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Synthesis and long wavelength hyper-Rayleigh scattering measurements of extended μ-vinylidene di-iron donor based organometallic merocyanines☆

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Dedicated to Professor Dr. Dieter Sellman on the occasion of his 60th Birthday

Abstract

The synthesis is reported of a series of extended π-bridged organometallic merocyanines linking the dicyanovinyl electron accepting group with the electron donating $[(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH\text{–})]$ fragment. The chromophores exhibited inverse solvatochromic shifts with increased medium polarity, which is because of interactions between dipolar or protic solvents and the dicyanovinyl unit. The nonlinear optical (NLO) properties of the chromophores have been investigated using long wavelength (1500 nm) hyper-Rayleigh scattering techniques to avoid both resonance and two-photon absorption enhancement of the first hyperpolarisabilities. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organometallic; Merocyanine; Dicyanovinyl; Solvatochromism; Nonlinear optics (NLO); Long wavelength hyper-Rayleigh scattering (HRS)

1. Introduction

Recently interest in the area of non-linear optical (NLO) materials has intensified due to the many proposed applications in communication technology. Most efforts have concentrated on organic chromophores [1] though there is growing interest in organometallic systems [2]. It has been suggested that coplanarity of the metals with the π electrons may increase the extent of electronic coupling within the π-framework and benefit NLO efficiency [3]. The optical properties of a series of merocyanine chromophores utilising the $(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH\text{–})$ unit as an electron donor, thiobarbituric acid as the electron acceptor linked via 1–3 olefinic bonds were studied using electrical field induced second harmonic generation (EFISH) [4]. The larger $\mu\beta_0$ values (a dot product of the dipole moment and the static first hyperpolarisibility) obtained relative to the organic trimethylindoline donor based analogues demonstrated the effective electron donating capabilities of these metal-in-plane organometallic termini. Moreover, studies on organometallic merocyanines containing the $(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–})^+$ cationic fragment as an electron accepting terminus concur with such a motif and have established the potential and versatility of incorporating these moieties into NLO candidates [5]. In this work, we report the synthesis and 1500 nm hyper-Rayleigh scattering (HRS) studies of a related series of organometallic merocyanines demonstrating the effects of π-bridge modifications and the influence of the surrounding medium on the molecular electronic make-up and the second-order non-linear optical activity.

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2. Results and discussion

2.1. Synthesis

Attempts to synthesis extended μ-vinylidene complexes of the type [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–R)] via the reaction of the formyl substituted complex [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CHO)] (**1**) [6] with Wittig reagents were unsuccessful. This lack of reactivity towards phosphorane nucleophiles can be easily understood if we consider the three mesomeric forms depicted in Fig. 1 and their relative contribution to the overall ground state electronic distribution. The presence of the strong electron-donating dinuclear carbene stabilises the resonance form **C** and renders the formyl group less susceptible to nucleophilic attack. This is verified by simply comparing the spectroscopic data of **1** with the related μ-ethenylidene complex [(CpFeCO)$_2$(μ-CO)(μ-C=CH$_2$)] (**2**) [7] (Table 1). The carbonyl ligands of **1** absorb at higher wavenumbers than those of **2** as a result of decreased M–CO back bonding and the μ-C signal in the ^{13}C-NMR spectrum of **1** is shifted downfield relative to that of **2** due to increased positive charge localisation on the Fe$_2$μ-C centre.

On the other hand the reaction of **1** with the more reactive Wittig–Horner–Wadsworth–Emmons (WHWE) reagents were successful. Thus the di-iron μ-C complexes [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–Br)] (**3**) and [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–Br)] (**4**) were obtained in high yields by the reaction of **1** with 4-Br–C$_6$H$_4$–CH$_2$P(O)(OEt)$_2$ [8] and 2-Br–C$_4$H$_2$S–5–CH$_2$P(O)(OEt)$_2$ [9] in the presence of *t*-BuOK (Scheme 1). Lithium–halogen exchange followed by DMF quenching revealed the extended formyl vinylidenes [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–CHO)] (**5**) and [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–CHO)] (**6**). These organometallic aldehydes underwent Knoevenagel condensations with malonitrile to yield the intensely coloured dicyanovinyl merocyanines [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–CH=(CN)$_2$)] (**7**) and [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–CH=(CN)$_2$] (**8**) (Scheme 1).

