyzer Model-600A. The measurements were carried out in a standard one-compartment cell equipped with a Ag^+/Ag reference electrode, a platinum-wire counter electrode and a platinum-disk working electrode (ID: 1.6 mm). The fast atom bombardment mass spectra (FABMS) were obtained from a JEOL JMS-700 (matrix, *m*-nitrobenzylalcohol) spectrometer. Electrospray ionization mass spectrometry (ESIMS) was recorded on a ThermoQuest Finnigan LCQ Duo. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

Syntheses

$FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$. A solution of ferrocenecarboxaldehyde (1.1 g, 5.0 mmol) and $H_2NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ (886 mg, 5.0 mmol) in toluene (100 cm^3) was heated at 75 °C for 12 h in the presence of MS4A (molecular sieves 4 Å, 1.0 g). After removal of MS4A, evaporation of the solution to dryness produced $FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ as a brown solid which was washed with hexane (20 cm^3) (1.37 g, 3.7 mmol, 74%). Anal. calc. for $C_{22}H_{23}ONFe$: C, 70.79; H, 6.21; N, 3.75. Found: C, 70.82; H, 6.39; N, 3.66%. IR (KBr): $\nu = 1636$ (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 2.52 (m, 2H, OCH_2CH_2), 3.99 (t, 2H, OCH_2, $J = 7$ Hz), 4.15 (s, 5H, C_5H_5), 4.35 (m, 2H, C_5H_4), 4.58 (s, 2H, NCH_2), 4.66 (m, 2H, C_5H_4), 5.09 (dd, 1H, $CH{=}CH_2$, $J = 10, 2$ Hz), 5.15 (dd, 1H, $CH{=}CH_2$, $J = 17, 2$ Hz), 5.89 (ddt, 1H, $CH{=}CH_2$, $J = 17, 10, 7$ Hz), 6.87 (d, 2H, C_6H_4, $J = 8$ Hz), 7.19 (d, 2H, C_6H_4, $J = 8$ Hz), 8.19 (s, 1H, NCH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, r. t.): δ 33.6 (OCH_2CH_2), 64.4, 67.2, 68.6, 69.0 (C_5H_5), 70.4, 80.5 (C_5H_4), 114.6, 116.9, 129.0, 131.6, 134.5, 157.9, 161.7 (C=N).

$FcCH{=}NCH_2C_6H_4CH{=}CH_2$. A solution of ferrocenecarboxaldehyde (3.6 g, 17 mmol) and *p*-vinylbenzylamine (2.2 g, 17 mmol) in toluene (200 cm^3) was heated at 60 °C for 28 h in the presence of MS4A (4.5 g). After removal of MS4A, evaporation of the solution to dryness produced $FcCH{=}NCH_2C_6H_4CH{=}CH_2$ as a brown solid which was washed with hexane (50 cm^3) (3.4 g, 10 mmol, 59%). Anal. calc. for $C_{20}H_{19}NFe$: C, 72.97; H, 5.82; N, 4.25. Found: C, 72.81; H, 5.70; N, 4.25%. IR (KBr): $\nu = 1636$ (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 4.16 (s, 5H, C_5H_5), 4.36 (m, 2H, C_5H_4), 4.63 (s, 2H, NCH_2), 4.66 (m, 2H, C_5H_4), 5.20 (d, 1H, $CH{=}CH_2$, $J = 11$ Hz), 5.72 (d, 1H, $CH{=}CH_2$, $J = 18$ Hz), 6.69 (dd, 1H, CH, $J = 18, 11$ Hz), 7.25 (d, 2H, C_6H_4, $J = 8$ Hz), 7.38 (d, 2H, C_6H_4, $J = 8$ Hz), 8.22 (s, 1H, NCH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, r. t.): δ 64.5 (NCH_2), 68.3 (C_5H_4), 68.8 (C_5H_5), 70.2 (C_5H_4), 80.2 (C_5H_4), 113.2 ($CH{=}CH_2$), 126.0 (C_6H_4), 127.7 (C_6H_4), 135.9 (C_6H_4), 136.3 ($CH{=}CH_2$), 139.1 (C_6H_4), 161.8 (NCH). Assignment of these signals was supported by ^{13}C{^{1}H}–^{1}H COSY NMR spectroscopy.

