

Syntheses and NLO Properties of Chromium Carbonyl Arene Complexes with Conjugated Side Chains: The Amphoteric Nature of Chromium Carbonyl Complexation in Push–Pull Chromophores

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Received September 8, 1999

Donor- and acceptor-substituted alkynylated chromium carbonyl arene complexes $\text{Cr}(\text{CO})_2\text{L}(\eta^6\text{-R}^1\text{-C}_6\text{H}_4)(\text{C}\equiv\text{C})_n\text{R}^2$ (**1**, $n = 1$, $\text{L} = \text{CO}$, PPh_3 , $\text{R}^1 = \text{H}$, σ -formyl, $\text{R}^2 = p\text{-C}_6\text{H}_4\text{-NMe}_2$, $p\text{-C}_6\text{H}_4\text{-NO}_2$, ferrocenyl; **3**, $n = 2$, $\text{L} = \text{CO}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = p\text{-C}_6\text{H}_4\text{-NMe}_2$, $p\text{-C}_6\text{H}_4\text{-NO}_2$, ferrocenyl) are easily accessible by Sonogashira alkynylations of chloroarene complexes and Cadiot–Chodkiewicz couplings of bromoalkynes with the complexed phenyl acetylene **1a** ($n = 1$, $\text{L} = \text{CO}$, $\text{R}^1 = \text{R}^2 = \text{H}$), respectively. The Horner–Emmons–Wadsworth olefinations of the $\text{Cr}(\text{CO})_3$ -complexed benzylphosphonate and (hetero)aromatic aldehydes give rise to numerous alkenylated chromium carbonyl arene complexes $(E)_n\text{-Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5)(\text{CH}=\text{CH})_n\text{R}^1$ (**6**, $n = 1\text{--}3$, $\text{R}^1 = p\text{-C}_6\text{H}_4\text{-NMe}_2$, $p\text{-C}_6\text{H}_4\text{-NO}_2$, 2-(4-nitrothienyl)). The linear (UV/vis spectra) and the nonlinear optical properties (hyper Rayleigh scattering measurements) of the complexes **1**, **3**, and **6** reveal that the chromium carbonyl arene fragment behaves electronically amphoteric, i.e., as an electron donor or electron acceptor depending on the substituent on the far end of the conjugating bridge. The first hyperpolarizability β -values ($\beta_{333}^0 = (8\text{--}41) \times 10^{-30}$ esu) are found to be similar to those of related ferrocenyl compounds.

Introduction

The rapidly increasing demand for novel chromophores suitable for photonic applications such as frequency doubling and the electrooptical effect¹ has initiated an eager search for highly polarizable organometallic chromophores and auxochromes.² Since nonlinear optical (NLO) properties of quite a number of organic chromophores have been thoroughly studied, both experimentally and theoretically, some common structural features could be deduced such that the lead

structure consists of an electron-donating group, a conjugated π -bridge (alkyne, alkene or (hetero)arene), and an electron-accepting group, generally referred to as a push–pull system. Typically, these push–pull chromophores are structurally prerequisite for designing NLO systems with large second-order hyperpolarizabilities β^0 ($>10 \times 10^{-30}$ esu). Especially, extended conjugated π -systems such as donor–acceptor α,ω -diaryl polyenes and polyynes are classes of organic molecules that display considerable NLO responses.³ Many transition-metal π -complexes are also highly polarizable. The facile excitation of metal-to-ligand transitions upon irradiation with visible light and the formation of stable specimens of higher oxidation states has made π -complexes attractive and advantageous for the construction of organometallic NLO chromophores with extended π -conjugation.^{1a,d,2a,b} In particular, due to its high polarity, its amphoteric electronic nature, and its rich chemistry⁴ the (arene)chromium carbonyl fragment could be a promising auxochrome for novel organo-

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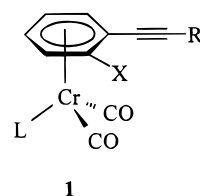
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metallic NLO systems, either electron donating or withdrawing depending on the attached electronic environment. Interestingly, there have been extensive calculations^{1d,5} on the NLO properties of alkenylated chromium arene complexes, but only one synthetic approach has been reported⁶ so far, which unfortunately gives no details on the optical nonlinearities of those systems. Here, we describe the synthesis and structures as well as our first findings on the linear and nonlinear optical properties of alkynylated and alkenylated donor- and acceptor-substituted chromium-complexed arenes.

