

Bimetallic π -conjugated complexes modulated by a carbonyl spacer: synthesis of arenetricarbonylchromium–ferrocene derivatives

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Received 2 October 2000; accepted 20 October 2000

Dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract

Heterobimetallic complexes modulated by a carbonyl spacer have been prepared in the case of arenetricarbonylchromium and ferrocene derivatives via Claisen–Schmidt condensations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Arenetricarbonylchromium complexes; Carbonyl spacer; NLO; Claisen–Schmidt; Ferrocene

1. Introduction

In the past decade, highly active chromophores with large quadratic hyperpolarisability β have attracted much attention because of their interesting non linear optical (NLO) response. Their particular properties have usually been observed when connecting an organic electron donor to an organic electron acceptor via a π -conjugated backbone [1].

However, in a recent publication Persoons and co-workers [2] pointed out the crucial role played by non conventional keto spaced chromophores based on dithienyl derivatives, in tuning the charge transfer along the push–pull conjugated system. Indeed, these authors suggested that the carbonyl spacer did not interrupt the charge delocalisation between the terminal donor and acceptor groups leading to high NLO efficiencies. Moreover, conjugation between the electron withdrawing and the electron donating tails of the substituted

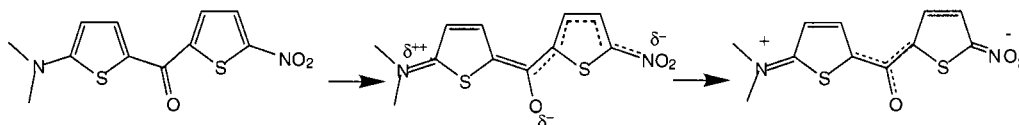
dithienylketone structure was proposed through the following zwitterion-like species (Scheme 1).

They observed two different stages, the first one for an external electric field below 6×10^7 V cm⁻¹, the charge delocalisation occurred from the donor to the carbonyl, the spacer playing the role of the main acceptor group. Beyond 6×10^7 V cm⁻¹ the spacer was saturated and transmitted electrons from the donor to the acceptor. Thus increasing the external field allowed charge redistribution in the molecule leading to polar species. As there is a large difference of dipolar moment $\Delta\mu$ between the ground and the excited states, which are separated by a large enough band gap energy, such organic molecules exhibit high second-order polarisability β .

According to these results and knowing that organometallic complexes have been shown to exhibit good NLO properties [3], we were tempted to investigate the behavior of bimetallic complexes containing such keto-spacers. We report here the preparation of new Cr–Fe dinuclear complexes where the chromium fragment is linked to the ferrocene entity by conjugated carbonyl spacers (Fig. 1).

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Scheme 1. Schematic representation of the evolution of the molecule upon application of an external electric field.

2. Results and discussion

One of the most useful way to obtain keto spacers with concomitant creation of carbon–carbon bonds is to use the efficient addition of carbanions to aldehydes or ketones. Few reports deal with Claisen type reactions involving an organometallic carbanion and aldehydes or ketones. For example, complexed benzylic carbanions obtained from allyl or alkylbenzenetricarbonylchromium derivatives [4] in basic medium lead to the formation of ketones after addition of aldehydes and subsequent oxidation [5] (Scheme 2).

On the other hand, it has been shown that condensation of α -alkylmethylketone anions to benzaldehydetricarbonylchromium complex afforded the corresponding ketol derivative at low temperature. Deshydration of the ketol gave rise to chalcone structures at higher temperatures for prolonged reaction times [6] (Scheme 3).

To the best of our knowledge, no Claisen type reaction has been described involving two organometallic reactants. This strategy was chosen for the preparation of new bimetallic complexes.

As depicted in Scheme 4, complex **1** was obtained through two successive so called Claisen–Schmidt condensations [7] starting either from benzaldehydetricarbonylchromium **2** [8] (pathway a) or ferrocene carboxaldehyde **3** (pathway b).

