



Organochromium/organoiron dipoles comprising (η^6 -arene)chromium and (η^5 -cyclohexadienyl)iron(1+) complexes linked with conjugated spacers

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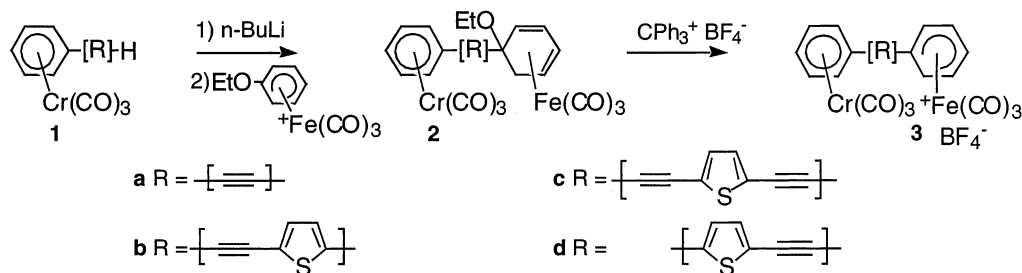
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Abstract—The synthesis of novel bimetallic organochromium/organoiron monocation dipoles comprising π -conjugated complexes linked with conjugated spacers has been performed utilising Stille and Sonogashira coupling reactions. This work establishes a general strategy for the synthesis of mixed-metal chromium/dipole complexes for evaluation for nonlinear optical effects by hyper-Rayleigh scattering. © 2001 Elsevier Science Ltd. All rights reserved.

The development of hyper-Rayleigh scattering (HRS)¹ is a photophysics technique that determines the molecular parameter β to assess second harmonic generation (SHG) in nonlinear optics (NLO). It has proved to be a stimulus for rapid progress in the design of molecular architectures, since simple evaluation in solution is possible by this method. So it avoids the complexities of requirements for crystal engineering to establish non-centrosymmetric solid-state forms, and of the interpretation of contributions from intermolecular solid-state effects in crystals and poled films. Since the first report of NLO effects with ferrocene² as an electron reservoir linked by an alkene to a nitroarene, many organometallic π -complexes³ have been evaluated for NLO effects, and the topic has been the subject of recent reviews.⁴

Our interest in this field stems from the expectation⁵ that bimetallic dipoles with an organometallic polarising group at each end may have exceptional properties, indeed simple structures combining ferrocene and cationic (η^5 -cyclohexadienyl)iron complexes have significant β values ($>100 \times 10^{-30}$ esu).⁶ Metallocene-type complexes linked with alkene,⁷ arene and thiophene⁸ as spacers have also been described and some of them exhibit large second-order optical nonlinearities.^{4a}

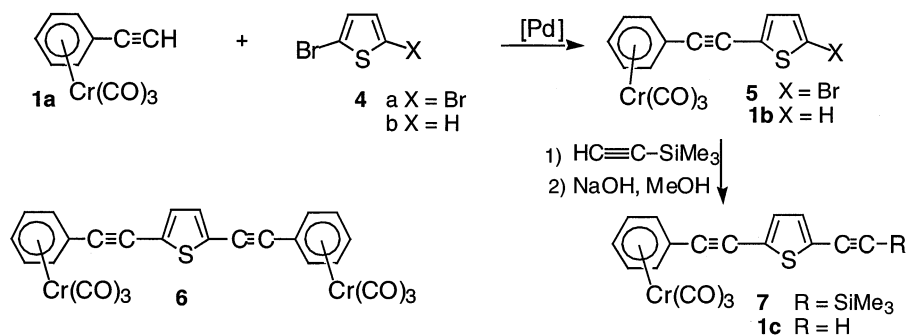
The combination of synthetic techniques has allowed us to explore⁹ the possibility of preparing bimetallic π -conjugated complexes based on (η^5 -cyclohexadienyl)iron(1+) and (η^6 -arene)chromium moieties joined by spacers containing triple bond(s) and/or thiophene



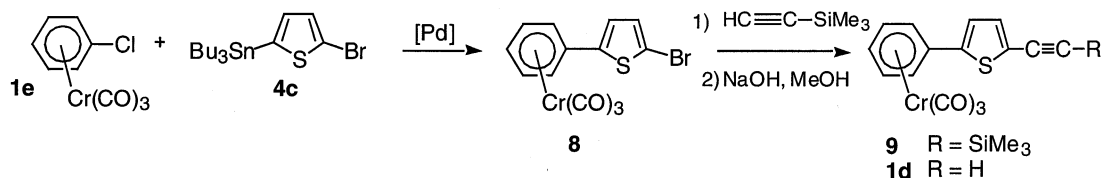
Scheme 1.

Keywords: nonlinear optics; bimetallic dipoles; alkyne; thiophene; tricarbonylarenechromium; tricarbonylcyclohexadienyliron.

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Scheme 2.



Scheme 3.

components. In this communication, we describe the synthesis of new η^6 – η^5 dipoles by means of palladium catalysed Stille and Sonogashira coupling reactions in the presence of stoichiometric organometallic moieties, and the use of nucleophile additions to electrophilic π -complexes to join (η^6 -arene)tricarbonylchromium complexes substituted by a triple bond or a thiophene residue, and a cationic tricarbonyl(η^5 -cyclohexadienyl)iron complex.

