Synthesis and non-linear properties of conjugated poly-unsaturated amino carbene complexes[☆]

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Abstract

A series of poly-unsaturated pyrrolidino carbene complexes have been synthesized and their first β hyperpolarizabilities evaluated using the Hyper Rayleigh Scattering (HRS) technique. Some of these complexes have good to high β values (up to 543×10^{-30} esu). A comparison of the non-linear responses of the complexes with those of the corresponding amides (their isolobal organic analogues) highlighted the potential usefulness of the pentacarbonylchromium carbene moiety as an electron-accepting group in the design of second order non-linear optical (NLO) materials. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The discovery of non-linear behaviour in materials or molecules under the influence of a strong electric field such as that supplied by a laser beam has aroused considerable scientific interest over recent years. This is due to the essential contribution that these studies have made to the current evolution from electronic to photonic devices, an evolution that is likely to be implemented in the near future [1]. As a consequence of the active research being conducted in relation to this physical phenomenon, many inorganic materials with appreciable non-linearities have been discovered and some of them are now finding concrete applications. However the high cost of inorganic materials, their low optical damage threshold, and the problems encountered when they are processed have more recently led researchers to consider organic materials, which have the advantages of being cheaper, easier to process and, more flexibly

synthesized. Furthermore, many organic materials have greater non-linear properties than even the best inorganic materials. It has also been possible to investigate and clarify the molecular structural factors which are crucial to their non-linear response. For example, non centro-symmetric molecules are good candidates for second order non-linear activity and, in particular, large first β hyperpolarizability can be observed in type **1** conjugated poly-unsaturated organic systems in which a π-system connects electron-donating **D** to accepting **A** groups (the so called "push-pull" molecules) (Fig. 1).

Empirical models have been proposed to correlate the β tensor with the physical and electronic parameters of such molecules. The two-state model of Oudar [2] indicates that good candidates for NLO should have: (1) a dipolar moment in the excited charge transfer state that is very different from that in the ground state; (2) a small difference in energy between the ground and excited states; and (3) large electronic transition dipolar moment.
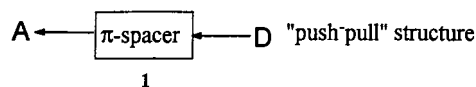
Fig. 1.

Several types of π-spacers (enes, ynes, oligoaromatics, oligoheteroaromatics and their combinations), coupled with different kind of donor (–NR$_2$, OR, SR, R$_2$N–N=CH–) and accepting groups (–NO$_2$, –(CN)C=C(CN)$_2$, –COR, SO$_2$R), have already been studied and been found to have very interesting β values [3]. Attention in this field has more recently been directed to "push-pull" molecules containing organometallic moieties because transition metals introduce new variables such as their different oxidation states, differences in the nature and number of the ligands that allow the modulation of their electron-withdrawing or releasing properties and optimization of their interaction with the π-spacer in order to create the best non-linear response [4].

Among the stable and isolable organometallic compounds containing transition metals, Fischer-type carbene complexes **2** have recently become very popular as useful reagents in organic synthesis ([5], Fig. 2).

The pentacarbonyl(metal)carbene unit in these complexes behaves as a strong electron-withdrawing group that is similar to a Lewis acid complexed carbonyl function. Furthermore Fischer-type carbene complexes have a low energy metal to ligand charge transfer (MLCT) transition in which the metal donates electrons to the empty p orbital of the carbenic carbon atom. This situation is the opposite of that observed in the ground state, in which the heteroatom bonded to the carbene carbon atom acts as a π-donor towards the metal (Fig. 3).

Under the two-state approximation proposed by Oudar, the consequence of these factors should be a greater difference between the dipolar moment in the excited charge transfer state and in that the ground state ($\Delta\mu$) and a higher β value would be expected for carbene complexes in comparison with the corresponding carbonyl derivatives that represent their isolobal analogues (Eq. (1)).

$$\beta(-2\omega;\omega,\omega) = \frac{3\Delta\mu\,\mu_{eg}^2}{E_{CT}^2}\frac{\omega_{CT}^2}{[1-(2\omega)^2(\omega_{CT})^2][(\omega_{CT})^2-\omega^2]}$$

$$= \beta_0\frac{\omega_{CT}^2}{[1-(2\omega)^2(\omega_{CT})^2][(\omega_{CT})^2-\omega^2]} \quad (1)$$

The possibility of inserting this unit into "push-pull" systems appeared to us to be very attractive. In addition, by acting on the π-donor capabilities of the het-
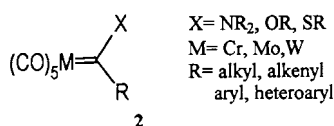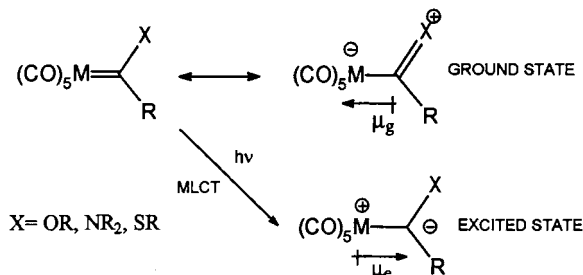

Fig. 3. Representation of ground and excited state gor Fischer-type carbene complexes.

eroatom X, it is theoretically possible to modulate the electron-withdrawing strength of the pentacarbonyl(metal)carbene unit and its interaction with an unsaturated system.

2. Results and discussion

β values comparable with those of *para*-nitroaniline ($\beta = 16.9 \times 10^{-30}$ esu), have recently been determined in simple "push-pull" Fischer-type carbene complexes **3a,b** synthesized by us ([6], Fig. 4), and these preliminary results stimulated us to investigate further the synthesis of other carbene complexes with more extended π-spacers.

We report here the synthesis of poly-unsaturated aminocarbene complexes and the measurements of their first β hyperpolarizability. The β values of these complexes were compared with those of their corresponding amides with the aim of evaluating the real effectiveness of the pentacarbonylaminocarbene moiety in determining significant non-linear responses.