2.2. Spectroscopic data

The ground state (GS) description of these complexes is easily formulated by analysing the IR and NMR spectroscopic data (table 2). The solution IR spectra for **3**–**8** contain three bands in the carbonyl region with similar stretching frequencies to those of other di-iron μ-alkenylidene complexes [6,7,10]. The relative intensities are consistent with the presence of a *cis*(Cp)$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-C–) arrangement [7]. In the ^{1}H-NMR spectra of **3**–**8** there are two Cp resonances which illustrates the lack of rotation about the μ-C=CH bond [4,6,10]. The same is not true in di-iron vinyl carbyne complexes where only one Cp signal is ob-

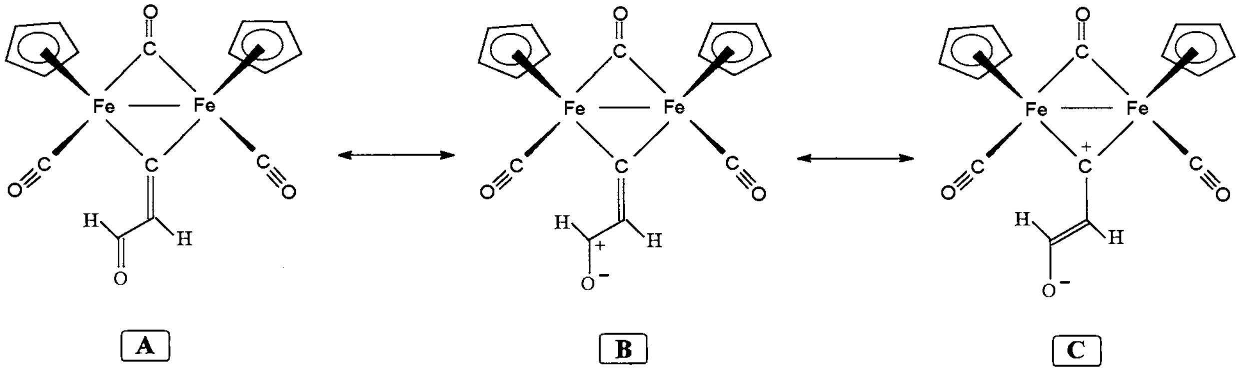


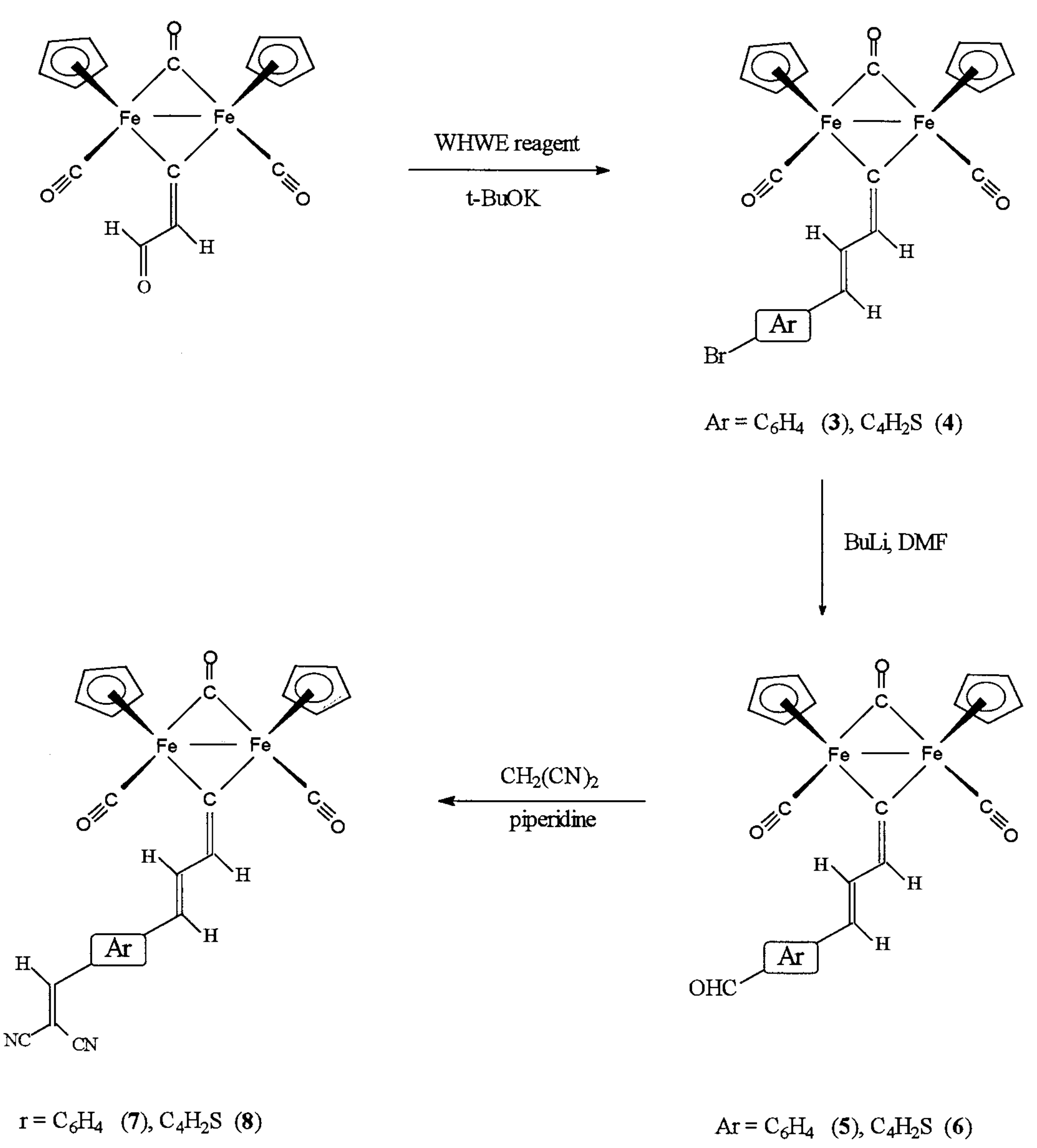
Fig. 1. Resonance forms of **1**.