Conjugated ketone **4** was first prepared using acetone and benzaldehydetricarbonylchromium in the presence of aqueous potassium hydroxide. Carefull deprotonation using LDA and subsequent addition of ferrocene carboxaldehyde **3** directly afforded complex **1** (Scheme 4, path a). As a result of the well-known stabilization effect of the $\text{Cr}(\text{CO})_3$ entity, the reactivity of the carbanion of **4** is weakened, giving consequently a poor 4% yield together with several unidentified polycondensation products. Complex **5** could be obtained from ferrocene carboxaldehyde **3** and acetone in the presence of aqueous potassium hydroxide. In contrast, treatment of **5** with LDA gave a more reactive carbanion, destabilized by the donor effect of ferrocene. Addition to benzaldehyde tricarbonylchromium **2**, allowed the preparation of complex **1** in an overall 60% yield.

The $^1\text{H-NMR}$ spectrum of **1** showed a characteristic vicinal coupling constant of 15 Hz for H7 and H8 protons in good agreement with a *trans* configured double bond created by the Claisen–Schmidt condensation.

We extended this strategy to the building of a more rigid keto-spaced backbone and we performed the same kind of condensation with a cyclic ketone (Scheme 5).

Condensation of cyclohexanone carbanion with ferrocene carboxaldehyde **3** afforded **6** in 60% yield a further lithiation–condensation sequence using LDA and benzaldehydetricarbonylchromium **2** gave the expected complex **7** in 45% yield.

We also tried to extend the spacer's length with a thienyl unit known for its intrinsic properties in NLO materials [9]. Indeed, since the ground state aromaticity of thiophene is lower than that of benzene, much attention has been paid to chromophores containing this unit. Unfortunately reaction of ferrocenyl derivative **5** with aldehyde **8** did not afford complex **9** (Scheme 6). According to NMR spectra, the crude mixture showed the presence of polycondensation products that we were unable to separate and to analyze, due to their high instability.

We generalized this method to the synthesis of other bimetallic complexes with various spacer's lengths using acetylferrocene carbanion.

As mentioned above, LDA was used as base to afford deprotonated acetyl ferrocene species. Subsequent reaction with benzaldehydetricarbonyl chromium **2** gave 60% yield of complex **11**.

Complex **12** was obtained in 21% yield under similar conditions using 5-(η^6 -thiophene-2-carboxaldehyde)-benzenetricarbonylchromium **8**.