We have recently reported that the conjugated base of the propenyl(pyrrolidino)carbene complex **4** reacts with aldehydes to produce the corresponding aldol addition products in high chemical yields and complete γ-regioselectivity [7]. On the hypothesis that the dehydration of these aldols would allow a simple and direct entry to poly-unsaturated aminocarbene complexes, we investigated the aldol addition complexes **6a–c**, respec-
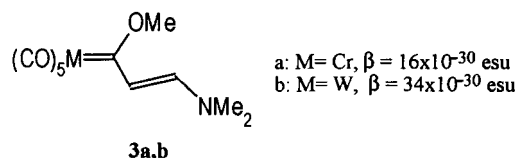

X= NR$_2$, OR, SR
M= Cr, Mo, W
R= alkyl, alkenyl
aryl, heteroaryl

2

Fig. 2. General structure of Fischer-type carbene complexes.

a: M= Cr, β = 16x10^{-30} esu
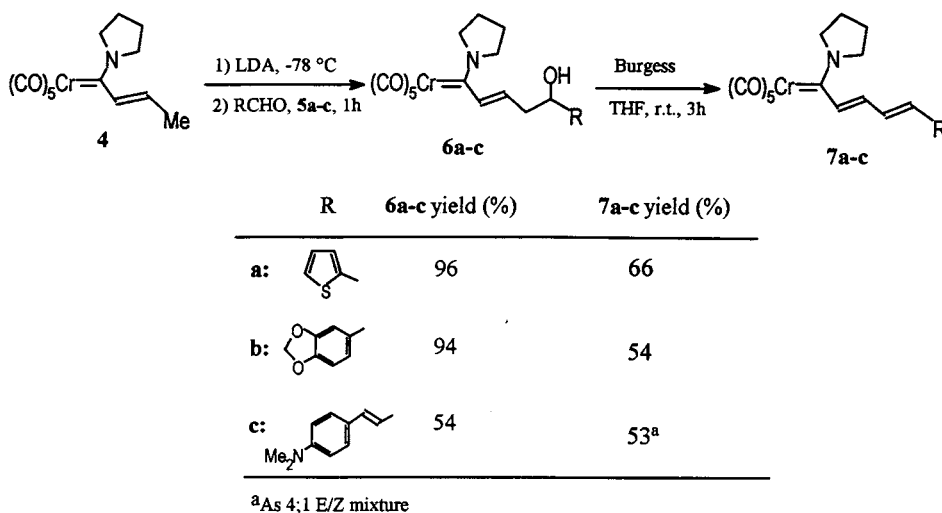b: M= W, β = 34x10^{-30} esu

3a,b

Fig. 4. Simple Fischer-type carbene complex based "push-pull" structures.

Scheme 1. Synthesis of poly-unsaturated Fischer-type amino carbene complexes.

tively, obtained from the reaction of **4** with 2-thiophen-carbaldehyde **5a**, piperonal **5b** and 4-dimethylaminocinnamaldehyde **5c** (Scheme 1). The dehydration of **6a–c** was expected to lead directly to "push-pull" poly-unsaturated aminocarbene complexes in which the donor groups are represented by the thiophene, 3,4-methylenedioxyphenyl and 4-dimethylaminophenyl rings.

The treatment of **6a–c** with three equivalents of methyl-N-(triethylammoniosulfonyl)carbamate (Burgess reagent) [8], a convenient and commercially available reagent for the direct dehydration of secondary alcohols, in THF solution at room temperature, allowed the corresponding poly-unsaturated amino carbene complexes **7a–c** to be obtained in synthetically useful yields. In carbenes **7a** and **7b**, the new double bond was formed in the (E) configuration, whereas ^{1}H-NMR data showed that **7c** was obtained as a 4:1 trans/cis mixture. The pure E,E,E, isomer of **7c** was obtained after two crystallizations from diisopropyl ether at −78°C (Scheme 1).

The NLO properties of these complexes were evaluated by measuring the first β hyperpolarizability using the Hyper Rayleigh Scattering (HRS) technique [9] in a dichloromethane solution and an Nd:YAG laser operating at 1064 nm (see Table 1).

Complexes **7a** and **7b** both had modest β values of around 50×10^{-30} esu (although these are appreciably higher than those of the complexes **3** and of the para-nitroaniline external reference). This is in agreement with the still relatively short length of the π-spacer and the poor donating properties of the methylendioxyphenyl and thiophene rings. A further increase in the spacer length and the donor properties of the phenyl ring (as in complex **7c**) lead to a considerable enhancement of the β value up to 350×10^{-30} esu.

Since the (CO)$_5$Cr=C unit is considered to be isolobal [10] to a carbonyl function, the amides **8a** and **8b** can be seen as the organic analogues of complexes **7b** and **7c**. To the best of our knowledge there is no reference in the literature to the NLO properties of polyunsaturated amides. These amides were prepared by oxidising complexes **7b** and **7c**. We found that ceric ammonium nitrate gave the best yields in the oxidation of **7b** to **8a** (73% yield); the exposure of an acetone solution of complex **7c** to atmospheric oxygen in the presence of sunlight gave the amide **8b** in 35% yield (Scheme 2).

The NLO properties of amides **8a** and **8b** were measured using HRS technique and compared with those of the complexes **7a–c** in the Table 1.

This comparison clearly shows that the substitution of an amide functionality with an aminocarbene moiety positively influences the NLO response, particularly in the case of **7c** with respect to **8b** [11]. Two principal parameters may explain this effect: (1) the interaction of the donor and accepting groups with the spacer; and (2) the polarizability of the spacer itself. Since the donor groups are identical, only a different interaction between the spacer and the pentacarbonylchromium carbene moiety in **7** and the amide function in **8** should

Table 1
First β and β_0 hyperpolarizability of complexes **7a–c** and amides **8a** and **8b**

Compound	λ_{max} (nm, log ε_{max}) [a]	β (10^{-30} esu)	β_0 (10^{-30} esu)
7a	342	50	26
7b	345 (4.5)	55	28
7c	395 (4.7)	350	154
8a	342 (4.4)	49	
8b	401 (4.6)	260	

[a] Measures performed in CH$_2$Cl$_2$.
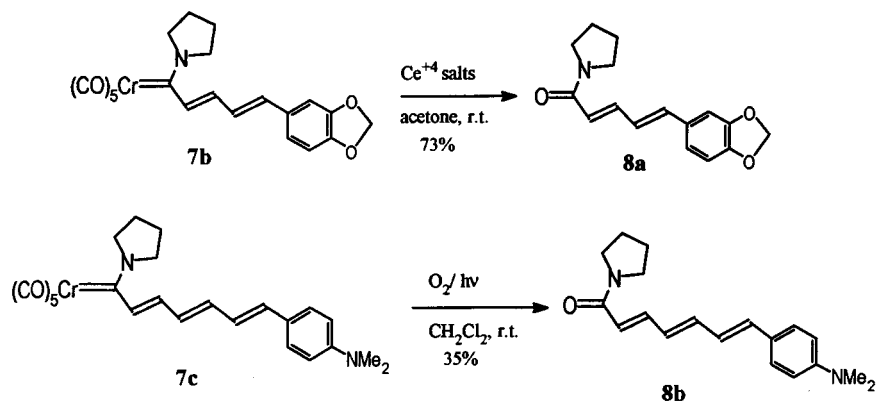
Scheme 2. Synthesis of poly-unsaturated amides.

be expected. The ^{1}H- and ^{13}C-NMR data for the complexes **7**, and those reported for other α,β-unsaturated alkoxy and aminocarbene complexes [12], strongly suggest that the planes containing the M = C moiety and the π-system are perpendicular to each other, and so only an inductive electron-withdrawing effect can be exerted by the (CO)$_5$Cr=C moiety on the spacer. The ground state of complexes **7** is therefore better described by the resonance structures **A** and **B** (Fig. 5). Given that non-linear responses are related to an asymmetric distribution of the π-electrons in "push-pull" structures, it is likely that the response observed in complexes **7** mainly originated from the polarization of the π-electrons of the spacer by the (CO)$_5$Cr=C moiety (a inductive polarization of the π-electrons of the spacer has previously been observed in poly-unsaturated structures bearing onium groups [3a]). A different situation can be expected for amides **8**, in which the better π-overlap between the amide function and the unsaturated spacer means that the ground state is better described by the resonance structures **B** and **C**, and that the charge-separated structure **C** is responsible for their non-linear behaviour (Fig. 5).