$[FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CH_2](PF_6)$ (1a). $FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$ (1.1 g, 3.0 mmol) was dissolved in MeOH (25 cm^3) at room temperature. $NaBH_4$ (894 mg, 24 mmol) was added to the solution in one portion and the mixture was stirred for 2 h at room temperature. Quenching the mixture with 4 M HCl(aq) (75 cm^3) and further stirring for 30 min caused the separation of $[FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CH_2]Cl$ as a yellow solid from the solution. The solid product was washed with Et_2O (10 cm^3 × 2) and dried under reduced pressure (1.1 g, 2.7 mmol, 90%). To an acetone (25 cm^3) suspension of the obtained $[FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CH_2]Cl$ (823 mg, 2.0 mmol) was added NH_4PF_6 (1.7 g, 10 mmol) in acetone (25 cm^3), and the mixture was stirred for 2 h at room temperature. The precipitated salt was removed by filtration. Evaporation of the filtrate gave **1a** as a yellow solid which was washed with water (10 cm^3 × 5), and then with Et_2O (10 cm^3 × 5), and dried under reduced pressure (598 mg, 1.2 mmol, 60%). Anal. calc. for $C_{22}H_{23}ONFe$: C, 50.69; H, 5.03; N, 2.69. Found: C, 50.69; H, 5.39; N, 2.78%. IR (KBr): $\nu =$ 3260 (N–H), 3237 (N–H), 826 (P–F), 559 (P–F) cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN, r. t.): δ 2.50 (tddd, 2H, OCH_2CH_2, $J = 7$, 7, 1, 1 Hz), 4.02 (s, 2H, NCH_2), 4.04 (t, 2H, OCH_2, J = 7 Hz), 4.04 (s, 2H, NCH_2), 4.20 (s, 5H, C_5H_5), 4.27 (m, 2H, C_5H_4), 4.37 (m, 2H, C_5H_4), 5.08 (ddt, 1H, CH=CH_2, J = 10, 2, 1 Hz), 5.16 (ddt, 1H, CH=CH_2, J = 17, 2, 1 Hz), 5.91 (ddt, 1H, CH=CH_2, J = 17, 10, 7 Hz), 6.71 (brs, 2H, NH_2), 6.95 (d, 2H, C_6H_4, J = 9 Hz), 7.33 (d, 2H, C_6H_4, J = 9 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, r. t.): δ 34.2 (OCH_2CH_2), 48.5 (NCH_2), 51.5 (NCH_2), 68.2 (OCH_2), 69.9 (C_5H_5), 70.5 (C_5H_4), 71.4 (C_5H_4), 76.5 (C_5H_4), 115.8 (C_6H_4), 117.3 (CH=CH_2), 123.3 (C_6H_4), 132.6 (C_6H_4), 135.7 (C_6H_4), 160.8 (CH=CH_2). The assignments were supported by $^{13}C\{^1H\}$–^1H COSY NMR spectroscopy.