Table 1
Spectroscopic data for the complexes [(CpFeCO)$_2$(μ-CO)(μ-B)]

B	IR (cm^{-1}) [a]			^{13}C-NMR [b]	
	ν(CO)	ν(μ-CO)	ν(CHO)	μ-C	μ-CO
C=CH–CHO (**1**)	2008, 1972	1809	1634	319.5	265.7
C=CH$_2$ (**2**)	1992, 1953	1788		276.9	272.1

[a] In CH$_2$Cl$_2$.

[b] δ in ppm from TMS; CDCl$_3$ solvent.



Scheme 1. Synthetic route to the organometallic merocyanines.

served, which is consistent with facile rotation about the μ-C–CH bond [5,6,10d,11]. The chemical shift of the μ-C in the ^{13}C-NMR spectra of dinuclear carbonyl complexes is an excellent diagnostic towards the extent of charge delocalisation in the ground state.

While the IR and NMR data demonstrate nicely the predominantly neutral GS structures of **3**–**8**, as depicted in Fig. 2, they also verify the expected, though subtle, trends and contributions of the charge separated form to the GS structure. The greater is the extent of charge separation, the higher will be the energy for the CO stretching mode and the more deshielded the μ-C ^{13}C-NMR. Most notable is that: (i) comparing the data of **1** with the extended aldehydic complexes **5** and **6** reveals that extending the π-bridge with phenyl units reduces the GS donor–acceptor communication, (ii) for the thienyl complexes the ν(CO) modes are found at lower wavenumbers and the μ-C ^{13}C-NMR resonances are found consistently downfield when compared to the phenyl analogues and (iii) with increasing acceptor strength i.e. $CH{=}(CN)_2 > CHO > Br$, the ν(CO) are found at higher wavenumbers and the μ-C signal is more deshielded.

The electronic absorption spectra of these complexes contain one intense band in the visible region which is sensitive to both π-bridge and acceptor-strength modifications (Table 2). The introduction of the less aromatic thiophene in place of the phenyl unit produces a red shift of the λ_{max} in all cases (Fig. 3). As expected, increasing the acceptor strength also results in the low-energy band being shifted to longer wavelengths. Another important electronic absorption characteristic, which is used to indicate possible NLO activity, is the solvatochromic behaviour of chromophores [12]. Strong

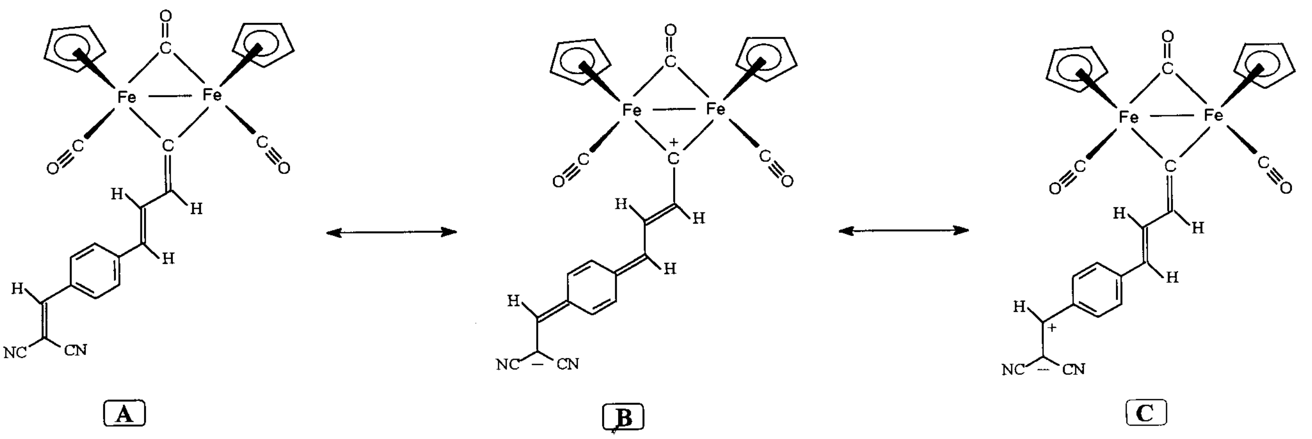


Fig. 2. Resonance forms for complex 7.

solvatochromism i.e. the variation of λ_{max} in solvents of different polarities, is often used as an indication of a large dipole moment difference between the ground and first excited states. On going from hexane to CH_2Cl_2 complexes **3**–**8** exhibit positive solvatochromism (i.e. as the polarity of the solvent increases the λ_{max} moves to longer wavelengths). This effect is strongest in complexes **7** and **8** and indicates charge transfer from the di-iron centre to the dicyanovinyl acceptor terminus upon excitation resulting in a more polar excited state (Table 2).