The differences in the β values observed between the complexes **7** and amides **8** can be interpreted as a better polarization, and a consequently greater asymmetric distribution of the π-electrons of the spacer, due to the fact that the electron-withdrawing power of the (CO)$_5$Cr=C group is stronger than that of the amide function. In amide **8a**, the asymmetric electronic distri-

bution resulting from the conjugation of the amide function with the π-spacer (structure **C**, Fig. 5) could be of the same magnitude as that induced by the polarization of the spacer's π-electrons by the pentacarbonylchromium amino carbene moiety in **7b**, thus justifying the similar non-linear response observed for these compounds. In complex **7c** and the corresponding amide **8b**, the π-electrons are decidedly more polarizable as a result of the presence of the better −NMe$_2$ donor group and longer spacer in comparison with **7b** and **8a**, and this would justify the enormous improvement in non-linear response going from **7b** to **7c** and from **8a** to **8b**. A similar trend has been observed in similar organic "push-pull" structures [3c]. The considerable difference in the β values of **7c** and **8b** reflects the greater asymmetric electronic distribution induced by the amino carbene moiety in comparison with the amide function.

The high β value of complex **7c** prompted us to synthesize complexes with a more extended π-system.

The tailoring of new NLO materials has mainly concentrated on "push-pull" molecules containing oligothiophene or mixed thiophene-ene π-spacers [13], since the introduction of this heterocycle offers distinct advantages over pure polyenes or polyphenyl spacers: for example, the thiophene ring is particularly stable under thermal and oxidative conditions, and so oligothiophene spacers are more stable than the corresponding conjugated polyenes; furthermore it has a less aromatic character than a phenyl ring, an this allows better electronic communication between the donor and the accepting groups than in polyphenyl-based "push-pull" structures. We therefore considered carbene **9**, in which
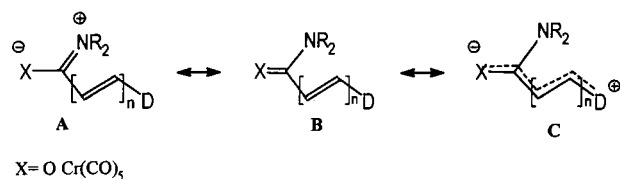

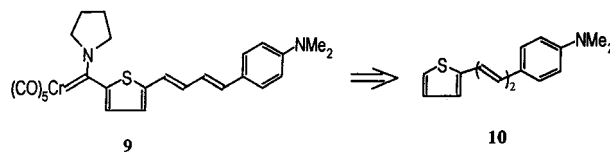Fig. 5. Resonance structures for poly-unsaturated aminocarbene complexes and amides.

Fig. 6.

two of the four double bonds are included in a thiophene ring. Retrosynthetic analysis identifies compound **10**, as suitable starting material for the synthesis of complex **9** (Fig. 6).

Compound **10** was directly synthesized by means of a Wittig–Horner reaction between the 2-thiophene-ethylphosphonate **11** [14] and **5c**. Selective metallation with *n*-BuLi at the free 5-position of thiophene ring in **10**, followed by reaction with $Cr(CO)_6$ and alkylation of the resulting acylanion intermediate with Meerwein's salt afforded the corresponding alkoxycarbene **12** in an overall yield of 62%. Aminolysis of **12** with pyrrolidine gave **9** in 52% yield (Scheme 3).

Complex **9** has a β value of 543×10^{-30} esu, the highest β value so far observed for a Fischer-type based "push-pull" molecule. This improvement probably parallels the greater polarizability of the spacer in complex **9** in comparison with that in complex **7c**. Furthermore the maximum absorption of **9** at 403 nm (log $\varepsilon_{max} = 4.7$), a higher level of energy than the 432 nm observed in the case of simple mono-thiophene amino carbene complexes [15], suggests that the metal-carbene moiety in complex **9**, does not conjugate with the thiophene ring; the NMR of thiophene ring protons in **9** confirms this situation. Absorption at 403 nm is far enough from 532 nm (the second harmonic of the 1064 nm laser used) to exclude any appreciable contribution by resonance enhancement to the β value. Furthermore this complex has a good static β_0 hyperpolarizability (195×10^{-30} esu).

The results obtained in this study clearly underline the interesting potential of the pentacarbonyl(chromium)aminocarbene moiety as the accepting group in the design of new "push-pull" molecules with NLO properties as well as the fact that this potential is greater than that of a carbonyl function which represents its corresponding organic analogue. The good NLO behaviour of these complexes can be attributed to the good polarization of the π-electron system of the spacer produced by the strong electron-withdrawing character of the $(CO)_5Cr=C$ group and, to some extend, probably attributed to the presence of MLCT absorp-

tion (which should contribute in increasing the difference between the dipolar moment in the ground and excited states). The low π-interaction is only a partial drawback to the electronic communication with the donor group at the other end of the spacer because it positively contributes towards keeping the maximum absorption of these complexes at around 400 nm, thus limiting the contribution of resonance enhancement to the measured β values. Chiral amines can be easily introduced in the aminocarbene complex moiety. Their presence ensures a non-centrosymmetric packing of the molecules, an important macroscopic feature for NLO activity. Finally, the presence of the $Cr(CO)_5$ group means that Fischer-type carbene complexes are often solid and crystalline compounds with appreciable solubility even in low polar solvents such as hydrocarbons and ethers. In our opinion, the potential of these particular characteristics of carbene complexes makes them worthy of further studies with the aim of making better-tailored spacers and donor groups, and investigating different metals.