[$FcCH_2NH_2CH_2C_6H_4CH{=}CH_2$]($PF_6$) (1b). $FcCH{=}NCH_2$-$C_6H_4CH{=}CH_2$ (2.5 g, 7.6 mmol) was dissolved in MeOH (200 cm^3) at room temperature. $NaBH_4$ (289 mg, 7.6 mmol) was added to the solution and the mixture was stirred for 4 h at room temperature. An extra portion of $NaBH_4$ (290 mg, 7.6 mmol) was added, and the mixture was stirred for a further 14 h, before being treated with 4 M HCl(aq) (40 cm^3) for 30 min. After reducing the volume of the solution to *ca.* 100 cm^3 by evaporation, the solid product was partitioned between 2 M KOH(aq) (100 cm^3) and CH_2Cl_2 (100 cm^3). The aqueous layer was separated and extracted with CH_2Cl_2 (100 cm^3). The combined organic extracts were washed with water (200 cm^3) and dried over $MgSO_4$. Evaporation of the solvent gave $FcCH_2NHCH_2C_6H_4CH{=}CH_2$ as a brown oil (1.4 g, 4.3 mmol, 56%). A MeOH solution (40 cm^3) of the obtained $FcCH_2NHCH_2C_6H_4CH{=}CH_2$ (1.3 g, 4.0 mmol) was treated with 4 M HCl(aq) (30 cm^3) for 1 h at room temperature to afford a yellow solid which was collected by filtration. To an acetone (50 cm^3) suspension of the solid was added NH_4PF_6 (3.4 g, 21 mmol) in acetone (100 cm^3), and the mixture was stirred for 1 h at room temperature. The precipitated salt was removed by filtration and the evaporation of the filtrate gave **1b** as a yellow solid which was washed with water (20 cm^3 × 10) and then hexane (20 cm^3 × 5), and dried *in vacuo* (1.5 g, 3.1 mmol, 78%). Anal. calc. for $C_{20}H_{22}NFePF_6$: C, 50.34; H, 4.65; N, 2.94. Found: C, 49.95; H, 4.72; N, 2.86%. IR (KBr): ν = 3235 (N–H), 3260 (N–H), 847 (P–F) cm^{-1}. ^1H NMR (300 MHz, CD_3CN, r. t.): δ 4.06 (s, 2H, NCH_2), 4.10 (s, 2H, NCH_2), 4.21 (s, 5H, C_5H_5), 4.28 (m, 2H, C_5H_4), 4.38 (m, 2H, C_5H_4), 5.33 (dd, 1H, CH=CH_2, J = 11, 1 Hz), 5.86 (dd, 1H, CH=CH_2, J = 18, 1 Hz), 6.77 (brs, 2H, NH_2), 6.77 (dd, 1H, CH, J = 18, 11 Hz), 7.38 (m, 2H, C_6H_4), 7.51 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, r. t.): δ 48.9 (NCH_2), 51.6 (NCH_2), 70.0 (C_5H_5), 70.6 (C_5H_4), 71.5 (C_5H_4), 76.4 (C_5H_4), 116.2 (CH=CH_2), 127.7 (C_6H_4), 130.9 (C_6H_4), 131.4 (C_6H_4), 136.9 (CH=CH_2), 139.9 (C_6H_4). Assignment of these signals was supported by $^{13}C\{^1H\}$–^1H COSY NMR spectroscopy.

[($FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CH_2$)(DB24C8)]($PF_6$) (2a). An NMR tube was charged with **1a** (3.6 mg, 6.9 × 10^{-3} mmol) and DB24C8 (3.1 mg, 6.9 × 10^{-3} mmol) which were then dissolved in CD_3CN (0.7 cm^3). ^1H NMR quickly showed the formation of **2a**. ^1H NMR (300 MHz, CD_3CN, 20 °C): δ 2.44 (tddd, 2H, OCH_2CH_2, J = 7, 7, 2, 2 Hz), 3.55–4.21 (30H, C_5H_4, CH_2-DB24C8, OCH_2-axle), 3.93 (s, 5H, C_5H_5), 4.37 (m, 2H, NCH_2), 4.50 (m, 2H, NCH_2), 5.08† (1H, CH=CH_2, J = 10 Hz), 5.15 (ddt, 1H, CH=CH_2, J = 17, 2, 1 Hz), 5.89 (ddt, 1H, CH=CH_2, J = 17, 10, 7 Hz), 6.55 (d, 2H, C_6H_4-axle, J = 9 Hz), 6.86–6.92† (8H, C_6H_4-DB24C8), 7.14 (brs, 2H, NH_2), 7.17 (d, 2H, C_6H_4-axle, J = 9 Hz). Peaks with a dagger were significantly overlapped with the signals of **1a** and DB24C8. ESIMS: Calc. for $C_{46}H_{58}O_9NFe$: 824.3 Found: m/z = 824.1 [M − PF_6]$^+$.