However, when protic or dipolar solvents are used an inversion of solvatochromism from positive to negative is observed, particularly in the chromophores **7** and **8**. This phenomenon is often taken as evidence of changes in the GS electronic structure [13]. Thus this effect could be interpreted here as indicating that the GS structure changes from the neutral structure **A** (Fig. 2) in hexane via the intermediate polymethine-like structure in CH_2Cl_2 to the quinonoid charge separated structure **B** in more polar solvents. It is certainly true that the geometry and therefore the potency of π-substituted systems with strong donors and acceptors often depend strongly on specific interactions such as hydrogen bonding and dipole–dipole interactions between the molecule and the surrounding medium [13f,14]. However, we believe that the interaction here is more likely just between the solvent and a specific part of the molecule.

Analysing the changes in the ^{1}H-NMR spectra of the chromophores **7** and **8** in CD_2Cl_2 and CD_3CN or $(CD_3)_2CO$ we see that the dicyanovinyl proton is shifted downfield by more than 0.5 ppm. We attribute this to the stabilisation of resonance structure **C** by dipolar or protic solvents with the concomitant downfield shift of the dicyanovinyl proton. Also there is very little change in the chemical shift (< 0.1 ppm), and the $J_{H\text{–}H}$ coupling constants (< 0.3 Hz) of the μ-C=CH–CH=CH π-bridge protons which would indicate a strong contribution from resonance structure **B** to the GS. Thus, increased contribution of resonance form **C** to the GS reduces the electron-accepting ability of the dicyanovinyl unit and results in a hypsochromic shift of the λ_{max} with increased solvent polarity.

2.3. Hyperpolarisability measurements

These complexes were subjected to hyper-Rayleigh scattering (HRS) studies [15] but as they absorb substantially in the area of 532 nm (i.e. $I(2\omega)$ when the incident light has a wavelength of $I(\omega) = 1064$ nm), a shift to higher incident wavelength (1500 nm) was attempted in order to reduce strong resonance enhancement. Another and more important reason for using the higher wavelength incident beam, is an attempt to discriminate between a true SHG signal and a two-photon absorption fluorescence (TPAF) enhanced signal [20, 16]. A recent publication has documented the problems in comparing EFISH and HRS data as well as comparing the results obtained at different wavelengths [17] and therefore no comparisons will be drawn between the NLO properties of the chromophores in this work and the di-iron series of Wu et al. [4].

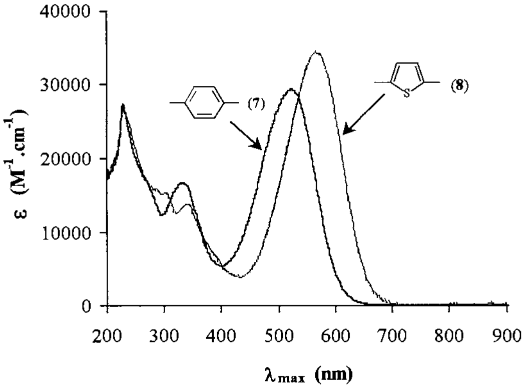


Fig. 3. Electronic absorption spectra of the dicyanovinyl chromophores in CH_2Cl_2.

The 1500 nm incident beam HRS examinations were achieved using a tuneable optical parametric oscillator (OPO) based set-up [18]. All the measurements were carried out using Disperse Red 1 (DR1) as an external standard and the results are presented in table 2. The reference hyperpolarisability β of DR1 in CH_2Cl_2 was calculated by comparing the slopes of the standard in CH_2Cl_2 and $CHCl_3$ to obtain the ratio of β_{solute} [19]. Using the value $\beta(CHCl_3) = 80 \times 10^{-30}$ esu [20] the hyperpolarisibility of DR1 in CH_2Cl_2 is estimated to be 70×10^{-30} esu. The effect of the refractive indices of the solvents was corrected using the simple Lorentz local field [21].

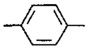
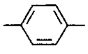
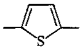
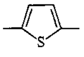
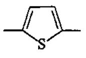
Comparing the β values of **7** (156×10^{-30} esu) and **8** (227×10^{-30} esu) reveals a 1.5 fold increase on replacing the phenyl π-spacer by a thiophene unit and this is attributed to the lower delocalisation energy of thiophene. The extremely low extinction coefficients for complexes **7** and **8** at $I(2\omega)$ (less than 50 M^{-1} cm^{-1}), means that the calculation of the static hyperpolarisabilities (β_0) using the two-level model [12b,c] results in significantly more reliable values (β_0 (**7**) $= 68 \times 10^{-30}$ esu and β_0 (**8**) $= 84 \times 10^{-30}$ esu). Static hyperpolarisabilities of 169×10^{-30} esu for a donor substituted truxenone derivative (measured in $CHCl_3$ using *p*-dimethylaminocinnamaldehyde as external reference) [20] and 121×10^{-30} for a tricyanovinyl substituted triarylamine (measured in CH_3CN using *p*-dimethylaminocinnamaldehyde as external reference) [22] have been reported. However, the 1500 nm HRS technique is relatively new and therefore the body of work to draw comparisons and conclusions from for these organometallic chromophores are limited.