3. Experimental

3.1. General

Complex **4** was prepared by literature procedures [16]. The aldehydes **5a–c** were purchased by Aldrich Chemical Co.; **5a,c** used as received, **5b** distilled just before use. The amide **8a** is a known compound [17]. The reagent *n*-BuLi (1.6 M hexane solution) was purchased from Merck Co. and titred just before use. THF was dried by refluxing over Na/benzophenone ketyl. All manipulations were performed under inert atmosphere. Flash and dry chromatography were performed with silica gel 60 Merck 230–400 mesh. Melting points were measured with a Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1725X FT-IR spectrometer. NMR spectra were obtained using a Bruker WP 80 and AC300 or Varian XL300 and Gemini 200 MHz. Mass spectra (EI, FAB)
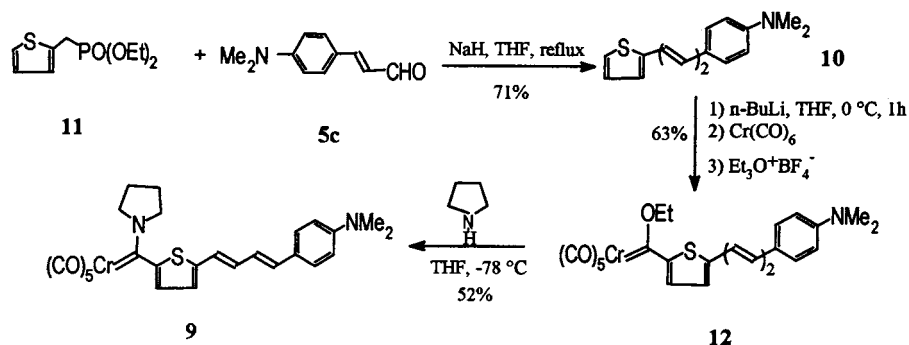
Scheme 3.

were collected using a VG Analytical 7070 EQ instrument. UV/vis spectra were recorded on JASCO V-520 UV/vis spectrometer using deoxygenated solvents.

3.2. General procedure for the preparation of the complexes 6a–c

To a tetrahydrofuran solution of the conjugated base of the complex **4** [generated by treating 1 mmol of **4** with 1.3 mmol of freshly prepared LDA (from distilled diisopropylamine and *n*-BuLi) at –78°C for 20 min] the aldehydes **5a–c** (1.2 equivalents) were added at − 78°C under inert atmosphere. The mixture was allowed to react at − 78°C and the progress of the reaction was monitored by TLC analysis (eluent: CH_2Cl_2/light petroleum 1:1). After 1 h the reaction was practically complete. The reaction was quenched by adding 10 ml of a saturated aqueous ammonium chloride solution, followed by extraction with CH_2Cl_2 (2 × 50 ml). The organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of dry flash chromatography (**6a** and **6b** eluent: light petroleum/CH_2Cl_2, 1:1, **6c** eluent: light petroleum/diethyl ether 1:1). The chemical yields of recovered complexes **6a–c** are reported in Scheme 1.

3.2.1. Complex 6a

Yellow solid m.p. 70°C (from diisopropyl ether/hexane); IR (nujol) cm^{-1}: 3369 (v OH), 2051 (v CO *trans*), 1972–1852 (broad, v CO *cis*), 1641 (v C=C), 1601 (v C=C, thiophene ring); ^{1}H-NMR (300 MHZ, CDCl$_3$) δ ppm: 1.94 (m, 2H, N_E–CH$_2$–CH_2), 2.08 (m, 2H, CH_2–CH$_2$–$_Z$N), 2.18 (d, 1H, J_{vic} = 3.8 Hz, OH), 2.70 (m, 2H, –CH=CH–CH_2–), 3.47 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.08 (m, 2H, CH$_2$–CH_2–$_Z$N), 5.04 (m, 1H, CH–OH), 5.20 (dt, 1H, J_{trans} = 16.4 Hz, J_{vic} = 7.0 Hz –CH=CH–CH$_2$–), 6.50 (broad d, 1H, J_{trans} = 16.1 Hz), 6.95–7.25 (m, 1H, thiophene ring.), 6.97 (m, 2H, thiophene ring); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.0 (N$_E$–C–C–), 25.3 (C–C–$_Z$N), 42.4 (–CH=CH–CH$_2$–), 55.1 (N$_E$–C–C), 59.1 (C–C–$_Z$N), 69.7 (CH–OH), 119.8 (Cr=C–CH=CH–CH$_2$–), 124.1 (CH, thiophene ring), 124.8 (CH, thiophene ring), 126.7 (CH, thiophene ring), 143.8 (Cr=C–CH=CH–CH$_2$–), 147.7 (C$_q$, thiophene ring), 218.0 (CO$_{cis}$), 223.6 (CO$_{trans}$), 263.8 (Cr=C–C);. Elem. Anal. Found: C = 50.45%, H = 3.91%, N = 3.21%. C$_{18}$H$_{17}$NCrO$_6$S, MW 427,39. Anal. Calc. C = 50.58%, H = 3.98%, N = 3.28%.

3.2.2. Complex 6b

Yellow oil; IR (neat) cm^{-1}: 3386 (v OH), 2055 (v CO *trans*), 1981–1866 (broad, v CO *cis*), 1642 (v C=C); ^{1}H-NMR (80 MHz, CDCl$_3$) δ ppm: 2.10 (m, 5H, CH_2–CH$_2$–$_Z$N$_E$– CH$_2$–CH_2– + OH), 2.56 (t, 2H, J_{vic} = 7.0 Hz, –CH=CH–CH_2–), 3.47 (m, 2H, N$_E$–

CH_2–CH$_2$–), 4.10 (m, 2H, CH$_2$–CH_2–$_Z$N), 4.72 (broad t, 1H, J_{vic} = 3.2 Hz, CH–OH), 5.16 (dt, 1H, J_{trans} = 16.1 Hz, J_{vic} = 7.0 Hz –CH=CH–CH$_2$–), 5.94 (s, 2H, –O–CH$_2$–O–), 6.48 (broad d, 1H, J_{trans} = 16.1 Hz), 6.83 (m, 3H, arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.5 (N$_E$–C–C–), 25.8 (C–C–$_Z$N), 42.9 (–CH=CH–CH$_2$–), 55.6 (N$_E$–C–C), 59.7 (C–C–$_Z$N), 74.2 (CH–OH), 101.6 (s, 2H, –OCH$_2$–O–) 106.9 (CH, arom.), 108.7 (CH, arom.), 119.9 (CH, arom.), 121.3 (Cr=C–CH=CH–CH$_2$–), 138.6 (C$_q$, arom.), 144.1 (Cr=C–CH=CH–CH$_2$–), 147.7 (C$_q$, arom.), 148.5 (C$_q$, arom.), 218.7 (CO$_{cis}$), 224.1 (CO$_{trans}$), 265.3 (Cr=C–C); MS (FAB$^+$), m/z: 465 (M$^+$, low intensity), 409 (M$^+$-2CO), 381 (M$^+$-3CO), 363 (M$^+$-4CO), 335 (M$^+$-5CO). Elem. Anal. Found: C = 53.78%, H = 3.92%, N = 2.91%. C$_{21}$H$_{19}$N$_1$CrO$_8$, MW 465.38. Anal. Calc. C = 54.19%, H = 4.08%, N = 3.01%.