[($FcCH_2NH_2CH_2C_6H_4CH{=}CH_2$)(DB24C8)]($PF_6$) (2b). An NMR tube was charged with **1b** (3.3 mg, 6.9 × 10^{-3} mmol) and DB24C8 (3.1 mg, 6.9 × 10^{-3} mmol) which were then dissolved in CD_3CN (0.7 cm^3). ^1H NMR showed the formation of **2b**. ^1H NMR (300 MHz, CD_3CN, 20 °C): δ 3.59 (m, 8H, CH_2-DB24C8), 3.79 (m, 8H, CH_2-DB24C8), 3.93 (s, 5H, C_5H_5), 4.02–4.16 (m, 10H, C_5H_4, CH_2-DB24C8), 4.18 (m, 2H, C_5H_4), 4.38 (m, 2H, NCH_2), 4.59 (m, 2H, NCH_2), 5.22 (dd, 1H, CH=CH_2, J = 11, 1 Hz), 5.67 (dd, 1H, CH=CH_2, J = 18, 1 Hz), 6.58 (dd, 1H, CH=CH_2, J = 18, 11 Hz), 6.90 (m, 8H, C_6H_4-DB24C8), 7.14 (d, 2H, C_6H_4, J = 8 Hz), 7.12–7.28 (br, 2H, NH_2), 7.25 (d, 2H, C_6H_4, J = 8 Hz). ESIMS: Calc. for $C_{44}H_{54}O_8NFe$: 780.3 Found: 780.3 [M − PF_6]$^+$.

Yellow crystals of **2b** were obtained by recrystallization from a CH_2Cl_2–Et_2O solution of **1b**–DB24C8 (**1b**–DB24C8 = 48 : 55 mg) at room temperature (13% yield). Anal. calc. for $C_{44}H_{54}O_8NFePF_6$: C, 57.09; H, 5.88; N, 1.51. Found: C, 57.18; H, 5.65; N, 1.46%. IR (KBr): ν = 3156 (N–H), 3085 (N–H), 840 (P–F) cm^{-1}.

[($FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CHCOOC_6H_3$-3,5-$Me_2$)-(DB24C8)]($PF_6$) (3). **1a** (52 mg, 0.10 mmol) was dissolved in 2 cm^3 of CH_2Cl_2 containing DB24C8 (54 mg, 0.12 mmol), followed by addition of 3,5-dimethylphenyl acrylate (35 mg, 0.20 mmol) and Ru catalyst (4.2 mg, 5 × 10^{-3} mmol). The mixture was refluxed for 15 h and the solvent was removed by evaporation to form a brown oil. Reprecipitation of the crude product from CH_2Cl_2–Et_2O (2.5 : 30 cm^3) gave a brown solid which was collected, washed with Et_2O (10 cm^3 × 2) and dried under reduced pressure to give **3** (80 mg, 0.072 mmol, 72%). Anal. calc. for $C_{55}H_{66}O_{11}NF_6FeP(H_2O)$: C, 58.15; H, 6.03; N, 1.23. Found: C, 57.87; H, 6.12; N, 1.24%. IR (KBr): ν = 3162 (N–H), 3073 (N–H), 1734 (C=O), 841 (P–F), 558 (P–F) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, r. t.): δ 2.29 (s, 6H, Me), 2.73 (br, 2H, CH_2CH=CH), 3.41–3.85 (16H, CH_2-DB24C8), 4.01–4.50 (21H, NCH_2, C_5H_5, C_5H_4, OCH_2-axle, CH_2-DB24C8), 4.60 (br, 2H, NCH_2), 6.13 (d, 1H, C(=O)CH, J = 15 Hz), 6.70–6.72 (4H, C_6H_4-axle, C_6H_3), 6.85 (s, 1H, C_6H_3), 6.88–6.97 (8H, C_6H_4-DB24C8), 7.23 (d, 1H, CH_2CH), 7.34 (br, 2H, C_6H_4-axle), 7.35 (br, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, r. t.): δ 21.3 (Me), 32.1 (CHCH_2), 47.7 (NCH_2), 51.6 (NCH_2), 65.9 (OCH_2-axle), 68.5 (CH_2-DB24C8), 68.8 (C_5H_5), 69.4 (C_5H_4), 69.7 (C_5H_4), 70.3 (CH_2-DB24C8), 70.8 (CH_2-DB24C8), 113.0, 114.5, 119.1, 121.8, 122.7, 124.4, 127.4, 131.0, 139.1, 147.0, 147.6, 150.5, 159.0, 164.8 (C=O). C_5H_4-*ipso* was not observed due to their low intensity. Assignment of these signals was supported by ^1H–^1H and $^{13}C\{^1H\}$–^1H COSY NMR spectroscopy. ESIMS: Calc. for $C_{55}H_{68}O_{12}NFe$: 972.4. Found: m/z = 972.5 [M − PF_6]$^+$.