Our first investigation addressed the preparation of the ethyne-linked chromium/iron analogue of the diiron complex.⁶ Tricarbonyl(η^6 -phenylethynyl)chromium complex **1a**¹⁰ was lithiated at -78°C in THF with 1 equiv. of *n*-BuLi to form an acetylide that reacted with (η^5 -1-ethoxycyclohexadienyl)Fe(CO)₃⁺PF₆[−] to give the dinuclear complex **2a** in 45% yield. Removal of the ethoxy group using CPh₃⁺BF₄[−]¹¹ to reform the η^5 bonding mode gave complex **3a** in 99% yield (Scheme 1; a).

Turning to the question of longer linkers (Scheme 1; b–d), our next goal was to introduce a thiophene unit together with triple bonds as a spacer. Cross-coupling between the chromium(0) complex **1a** and 2,5-dibromothiophene **4a** afforded the expected bromothiophenyl derivative **5** in 42% yield as a red-orange compound, together with a red by-product hexacarbonyl[2,5-di(η^6 -phenylethynyl)thiophene]dichromium, **6**, which was formed in 12% yield. Trimethylsilylthyne reacted with **5** under palladium catalysis giving **7**, which, after desilylation, afforded complex **1c** in 90% overall yield (Scheme 2). Similarly, complex **1a** and 2-bromothiophene **4b** gave complex **1b** in 35% yield.

As reported by Wright,¹² complex **1d** (in which the order of the alkyne and thiophene components is reversed relative to **1b**) was not available through the Stille coupling reaction of [tri-*n*-butyl(η^6 -

phenyl)tin]Cr(CO)₃ and bromothiophene derivatives.¹³ Thus, in order to gain access to the dipole **3d**, we needed to develop an alternative procedure. This was achieved by the preparation of complex **8** in 50% yield, reacting 2-tri-*n*-butylstannyl-5-bromothiophene **4c** with (η^6 -chlorobenzene)Cr(CO)₃ (**1e**) using a modified catalytic system.¹⁴ A Sonogashira coupling reaction with trimethylsilylacetylene afforded **9** which was taken on by desilylation with NaOH in MeOH giving the expected mononuclear complex **1d** in 41% (Scheme 3).

Treatment of complexes **1b**–**d** with *n*-BuLi and then the (η^5 -1-ethoxycyclohexadienyl)iron(1+) complex, followed by removal of OEt from complexes **2b**–**d** with CPh₃⁺BF₄[−], yielded complexes **3b**–**d** in 19, 20 and 25% overall yields, respectively, as red or brown bimetallic complexes (Scheme 1).¹⁵

In conclusion, we have demonstrated a general method for the preparation of new bimetallic monocation dipoles containing for the first time a combination of (arene)tricarbonylchromium(0) and cationic tricarbonyl(η^5 -cyclohexadienyl)iron(1+) complexes spaced with alkynes and thiophene units. Further work is in progress to study the nonlinear optical properties of these new bimetallic dipoles, which are stable in air in the solid state, by measurement of SHG by hyper-Rayleigh scattering.

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13. We did not succeed in obtaining **8** by a Stille reaction using 2,5-dibromothiophene and [tri-*n*-butyl(η^6 -phenyl)tin]Cr(CO)₃ prepared by trapping [η^6 -phenyl-lithium]Cr(CO)₃ with Bu₃SnCl.
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15. All new compounds showed satisfactory spectroscopic and analytical data. Typical procedure for product **3a**: [(η^6 -phenyl)ethynyl]Cr(CO)₃ complex **1a**¹⁰ (238 mg, 1 mmol) in THF (10 mL) was lithiated with *n*-BuLi (0.67 mL, 1 mmol) at –78°C for 1 h and reacted with (η^5 -1-ethoxycyclohexadienyl)Fe(CO)₃⁺PF₆[–] (364 mg, 1 mmol) dissolved in THF (10 mL). The reaction mixture was stirred at –78°C for 1 and 5 h at rt, and evaporated under reduced pressure. Flash silica gel (60 μ) chromatography column eluted with a mixture of petroleum ether and diethyl ether (80:20) afforded dinuclear complex **2a** (220 mg, 0.45 mmol) in 45% yield. The crude complex **2a** was treated with CPh₃⁺BF₄[–] (220 mg, 0.67 mmol) in CH₂Cl₂ (10 mL) at rt for 30 min. By adding Et₂O (30 mL), the dinuclear complex **3a** precipitated and was collected by filtration as a brown-red powder (240 mg, 99% yield). **3a**: ¹H NMR (acetone-*d*₆, 200 MHz), δ 2.54 (1H, d, *J*=15 Hz, H_{1_{exo}}); 3.38 (1H, dd, *J*=15 and 6 Hz, H_{1_{endo}}); 4.96 (1H, t, *J*=6 Hz, H₂ η^5); 5.63–5.95 (5H, m, ArCr); 6.33 (1H, t, *J*=7 Hz, H₃ η^5); 6.52 (1H, d, *J*=5 Hz, H₅ η^5); 7.55 (1H, t, *J*=5 Hz, H₄ η^5). ¹³C NMR (acetone-*d*₆, 100 MHz): 69.08 (C₁); 93.55, 94.3 (C₁₀, C₁₁, C₁₃, C₁₄); 94.80 (C₁₂); 92.9, 96.45, 96.7, 98.0 (C₆, C₇, C₈, C₉); 129.5, 130.1, 132.6 (C₃, C₄, C₅); 131.75 (C₂); 233.1, 233.7 (CO). IR (CH₂Cl₂) cm^{–1}: 1885, 1965, 2020 (CO), 2100 (C₇, C₈); UV–vis (CH₂Cl₂) nm: λ_{\max} (ϵ)=315 (67900); (CH₃NO₂) λ_{\max} (ϵ)=377 (17900).