3.2.3. Complex 6c

Orange oil; IR (neat) cm^{-1}: 3390 (v OH), 2051 (v CO *trans*), 1968–1901 (broad, v CO *cis*), 1609 (v C=C); ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 1.90 (m, 2H, N$_E$–CH$_2$–CH_2–), 2.05 (m, 3H, CH_2–CH$_2$–$_Z$N=OH), 2.48 (m, 2H, –CH=CH–CH_2–), 2.95 (s, 6H, NMe$_2$) 3.57 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.09 (m, 2H, CH$_2$–CH_2–$_Z$N), 4.38 (m 1H, CH–OH), 5.30 (dt, 1H, J_{trans} = 16.4 Hz, J_{vic} = 7.0 Hz –CH=CH–CH$_2$–), 6.12 (dd, 1H, J_{trans} = 16.2 Hz, J_{vic} = 6.47 Hz, CH(OH)–CH=CH–Ar), 6.52 (broad d, 1H, J_{trans} = 16.4 Hz), 6.51 (d, 1H, J_{trans} = 16.2 Hz CH(OH)–CH=CH–Ar), 6.66 (d, 2H, J_{ortho} = 7.5 Hz, arom.), 7.24 (d, 2H, J_{ortho} = 7.5 Hz, arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 24.9 (N$_E$–C–C–), 25.8 (C–C–$_Z$N), 40.3 (NMe$_2$), 40.7 (–CH=CH–CH$_2$–), 55.3 (N$_E$–C–C), 59.1 (C–C–$_Z$N), 72.4 (CH–OH), 112.3 (CH, arom.), 120.9 (Cr=C–CH=CH–CH$_2$–), 124.7 (C$_q$, arom.), 127.1 (CH(OH)–CH=CH–Ar.), 127.3 (CH, arom.), 131.0 (CH(OH)–CH=CH–Ar), 143.3 (Cr=C–CH=CH–CH$_2$–), 150.2 (C$_q$, arom.), 218.0 (CO$_{cis}$), 223.5 (CO$_{trans}$), 264.1 (Cr=C–C); MS (FAB$^+$), m/z: 490 (M$^+$, low intensity), 434 (M$^+$-2CO), 406 (M$^+$-3CO), 378 (M$^+$-4CO), 350 (M$^+$-5CO). Elem. Anal. Found: C = 58.58%, H = 5.23%, N = 5.58%. C$_{24}$H$_{26}$N$_2$CrO$_6$, MW 490.48. Anal. Calc. C = 58.77%, H = 5.31%, N = 5.71%.

3.3. General procedure for the preparation of the complexes 7a–c

To a solution of 1 mmol of the aldol complexes **6a–c** in THF (5 ml), the Burgess reagent (three equivalents) dissolved in THF (7 ml) was added dropwise over 5 min at room temperature and under inert atmosphere. The mixture was allowed to react at the same temperature, monitoring the progress of the reaction by TLC analysis (eluent: CH_2Cl_2 /light petroleum 1:1). After 4 h

the reaction was practically complete and the solution appeared red or orange in colour. The reaction was quenched by adding 5 ml of water and the organic solvent removed under reduced pressure. The crude oil was taken up with dichloromethane (50 ml) and washed twice with 10 ml of water. The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude reaction mixture was purified by means of flash chromatography (eluent: light petroleum/CH_2Cl_2, 1:1). The chemical yields of recovered complexes **7a–c** are reported in Scheme 1.

3.3.1. Complex 7a

Orange oil; IR (neat) cm^{-1}: 2060 (ν CO *trans*), 1992–1870 (broad, ν CO *cis*), 1630 (ν C=C), 1605 (ν C=C thiophene); ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 2.12 (m, 4H, CH_2–CH$_2$–$_Z$N$_E$–CH$_2$–CH_2–), 3.15 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.15 (m, 2H, CH$_2$–CH_2–$_Z$N), 6.04 (dd, 1H, J_{vic1} = 15.7 Hz, J_{vic2} = 10.4 Hz, Cr=C–CH=CH–CH=CH–thiophene), 6.57 (dd, 1H, J_{vic1} = 15.3 Hz, J_{vic2} = 10.4 Hz, Cr=C–CH=CH–CH=CH–thiophene), 6.67 (d, 1H, J_{vic1} = 15.7 Hz, Cr=C–CH=CH–CH=CH–thiophene), 6.78 (d, 1H, J_{vic1} = 15.7 Hz, Cr=C–CH=CH–CH=CH–thiophene), 6.98 (m, 2H, thiophene ring), 7.19 (d, 1H, J = 5.0 Hz, thiophene ring); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.3 (N$_E$–C–C–), 25.5 (C–C–$_Z$N), 55.5 (N$_E$–C–C), 59.4 (C–C–$_Z$N), 120.3 (Cr=C–CH=CH–CH=CH–thiophene), 124.2 (Cr=C–CH=CH–CH=CH–thiophene), 127.3 (Cr=C–CH=CH–CH=CH–thiophene), 126.3 (CH, thiophene), 127.7 (CH, thiophene), 128.8 (CH, thiophene), 141.4 (C$_q$, thiophene), 143.5 (Cr=C–CH=CH–CH=CH–thiophene), 217.9 (CO$_{cis}$), 223.7 (CO$_{trans}$), 262.7 (Cr=C–C); MS (FAB$^+$), m/z: 409 (M$^+$, low intensity), 381 (M$^+$-CO), 353 (M$^+$-2CO), 325 (M$^+$-3CO), 297 (M$^+$-4CO), 269 (M$^+$-5CO). Elem. Anal. Found C = 52.48%, H = 3.57%, N = 3.38%. C$_{18}$H$_{15}$NCrO$_5$S, MW 409.38. Anal. Calc. C = 52.81%, H = 3.67%, N = 3.42%.

3.3.2. Complex 7b

Light orange solid, m.p. 97°C (from hexane); IR (Nujol) cm^{-1}: 2055 (ν CO *trans*), 1981–1866 (broad, ν CO *cis*), 1625 (ν C=C), 1606 (ν C=C, arom.); ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 2.07 (m, 2H, N$_E$–CH$_2$–CH_2–), 2.18 (m, 2H, CH_2–CH$_2$–$_Z$N), 3.67 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.18 (m, 2H, CH$_2$–CH_2–$_Z$N), 5.92 (s, 2H, –O–CH$_2$–O–), 6.06 (dd 1H, J_{trans} = 15.8 Hz, $J_{vic.}$ = 7.8 Hz, Cr=C–CH=CH–CH=CH–Ar), 6.53–6.63 (m, 2H, Cr=C–CH=CH–CH=CH–Ar), 6.68 (d, 1H, J_{trans} = 15.5 Hz, Cr=C–CH=CH–CH=CH–Ar), 6.76 (d, 1H, J_{ortho} = 8 Hz, 1H arom.), 6.85 (dd, 1H, J_{ortho} = 8 Hz, J_{meta} = 1.5 Hz, 1H arom.), 6.95 (d, 1H, J_{meta} = 1.5 Hz, 1H arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.1 (N$_E$–C–C–), 25.5 (C–C–$_Z$N), 55.5 (N$_E$–C–C), 59.4 (C–C–$_Z$N), 101.2 (–OCH$_2$–O–), 105.5