Results and Discussion

Syntheses. General Considerations. Since the direct complexation of the free hydrocarbon ligand is either unselective or inefficient, we have transposed olefination⁷ and palladium-catalyzed alkynylation⁸ methodologies to the synthesis of conjugated side chains on the η^6 -coordinated arene ligand. In particular, this approach has been shown to be successful in the construction of [(cyclobutadienylcobalt)ethynylene(arylene)ethynylene] copolymers with liquid crystalline properties.⁹ Prior to this work the Wittig reaction of $\text{Cr}(\text{CO})_3$ -complexed benzaldehydes and aryl phosphonium salts has already been successfully applied to the construction of ethenyl bridges on the organometallic template.^{6,10} However, due to the low stereoselectivity (*E* vs *Z* configuration of the double bond) in these cases and the tedious preparation of allyl phosphonium salts for extended π -systems, we sought more general and even more straightforward strategies of alkenylation and alkynylation starting from easily accessible chromium carbonyl arene complexes. Chemically, the $\text{Cr}(\text{CO})_3$ complexation activates chloroarenes considerably toward the oxidative addition¹¹ and thus has opened the

Chart 1



1a L = CO, X = H, R = H

1b L = CO, X = H, R =

1c L = CO, X = H, R =

1d L = CO, X = H, R =

1e L = PPh_3 , X = H, R =

1f L = CO, X = CHO, R =

possibility of palladium-catalyzed alkynylations.^{8,12} Furthermore, $\text{Cr}(\text{CO})_3$ -complexed benzylphosphonates can be easily condensed with aldehydes in the sense of a Horner–Emmons–Wadsworth olefination.⁷

Syntheses of Alkynylated (Arene)chromium Carbonyl Complexes. Chlorobenzene– $\text{Cr}(\text{CO})_3$ complexes are by far more reactive in palladium-catalyzed cross-coupling reactions than uncomplexed iodobenzenes.^{11,12a} Recently, we synthesized the alkynylated complexes **1** upon coupling the corresponding chlorobenzene chromium carbonyl complexes with terminal alkynes under Sonogashira conditions¹³ in good to excellent yields (Chart 1).^{8b,f}

The $\text{Cr}(\text{CO})_3$ -complexed phenylacetylene^{8a} **1a** reacts in a Cadiot–Chodkiewicz coupling¹⁴ with bromoalkynes **2** to give the dumbbell-shaped rigid-rod homologous butadiynylated complexes **3** in excellent yields (Scheme 1). Characteristically, the appearance of four quaternary alkynyl carbon resonances in the ¹³C NMR spectra and the significant alkynyl stretching vibrations in the IR spectra at 2200 cm^{-1} unambiguously support the structure of these novel unsymmetrically substituted organometallic diynes. The carbonyl resonances in the ¹³C NMR spectra appear in the expected region between δ 232.8 and 233.3, displaying only a small substituent influence.

Syntheses of Alkenylated (Arene)chromium Carbonyl Complexes. Benzylic anions are efficiently stabilized by chromium carbonyl complexation.^{4e} Thus, the $\text{Cr}(\text{CO})_3$ -complexed benzylphosphonate **4**^{7b} is successfully applied in Horner–Emmons–Wadsworth ole-