The ^1H-NMR and solvatochromism data illustrate nicely the effect which the surrounding medium has on the electronic structures of these organometallic merocyanines. Hence, one may expect that the first hyperpolarisabilities may also be solvent dependent and therefore we carried out HRS measurements in CH_3CN. In order to analyse the experimental β values properly one must not compare directly the calculated values in CH_3CN which were β (DR1) $= 110 \times 10^{-30}$ esu (obtained by the procedure outlined above), β (**7**) $= 134 \times 10^{-30}$ esu and β (**8**) $= 256 \times 10^{-30}$ esu with the analogous CH_2Cl_2 values. Instead we compare the first hyperpolarisabilities β (**7**) $= 2.2 \times \beta$ (DR1) in CH_2Cl_2 and β (**7**) $= 1.2 \times \beta$ (DR1) in CH_3CN and observe a halving of the β value of complex **7** in the more dipolar solvent. A similar comparison of the first hyperpolarisabilities for the thienyl chromophore **8** in CH_2Cl_2 and CH_3CN reveals a 0.7 fold decrease in the β value. This is in complete agreement with the linear optical property observations that the dicyanovinyl group is a weaker acceptor in dipolar solvents and therefore exhibits a lower NLO response. Moreover, our results are consistent with recent studies demonstrating the effect of the medium on the hyperpolarisability–structure relationships [13a,b,23].

3. Conclusions

We have outlined a facile method for the synthesis of extended organometallic merocyanines based on the electron donating [(CpFeCO)$_2$(μ-CO)(μ-C=CH–)] fragment. A 1500 nm laser excitation was used to evaluate the first hyperpolarisability to eliminate experimental complications often experienced with the 1064 nm excitation wavelength. The linear and non-linear optical results illustrate the effect of the medium on the electron accepting ability of the dicyanovinyl group and hence the NLO response. It is hoped that further

Table 2
Spectroscopic data for complexes [(CpFeCO)$_2$(μ-CO)(μ-C=CH-CH=CH-π-B-Acc)].

π-B	Acc	Solution IR (cm^{-1})$^{(a)}$		^{13}C NMR$^{(b)}$	UV-vis (λ_{max} nm)				β$^{(c)}$
		ν(CO)	ν(μ-CO)	μ-*C*=CH	hexane	CH_2Cl_2	CH_3CN	EtOH	10^{-30} esu
 (3)	Br	1996, 1959	1793	287.2	352	357	356	353	-----
 (5)	CHO	1997, 1961	1796	292.4	395	414	410	410	-----
 (7)	CH=(CN)$_2$	1999, 1963	1800	297.0	507	523	509	519	156
 (4)	Br	1997, 1960	1796	288.3	365	370	369	369	-----
 (6)	CHO	1999, 1963	1798	296.7	429	450	446	455	-----
 (8)	CH=(CN)$_2$	2001, 1965	1802	303.0	541	565	556	567	227

(a) solvent CH_2Cl_2; (b) δ in ppm from TMS; $CDCl_3$ solvent; (c) measured in CH_2Cl_2 at λ = 1500 nm.

modifications such as changing the electron acceptor to phenylisoxazolone or tropylium may indicate whether these effects are unique to the dicyanovinyl unit.

4. Experimental

CH_2Cl_2 and THF were dried by refluxing over CaH_2 and distilled prior to use. THF was further distilled from sodium benzophenone. IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrometer. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 6 spectrometer and a Perkin–Elmer model 554. NMR spectra were recorded on a JEOL JNM-GX 270 FT and Varian Gemini 200 BB spectrometers using TMS as an internal standard. Elemental analysis was carried out by the Microanalytical laboratory, University College, Dublin and in the Institut für Anorganische und Angewandte Chemie, Universität Hamburg.

*4.1. General procedure for the reaction of [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CHO)] (**1**) with phosphonates (Wittig–Horner–Wadsworth–Emmons reaction)*

t-BuOK (0.13 g, 1.16 mmol) was added to a solution of **1** (0.3 g, 0.79 mmol) and the phosphonate (1.1 equivalents) in dry THF (50 ml). Stirring was continued for 1 h under nitrogen, water (30 cm^3) was added and the reaction mixture extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed. The residue was taken up in CH_2Cl_2 and chromatographed on alumina. The products were eluted with CH_2Cl_2 and recrystallised from CH_2Cl_2–hexane.

