

Preliminary communication

Nonlinear optical properties in bimetallic monocation π -complexes of iron

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Abstract

Acetylide addition to 1-alkoxy-substituted cyclohexadienyliron complexes and acid promoted dealkoxylation have been used to prepare bimetallic monocation alkyne-linked dipoles which have been shown to exhibit NLO effects by hyper-Rayleigh scattering measurements. © 1997 Elsevier Science S.A.

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1. Introduction

Dipolar structures with nonlinear optical (NLO) properties typically employ organic donor and acceptor groups (Fig. 1: D = C₆H₄OMe, C₆H₄NMe₂; A⁺ = C₆H₄NO₂) to polarise unsaturated spacers [1]. Organometallic complexes can also be used [2] and, because of its great stability, ferrocene has become popular as an organometallic donor. ¹ Structure 1 [D = C₅H₄FeCp, A⁺ = C₆H₄NO₂ (*n* = 1)] has been shown [3] to exhibit good NLO properties with a level of second-harmonic generation (SHG) 62 times greater than that of the reference compound urea. The hyperpolarisability (β) [4] of this complex was subsequently

measured (31 [3d]–34 [3c] $\times 10^{-30}$ esu), and increasing the length of the polyene to *n* = 2 has been shown to increase β to 52 [3c]–66 [5d] $\times 10^{-30}$ esu. A variety of ferrocene-based NLO compounds have now been described [3,5], NLO properties of ferrocene-containing polymers have been measured [6], and ferrocene-bearing tetrathiafulvalenes [7] and polymeric systems with conjugated backbones [8] have been synthesised. Besides ferrocene, there has been considerable interest in other organometallics and, since a survey of over 60 simple complexes in 1986 [9], a wide variety of structures have been studied. Recent examples include organometallic and metalloorganic complexes of tungsten [10], nickel [11], molybdenum [12], ruthenium [13], and platinum [14]. Unsubstituted tricarbonyliron diene complexes are known to exhibit SHG properties to a small extent when present in host/guest inclusion complexes [15].

In Norwich, we have been examining alkyne-linked bimetallic monocation complexes in which the alkyne is placed as a substituent at C-1 of a tricarbonyl(cyclohexadienyl)iron(1+) complex. We have recently described [16] the preparation of the first alkyne-substituted dienyliron moiety, using phenylethyne as the alkyne. The method used shows promise as a general procedure, and has been extended to give a convenient route to the bimetallic dipole structures of type 2. A related alkyne-linked ferrocene-containing dipole 2 [D = (C₇H₇)Cr(CO)₃⁺; A = CpFe(C₅H₄)] has been shown

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¹ Although the iron in ferrocene is Fe(II), this neutral π -complex is electron rich and typically stabilises adjacent positive charge in the ferrocenyl cation [which is also Fe(II)]. This feature of ferrocene chemistry lends significance to alternative canonical representations of compounds in which ferrocene is in conjugation with positively charged substituents, and leads to better charge stabilisation and a significant degree of delocalisation in such structures. With alkyne links, however, this delocalisation of charge is restricted by the need for cumulated bonding in the linking region of the alternative canonical representation, so charge separation is retained. We refer to this concept as 'bonding-locked charge separation' in the compounds prepared for NLO studies in this work, since for our purpose we require a large dipole and good polarisability, and need to avoid structures with roughly equal positive charge at each end.



Fig. 1. Polyene and polyyne dipoles.

to have an exceptionally high β value [17]. The cyclohexadienyl complexes targeted in this investigation contain the same ferrocenylethyne donor/linker motif but have the advantage that the electron-accepting organometallic end-group is chiral.

2. Results and discussion

Reaction of the lithiated acetylene **3** [18] (generated with *n*-BuLi from ferrocenylethyne) with the 1-ethoxy-cyclohexadienyl complex **4a** ($R = \text{Et}$, $X = \text{H}$) afforded the expected intermediate **5a** in 79% yield (Scheme 1). A sample of the lithiated ferrocenylethyne and advice on the preparation [10] of this reagent (yields quoted were obtained by the use of freshly prepared samples of the nucleophile) were given by Professor J. Heck (Universität Hamburg). Reaction of **5a** with hexafluorophosphoric acid produced the required ferrocenylethyne-substituted cyclohexadienyl complex **6a** in 71% yield. The product was precipitated as a red powder ($\lambda_{\text{max}} = 350, 405, \text{ and } 500 \text{ nm}$ in CH_3CN), much darker in colour than the yellow phenylethyne-substituted structures obtained [16] in our earlier work, and was fully characterised by standard spectroscopic and mass spectrometric techniques (Table 1). The same reaction sequence was employed with the 1,4-dimethoxy-substituted electrophile **4b** ($R = \text{Me}$, $X = \text{OMe}$), though in this case the reaction sequence proved somewhat less efficient. Intermediate **5b** was obtained in 58% yield, and the salt formation also proceeded in 58%, affording **6b** (Table

1). The methoxy substituent on the cyclohexadienyl ligand extends the chromophore, and **6b** was even darker in colour than **6a**, having a purple/black appearance ($\lambda_{\text{max}} = 375, 420, \text{ and } 540 \text{ nm}$ in CH_3CN). NLO properties of **6a** were measured in dichloromethane solution by the hyper-Rayleigh scattering method [19] using an Nd:YAG laser ($\lambda = 1064 \text{ nm}$), giving a β value of $100 \times 10^{-30} \text{ esu}$. The hyperpolarisability of 4-nitroaniline in dioxane ($16.9 \times 10^{-30} \text{ esu}$ [20]) was used as an external reference. Measurements on **6b** were hampered by the darker colour of this compound, but hyperpolarisability (β) is at least $140 \times 10^{-30} \text{ esu}$. The increase in β for compound **6b** is attributed to the resonance enhancement of the first hyperpolarisability by the lowest absorption band (500–540 nm).

