PERKIN 2

A novel solvatochromic 2-nitroacrylonitrile derived from octamethylferrocenecarbaldehyde

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Octamethylferrocenecarbaldehyde reacts with excess nitromethane in the presence of potassium *tert*-butanoxide to give, after silylation and hydrolysis, 2-nitro-3-(octamethylferrocenyl)acrylonitrile in moderate yield. This compound exhibits visible positive solvatochromism. The molar transition energies E_T in 26 different solvents are correlated with the dipolarity-polarizability parameter π^* and the hydrogen bond donor acidity α. The results from temperature-dependent Mössbauer spectroscopy suggest that the cyclopentadienyl ring rotation and libration ('gear wheel' effect) is inhibited up to a temperature within a few degrees below the melting point, presumably due to the steric requirements of the side chain. The crystal structure has been determined.

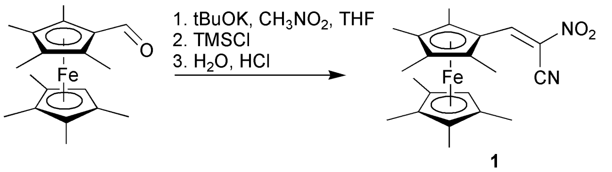
Introduction

Ferrocene based donor-acceptor type chromophores[1] are a current topic in research, *e.g.* as non-linear optical (NLO) materials.[2] Second harmonic generation by molecules containing conjugated bridges between ferrocene and nitro groups[3] and redox-switchable NLO properties[4] are key features of such donor-acceptor assemblies. The donor strength of the metallocene is enhanced by introduction of alkyl groups as in octamethylferrocene (OMF). An inviting concept to achieve novel molecular devices is the vinylenic elongation and terminal functionalisation of readily accessible, versatile starting chemicals like OMF carbaldehyde. In the course of our ongoing studies of conjugated ferrocenes,[5] we obtained an unexpected but very interesting product. A simple one-pot synthesis of the novel 2-nitro-3-(octamethylferrocenyl)acrylonitrile (**1**) is reported, and the structural and spectroscopic data of this new compound are presented.

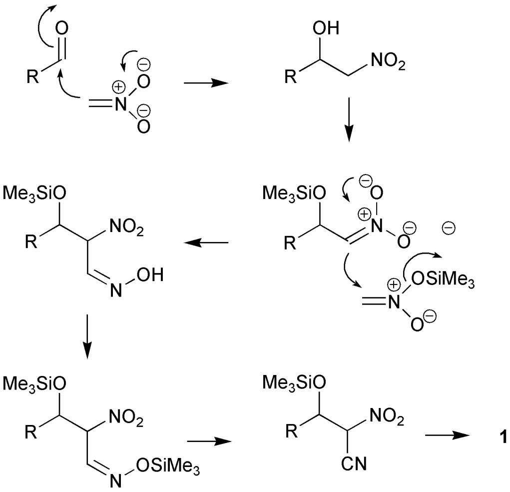
Results and discussion

Proposed reaction mechanism

It was found that OMF carbaldehyde reacted with excess nitromethane in the presence of two equivalents potassium *tert*-butanoxide to give, after silylation and hydrolysis, (*E*)-2-nitro-3-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)acrylonitrile (**1**) (Scheme 1). The first step in the proposed reaction pathway (Scheme 2) is assumed to be a conventional nitro-aldol addition, followed after silylation by attack of the mono-silyl nitronate at the deprotonated nitro-aldol leading to an oxime[6] [the formation of a bis(trimethylsilyl) nitronate is reportedly[7] very slow with chlorotrimethylsilane as a silylating agent]. The oxime is transformed into the nitrile by an excess of base and silylating agent. Elimination during work-up finally yields the unsaturated **1** as the only isolable product, albeit in modest yield. The conversion of a nitro compound into an unsaturated nitrile by a cascade of silylations and eliminations, which bears some resemblance to the present reaction, has been reported recently.[8] To our knowledge, however, the one-pot reaction described here represents an unprecedented sequence of normal and reversed reactivity of nitromethane which holds promise for broader synthetic applicability.



Scheme 1 Preparation of **1** from octamethylferrocenecarbaldehyde and nitromethane.