*4.1.1. [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–4-Br)] (**3**)*

Yield: 0.29 g (68.9%). ^{1}H-NMR ($(CD_3)_2CO$): δ 8.22 (d, 1H, *J* = 10.1 Hz, μ-C=C*H*), 7.44 (d, 2H, *J* = 8.4 Hz, C_6H_4), 7.30 (d, 2H, *J* = 8.4 Hz, C_6H_4), 7.19 (dd, 1H, *J* = 10.1, 15.6 Hz, μ-C=CH–C*H*=CH), 6.28 (d, 1H, *J* = 15.6 Hz, μ-C=CH–CH=C*H*), 4.91 (s, C_5H_5), 4.83 (s, C_5H_5). ^{13}C-NMR ($CDCl_3$): δ 287.17 (μ-C), 270.17 (μ-CO), 210.26, 210.14 (CO), 143.46, 131.84, 121.07 (μ-C=CH–CH=CH), 137.68, 131.31 (C*q*–C_6H_4), 128.72, 126.82 (C_6H_4), 87.97, 87.36 (C_5H_5). IR: (CH_2Cl_2): ν(CO) 1996 (10), 1959 (1.9); ν(μ-CO) 1793 (3.4); ν(C=C) 1605 (1.5), 1560 (1.4), 1552 (1.5), 1485 (1.4) cm^{-1}. KBr: ν(CO) 1978 (10), 1942 (4.5); ν(μ-CO) 1775 (7.1); ν(C=C) 1604 (1.9), 1556 (2.4), 1484 (1.8) cm^{-1}. Elemental analysis: Anal. Calc. for $C_{23}H_{17}BrFe_2O_3$: C, 51.78; H, 3.19. Found: C, 51.18; H, 3.41%.

*4.1.2. [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–2-Br)] (**4**)*

Yield: 0.30 g (70.5%). ^{1}H-NMR ($CDCl_3$): δ 8.12 (d, 1H, *J* = 10.3 Hz, μ-C=C*H*), 6.96 (dd, 1H, *J* = 10.3, 15.4 Hz, μ-C=CH–C*H*=CH), 6.91 (d, 1H, *J* = 3.9 Hz, C_4H_2S), 6.63 (d, 1H, *J* = 3.9 Hz, C_4H_2S), 6.36 (d, 1H, *J* = 15.4 Hz, μ-C=CH–CH=C*H*), 4.90 (s, C_5H_5), 4.82 (s, C_5H_5). ^{13}C-NMR ($CDCl_3$): δ 288.32 (μ-C), 269.67 (μ-CO), 210.08 (CO), 146.00, 108.08 (C-2, C-5–C_4H_2S), 142.67, 131.92, 130.36 (μ-C=CH–CH=CH), 123.58, 114.77 (C-3, C-4–C_4H_2S), 87.85, 87.31 (C_5H_5). IR (CH_2Cl_2): ν(CO) 1997 (10), 1960 (2.1); ν(μ-CO) 1796 (3.7); ν(C=C) 1595 (1.1), 1560 (2.2), 1514 (1.2) cm^{-1}. KBr: ν(CO) 1991 (9.0), 1982 (10), 1957 (3.7), 1945 (4.3); ν(μ-CO) 1808 (6.1), 1790 (4.7); ν(C=C) 1593 (1.7), 1560 (2.6), 1513 (1.3) cm^{-1}. Elemental analysis: Anal. Calc. for $C_{21}H_{15}Fe_2BrO_3S\cdot(1/2CH_2Cl_2)$*[1] C, 46.75 (44.37); H, 2.78 (2.75). Found: C, 44.37; H, 2.75%.

*4.2. General procedure for the reaction of [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–4-Br)] (**3**) and [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–2-Br)] (**4**) with BuLi–DMF*

n-BuLi (1.1 equivalents) was added to a solution of **3** or **4** (0.5 g) in dry THF (75 cm^3) at −70°C. Stirring was continued at this temperature for 20 min, then DMF (2.5 equivalents) was added and temperature allowed to warm to 0°C. The reaction mixture was poured into an equivalent volume of iced water and then extracted with diethylether (100 cm^3). The organic layer was dried over $MgSO_4$ and the solvent was removed. The residue was taken up in CH_2Cl_2 and chromatographed on alumina. The products were eluted with CH_2Cl_2 and recrystallised from CH_2Cl_2–hexane.

*4.2.1. [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–4-CHO)] (**5**)*

Yield: 0.26 g (57.5%). ^{1}H-NMR ($CDCl_3$): δ 9.95 (s, 1H, CHO), 8.29 (d, 1H, *J* = 10.4 Hz, μ-C=C*H*), 7.84 (d, 2H, *J* = 8.4 Hz, C_6H_4), 7.55 (d, 2H, *J* = 8.4 Hz, C_6H_4), 7.38 (dd, 1H, *J* = 10.4, 15.5 Hz, μ-C=CH–C*H*=CH), 6.38 (d, 1H, *J* = 15.5 Hz, μ-C=CH–CH=C*H*), 4.94 (s, C_5H_5), 4.86 (s, C_5H_5). ^{13}C-NMR ($CDCl_3$): δ 292.35 (μ-C), 269.31 (μ-CO), 210.14, 209.96 (CO), 191.64 (CHO), 145.79, 133.82 (C*q*–C_6H_4), 143.73, 134.87, 120.92 (μ-C=CH–CH=CH), 130.38, 125.79 (C*q*–C_6H_4), 88.04, 87.44 (C_5H_5). IR (CH_2Cl_2): ν(CO) 1997 (10), 1961 (2.5); ν(μ-CO) 1796 (4.0); ν(CHO) 1691 (2.8); ν(C=C) 1606 (1.5), 1590 (32.1), 1548 (5.5) cm^{-1}. KBr: ν(CO) 1988 (10), 1952 (4.9); ν(μ-CO) 1792 (5.4); ν(CHO) 1685 (3.1); ν(C=C) 1587 (3.7), 1544 (6.1) cm^{-1}. Elemental analysis: Anal. Calc. for $C_{24}H_{18}Fe_2O_4(H_2O)$*: C, 59.75 (57.60)*; H, 3.73 (4.0)*. Found: C, 57.15; H, 4.19%.