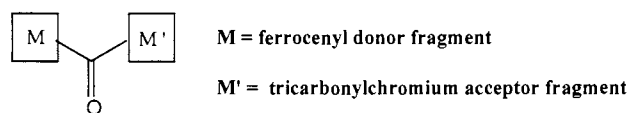
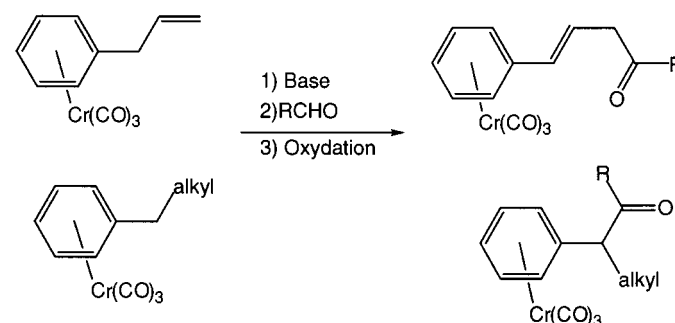
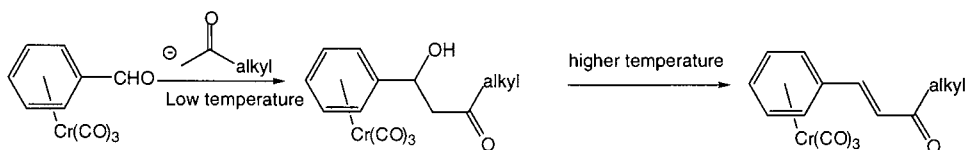
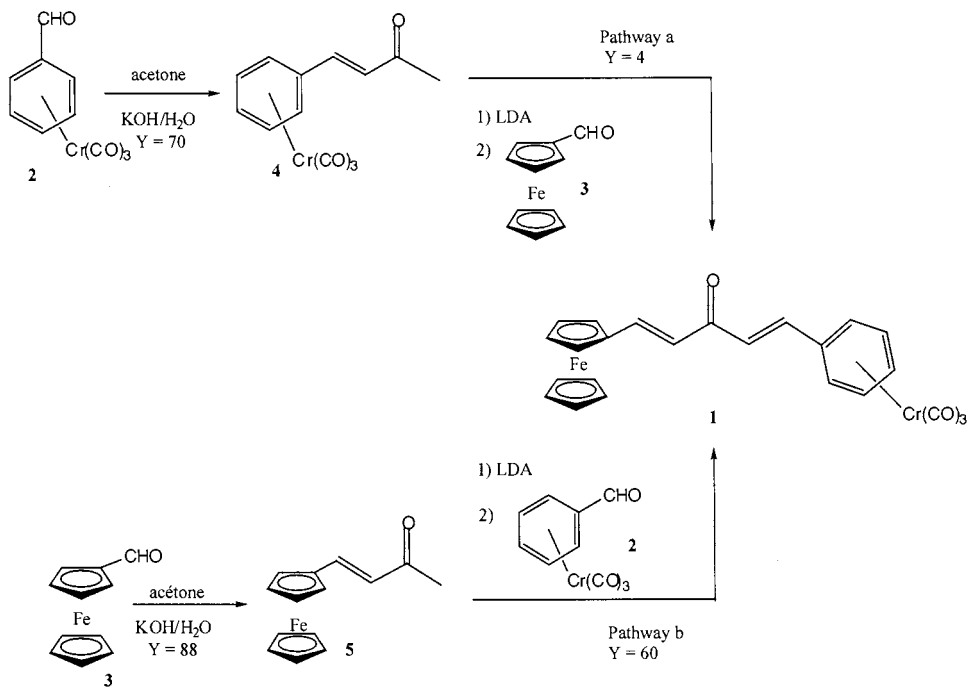
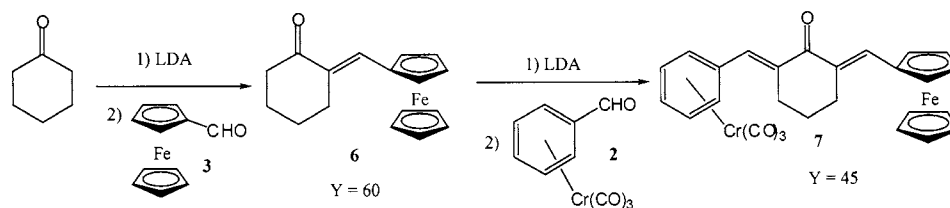
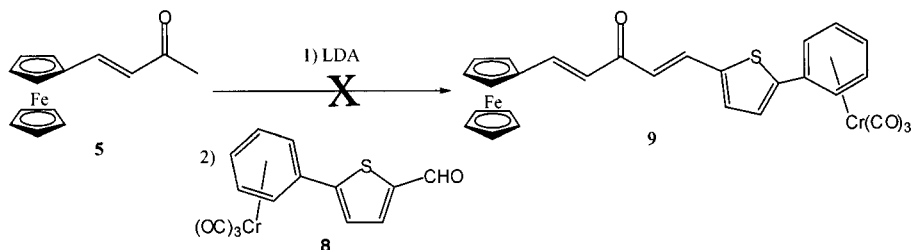


Fig. 1. Design of new bimetallic Cr–Fe complexes.

Scheme 2. Condensation of allyl or alkyl $\text{Cr}(\text{CO})_3$ carbanion.

Scheme 3. Preparation of chalcone- $\text{Cr}(\text{CO})_3$ derivatives.Scheme 4. Preparation of conjugated arene- $\text{Cr}(\text{CO})_3$ -ferrocene derivatives.Scheme 5. Preparation of arene- $\text{Cr}(\text{CO})_3$ -ferrocene derivatives.

Scheme 6. Condensation of ferrocenyl derivatives with aldehyde 8.

In contrast, the reaction of complex 13 with complex 10 carbanion, gave significant resinification. The expected product could not be detected. As observed above, both double bonds created in com-

plexes 11 and 12 were found to be *trans* configured. These complexes differ from 1 and 7 by a direct link between ferrocene and the carbonyl moiety (Scheme 7).

It is worthy to note that benzaldehydicarbonylchromium complex **2** is the most electrophilic candidate under Claisen–Schmidt condensation conditions used in our study. The best results were obtained in reacting complex **2** with carbanions of ketone **10** or enones **5** and **6**. As soon as the aldehyde function is moved away from the coordinated cycle such as in complex **8**, the electron withdrawing effect of $\text{Cr}(\text{CO})_3$ group is less efficient and yields of condensation decreased from 60% for complex **11** to 21% for complex **12**. As for the condensation of **8** with enone **5** anion, no bimetallic complex could be detected in the crude mixture (Scheme 6).