(CH, arom.), 108.5 (CH, arom.), 121.7 (CH, arom.), 126.4 (Cr=C–CH=CH–CH=CH–Ar), 127.1 (Cr=C–CH=CH–CH=CH–Ar), 131.4 (Cr=C–CH=CH–CH=CH–Ar), 134.7 (C$_q$, arom.), 141.0 (Cr=C–CH=CH–CH=CH–Ar), 147.7 (C$_q$, arom.), 148.2 (C$_q$, arom.), 218.0 (CO$_{cis}$), 222.3 (CO$_{trans}$), 261.7 (Cr=C–C); MS (FAB$^+$), m/z: 447 (M$^+$, low intensity), 391 (M$^+$–2CO), 363 (M$^+$-3CO), 335 (M$^+$-4CO), 307 (M$^+$-5CO). Elem. Anal. Found: C = 56.18%, H = 2.85%, N = 3.08%. C$_{21}$H$_{17}$N$_1$CrO$_8$, MW 447.38. Anal. Calc. C = 56.37%, H = 2.91%, N = 3.13%.

3.3.3. Complex 7c (E,E,E, isomer)

Red solid, m.p. 135°C (dec. from diisopropyl ether at −78°C); IR (nujol) cm^{-1}: 2051 (ν CO *trans*), 1968–1909 (broad, ν CO *cis*), 1609 (ν C=C); ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 1.90 (m, 2H, CH$_2$–CH$_2$–$_Z$N$_E$–CH$_2$–CH_2–), 2.00 (m, 2H, CH_2–CH$_2$–$_Z$N$_E$– CH$_2$–CH$_2$–), 2.97 (s, 6H, NMe$_2$) 3.67 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.16 (m, 2H, CH$_2$–CH_2–$_Z$N), 6.12 [dd, 1H, J_{vic1} = 15.3 Hz, J_{vic2} = 10.8 Hz, –(CH=CH)$_3$–], 6.27 [dd, 1H, J_{vic1} = 14.3 Hz, J_{vic2} = 10.8 Hz, –(CH=CH)$_3$–], 6.46–6.71 (m, 4H, 2H –(CH=CH)$_3$– = 2H arom.), 7.30 (d, 2H, J_{ortho} = 8.7. Hz, arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.1 (N$_E$–C–C–), 25.5 (C–C–$_Z$N), 40.4 (NMe_2), 55.3 (N$_E$–C–C), 59.4 (C–C–$_Z$N), 112.3 (CH, arom.), 126.1 (C$_q$, arom.), 129.0 (CH, arom.), 133.8 [Cr=C–CH=CH–(CH=CH)$_2$–Ar], 134.6 [Cr=C–CH=CH–CH=CH–CH=CH–Ar], 135.3 [Cr=C–CH=CH–CH=CH–CH=CH–Ar], 137.2 [Cr=C–CH=CH–CH=CH–CH=CH–Ar], 140.0 [Cr=C–CH=CH–CH=CH–CH=CH–Ar], 141.0 [Cr=C–CH=CH–CH=CH–CH=CH–Ar], 150.3 (C$_q$, arom.), 217.9 (CO$_{cis}$), 222.9 (CO$_{trans}$), 262.1 (Cr=C–C); MS (FAB$^+$), m/z: 440 (M$^+$-CO), 412 (M$^+$-2CO), 384.(M$^+$-3CO), 356 (M$^+$-4CO), 328 (M$^+$-5CO). Elem. Anal. Found: C = 60.89%, H = 5.13%, N = 5.85%. C$_{24}$H$_{24}$N$_2$CrO$_5$ MW 472.46. Anal. Calc. C = 61.02%, H = 5.08%, N = 5.95%.

3.4. Preparation of the amide 8a

To a solution of 1 mmol of the complex **7b** in acetone (25 ml), (NH$_4$)$_2$Ce(NO$_3$)$_6$ (three equivalents) dissolved in H$_2$O (1 ml) was added dropwise over 5 min at room temperature. The mixture was allowed to react at the same temperature, monitoring the progress of the reaction by TLC analysis (eluent: ethyl–acetate). After 30 min the reaction was complete. The solvent was evaporated under reduced pressure, the crude oil was taken up with dichloromethane (25 ml) and washed twice with 10 ml of water. The organic phase was dried over Na$_2$SO$_4$, filtered and the solvent removed under reduced pressure. The crude reaction mixture was purified by means of flash chromatography (eluent: ethyl–acetate) affording **8a** in 74% yield.

8a, pale yellow solid, m.p. 140–141°C (from ethyl–acetate/diisopropyl ether, lit. 142–143°C [16]); IR (nujol) cm^{-1}: 1640 (v C=O), ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 1.90 (m, 4H, CH_2–CH$_2$–N), 3.52 (m, 4H, N–CH_2–CH$_2$–), 5.95 (s, 2H, –O–CH$_2$–O–), 6.21 (d, 1H, –CO–CH=CH–CH=CH–Ar.), 6.58–7.01 (m, 5H, –CO–CH=CH–CH=CH–Ar, + H arom.), 7.42 (ddd, 1H, J_{trans} = 15.3 Hz, J_{vic1} = 7.1 Hz, J_{vic2} = 3.9 Hz, –CO–CH=CH–CH=CH–Ar); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 24.4 (N$_E$–C–C–), 26.2 (C–C–$_Z$N), 46.0 (N$_E$–C–C), 46.5 (C–C–$_Z$N), 101.3 (–OCH$_2$–O–), 105.7 (CH, arom.), 108.5 (CH, arom.), 121.4 (CH, arom.), 123.1 (OC–CH=CH–CH=CH–Ar), 127.6 (OC–CH=CH–CH=CH–Ar), 131.4 (Cr=C–CH=CH–CH=CH–Ar), 135.9 (C$_q$, arom.), 139.5 (C$_q$, arom.), 141.1 (OC–CH=CH–CH=CH–Ar), 165.0 (CO.); Elem. Anal. Found: C = 70.78%, H = 6.23%, N = 5.19%. C$_{16}$H$_{17}$N$_1$O$_3$, MW 271.32. Anal. Calc. C = 70.85%, H = 6.27%, N = 5.17%.

3.5. Preparation of the amide 8b

A solution of the carbene **7c** (1.3 mmol) in acetone (100 ml) was exposed, under stirring, for 5 days to the atmospheric oxygen and to the sun-light. The solvent was evaporated under reduced pressure and the crude reaction mixture was purified by gravimetric column chromatography over silica gel (eluent: light petroleum/ethyl acetate 3:1, then ethyl acetate) yielding **8b** in 35% yield.