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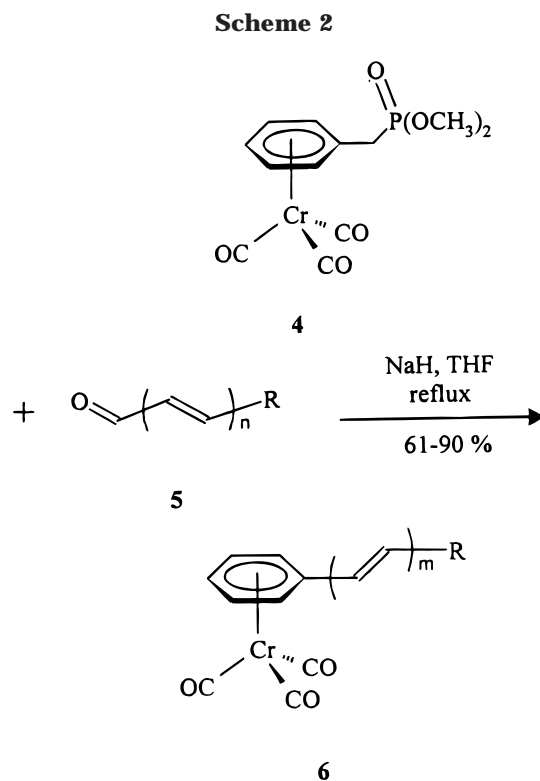
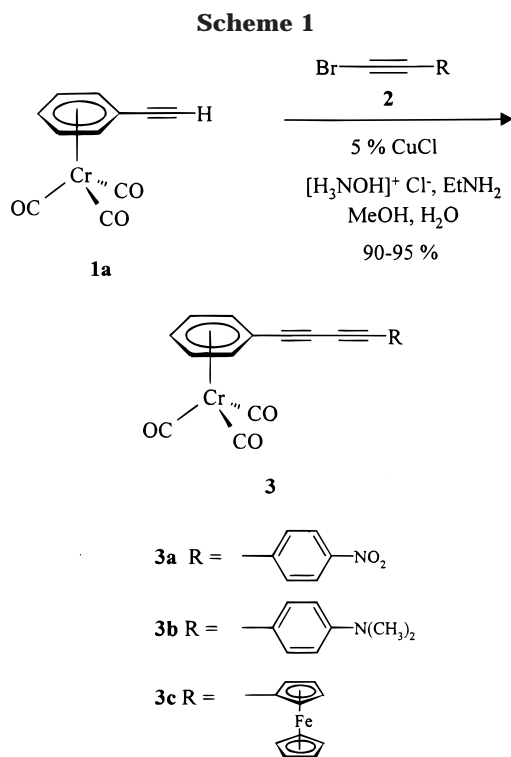
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finations⁷ with *p*-dimethylamino- and *p*-nitro-substituted aromatic and heteroaryl aldehydes **5** to furnish the alkenylated (arene)Cr(CO)₃ complexes **6** as orange to deep red crystalline solids in good yields (Scheme 2).

The carbonyl resonances in the ¹³C NMR spectra appear in the expected region between δ 234.0 and 234.7, displaying only a small substituent influence. In the proton and carbon NMR spectra the characteristic high-field shift of the complexed arene carbon and proton resonances not only facilitates the unambiguous assignment of the arene signals but also clearly indicates that in the case of the donor-substituted systems a shift of the chromium carbonyl tripod to the more electron-rich arene rings can definitely be excluded. According to the vicinal coupling constants (³*J* = 15.3–16.5 Hz) the *E* configuration of newly formed double bonds supports the highly stereoselective olefination. In the case of the conjugated dienes (**6b** and **6f**) and triene (**6d**) the additional vicinal coupling constants (³*J* = 9.7–10.3 Hz) establish the preferred *s-trans* conformation of the conjugated side chains.

According to X-ray crystal structure analyses¹⁵ of two alkenyl-bridged representatives, the deep red stilbazole complex **6a** (Figure 1, Table 1) and the orange dimethylamino-substituted stilbene complex **6e** (Figure 2, Table 1), the chromium arene fragments, the olefin bridges, and the arene substituents are almost coplanar. Therefore, an ideal overlap of the π -system and a strong electronic coupling can be assumed in the solid state. This is consistent with previously published structural details on several complexed stilbenes.⁶ In both cases, as already supported by NMR spectroscopy, the double

bonds are *trans*-configured. The chromium–centroid distances (1.70 and 1.71 Å) are in the expected range.¹⁶

Linear Optical Properties of the Complexes 1, 3, and 6 (Electronic Spectra and Solvochromicity). In the UV/vis spectra of the alkynylated (**1** and **3**) and the alkenylated complexes (**6**) recorded in chloroform, the appearance of the intense longest wavelength absorption band between 378 (**1f**) and 488 nm (**6g**) can be assigned to the metal-to-ligand charge-transfer (MLCT) band arising from a charge transition from the chromium center to the π - and σ -bound ligands.^{5,17} The next band between 309 (**1b**) and 383 nm (**6f**) is the most intense absorption and arises from intraligand (IL)

(15) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-127408 (**6a**) and CCDC-127407 (**6e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, + 44-1223/336-033; e-mail, deposit@cdc.cam.ac.uk).