In conclusion we have prepared different hetero-bimetallic complexes by introducing keto-spacers of various natures. Further work will be directed in the characterization of the second order polarisability β of these new bimetallic complexes.

3. Experimental

3.1. General

All experiments were always protected from exposure to light and oxygen. Workup procedures were done in air. Tetrahydrofuran (THF) used was distilled from

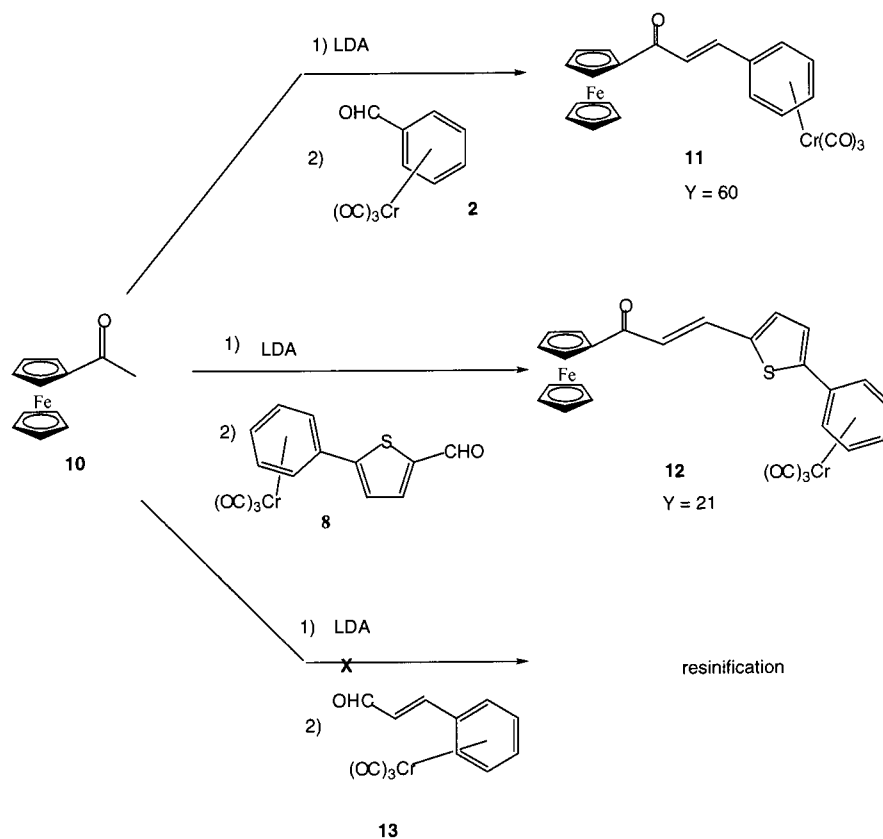
sodium benzophenone ketyl under dry nitrogen. ^1H - and ^{13}C -NMR spectra were obtained with Bruker 200 and ARX 400 spectrometers. Infrared spectra were recorded with Perkin–Elmer 1420. Melting points were measured with a Reichert apparatus.

3.2. Preparation of enones **4** and **5**

An aqueous solution of KOH (5 ml, 0.474 mmol, 1 M) was added at 0°C to a solution of the organometallic aldehyde (1.153 mmol) in acetone (10 ml). The reaction mixture was stirred for 1 h at 0°C and poured into cold water. The precipitate was filtered off and purified by silica gel chromatography using a mixture of petroleum ether and ether (9:1) as eluant to afford the corresponding enone.

Enone **4**: 70% yield. ^1H -NMR (CDCl_3 , 200 MHz): 7.03 (d, $J = 16$ Hz, 1H, $\text{CH}=\text{}$), 6.50 (d, $J = 16$ Hz, 1H, $\text{CH}=\text{}$), 5.55 (d, $J = 6$ Hz, 2H, C_6H_5), 5.46 (t, $J = 6$ Hz, 1H, C_6H_5), 5.34 (t, $J = 6$ Hz, 2H, C_6H_5), 2.35 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3 , 50 MHz): 231.7 ($\text{Cr}(\text{CO})_3$), 197.1 (CO), 140.2 ($\text{CH}=\text{}$), 127.5 ($\text{CH}=\text{}$), 98.8 (C, C_6H_5), 93.1, 92.8 and 91.2 (CH, C_6H_5), 28.1 (CH_3). IR (CH_2Cl_2) cm^{-1} : 1958, 1892, 1645.