Scheme 2 Proposed reaction pathway; R = octamethylferrocenyl.

Solvatochromism

Compound **1** exhibits visible positive solvatochromism:[9] blue in heptane, green in dimethyl sulfoxide. The absorption spectrum shows two bands in the visible region. The low-energy transition is assigned as a metal to ligand charge transfer and the high-energy transition as an intraligand charge transfer excitation.[10] The low-energy band is shifted bathochromically

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Table 1 Electronic absorption maxima and molar transition energies for **1** in different solvents

Solvent	π^{*a}	α^a	λ_{max1}/nm	λ_{max2}/nm	E_{T1}/kJ mol^{-1}	E_{T2}/kJ mol^{-1}
Non-HBD solvents						
Dimethyl sulfoxide	1.00	0	408	646	293.2	185.2
Dimethylformamide	0.88	0	403	644	296.8	185.8
Dimethylacetamide	0.88	0	402	641	297.6	186.6
Pyridine	0.87	0	405	643	295.4	186.0
Benzene	0.59	0	395	631	302.8	189.6
Tetrahydrofuran	0.58	0	396	628	302.1	190.5
Dioxane	0.55	0	392	624	305.2	191.7
Ethyl acetate	0.55	0	392	625	305.2	191.4
Toluene	0.54	0	394	621	303.6	192.6
Butyl acetate	0.46	0	389	623	307.5	192.0
Tetrachloromethane	0.28	0	386	613	309.9	195.1
Diethyl ether	0.27	0	387	616	309.1	194.2
Triethylamine	0.14	0	383	611	312.3	195.8
Cyclohexane	0.00	0	379	600	315.6	199.4
Hexane	−0.04	0	376	599	318.2	199.7
Heptane	−0.08	0	376	598	318.2	200.0
Non-hydroxylic HBD solvents						
Formamide	0.97	0.71	408	645	293.2	185.5
Dichloromethane	0.82	0.13	403[b]	640[c]	296.8	186.9
Acetonitrile	0.75	0.19	401	640	298.3	186.9
Acetone	0.71	0.08	399	636	299.8	188.1
Butan-2-one	0.67	0.06	397	633	301.3	189.0
Hydroxylic HBD solvents						
Methanol	0.60	0.98	396	633	302.1	189.0
Ethanol	0.54	0.86	397	634	301.3	188.7
Propan-2-ol	0.48	0.76	394	631	303.6	189.6
Butan-1-ol	0.47	0.84	394	628	303.6	190.5
tert-Butyl alcohol	0.41	0.42	394	622	303.6	192.3
Δ (DMSO–heptane)			32	48	−25.0	−14.8

[a] Values taken from ref. 17. [b] Log (ε/dm^3 mol^{-1} cm^{-1}) = 4.09. [c] Log (ε/dm^3 mol^{-1} cm^{-1}) = 3.54.

48 nm and the high-energy band 32 nm on changing the solvent from heptane to dimethyl sulfoxide, indicative of increased polarity in the excited state. This solvatochromic shift is slightly more than the one observed for the related (*E*)-2-nitroethenylferrocene[11] (312 and 496 nm in heptane, 337 and 543 nm in DMSO). The electronic absorption maxima in 26 different solvents and the corresponding molar transition energies E_T, as calculated by eqn. (1), are summarized in Table 1.

$$E_T/\text{kJ mol}^{-1} = hcN/\lambda = 119625/(\lambda/\text{nm}) \qquad (1)$$

For non-hydrogen bond donor (non-HBD) solvents excellent correlations of the transition energies with the dipolarity-polarizability parameter π^*[12] alone are obtained. The coefficient of correlation for the high-energy transition [eqn. (2)] is r = 0.992, standard deviation is σ = 1.0 kJ mol^{-1}; for the low-energy transition [eqn. (3)] r = 0.991 and σ = 0.7 kJ mol^{-1}.

$$E_{T1}/\text{kJ mol}^{-1} = 316.29–22.49\pi^* \qquad (2)$$

$$E_{T2}/\text{kJ mol}^{-1} = 198.84–14.16\pi^* \qquad (3)$$

Inclusion of non-hydroxylic HBD solvents does not change the quality of the correlation significantly. However, when hydroxylic solvents are included, a dual linear free energy relationship which takes the HBD acidity α[13] into account [eqn. (4)] is required to improve the fit.