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Table 1. Crystal Data and Structure Refinement Details for 6a and 6e¹⁵

	6a	6e
empirical formula	C ₁₆ H ₁₁ CrNO ₃	C ₁₉ H ₁₇ CrNO ₃
color, form	red sticks	orange sticks
fw	317.28	359.37
temp, K	294(2)	297(2)
wavelength (Å), radiation	0.710 69 (Mo Kα)	0.710 93 (Mo Kα)
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
unit cell dimens		
<i>a</i> , Å	7.930(21)	11.424(2)
<i>b</i> , Å	13.164(3)	8.995(1)
<i>c</i> , Å	13.388(2)	18.660(3)
α, deg	90	90
β, deg	96.37(2)	91.32(1)
γ, deg	90	90
<i>V</i> , Å ³	1389.0(5)	1725.2(5)
<i>Z</i>	4	4
density (calcd), g/cm ³	1.517	1.384
abs coeff, mm ⁻¹	0.81	0.66
<i>F</i> (000)	648	744
cryst size, mm	0.4 × 0.225 × 0.225	0.65 × 0.35 × 0.075
θ range for data collec, deg	2.18–22.97	1.78–22.97
index ranges	−8 ≤ <i>h</i> ≤ 1, 0 ≤ <i>k</i> ≤ 14, −14 ≤ <i>l</i> ≤ 14	−12 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 8, −20 ≤ <i>l</i> ≤ 20
no. of rflns collected	2093	4646
no. of indep rflns	1929 (<i>R</i> (int) = 0.0410)	2397 (<i>R</i> (int) = 0.0422)
abs cor	empirical from ψ-scans	empirical from ψ-scans
max and min transmissn	0.995 and 0.586	0.838 and 0.717
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	1927/3/208	2397/8/302
goodness of fit on <i>F</i> ²	1.063	1.058
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))		
<i>R</i> 1	0.0561	0.0418
<i>wR</i> 2	0.1469	0.1057
<i>R</i> indices (all data)		
<i>R</i> 1	0.0663	0.0609
<i>wR</i> 2	0.1650	0.1192
largest diff peak and hole, e/Å ³	0.961 and −0.652	0.376 and −0.341

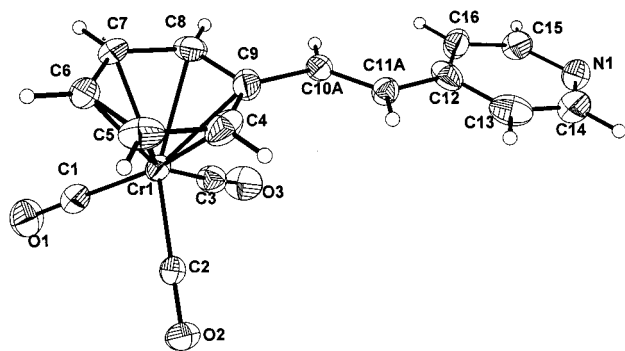


Figure 1. X-ray crystal structure of **6a**. Selected bond lengths (Å) and torsional angles (deg): Cr–arene centroid, 1.714; C(9)–C(10A), 1.553(13); C(10A)–C(11A), 1.307(13); C(11A)–C(12), 1.480(11); C(4)–C(9)–C(10A)–C(11A), −4.3(13); C(10A)–C(11A)–C(12)–C(16), 2.1(13); C(10A)–C(11A)–C(12)–C(13), −177.3(7).

transitions with high oscillator strength, to the most extent from π – π^* transitions.⁵ This rationale is also supported by the inspection of the solvchromicities of these complexes. In all cases the MLCT band displays a small to moderate negative solvchromicity, indicating that the electronic ground state is more polar than the first excited state, and therefore an increase in solvent polarity causes a hypsochromic shift.¹⁸ This is also in agreement with the highly polar nature of chromium carbonyl complexes, which can be attributed

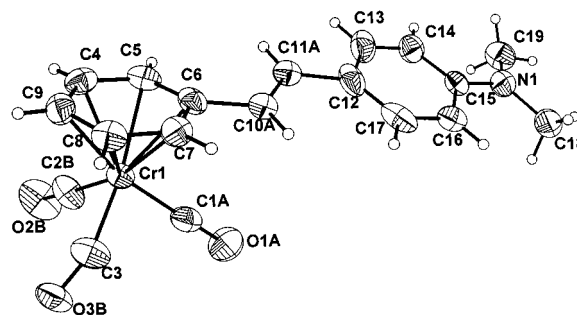


Figure 2. X-ray crystal structure of **6e**. Selected bond lengths (Å) and torsional angles (deg): Cr–arene centroid, 1.703; C(6)–C(10A), 1.510(3); C(10A)–C(11A), 1.308(12); C(11A)–C(12), 1.499(9); C(15)–N(1), 1.367(4); N(1)–C(18), 1.435(5); N(1)–C(18), 1.440(5); C(5)–C(6)–C(10A)–C(11A), 17.7(8); C(10A)–C(11A)–C(12)–C(13), 177.8(5); C(14)–C(15)–N(1)–C(19), −8.2(5); C(16)–C(15)–N(1)–C(18), 7.4(5).