Enone **5**: 88% yield. ^1H -NMR (CDCl_3 , 200 MHz): 7.42 (d, $J = 16$ Hz, 1H, $\text{CH}=\text{}$), 6.33 (d, $J = 16$ Hz, 1H, $\text{CH}=\text{}$), 4.50 (brs, 2H, C_5H_4), 4.44 (brs, 2H, C_5H_4), 4.15



Scheme 7. Condensation of aldehydes with acetylferrocene.

(brs, 5H, C₅H₅), 2.29 (s, 3H). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 194.0 (CO), 144.1 (CH=), 123.6 (CH=), 78.0 (C, C₅H₄), 70.2 and 68.7 (CH, C₅H₄), 67.8 (CH, C₅H₅), 26.2 (CH₃). IR (CH₂Cl₂) cm⁻¹: 1655.

3.3. Complex 1 prepared from enone 5

A solution of ⁿBuLi (0.408 ml, 0.613 mmol, 1.6 M) in THF (5 ml) was added at 0°C, under N₂ to (iPr)₂NH (0.0846 ml, 0.645 mmol) in dry THF (3 ml). The reaction mixture was stirred at 0°C for 10 min and a solution of complex 3 (184 mg, 0.645 mmol) in dry THF (3 ml) was added. The resulting mixture was stirred at 0°C for 45 min. A solution of ferrocenecarboxaldehyde (222 mg, 0.774 mmol) in dry THF (3 ml) was then added dropwise at the same temperature. The mixture was stirred at room temperature (r.t.) for 24 h, poured into ice cold water (50 ml) and extracted twice with diethylether (2 × 30 ml). The organic phases were washed with water (2 × 30 ml), saturated solution of ammoniumchloride (50 ml) and evaporated to dryness under reduced pressure. Purification by silica gel chromatography using a mixture of petroleum ether and ether (7:3) as eluant afforded red crystals of complex 1.

Complex 1: 60% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.62 (d, *J* = 16 Hz, 1H, CH=), 7.14 (d, *J* = 16 Hz, 1H, CH=), 6.76 (d, *J* = 16 Hz, 1H, CH=), 6.51 (d, *J* = 16 Hz, 1H, CH=), 5.59 (d, *J* = 6 Hz, 2H, C₆H₅), 5.36 (m, 3H, CH₃), 4.52 (brs, 2H, C₅H₄), 4.45 (brs, 2H, C₅H₄), 4.13 (brs, 5H, C₅H₅). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 232.3 (Cr(CO)₃), 187.2 (CO), 147.0 (CH=), 139.4 (CH=), 126.6 (CH=), 123.2 (CH=), 100.0 (C, C₆H₅), 98.9, 93.3 and 91.5 (CH, C₆H₅), 77.7 (C, C₅H₄), 70.3, 69.5 and 69.2 (CH, C₅H₄, C₅H₅). M.p.: 92°C. IR (CH₂Cl₂) cm⁻¹: 1978, 1900 (Cr(CO)₃), 1615 (CO). Anal. Found: C, 60.41; H, 3.88. Calc. for C₂₄H₁₈O₄CrFe: C, 60.28; H, 3.79%.

Complex 1 was also prepared from enone 4 using the above described procedure.

3.4. Preparation of complex 6

A solution of ⁿBuLi (1.327 ml, 2.12 mmol, 1.6 M) in THF was added at 0°C, under N₂ to (iPr)₂NH (0.3 ml, 2.32 mmol) in dry THF (8 ml). The reaction mixture was stirred for 10 min at 0°C and added to a solution of cyclohexanone (0.2 ml, 1.93 mmol) in dry THF (9 ml) at the same temperature. After 45 min at 0°C, ferrocenecarboxaldehyde (650 mg, 2.32 mmol), in dry THF (8 ml) was added and the mixture was stirred at r.t. for 3 h. Diethylether (20 ml) was then added and the reaction mixture was poured into ice cold water (50 ml). The organic layer was extracted twice with water (2 × 20 ml) and with saturated solution of ammoniumchloride (50 ml). The organic phase was dried with MgSO₄ and evaporated under reduced pressure. Purifi-

ation by silica gel chromatography using a mixture of petroleum ether and ether (98:2) as eluant afforded red crystals of complex 6.