Compounds **6a,b** provide an interesting comparison to the related compounds prepared in Hamburg [17], which employ an η^7 -tropylium complex as the acceptor group ($\beta = 570 \times 10^{-30} \text{ esu}$). While open [21] π -complexes have been used in Norwich, the Hamburg group has worked with closed π -systems; both types of structure are capable of imparting NLO effects, though the larger closed tropylium complex shows the greater hyperpolarisability. On the other hand, the planar chirality of the cyclohexadienyl complexes (used here in racemic form) offers the advantage of the possibility of crystallisation in a non-centrosymmetric space group without the need of an external chiral auxiliary when working in the enantiopure series.

This investigation has provided the first example of the use of cationic tricarbonyl(cyclohexadienyl)iron complexes as acceptor groups in NLO-active compounds, and has established the practicality of hyperpolarisability measurements on structures of this type despite the presence of potentially photolabile metal carbonyl groups. Bimetallic monocation iron complexes with a single alkyne spacer show significant levels of

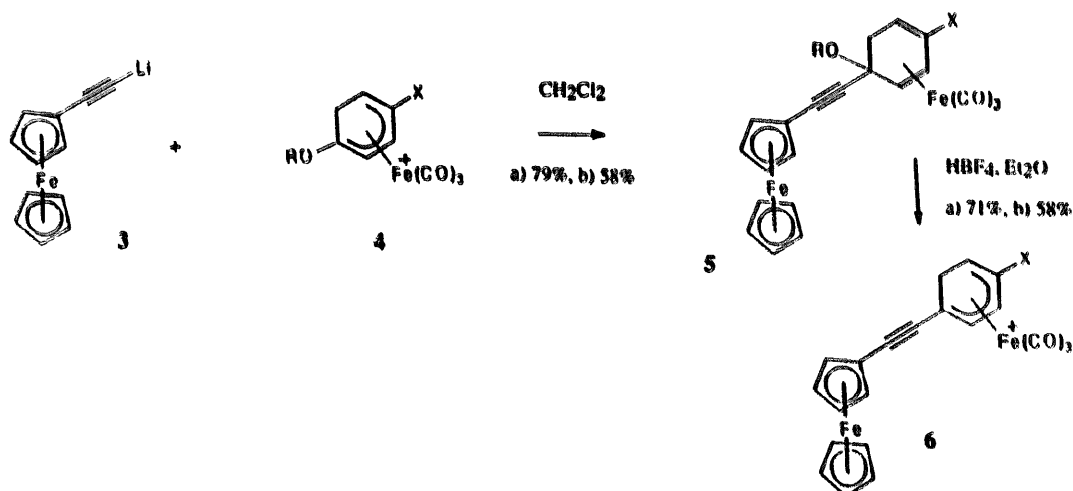
Scheme 1. a) $R = \text{Et}$, $X = \text{H}$; b) $R = \text{Me}$, $X = \text{OMe}$.

Table 1

Spectroscopic and mass spectrometric data for ferrocenyl-substituted ethynylcyclohexadienyl complexes

<p>6a: $\beta = 100 \times 10^{-30}$ esu^a; ¹H NMR (270 MHz, CD₃CN, 25 °C, TMS): $\delta = 7.08$ [t, $J = 5.5$ Hz, H^3], 5.94 [t, $J = 6$ Hz, H^4], 5.85 [ddd, $J = 5, 2,$ and 1.5 Hz, H^2], 4.6–4.4 [m^b, H^5 and m, C₅H₄], 4.30 [bs, Cp], 3.18 [dd, 16, $J = 6$ Hz, H^{6B}], 2.38 [d, $J = 16$ Hz, H^{6A}]; IR (CH₂Cl₂) $\nu = 2188$ cm⁻¹ (C≡C), 2109, 2062 cm⁻¹ (C≡O); FAB-MS: m/z 426.9732: M⁺ – BF₄ [C₂₁H₁₅O₃Fe₂; Calc. mass 426.9720].</p> <p>6b: $\beta = 140 \times 10^{-30}$ esu^a; ¹H NMR (270 MHz, CD₃CN, 25 °C, TMS): $\delta = 6.86$ [dd, $J = 6$ and 2.5 Hz, H^3], 5.94 [d, $J = 6$ Hz, H^2], 4.6–4.4 [m, C₅H₄], 4.29 [bs, Cp], 4.13 [dm, $J = 5$ Hz, H^5], 3.79 [s, OMe], 3.25 [dd, $J = 15$ and 6 Hz, H^{6B}], 2.49 [d, $J = 15$ Hz, H^{6A}]; IR (CH₂Cl₂) $\nu = 2194$ cm⁻¹ (C≡C), 2107, 2059 cm⁻¹ (C≡O); FAB-MS: m/z 456.9830: M⁺ – BF₄ [C₂₂H₁₇O₄Fe₂; Calc. mass 456.9826].</p>
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^a Referenced to 4-nitroaniline ($\beta = 16.9 \times 10^{-30}$ esu).^b Overlapping with signals from C₅H₄.^c NOBA matrix (recorded by the EPSRC Mass Spectrometry Service, Swansea).

second-harmonic generation. The effect of spacer type and length on SHG is now under investigation.

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