$$XYZ = (XYZ)_0 + s\pi^* + a\alpha \qquad (4)$$

Thus, by analysis of the spectroscopic data in the 26 solvents used, the following solvatochromic eqns. (5) and (6) were derived.

$$E_{T1}/\text{kJ mol}^{-1} = 316.12–22.42\pi^*–2.26\alpha \qquad (5)$$

$$E_{T2}/\text{kJ mol}^{-1} = 198.67–13.97\pi^*–1.86\alpha \qquad (6)$$

The correlation between calculated and measured data is excellent, with r = 0.990 and standard deviation σ = 1.0 kJ mol^{-1} for eqn. (5), r = 0.987 and σ = 0.7 kJ mol^{-1} for eqn. (6). The s/a ratio is 9.9 and 7.5, respectively, indicating that the probe **1** registers mainly the dipolarity-polarizability of its environment but is not completely insensitive to hydrogen bonding, either.

Mössbauer spectroscopy

As is true of all diamagnetic ferrocene-related complexes, the ^{57}Fe Mössbauer resonance spectra of **1** consist of a well resolved doublet with no evidence of more than one iron site. The temperature dependence of the isomer shift, IS(90 K)/mm s^{-1} = 0.531(2), shows some curvature over the entire range (90 ≤ T ≤ 330 K) but the data over the range 150 ≤ T ≤ 320 are reasonably fit by a linear regression with a slope of (dIS/dT)/mm s^{-1} K^{-1} = − (4.16 ± 0.07) × 10^{-4} and a correlation coefficient of 0.994 for 9 data points. This value leads to an effective vibrating mass, M_{eff}/Da = 100, similar to the values reported for related ferrocenyl complexes.[14] The quadrupole splitting, QS(90 K)/mm s^{-1} = 2.132(4), is essentially temperature-independent over the entire temperature range. The temperature dependence of the recoil-free fraction, as extracted from the area under the resonance curve, again shows some curvature over the entire range (up to 330 K). The data over the range 150 ≤ T ≤ 330 K are reasonably well fit by a linear regression, with a slope of dln[$A(T)/A$(90 K)]/d(T/K^{-1}) = −(9.33 ± 0.39) × 10^{-3} and a correlation coefficient of 0.992 for 9 data points. This value, in conjunction with the −dIS/dT value quoted above, leads to a Mössbauer lattice temperature of ~91

K. The data acquired at 350 K show a sudden diminution in ln *A* (the resonance effect magnitude is only 0.14%, but in excess of 13.9 million counts per channel were accumulated in this experiment) indicating a major increase in the mean-square-amplitude of the metal atom vibration (MSAV) at this temperature. However, it should be noted that this decrease in ln *A* occurs at a reduced temperature, $T_R = T/T_{mp}$, of 0.96, in contrast to the behaviour noted for other octamethylferrocene complexes reported earlier (Fig. 1).[15] These results suggest that the onset of cyclopentadienyl (Cp) ring rotation and libration ('gear wheel' effect), which leads to a large increase in MSAV at temperatures well below T_{mp} for octamethylferrocene, nonamethylferrocene, ethynyl(octamethyl)ferrocene, and ethenyl(octamethyl)ferrocene,[14] is inhibited in **1**, presumably due to the steric requirements of the side chain carrying the cyano and nitro substituents as well as dipole–dipole interactions in the lattice. The presence of a hydrogen substituted ring site in one of the Cp rings notwithstanding, the iron atom does not participate in an anomalous vibrational behaviour until a temperature within a few degrees of T_{mp} (363 K) is reached. A similar observation has been made in the case of octamethylferrocenylacetonitrile, in which the ln *A*(*T*) characteristics are very similar to those in **1**, suggesting that a three-atom side chain on one of the two Cp rings is sufficient to inhibit significantly the 'anomalous' ln *A*(*T*) behaviour observed in the ethynyl and ethenyl analogues. Finally, it is worth noting that over the available temperature range (to 0.96 T_R), there is no evidence of significant vibrational anisotropy (Gol'danskii–Karyagin effect) observable in **1**, and thus it is inferred that the iron atom motion is essentially isotropic, at least up to 333 K.