Complex 6: 60% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.60 (s, 1H, CH=), 4.54 (brs, 2H, C₅H₄), 4.41 (brs, 2H, C₅H₄), 4.16 (brs, 5H, C₅H₅), 2.72 (t, *J* = 5.5 Hz, 2H, CH₂CO), 1.84 (m, 2H, CH₂), 1.57 (m, 4H, (CH₂)₂). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 213.0 (CO), 137.7 (CH = C), 80.0 (C = CH), 74.1 (C, C₅H₄), 71.4 and 70.9 (CH, C₅H₄), 69.7 (CH, C₅H₅), 28.4 (COCH₂), 20.0, 20.05 and 20.1 (CH₂). IR (CH₂Cl₂) cm⁻¹: 1710.

3.5. Preparation of complex 7

A solution of ⁿBuLi (0.297 ml, 0.474 mmol, 1.6 M) in THF was added at 0°C, under N₂ to (iPr)₂NH (0.064 ml, 0.494 mmol) in dry THF (3 ml). After 10 min at 0°C a solution of complex 6 (186 mg, 0.494 mmol) in dry THF (3 ml) was added and the reaction mixture was stirred for 45 min at the same temperature. A solution of tricarbonylchromium benzaldehyde (119 mg, 0.491 mmol) in dry THF (3 ml) was then added dropwise in 1 h. After 24 h at r.t. the reaction mixture was poured into ice cold water (50 ml). The organic layer was extracted twice with water (2 × 20 ml) and with a saturated solution of ammoniumchloride (50 ml). The organic phase was dried with MgSO₄ and evaporated under reduced pressure. Purification by silica gel chromatography using a mixture of petroleum ether and ether (7: 3) as eluant afforded red crystals of complex 7.

Complex 7: 45% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.63 (s, 1H, CH=), 7.29 (s, 1H, CH=), 5.52 (m, 2H, C₆H₅), 5.36 (m, 3H, C₆H₅), 4.55 (brs, 2H, C₅H₄), 4.45 (brs, 2H, C₅H₄), 4.16 (brs, 5H, C₅H₅), 2.84 (t, *J* = 6 Hz, 2H, CH₂), 2.71 (t, *J* = 6 Hz, 2H, CH₂), 1.83 (m, 2H, CH₂). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 232.2 (Cr(CO)₃), 187.4 (CO), 140.1 (CH=), 139.7 (C=), 132.1 (CH=), 131.3 (C=), 94.8, 91.5 and 91.1 (CH, C₆H₅), 92.8 (C, C₆H₅), 78.3 (C, C₅H₄), 71.5 and 71.2 (CH, C₅H₄), 69.6 (CH, C₅H₅), 28.5, 28.0 and 22.5 (CH₂). IR (CH₂Cl₂) cm⁻¹: 1609. Anal. Found: C, 62.41; H, 4.20. Calc. for C₂₇H₂₂O₄CrFe: C, 62.57; H 4.28%.

3.6. Preparation of complex 8

A solution of ⁿBuLi (5.41 ml, 9.57 mmol, 1.6 M) in THF was added at -78°C, under N₂ to 2-bromo-5-dioxolanylthiophene (2.045 g, 8.7 mmol) in dry THF (10 ml). The reaction mixture was stirred for 1 h at -78°C and tributylstannylchloride (2.35 ml, 8.7 mmol) was added. After 1 h and 30 min, water (5 ml) and diethylether (15 ml) were added. The organic layer was extracted twice with water (2 × 20 ml) and a saturated solution of ammoniumchloride (50 ml). The organic phase was dried with MgSO₄ and evaporated under

reduced pressure. 2-Tributylstannyl-5-dioxolanylthiophene was purified by distillation.

2-Tributylstannyl-5-dioxolanylthiophene: 75% yield. B.p._{4mmHg}: 50°C. ¹H-NMR (CDCl₃, 200 MHz): 7.26 (d, *J* = 3 Hz, 1H, C₄H₂S), 7.04 (d, *J* = 3 Hz, 1H, C₄H₂S), 6.10 (s, 1H, CH(OCH₂)₂), 4.08 (m, 2H, OCH₂), 3.99 (m, 2H, OCH₂), 1.62 (m, 6H, SnCH₂), 1.30 (m, 6H, CH₂), 1.07 (m, 6H, CH₂), 0.88 (m, 9H, CH₃). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 138.8 (C, C₄H₂S), 135.1 and 127.6 (CH, C₄H₂S), 116.2 (C, C₄H₂S), 100.4 (CH(OCH₂)₂), 65.3 (CH(OCH₂)₂), 28.9, 27.3 and 13.8 (CH₂), 10.8 (CH₃).