to the dominant μ_x -dipole vector component directed from the arene to the chromium carbonyl tripod (Figure 3).⁵

Interestingly, the π – π^* transitions directed along the μ_x -dipole axis display a different solvchromic behavior. For most of the alkynyl-bridged chromophores this band shows a negative solvchromicity. However, for alkenyl-bridged chromophores this intraligand charge-transfer (ILCT) band is shifted bathochromically upon the increase of solvent polarity. Clearly, there seems to be a strong dependence on the hybridization of the conjugated π -bridge. In contrast to alkynes the canonical resonance structures of alkenes still retain a double

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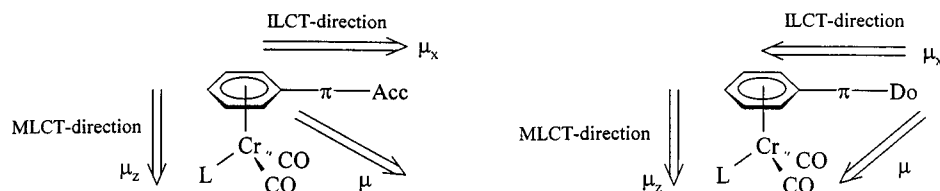
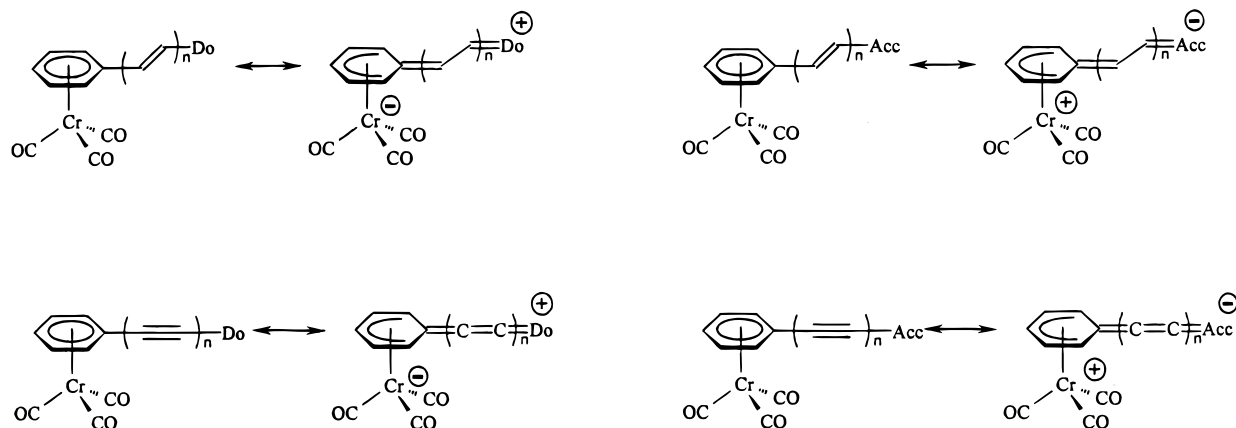


Figure 3. Additive nature of ground-state dipole vectors of chromium carbonyl complexed arenes with conjugated side chains.

Scheme 3. Resonance Hybrids of Alkenyl- (Top) and Alkynyl-Bridged (Bottom) Donor- and Acceptor-Substituted Chromium Carbonyl Arene Complexes



bond alternation without adopting unfavorable cumulogous resonance hybrids as with alkynes (Scheme 3). Since the solvochromicity reflects the polarizability of a chromophore, large solvochromicities can hint to the magnitude of expected optical nonlinearities.^{18b} In all cases the relevant bands for the polarizability are the ILCT bands. The dipole moment of the MLCT bands is perpendicular (μ_z) and does not coincide with that of the principal ILCT direction (μ_x).⁵ Therefore, the largest solvochromicities for the π - π^* transitions are found expectedly for long acceptor substituted alkenylated complexes **6c,d** and, surprisingly, also for long donor substituted alkynylated complexes **3b** and the short acceptor substituted alkynylated chromium dicarbonyl phosphane complex **1e**.