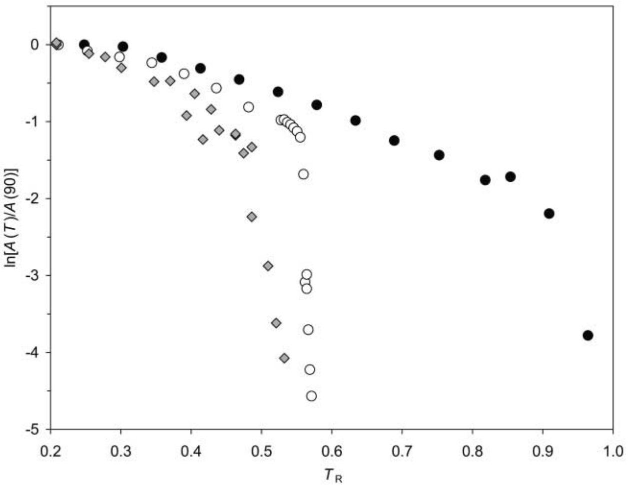

Fig. 1 Dependence of the recoil-free fraction (related to the mean square-amplitude of vibration) on reduced temperature ($T_R = T/T_{mp}$) in three related OMF complexes. The 'gear wheel' effect is clearly demonstrated in ethenyl OMF (◇) and ethynyl OMF (○), and absent in **1** (●).

Molecular structure

Compound **1** crystallizes in a centrosymmetric space group with two independent molecules in the asymmetric unit (Fig. 2). Both molecules are nearly identical except the position of the Cp ring, where the atom C(1) of the second molecule is moved in the direction of C(4) by rotation. As a result of steric hindrance between the nitroacrylonitrile group and a methyl group of the Cp ring, the angles C(9)–C(10)–C(11), C(10)–C(11)–C(12) and C(11)–C(12)–C(13) are increased over 130°. The influence of the acceptor groups at the ethene group can be seen in the increased length of the double bond C(11)–C(12) (136.0 pm) and in the shortening of the single bond C(10)–C(11) to the OMF donor group (141.2 pm). These differences in the bond lengths are in the range of 3 pm compared with other OMF-ethenes with less electron-withdrawing groups at the double bond. The conformational rigidity observed by Mössbauer spectroscopy is reflected in the small size of the thermal ellipsoids of the methyl groups in the substituted Me_4Cp ring of the metallocene.

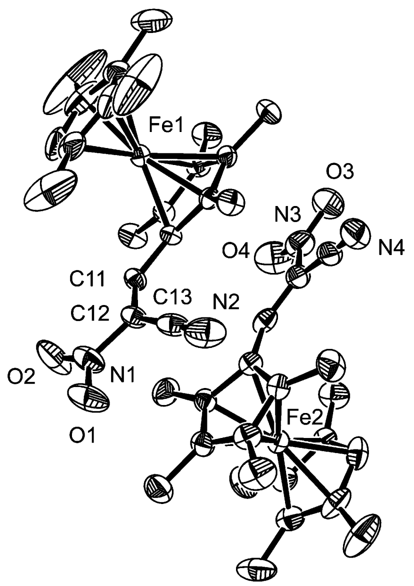

Fig. 2 ORTEP plot of **1** showing 50% thermal ellipsoids. Selected bond lengths (pm) and angles (°), values in square brackets are from the second independent molecule: N(1)–O(1) 123.3(4) [123.0(5)], N(1)–O(2) 122.6(5) [122.8(5)], N(1)–C(12) 145.1(5) [147.1(6)], N(2)–C(13) 114.8(5) [114.2(6)], C(12)–C(13) 141.7(6) [141.3(7)], C(11)–C(12) 136.0(5) [135.6(6)], C(10)–C(11) 141.2(5) [142.0(5)], C(9)–C(10) 144.7(5) [144.8(5)], C(6)–C(10) 147.0(5) [146.3(5)], C(11)–C(10)–C(9) 132.7(3) [132.4(4)], C(12)–C(11)–C(10) 134.5(4) [135.0(4)], C(11)–C(12)–C(13) 130.5(4) [129.9(4)].