A solution of chlorobenzenetricarbonylchromium (1.20 g, 4.8 mmol) in degazed THF (10 ml) was added to Pd₂dba₃ (0.073 g, 0.08 mmol), AsPPh₃ (0.098 g, 0.32 mmol) [10] in degazed THF (5 ml). After 15 min, the above prepared stannylated thiophene (1.791 g, 4 mmol) was added and the mixture was stirred at r.t. for 18 h. Water (20 ml) and diethylether (20 ml) were added. The organic layer was extracted twice with water (2 × 20 ml) and a saturated solution of ammoniumchloride (50 ml). The organic phase was dried with MgSO₄ and evaporated under reduced pressure. Purification by silica gel chromatography using a mixture of petroleum ether and ether (9:1) as eluant afforded the expected coupling complex.

2-[(η⁶-Chlorobenzene)tricarbonylchromium]-5-dioxolanylthiophene: 60% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.15 (d, *J* = 4 Hz, 1H, C₄H₂S), 7.07 (d, *J* = 4 Hz, 1H, C₄H₂S), 6.06 (s, 1H, CH(OCH₂)₂), 5.66 (d, *J* = 6 Hz, 2H, C₆H₅), 5.44 (t, *J* = 6 Hz, 2H, C₆H₅), 5.28 (t, *J* = 6 Hz, 1H, C₆H₅), 4.09 (m, 2H, OCH₂), 3.99 (m, 2H, OCH₂). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 233.0 (Cr(CO)₃), 143.1 and 140.6 (C, C₄H₂S), 126.9 and 124.8 (CH, C₄H₂S), 100.1 (CH(OCH₂)₂), 99.6 (C, C₆H₅), 92.3, 91.1 and 90.5 (CH, C₆H₅), 65.4 (CH(OCH₂)₂).

An aqueous solution of HCl (50 ml, 1 mol l⁻¹) was added to 2-[(η⁶-chlorobenzene) tricarbonylchromium]-5-dioxolanylthiophene (0.061 g, 0.16 mmol) in diethylether (5 ml) and water (5 ml). After 5 h, an aqueous solution of Na₂CO₃ (30 ml, 1 mol l⁻¹) was added. The aqueous phase was extracted with diethylether (2 × 50 ml). The combined organic phases were dried with MgSO₄ and evaporated under reduced pressure. Purification by silica gel chromatography using a mixture of petroleum ether and ether (7:3) as eluant afforded complex **8**.

Complex **8**: 67% yield. ¹H-NMR (200 MHz, CDCl₃): 9.88 (s, 1H, CHO), 7.69 (d, *J* = 4 Hz, 1H, C₄H₂S), 7.36 (d, *J* = 4 Hz, 1H, C₄H₂S), 5.75 (d, *J* = 6 Hz, 2H, C₆H₅), 5.42 (m, 3H, C₆H₅). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 231.8 (Cr(CO)₃), 182.6 (CHO), 149.8 and 143.2 (C, C₄H₂S), 136.6 and 125.5 (CH, C₄H₂S), 99.8 (C, C₆H₅), 92.0, 91.6 and 91.1 (CH, C₆H₅).

3.7. Preparation of complex **13**

PPh₃CHCHO (660 mg, 2.16 mmol) was added in portions to a solution of benzaldehydetricarbonylchromium (250 mg, 1.032 mmol) in DMF (3 ml) and the reaction mixture was stirred for 8 h at r.t. An additional 24 h was necessary to ensure completion of the reaction. The reaction mixture was poured into water (50 ml) and extracted twice with diethylether (2 × 50 ml). After extraction, the organic phase was evaporated under reduced pressure and purified by silica gel chromatography using a mixture of petroleum ether and ether (6:4) as eluant to afford yellow–orange crystals of complex **13**.