Data for (*E,E,E*,) isomer: orange–brownish solid, m.p. 130–131°C (from ethyl acetate/hexane); IR (nujol) cm^{-1}: 1636 (v C=O), ^{1}H-NMR (80 MHz, CDCl$_3$) δ ppm: 1.90 (m, 4H, CH_2–CH$_2$–N), 2.96 (s, 6H, NMe$_2$) 3.52 (m, 4H, N–CH_2–CH$_2$–), 6.15–7.25 (m, 10H, –CO–(CH=CH)$_3$–Ar, + H arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 24.3 (N$_E$–C–C–), 26.1 (C–C–$_Z$N), 40.2 (NMe$_2$), 45.8 (N$_E$–C–C), 46.4 (C–C–$_Z$N), 112.2 (CH, arom.), 120.1 (CH), 124.0, (CH), 124.7 (C$_q$), 127.9 (CH, arom.), 128.4 (CH), 136.3 (CH), 140.6 (CH), 142.0 (CH), 150.3 (C$_q$, arom.), 165.1 (CO.); MS (EI) m/z: 296 (M$^+$); Elem. Anal. Found: C = 77.11%, H = 8.15%, N = 9.41%. C$_{19}$H$_{24}$N$_2$O MW 296.41. Anal. Calc. C = 77.03%, H = 8.11%, N = 9.46%.

3.6. Preparation of 10

To a suspension of sodium hydride (14.4 mmol) in THF (30 ml) p-*N,N*–dimethylamino–cinnamaldehyde **5c** (12 mmol) was added. The mixture was heated to 50°C and a solution of the phosphonate **11** (12 mmol) in THF (5 ml) was added dropwise in 5 min. The reaction mixture was heated for 5 h then the solvent evaporated under reduced pressure. The crude reaction mixture was taken up with water (100 ml) and extracted with dichloromethane (2 × 50 ml). The organic phase

was washed with water until neutral pH, dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The crude reaction mixture was purified by dry column chromatography (eluent: light petroleum/diethyl ether 5:1) affording 2.2 g of **10** (71%).

10: yellow solid, m.p. 177–178°C (from ethyl acetate); IR (nujol) cm^{-1}: 1595 (v C=C); UV/vis (CH$_2$Cl$_2$): v_{max} 384 nm; ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 2.99 (s, 6H, NMe$_2$), 6.54–6.83 (m, 6H, –(CH=CH)$_2$–Ar, + 2H arom.), 6.97 (m, 2H, thiophene ring.), 7.14 (dd, 1H, J_1 = 4.6 Hz, J_2 = 1.4 Hz; H thiophene ring), 7.33 (d, 2H, J = 8.8 Hz, H arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 41.4 (NMe$_2$), 112.4 (CH, arom.), 123.1 (CH), 123.6 (CH), 124.5 (CH), 125.0 (CH), 125.7 (C$_q$, thiophene ring), 127.5 (CH, arom.), 129.0 (CH, thiophene ring), 133.1 (CH thiophene ring), 143.5 (C$_q$), 150.3 (C$_q$, arom.); MS (EI), m/z: 255 (M$^+$); Elem. Anal. Found: C = 76.35%, H = 6.66%, N = 5.62%; C$_{16}$H$_{17}$NS MW 255.34. Anal. Calc. C = 76.38%, H = 6.71%, N = 5.48%.

3.7. Preparation of the complex 9

To a tetrahydrofuran solution (25 ml) of the **10** (2 mmol) cooled at 0°C 1.5 ml of 1.5 M hexane solution of *n*-BuLi (2.2 mmol) was added. An immediate change in colour of the solution from yellow to red was observed. The mixture was allowed to react for 1 h at 0°C and transferred by a cannula to a solution of Cr(CO)$_6$ (2 mmol) in THF (30 ml). After 1 h the solvent was removed under reduced pressure, the crude was taken up with CH$_2$Cl$_2$ (100 ml) and water (100 ml) and treated with Et$_3$O$^+$BF$_4^-$ until the aqueous phase reached the pH 3. The dark violet organic phase was dried over Na$_2$SO$_4$, the solvent evaporated under reduced pressure and the crude reaction mixture was rapidly purified by means of dry column chromatography (eluent: light petroleum/CH$_2$Cl$_2$, 3:1) collecting the dark violet band affording 0.62 g (62%) of **12**. The complex **12** was found difficult to obtain in analytically pure form for its complete characterization, thus it was immediately used in the synthesis of **9**. A THF solution (30 ml) of **12** (0.7 mmol) cooled at −78°C was treated with pyrrolidine (0.84 mmol). The colour of the solution changed immediately from dark violet into yellow–orange and the TLC analysis (eluent: light petroleum/diethyl ether, 5:1) showed that the reaction was complete. The solvent was removed and the crude purified by dry column chromatography (eluent: light petroleum/diethyl ether, 5:1) giving 0.2 g (52%) of **9**.

3.7.1. Complex 9

Orange–yellow solid, m.p. 179°C (dec., from CHCl$_3$/pentane); IR (nujol) cm^{-1}: 2051 (v CO *trans*), 1977–1891 (broad, v CO *cis*), 1594 (v C=C); ^{1}H-NMR (300 MHz, CDCl$_3$) δ ppm: 2.03 (m, 2H, N$_E$–CH$_2$–CH_2–),

2.12 (m, 2H, CH_2–CH$_2$–$_Z$N), 2.96 (s, 6H, NMe$_2$), 3.60 (m, 2H, N$_E$–CH_2–CH$_2$–), 4.27 (m, 2H, CH$_2$–CH_2–$_Z$N), 6.37 (d, 1H, $J = 3.7$ Hz, CH thiophene ring), 6.53–6.74 (m, 8H, –(CH=CH)$_2$–Ar + 2H arom.), 6.80 (d, 1H, $J = 3.7$ Hz, thiophene ring.), 7.31 (d, 2H, $J = 8.8$ Hz, H arom.); ^{13}C-NMR (75 MHz, CDCl$_3$) δ ppm: 25.3 (N$_E$–C–C–), 25.4 (C–C–$_Z$N), 40.4 (NMe$_2$), 56.5 (N$_E$–C–C), 59.7 (C–C–$_Z$N), 112.4 (CH), 118.6 (CH), 122.4 (CH), 124.3 (CH), 125.0 (CH), 125.6 (C$_q$), 127.6 (CH), 130.4 (CH), 133.5 (CH), 142.5 (C$_q$), 150.1 (C$_q$), 150.5 (C$_q$), 217.2 (CO$_{cis}$), 223.6 (CO$_{trans}$), 264.1 (Cr=C–C); UV/vis (CH$_2$Cl$_2$): ν_{max} 403 nm (log ε_{max} = 4.7); MS (FAB$^+$), m/z: 528 (M$^+$), 500 (M$^+$-1CO), 472 (M$^+$-2CO), 444 (M$^+$-3CO), 416 (M$^+$-4CO), 388 (M$^+$-5CO). Elem. Anal. Found: C = 58.93%, H = 4.59%, N = 5.25%. C$_{26}$H$_{24}$N$_2$CrO$_5$S, MW 528.38. Anal. Calc. C = 59.09%, H = 4.54%, N = 5.30%.