Nonlinear Optical Properties of the Complexes 1, 3, and 6 (First Hyperpolarizabilities). The first hyperpolarizabilities β of the complexes **1**, **3**, and **6** were measured by hyper Rayleigh scattering (HRS).¹⁹ Unlike the more common electric-field-induced second-harmonic-generation (EFISHG) method,²⁰ HRS allows us to determine β without the knowledge of the dipole moment. However, according to eq 2 (see Experimental Section), HRS does not allow us to determine the sign of β and, therefore, the β -values given in this paper are only absolute values. The HRS experiments were carried out in chloroform solutions of the complexes at 1500 nm fundamental wavelength. Conducting HRS experiments in a far off-resonant regime is a safeguard against resonance enhancement and multiphoton-induced fluorescence, which may lead to unphysically high β -values.²¹ Since all investigated complexes display no

fluorescence around 750 nm, fluorescence enhancement at the second-harmonic frequency can be excluded.

The extrapolation of the dynamic hyperpolarizabilities $\beta_{333}^{1500\text{nm}}$ to their static counterparts β_{333}^0 is accomplished by using the two-level model.^{3f} Since there might be a contribution of MLCT components to the nonlinear optical response of the chromium carbonyl arene complexes, the applicability of the two-level model, which is only valid for rodlike chromophores with a CT along the molecule axis, must be questioned.⁵ However, the β -value of the unsubstituted chromium tricarbonyl benzene π -complex is negligibly small (-0.8×10^{-30} esu at 1910 nm in toluene).^{1d,5,22} Furthermore, the inspection of the solvochromicities (vide supra) has clearly shown that the major contribution of the polarizability and ultimately the hyperpolarizability arises from ILCT terms in the absorption band. For these reasons, the assumption of rodlike geometry is justified and the two-level model should still be applicable to the corresponding π - π^* absorption bands.

Our results reveal that the magnitude of the β -values of chromium carbonyl arene complexes with conjugated substituents are comparable to those of related ferrocenyl systems.^{2a} Some important structure-property relationships can already be derived from the dynamic and static β -values of the complexes **1**, **3**, and **6** (Table 2). As expected, the increase in conjugation length by n multiple bonds results in an approximately n -fold enhancement of the β_{333}^0 -values and the efficiency of hyperpolarization depends on the hybridization of the side chain.^{1a,d} As already stated for the solvochromicity

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Table 2. Absorption Maxima, Solvochromicities, and Hyperpolarizabilities^a of the Complexes 1, 3, and 6

	acceptor-substituted complex							donor-substituted complex									
	MLCT			ILCT			β_{333}^0 ^d	MLCT			ILCT			β_{333}^0 ^d			
	λ_{CHCl_3} (nm)	λ_{DMSO} (nm)	$\Delta\tilde{\nu}$ (cm ⁻¹)	λ_{CHCl_3} (nm)	λ_{DMSO} (nm)	$\Delta\tilde{\nu}$ (cm ⁻¹)		1500 nm	0	λ_{CHCl_3} (nm)	λ_{DMSO} (nm)	$\Delta\tilde{\nu}$ (cm ⁻¹)	λ_{CHCl_3} (nm)		λ_{DMSO} (nm)	$\Delta\tilde{\nu}$ (cm ⁻¹)	1500 nm
DMAZ ^b				384			35	24	DMAZ ^b				384			35	24
1b	435	433 ^c	-106	309	308 ^c	-105	10	8	1c	405	400 ^c	-309	338	336 ^c	-176	11	9
3a	437	434	-158	322	320	-194	18	14	3b	414	410	-235	342	347	421	34	26
6b	455	451	-195	317	321	393	15	12	6e	418	413	-290	360	362	153	20	14
6c	457	451	-291	339	351	1008	33	25	6f	438	428	-533	383	388	336	38	27
6d	453	448	-246	377	384	484	44	31	1d	387	395 ^c	-523	328	327 ^c	-188	9	7
6g	488	485	-127	356	358	157	30	22	3c	419	411	-465	324	322	-191	11	9
1e	481	472	-396	318	310	-812	52	41	1f	378			344			52	39

^a Measured by the hyper Raleigh scattering (HRS) technique at a fundamental wavelength of 1500 nm in a chloroform solution.