Complex **13**: 77% yield. ¹H-NMR (CDCl₃, 200 MHz): 9.64 (d, *J* = 7 Hz, 1H, CHO), 6.99 (d, *J* = 16 Hz, 1H, CH=), 6.49 (dd, *J* = 16 Hz, 1H, CH=), 5.53 (m, 3H, C₆H₅), 5.35 (t, *J* = 6 Hz, 2H, C₆H₅). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 231.5 (Cr(CO)₃), 192.6 (CHO), 149.3 and 128.5 (CH=), 97.3 (C, C₆H₅), 93.6, 93.3 and 90.9 (CH, C₆H₅). IR (CH₂Cl₂) cm⁻¹: 1978, 1905, 1682.

3.8. Preparation of complexes **11** and **12**

A solution of ⁿBuLi (0.236 ml, 0.379 mmol, 1.6 M) in THF was added at 0°C, under N₂ to (iPr)₂NH (0.052 ml, 0.395 mmol) in dry THF (2.5 ml). The reaction mixture was stirred for 10 min at 0°C and a solution of acetylferrocene (80 mg, 0.395 mmol) in dry THF (2 ml) was added dropwise. After 45 min at 0°C, a solution of the appropriate aldehyde (0.474 mmol) in dry THF (2 ml) was added dropwise. The mixture was stirred at r.t. for 24 h and poured into water (50 ml). The organic layer was extracted twice with water (2 × 20 ml) and a saturated solution of ammoniumchloride (50 ml). The organic phase was dried with MgSO₄ and evaporated under reduced pressure. Purification by silica gel chromatography using a mixture of petroleum ether and ether (7:3) as eluant afforded red crystals of the expected complex.

Complex **11**: 60% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.28 (d, *J* = 16 Hz, 1H, CH=), 6.90 (d, *J* = 16 Hz, 1H, CH=), 5.66 (d, *J* = 6 Hz, 2H, C₆H₅), 5.41 (m, 3H, C₆H₅), 4.88 (brs, 2H, C₅H₄), 4.62 (brs, 2H, C₅H₄), 4.21 (brs, 5H, C₅H₅). ¹³C{¹H}-NMR (CDCl₃, 50 MHz): 232.1 (Cr(CO)₃), 191.7 (CO), 137.5 (CH=), 123.8 (CH=), 99.7 (C, C₆H₅), 93.3, 93.1 and 91.4 (CH, C₆H₅), 80.1 (C, C₅H₄), 73.3 (CH, C₅H₄), 70.4 (CH, C₅H₄); 69.8 (CH, C₅H₅). IR (CH₂Cl₂) cm⁻¹: 1975, 1900, 1648. Anal. Found: C, 58.24; H, 3.42. Calc. for C₂₂H₁₆O₄CrFe: C, 58.43; H, 3.57%.

Complex **12**: 21% yield. ¹H-NMR (CDCl₃, 200 MHz): 7.79 (d, *J* = 16 Hz, 1H, CH=), 7.45 (d, *J* = 4 Hz, 1H, C₄H₂S), 7.50 (d, *J* = 4 Hz, 1H, C₄H₂S), 7.17 (d, *J* = 16 Hz, 1H, CH=), 6.16 (d, *J* = 7 Hz, 2H, C₆H₅), 5.83 (m, 3H, C₆H₅), 4.99 (brs, 2H, C₅H₄), 4.77 (brs, 2H,

C_5H_4), 4.24 (brs, 5H, C_5H_5). $^{13}C\{^1H\}$ -NMR ($CDCl_3$, 50 MHz): 232.5 ($Cr(CO)_3$), 192.3 (CO), 141.9 and 141.3 (C, C_4H_2S), 132.5 and 132.1 (CH, C_4H_2S), 125.8 (CH=), 122.8 (CH=), 101.8 (C, C_6H_5), 94.9, 92.4 and 90.4 (CH, C_6H_5), 80.5 (C, C_5H_4), 72.9 (CH, C_5H_4), 70.2 (C, C_5H_4), 69.7 (C, C_5H_5). IR (CH_2Cl_2) cm^{-1} : 1968, 1889, 1651. Anal. Found: C, 58.25; H, 3.21. Calc. for $C_{26}H_{18}O_4SCrFe$: C, 58.44; H, 3.40%.

Acknowledgements

We thank CNRS and the EU Training and Mobility of Researchers program for financial support and for a postdoctoral fellowship to Z.F.P.

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