Acknowledgements

References

[1] For general reading on NLO: (a) N.J. Long, Angew. Chem. Int. Ed. Engl., 34 (1995) 21. (b) W. Nie, Adv. Mater., 5 (1993) 520. (c) D.R. Kanis, M.A. Ratner, T.J. Marks, Chem. Rev., 94. (d) R.W. Munn, C.N. Ironside, Principles and Applications of Nonlinear Optical Materials, Chapman & Hall, London (1993). (e) P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York (1991). (f) B.F. Levine, C.G. Bethea, J. Chem. Phys., 63 (1975) 2667. J. Zyss, Molecular Nonlinear Optics, Academic Press (1994), and references cited therein.

[2] (a) J.L. Oudar, D.S.J. Chemla, J. Chem. Phys., 66 (1977) 2664. (b) E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J.L. Bredas, J. Am. Chem Soc., 117 (1995) 3547.

[3] (a) C. Lambert, S. Stadler, G. Bourhill, C. Bräuchle, Angew. Chem. Int. Ed. Engl., 35 (1996) 644. (b) A. Bahl, W. Grahn, S. Stadler, F. Feiner, G. Bourhill, C. Bräuchle, Angew. Chem. Int. Ed. Engl., 34 (1995) 1485. (c) L.T. Chen, W. Tam, S.R. Marder, A.E. Steigman, G. Rikken, C.W. Spangler, J. Phys. Chem., 95 (1991) 10643. (d) A. Abbotto, S. Bradamante, A. Facchetti, G.A. Pagani, J. Org. Chem., 62 (1997) 5755, and references cited therein.

[4] (a) H.S. Nalwa, Appl. Organomet. Chem., 5 (1991) 349. (b) T.J.J. Müller, M. Ansorge, H.J. Lindner, Chem. Ber.,129 (1996) 1433. (c) U. Behreus, H. Brussard, H. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J.G.M. van der Linden, A. Persoons, A.L. Speck, N. Veldman, Chem. Eur. J., 2 (1996) 98. (d) E. Hendrickx, A. Persoons, S. Samson, G.R. Stephenson, J. Organomet. Chem., 542 (1997) 295. (e) M. Bougault, K. Baum, H. Le Bozec, I. Ledoux; G. Pucetti, J. Zyss, New J. Chem., 22 (1998) 517. (f) G. Roth, H. Fischer, T. Meyer-Friedrichsen, J. Heck, S. Houbrechts, A. Persoons, Organometallics, 17 (1998) 1511, and references cited therein.

[5] For general reading on the synthesis and applications of Fischer-type carbene complexes: (a) K.H. Dötz, H. Fischer, P. Hoffmann, F.R. Kreissel, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinhein, Germany (1984). (b) L.S. Hegedus, Acc. Chem. Res., 28 (1995) 299. (c) D.B. Grotjahn, K.H. Dötz, Synlett., (1991) 381. (d) K.H. Dötz, in Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field, A. de Meijere, H. tom Dieck (Eds), Springer, Berlin (1988). (e) W.D. Wulff, in Comprehensive Organic Synthesis, vol 5, pp 106, H.B. Trost, I. Fleming (Eds), Pergamon Press, New York (1991). (f) R. Aumann, K. Stein. M. Grehl, Synlett., (1993) 669. (g) A Parlier. M. Rudler, H. Rudler, R. Gaumont, J. Daran, J Vaissermann, Organometallics, 14 (1995) 2760.

[6] S. Maiorana, A. Papagni, E. Licandro, A Persoons, K. Clays, S. Houbrechts, W. Porzio, Gazz. Chim. It. 125 (1995) 377.

[7] C. Baldoli, P. Hellier, E. Licandro, S. Maiorana, R. Manzotti, A. Papagni, Tetrahedron. Lett. 38 (1997) 3769.

[8] E.M. Burgess, H.R. Penton, E.A. Taylor, J. Org. Chem. 38 (1973) 26.

[9] K. Clays, A. Persoons, Phys. Rev. Lett. 66 (1991) 2980.

[10] R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 711.

[11] S.R. Marder has recently reported β values of 88×10^{-30} esu for p-Me$_2$–N–C$_6$H$_4$–(CH=CH)$_3$–CHO (see Ref. [3c]) and 266×10^{-30} esu for p-Me$_2$–N–C$_6$H$_4$–(CH=CH)$_3$–NO$_2$ in Adv. Mater. 5 (1993) 804 both estimated using EFISH. Since we have used a different technique (HRS), for the evaluation of our β's, we have intentionally avoided any comparison with our values. However the real efficiency of the (CO)$_5$Cr=C group and a tertiary amide functionality clearly determines the NLO response of polyenes "push-pull" structures.

[12] (a) B.A. Anderson, W.D. Wulff, T.S. Powers, S. Tribbit, A.L. Rheingold, J. Am. Chem. Soc., 114 (1992), 10785. (b) E. Licandro, S. Maiorana, A. Papagni, A. Zanotti-Gerosa, F. Cariati, S. Bruni, M. Moret, A. Chiesi-Villa, Inorg. Chim. Acta, 220 (1994) 233.

[13] (a) J.O. Morley, J. Chem. Soc. Perkin Trans. 2, (1995) 177. (b) M.G. Hutchings, I. Ferguson, D.J. McGeein, J.O. Morley, J. Zyss, I. Ledoux, J. Chem. Soc. Perkin Trans. 2, (1995) 171. (c) F. Effenberger, F. Würthner, Angew. Chem. Int. Ed. Engl., 32 (1993) 719. (d) P.V. Bedworth, J. Cai, A Jen, S.R. Marder, J. Org. Chem., 61 (1996) 2242. (e) L. Lancellotti, R. Tubino, S. Luzzati, E. Licandro, S. Maiorana, A. Papagni, Synth. Metals, 93 (1998) 27, and references cited therein.

[14] (a) J. Nakayama, T. Fujimori, Heterocycles, 32 (1991) 991. (b) A. Berlin, S. Bradamante, R. Ferraccioli, G. Pagani, F. Sannicolò, J. Chem. Soc. Perkin Trans. 1, (1987) 2631.

[15] J.A. Connor, E.M. Jones, J. Chem. Soc. A, (1971) 1974.

[16] C. Baldoli, P. Del Buttero, E. Licandro, S. Maiorana, A. Papagni, A. Zanotti-Gerosa, Synlett., (1993) 935.

[17] F. Kiuki, N. Nakamura, Y. Tsuda, K. Kondo, M. Yoshimura, Chem. Pharm. Bull. 36 (1988) 2452.