Thus, an integrated approach was undertaken in which different techniques contribute to an overall understanding of structure, metal atom motion, conformational dynamics, and solvatochromism of a short donor-acceptor conjugate originating from an interesting sequence of reactions.

Experimental

General

The solvents were purchased in the highest available purity (Merck, Fluka, Aldrich). UV-VIS spectra were recorded using a Shimadzu UV-160A spectrophotometer which was calibrated with a solution of holmium perchlorate according to the British Pharmacopoeia, and infrared spectra were obtained on a Nicolet 510 FT-IR instrument. Mass spectra were measured with a MAT 95 (FAB) spectrometer, and NMR spectra were recorded on a Bruker AC 200 spectrometer. *J* values are given in Hz.

Synthesis of (*E*)-2-nitro-3-(1′,2,2′,3,3′,4,4′,5-octamethylferrocenyl)acrylonitrile (1)

To a solution of 1′,2,2′,3,3′,4,4′,5-octamethylferrocene-1-carbaldehyde (0.350 g, 1.07 mmol) in anhydrous THF (15 ml), nitromethane (0.17 ml, 3.22 mmol) was added. The solution was cooled to 0 °C and *t*BuOK (0.252 g, 2.26 mmol) was added. The mixture was refluxed overnight, then cooled again to 0 °C, and chlorotrimethylsilane (0.48 ml, 3.75 mmol) was added. After being stirred for 6 h at room temperature, the reaction was quenched with hydrochloric acid (30 ml 0.1 M) and the organic solvent was removed *in vacuo*. The resulting suspension was extracted with diethyl ether, the ethereal layer was washed with 50 ml water and dried over Na_2SO_4. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to yield **1** (0.093 g, 22 %) as a green solid, mp 90–92 °C (Found: C, 64.10; H, 6.76; N, 6.98. $C_{21}H_{26}FeN_2O_2$ requires C, 63.97; H, 6.65; N, 7.10); ν_{max}(KBr)/cm^{-1} 2966w, 2910w, 2220m, 1588s, 1275s, 1028m; δ_H(200 MHz; $CDCl_3$; Me_4Si) 1.60 (6H, s, Me), 1.62 (6H, s, Me), 1.92 (6H, s, Me), 1.94 (6H, s, Me), 3.50 (1H, s, CpH), 8.57 (1H, s, CH=C); HR-MS (FAB): *m*/*z* 394.1366 (M^+); $C_{21}H_{26}FeN_2O_2$ requires 394.1344.

Mössbauer spectroscopy

A sample of the neat solid was ground with BN to ensure random crystallite orientation, and transferred to a plastic sample holder. The ^{57}Fe thickness was ~4.5 × 10^{17} cm^{-2} and thus constituted an optically 'thin' absorber. This was mounted in the Mössbauer cryostat and examined in transmission geometry using a ~50 mCi ^{57}Co(Rh) source at room temperature. Details of temperature control, data reduction, and error analysis have been discussed previously.[16] All isomer shift data are with respect to the centroid of a room temperature α-Fe absorber spectrum, which was also used for spectrometer calibration.

Crystal structure determination

Single crystals were obtained by cooling a hot solution of **1** in *n*-hexane. Data were measured *via* ω-scans in the 2θ range 5–22° using a Bruker P4 diffractometer, Mo-Kα (λ = 0.71073 Å), and corrected for Lorentz and polarisation effects. Structure solution was by direct methods (SHELXS-86) and refinement against F^2 (SHELXL-93). Hydrogen atoms were placed in calculated positions. CCDC reference number 178357. See http://www.rsc.org/suppdata/p2/b2/b203395j/ for crystallographic files in .cif or other electronic format.

Crystal data

$C_{21}H_{26}FeN_2O_2$, M_r = 394.29, green crystal with size of 0.5 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/n$ (No.14), a = 13.540(2), b = 16.289(6), c = 17.898(3) Å, β = 101.35(1)°, V = 3870(2) Å^3, Z = 8, F(000) = 1664, ρ_{calcd} = 1.353 g cm^{-3}, T = 213 K, μ = 0.796 mm^{-1}; of 4836 reflections collected, 4493 were independent and 3410 with $I > 2\sigma(I)$; R_1 = 0.0406, wR_2 = 0.0892. GOF = 1.036.

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