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[1] An asterisk indicates "including solvent molecules" throughout this article.

4.2.2. *[(CpFeCO)$_2$(μ-C=O)(μ-C=CH–CH=CH–C$_4$H$_2$S–2–CHO)]* (***6***)

Yield: 0.28 g (61.9%). ^{1}H-NMR (CDCl$_3$): δ 9.80 (s, 1H, CHO), 8.22 (d, 1H, $J = 10.7$ Hz, μ-C=C*H*), 7.64 (d, 1H, $J = 4.2$ Hz, C$_4$H$_2$S), 7.32 (dd, 1H, $J = 10.7$, 15.5 Hz, μ-C=CH–C*H*=CH), 6.82 (d, 1H, $J = 4.2$ Hz, C$_4$H$_2$S), 6.45 (d, 1H, $J = 15.5$ Hz, μ-C=CH–CH=C*H*), 4.94 (s, C$_5$H$_5$), 4.85 (s, C$_5$H$_5$). ^{13}C-NMR (CDCl$_3$): δ 296.65 (μ-C), 269.06 (μ-CO), 210.34, 210.29 (CO), 182.71 (CHO), 156.51, 139.54 (C-2, C-5–C$_4$H$_2$S), 143.38, 138.71, 136.91 (μ-C=CH–CH=CH), 125.03, 114.64 (C$_3$, C$_4$–C$_4$H$_2$S), 88.52, 88.02 (C$_5$H$_5$). IR: (CH$_2$Cl$_2$): ν(CO) 1999 (10), 1963 (1.7); ν(μ-CO) 1798 (3.8): ν(CHO) 1655 (3.3); ν(C=C) 1584 (2.3), 1553 (2.8) cm^{-1}. KBr: ν(CO) 1989 (10), 1955 (4.5); ν(μ-CO) 1795 (5.7); ν(CHO) 1653 (4.4); ν(C=C) 1580 (3.1), 1548 (4.1) cm^{-1}. Elemental analysis: Anal. Calc. for C$_{22}$H$_{16}$Fe$_2$O$_4$S: C, 54.10; H, 3.28. Found: C, 53.61; H, 3.66%.

4.3. *General procedure for the reaction of [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–4–CHO)]* (***5***) *and [(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–2–CHO)]* (***6***) *with malonitrile*

A few drops of piperidine were added to a solution of malonitrile (1.1 equivalents) and **5** or **6** (0.3 g) in CHCl$_3$ (50 cm^3) and refluxed for 1 h. The reaction mixture was cooled, water was added and the organic layer was separated and dried over MgSO$_4$. The solvent was removed and the residue recrystallised from CH$_2$Cl$_2$–hexane.

4.3.1. *[(CpFeCO)(μ-CO)(μ-C=CH–CH=CH–C$_6$H$_4$–CH=C(CN)$_2$)]* (***7***)

Yield: 0.26 g (78.8%). ^{1}H-NMR (CD$_3$CN): δ 8.39 (d, 1H, $J = 10.4$ Hz, μ-C=C*H*), 8.15 (s, 1H, C*H*=C(CN)$_2$), 7.99 (d, 2H, $J = 8.4$ Hz, C$_6$H$_4$), 7.74 (d, 2H, $J = 8.4$ Hz, C$_6$H$_4$), 7.67 (dd, 1H, $J = 15.5$, 10.4 Hz, μ-C=CH–C*H*=CH), 6.39 (d, 1H, $J = 15.5$ Hz, μ-C=CH–CH=C*H*), 5.19 (s, C$_5$H$_5$), 5.08 (s, C$_5$H$_5$), 4.27 (s, 3H, OMe). ^{13}C-NMR (CDCl$_3$): δ 297.00 (μ-C), 268.50 (μ-CO), 210.07, 209.84 (CO), 158.75, 144.01, 136.35 (μ-C=CH–CH=CH), 146.70, 128.26 (C*q*–C$_6$H$_4$), 131.70, 126.14 (C$_6$H$_4$), 120.50 (*C*H=C(CN)$_2$), 114.84, 113.73 (–CH=C(*C*N)$_2$), 108.96 (–CH=*C*(CN)$_2$), 88.17, 87.57 (C$_5$H$_5$). IR (CH$_2$Cl$_2$): ν(CN) 2226 (2.1); ν(CO) 1999 (10), 1963 (2.6); ν(μ-CO) 1800 (4.2); ν(C=C) 1605 (6.0), 1566 (3.2), 1531 (11.0), 1504 (3.8) cm^{-1}. KBr: ν(CN) 2222 (2.1), 2193 (0.5); ν(CO) 1992 (10), 1950 (2.9); ν(μ-CO) 1815 (3.4), 1796 (3.7); ν(C=C) 1572 (3.3), 1529 (8.6), 1500 (4.3) cm^{-1}. UV–Vis: hexane: $\lambda_{max} = 507$ nm, CH$_2$Cl$_2$: λ_{max} (ε) = 523 nm (29 594 M^{-1} cm^{-1}), CH$_3$CN: λ_{max} (ε) = 509 nm (29 095 M^{-1} cm^{-1}), EtOH: $\lambda_{max} = 517$ nm. Elemental analysis: Anal. Calc. for C$_{27}$H$_{18}$Fe$_2$N$_2$O$_3$-[CH$_2$(CN)$_2$·H$_2$O]*: C, 61.13 (58.66)*; H, 3.40 (3.36)*; N, 5.28 (9.40)*. Found: C, 58.50; H, 3.74; N, 9.13%.