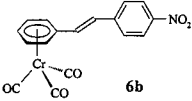
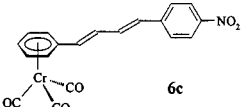
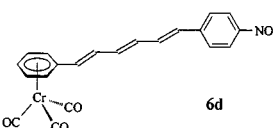
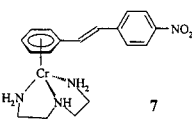
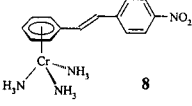
^b Reference chromophore *p*-dimethylamino cinnamic aldehyde (DMAZ).³³ ^c Measured in acetonitrile. ^d All β -values are given in 10⁻³⁰ esu (10⁻³⁰ esu \equiv 0.37 \times 10⁻⁵⁰ cm³ V⁻²); the β_{333}^0 -values were calculated by applying the two-level model on the π - π^* absorption band.

ties, alkenes tend to be more hyperpolarizable than alkynes. In addition, the substitution of the phenylene bridge (**6b**) by a thienylene bridge (**6g**) causes a 2-fold increase in the β -value due to the reduced aromaticity of thiophene.^{1a} Interestingly, comparable donor- and acceptor-substituted series of both alkynylated and alkenylated complexes display almost similar β_{333}^0 -values, and ferrocene as a donor in these systems (**1d** and **3c**) is not efficient. All this strongly supports the view that the chromium carbonyl arene fragment behaves electronically amphoteric, i.e., electron donating or electron withdrawing in NLO chromophores depending on the electronic nature of the attached auxochrome at the far end of the chromophore. Furthermore, the trend of the homologous series of alkenylated *p*-nitrophenyl-substituted complexes is reproduced correctly by ZINDO calculations⁵ based upon a three-level model (Table 3). Due to the pseudo-centrosymmetric electronic environment around the pseudo-octahedral ligand field of the chromium center these types of complexes inherently cannot display their higher total intrinsic hyperpolarizabilities.⁵

Therefore, the crucial question arises how the β -values can be enhanced for this kind of organometallic chromophores. One possibility is the additive enhancement of the push-pull character. The introduction of an electron-withdrawing *ortho* substituent on the complexed arene moiety of an alkynylated donor substituted complex (**1f**) not only causes a 4-fold enhancement of the β -value compared to the system **1c** but also opens a facile access to planar-chiral complexes. Especially, the introduction of chirality can be favorable for potential solid-state applications due to crystallization in non-centrosymmetric space groups.

Another option is the exchange of the carbonyl ligands on the metal. The exchange by phosphanes not only renders the chromium carbonyl center more electron rich in the sense of enhancing the push-pull character of acceptor-substituted complexes (**1e**) but also causes a break in the centrosymmetric electronic environment around the pseudo-octahedral ligand field, giving rise to a 5-fold increase in the β -values compared to the tricarbonylchromium complex **1b**. Most interestingly, computations on hypothetical triamminechromium arene complexes with short side chains such as **7** and **8** predict very large hyperpolarizabilities at a fundamental of 1900 nm (Table 3).^{1d,5} Although the synthesis of these structures involves quite some difficulty, we expect

Table 3. Comparison of Experimental β_{333}^0 -Values, ZINDO-Derived Molecular Hyperpolarizabilities^{1d,5} along the ILCT Dipole Axis β_{vec} , and Total Intrinsic Hyperpolarizabilities^{1d,5} β_{tot} at a Fundamental of 1900 nm^a

	β_{333}^0 ^{exp.}	β_{vec} ^{calc.}	β_{tot} ^{calc.}
	12	8.3	23.5
	25	11.5	28.4
	31	15.6	34.5
	-	543	-
	-	780	-

^a All β -values are given in 10⁻³⁰ esu (10⁻³⁰ esu \equiv 0.37 \times 10⁻⁵⁰ cm³ V⁻²).

comparable effects for phosphane-complexed systems simultaneously allowing extensive electronic fine-tuning on the metal. Further studies directed at optimizing the NLO properties of alkynyl- and alkenyl-bridged chromium carbonyl arene complexes are currently underway.