[($FcCH_2NH_2CH_2C_6H_4OCH_2CH_2CH{=}CHCOOCH_2Fc$)(DB24-C8)]($PF_6$) (4). **1a** (52 mg, 0.10 mmol) and DB24C8 (54 mg, 0.12 mmol) was dissolved in 2 cm^3 of CH_2Cl_2 followed by addition of $FcCH_2OCOCHCH_2$ (54 mg, 0.20 mmol) and Ru catalyst (4.2 mg, 5 × 10^{-3} mmol). The mixture was refluxed for 15 h. Repeated recrystallization of the crude product from CH_2Cl_2–Et_2O gave **4** (42 mg, 0.035 mmol, 35%). Anal. calc. for $C_{58}H_{68}O_{11}NFe_2PF_6(H_2O)$: C, 56.64; H, 5.74; N, 1.14. Found: C, 56.80; H, 5.88; N, 1.18%. IR (KBr): ν = 3166 (N–H), 3092 (N–H),

Table 2 Crystallographic data and structural refinement details

	$FcCH{=}NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$	**2b**	$Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$
Chemical formula	$C_{22}H_{23}FeNO$	$C_{44}H_{54}F_6FeNO_8P$	$C_{18}H_{18}FeO_4$
Molecular weight	373.28	925.72	354.18
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$ (no. 4)	$P2_1/a$ (no. 14)	$C2/c$ (no. 15)
a/Å	19.257(3)	38.521(4)	22.261(5)
b/Å	8.287(2)	10.253(2)	7.449(3)
c/Å	5.8376(7)	11.378(1)	11.557(3)
$\beta/°$	95.48(1)	96.222(8)	119.67(2)
V/Å^3	927.3(3)	4467(1)	1665.1(8)
Z	2	4	4
$F(000)$	392.00	1936.00	736.00
D_c/g cm^{-1}	1.337	1.376	0.921
Crystal size/mm	0.30 × 0.20 × 0.15	0.60 × 0.30 × 0.20	0.20 × 0.15 × 0.10
Unique reflections	2278	10267	1919
Used reflections	1894 [$I \geq 2.0\sigma(I)$]	3536 [$I \geq 3.0\sigma(I)$]	1439 [$I \geq 2.0\sigma(I)$]
No. of variables	250	604	114
R	0.074	0.058	0.039
R_w	0.107 [$I \geq 2.0\sigma(I)$]	0.091 [$I \geq 3.0\sigma(I)$]	0.055 [$I \geq 2.0\sigma(I)$]
Goodness of fit	1.31	0.96	1.00
Flack parameter	−0.1(2)	—	—

1717 (C=O), 841 (P–F), 558 (P–F) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 2.59 (m, 2H, $CH_2CH{=}CH$), 3.42–4.53 (42H, CH_2-DB24C8, C_5H_4, C_5H_5, $OCH_2C_5H_4$), 3.93 (2H, OCH_2CH_2CH), 4.07 (2H, NCH_2), 4.53 (2H, NCH_2), 4.68 (2H, C_5H_4), 5.82 (d, 1H, CH_2CH, J = 16 Hz), 6.65 (d, 2H, C_6H_4, J = 8 Hz), 6.85–6.91 (9H, C_6H_4-DB24C8, C(=O)H), 7.17 (brs, 2H, NH_2), 7.27 (d, 2H, C_6H_4-axle, J = 8 Hz). Signals observed at 3.4–4.6 ppm were overlapped significantly. Selected $^{13}C\{^1H\}$ NMR data (100 MHz, $CDCl_3$, r. t.): δ 31.9 ($CHCH_2$), 48.5 (NCH_2), 51.7 (NCH_2), 62.1, 62.2, 65.7 (OCH_2), 68.4 (CH_2-DB24C8), 70.3 (CH_2-DB24C8), 70.8 (CH_2-DB24C8), 112.8 (C_6H_4-DB24C8), 114.2 (C_6H_4-axle), 121.7, 122.6 (C_6H_4-DB24C8), 124.2, 130.7 (C_6H_4-axle), 144.7, 147.4, 158.8, 165.3 (C=O). Some of the signals due to the ferrocenyl groups were observed as a broad signal at 69–71 ppm. Assignment of these signals was supported by ^1H–^1H and $^{13}C\{^1H\}$–^1H COSY NMR spectroscopy. ESIMS: Calc. for $C_{58}H_{68}O_{11}NFe_2$: 1066.3 Found: m/z = 1066.5 $[M - PF_6]^+$.