4.3.2. *[(CpFeCO)$_2$(μ-CO)(μ-C=CH–CH=CH–C$_4$H$_2$S–CH=C(CN)$_2$)]* (***8***)

Yield: 0.21 g (63.7%). ^{1}H-NMR ((CD$_3$)$_2$CO): δ 8.38 (d, 1H, $J = 10.7$ Hz, μ-C=C*H*), 8.22 (s, 1H, –C*H*=C(CN)$_2$), 7.82 (d, 1H, $J = 4.2$ Hz, C$_4$H$_2$S), 7.56 (dd, 1H, $J = 10.7$, 15.2 Hz, μ-C=CH–C*H*=CH), 7.30 (d, 1H, $J = 4.2$ Hz, C$_4$H$_2$S), 6.57 (d, 1H, $J = 15.2$ Hz, μ-C=CH–CH=C*H*), 5.17 (s, C$_5$H$_5$), 5.11 (s, C$_5$H$_5$). ^{13}C-NMR (CDCl$_3$): δ 303.04 (μ-C), 267.58 (μ-CO), 209.68, 209.56 (CO), 159.26, 131.45 (C-2, C-5–C$_4$H$_2$S), 149.32, 141.00, 138.41 (μ-C=CH–CH=CH), 143.44, 124.80 (C-3, C-4–C$_4$H$_2$S), 115.38, 114.49 (–CH=C(CN)$_2$), 113.57 (–CH=C(CN)$_2$), 108.86 (–CH=C(CN)$_2$), 88.17, 87.66 (C$_5$H$_5$). IR (CH$_2$Cl$_2$): ν(CN) 2220 (3.2); ν(CO) 2001 (10), 1965 (3.2); ν(μ-CO) 1802 (3.9); ν(C=C) 1605 (5.8), 1586 (2.6), 1554 (5.7), 1542 (7.5) cm^{-1}. KBr: ν(CN) 2216 (3.3), ν(CO) 1987 (10), 1955 (4.2); ν(μ-CO) 1808 (5.5), 1795 (5.4); ν(C=C) 1584 (2.3), 1541 (8.2) cm^{-1}. UV–Vis: hexane: $\lambda_{max} = 541$ nm, CH$_2$Cl$_2$: λ_{max} (ε) = 565 nm (34 449 M^{-1} cm^{-1}), CH$_3$CN: λ_{max} (ε) = 556 nm (33 279 M^{-1} cm^{-1}), EtOH: $\lambda_{max} = 567$ nm. Elemental analysis: Anal. Calc. for C$_{25}$H$_{16}$Fe$_2$N$_2$O$_3$-S(H$_2$O)*: C, 56.00 (54.18); H, 3.01 (3.61)*; N, 5.22 (5.05)*; Found: C, 54.87; H, 3.34; N, 5.58%.

4.4. *HRS measurements (1500 nm) of the first hyperpolarisabilities*

Details for the experimental are similar to the set-up described in Ref. [18]. Instead of the third harmonic (355 nm) generated from a Nd:Yag laser with a wavelength of 1064 nm, the OPO [24] in use was pumped with the second harmonic frequency (532 nm). The signal intensity at 824 nm and the fundamental at 532 nm were removed from the Idler using dichroic mirrors (HR 650–850 and HR 532), a green light and a silicon filter (transmittent > 1000 nm). An additional Glan–Taylor polariser ensured the vertical polarisation of the beam into the measurement cell. All measurements were carried out in dry CH$_2$Cl$_2$ and CH$_3$CN with sample concentrations of 10^{-5} M using Disperse Red 1 as reference with values of β_{1500} (DR1) = 70×10^{-30} esu in CH$_2$Cl$_2$ and β_{1500} (DR1) = 110×10^{-30} esu in CH$_3$CN.

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