[(FcCH$_2$N(OAc)CH$_2$C$_6$H$_4$OCH$_2$CH$_2$CH=CHCOOC$_6$H$_3$-3,5-Me$_2$)(DB24C8)] (5). To a solution of rotaxane **3** (112 mg, 0.10 mmol) in MeCN (4.0 cm^3) were added triethylamine (70 μL, 0.50 mmol) and acetic anhydride (47 μL, 0.50 mmol), and the reaction mixture was allowed to stand at room temperature for 26 h. The reaction mixture was diluted by CH_2Cl_2 (4.0 cm^3), washed with water (5.0 cm^3 × 3), dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by preparative HPLC to give **5** (98 mg, 0.091 mmol, 91%). IR (KBr): ν = 1728 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 2.03 (s, 2H, COMe), 2.22 (s, 1H, COMe), 2.27 (s, 6H, $C_6H_3(CH_3)_2$), 3.13 (m, 2H, OCH_2CH_2-axle), 3.52–3.67 (8H, CH_2-DB24C8), 3.74–3.94 (8H, CH_2-DB24C8), 4.05–4.41 (23H, CH_2-DB24C8, OCH_2CH_2-axle, C_5H_4, C_5H_5, NCH_2), 6.38 (d, 1H, C(=O)CH, J = 16 Hz), 6.60 (s, 2H, *ortho*-C_6H_3), 6.66–6.90 (13H, C_6H_4-DB24C8, *para*-C_6H_3, C_6H_4-axle), 7.71 (dt, 1H, CH_2CH, J = 16, 7 Hz). HRFABMS: Anal. calc. for $C_{57}H_{67}NO_{12}Fe$: 1013.4014. Found: m/z = 1013.3987 $[M]^+$.

Fe(C$_5$H$_4$CH$_2$OCOCH=CH$_2$)$_2$. To a solution of $Fe(C_5H_4CH_2OH)_2$ (246 mg, 1.0 mmol) and NEt_3 (1.0 cm^3) in CH_2Cl_2 (7.0 cm^3) was added acryloyl chloride (222 mg, 2.5 mmol) at 0 °C. After stirring the mixture for 2 h at 0 °C, the insoluble solid was removed by filtration. The solution was washed with an aqueous solution of 0.1 M KOH and then with water, and dried over $MgSO_4$. The product was purified by chromatography on silica gel with hexane–ethyl acetate (10 : 1) as eluent. The solvent was removed at reduced pressure to give $Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$ as a yellow solid (87 mg, 0.25 mmol, 25%). Anal. calc. for $C_{18}H_{18}O_4Fe$: C, 61.04; H, 5.12. Found: C, 60.76; H, 4.92%. IR (KBr): ν = 1711 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 4.19 (br, 4H, C_5H_4), 4.28 (br, 4H, C_5H_4), 4.93 (s, 4H, OCH_2), 5.81 (dd, 1H, $CH{=}CH_2$, J = 10, 1 Hz), 6.09 (dd, 1H, $CH{=}CH_2$, J = 17, 10 Hz), 6.40 (dd, 2H, $CH{=}CH_2$, J = 17, 1 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, r. t.): δ 62.4 (CH_2), 69.3 (C_5H_4), 70.0 (C_5H_4), 81.9 (C_5H_4), 128.3, 130.9, 165.9 (C=O). Fig. 4 shows the molecular structure of $Fe(C_5H_4CH_2OCOCH{=}CH_2)_2$ determined by X-ray crystallography.

[{(FcCH$_2$NH$_2$CH$_2$C$_6$H$_4$OCH$_2$CH$_2$CH=CHCOOCH$_2$C$_5$H$_4$)$_2$-Fe}(DB24C8)$_2$](PF$_6$)$_2$ (6). **1a** (52 mg, 0.10 mmol) and DB24C8 (63 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (2.0 cm^3), followed by addition of $Fe(C_5H_4CH_2COOCHCH_2)_2$ (18 mg, 0.051 mmol) and Ru catalyst (8.5 mg, 1 × 10^{-2} mmol). The mixture was refluxed for 12 h and the solvent was removed by evaporation to form a brown oil. Purification of the crude product by preparative HPLC gave **6** (56 mg, 0.025 mmol, 50%). IR (KBr): ν = 3164 (N–H), 3081 (N–H), 1717 (C=O), 843 (P–F), 558 (P–F) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, r. t.): δ 2.61 (m, 4H, CH_2CH), 3.40–3.61 (16H, CH_2-DB24C8), 3.67–3.84 (16H, CH_2-DB24C8), 3.82 (s, 10H, C_5H_5), 3.94 (t, 4H, CH_2CH_2CH, J = 6 Hz), 3.99–4.19 (32H, CH_2-DB24C8, NCH_2, C_5H_4), 4.25 (m, 4H, C_5H_4), 4.52 (m, 4H, NCH_2), 4.91 (s, 4H, $OCH_2C_5H_4$), 5.91 (d, 2H, C(=O)H, J = 16 Hz), 6.64 (d, 4H, C_6H_4-axle, J = 8 Hz), 6.82–6.91 (16H, C_6H_4-DB24C8), 7.02 (dt, 2H, CH_2CH, J = 16, 7 Hz), 7.13 (br, 4H, NH$_2$), 7.23–7.26† (4H, C$_6$H$_4$-axle). The peak with a dagger was overlapping significantly with the signal of the solvent. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, r. t.): δ 31.9 (*C*H$_2$CH), 48.6 (NCH$_2$), 51.6 (NCH$_2$), 62.3 (O*C*H$_2$C$_5$H$_4$), 65.8 (*C*H$_2$CH$_2$CH), 68.3 (CH$_2$-DB24C8), 68.8 (C$_5$H$_5$), 69.3 (C$_5$H$_4$), 69.4 (C$_5$H$_4$), 69.9 (C$_5$H$_4$), 70.0 (C$_5$H$_4$), 70.3 (CH$_2$-DB24C8), 70.7 (CH$_2$-DB24C8), 76.3 (C$_5$H$_4$), 82.3 (C$_5$H$_4$), 112.8 (C$_6$H$_4$-DB24C8), 114.3 (C$_6$H$_4$-axle), 121.7 (C$_6$H$_4$-DB24C8), 123.0 (C(=O)*C*H), 124.2 (C$_6$H$_4$-axle), 130.8 (C$_6$H$_4$-axle), 145.4 (CH$_2$*C*H), 147.6 (C$_6$H$_4$-DB24C8-*ipso*), 158.9 (C$_6$H$_4$-axle), 165.9 (C=O). Assignment of these signals was supported by ^{1}H–^{1}H and ^{13}C{^{1}H}–^{1}H COSY NMR spectroscopy. ESIMS: Calc. for C$_{106}$H$_{126}$N$_2$O$_{22}$Fe$_3$: 1946.7 Found: $m/z = 974.0$ [M − 2(PF$_6$)]$^{2+}$.

Crystal structure determination

Crystals of FcCH=NCH$_2$C$_6$H$_4$OCH$_2$CH$_2$CH=CH$_2$, **2b**, and Fe(C$_5$H$_4$CH$_2$OCOCH=CH$_2$)$_2$ suitable for X-ray diffraction study were obtained by recrystallization from Et$_2$O, CH$_2$Cl$_2$–Et$_2$O, and CH$_2$Cl$_2$–Et$_2$O respectively and mounted on a glass capillary tube. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. The data were collected using the ω scan technique to a maximum 2θ value of 55.0°. Calculations were carried out by using a program package CrystalStructure™ for Windows.[35] Crystal data for the compounds are summarized in Table 2.

Details of the structure of **2b** (CCDC reference number 292617) have already been published[23] and the details of the structure of **2b** are in the CCDC as REFCODE WECVUW.

CCDC reference numbers 637664 (FcCH=NCH$_2$C$_6$H$_4$O-CH$_2$CH$_2$CH=CH$_2$) and 637665 (Fe(C$_5$H$_4$CH$_2$OCOCH=CH$_2$)$_2$).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702785k

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