Conclusion

Chromium carbonyl arene complexes with conjugated side chains are easily accessible by palladium/copper-catalyzed alkynylations of chloroarene complexes, Cadiot-Chodkiewicz couplings of bromoalkynes with a

complexed phenylacetylene, and Horner–Emmons–Wadsworth olefinations of a complexed benzylphosphonate and aromatic aldehydes. This approach of side chain construction on the metal template not only proceeds in good yields but also circumvents the regioselectivity problems of the direct complexation of the corresponding free ligands. The linear (electronic spectra and the solvchromicities) as well as the nonlinear optical properties (β -values from HRS measurements) of the alkynylated and alkenylated complexes reveal that chromium arene auxochromes at the α -terminus behave electronically amphoteric, i.e., as electron donors or electron acceptors depending on the counterpart at the ω -terminus, with a medium-sized magnitude of the β -values similar to those of ferrocenyl structures. Two possible strategies for optimizing the nonlinearities of chromium carbonyl complexes arise from these investigations: the organic synthetic approach would emphasize the additive enhancement of the push–pull character of the π -ligand and the organometallic strategy would be to disturb the electronic pseudosymmetry about the metal center by CO–phosphane exchange.

Experimental Section

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures.²³ Column chromatography: silica gel 60 (0.063–0.2 mm/70–230 mesh, Firma Merck). TLC: silica gel plates (60 F₂₅₄ Merck, Darmstadt, Germany). Melting points (uncorrected values): Reichert–Jung Thermovar. The alkynylated chromium carbonyl arene complexes **1**^{a,b,f} and the chromium tricarbonyl complexed benzylphosphonate **4**⁷ were prepared according to our previously published protocols. The bromoalkyne **2a**²⁴ was prepared by literature methods, and the bromoalkynes **2b,c** were prepared by lithiation (*n*-BuLi) and subsequent NBS bromination in THF at –78 °C of the corresponding terminal alkynes.²⁵ The aromatic aldehydes **5a,b,e,g**, sodium hydride (95%), hydroxylamine hydrochloride, copper(I) chloride, and aqueous ethylamine (70%) were purchased from Merck, Aldrich, or Fluka and used without further purification; the aldehydes **5c**,²⁶ **5d**,²⁷ and **5f**²⁸ were prepared according to literature methods. ¹H and ¹³C NMR spectra: Bruker ARX 300, Varian VXR 400S, Bruker WM 300, and Bruker AC 300 spectrometers, [D₆]DMSO or CDCl₃. IR: Perkin-Elmer FT-IR Paragon 1000 PC, samples were pressed into KBr pellets. UV/vis: Beckman DK-2-A, Beckman UV 5240, and Perkin-Elmer Lambda 16 instruments. MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90, and MAT 95 Q spectrometers. The structure was solved by direct methods and refined anisotropically on *F*² (programs SHELXS-86 and SHELXL-93 by G. M. Sheldrick, University of Göttingen). Elemental analyses were carried out in the Microanalytical Laboratories of the Institut für Organische Chemie, Technische Universität Darmstadt, and the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

Cr(CO)₃[η^6 -*o*-OHC(C₆H₄)]C≡C(*p*-C₆H₄)N(CH₃)₂ (1f**).** According to our previously published standard procedure, 440

mg (1.60 mmol) of the complexed *o*-chlorobenzaldehyde²⁹ and 250 mg (1.72 mmol) of (*p*-dimethylamino)phenyl)acetylene³⁰ gave after chromatography on silica gel (diethyl ether/pentane 1:1) 440 mg (71%) of pure **1f** as a red-orange solid. Mp: 110–111 °C. ¹H NMR (CDCl₃, 300 MHz): δ 3.01 (s, 6 H), 5.20 (dd, *J* = 6.2, 6.5 Hz, 1 H), 5.38 (d, *J* = 6.5 Hz, 1 H), 5.73 (dd, *J* = 6.3, 6.6 Hz, 1 H), 6.12 (d, *J* = 6.6 Hz, 1 H), 6.64 (m, AA'BB', *J* = 8.7 Hz, 2 H), 7.40 (m, AA'BB', *J* = 8.6 Hz, 2 H), 10.14 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 40.05 (CH₃), 79.67 (C_{quat}), 87.20 (CH), 91.29 (CH), 91.58 (CH), 93.75 (C_{quat}), 94.44 (CH), 97.69 (C_{quat}), 98.59 (C_{quat}), 107.10 (C_{quat}), 111.63 (CH), 133.31 (CH), 150.99 (C_{quat}), 188.28 (CH), 230.20 (C_{quat}, CO). MS (EI, 70 eV; *m/z* (%)): 335 (M⁺ – C₄H₂, 15), 249 (M⁺ – Cr(CO)₃, 8), 235 (M⁺ – Cr(CO)₃ – CH₂, 33), 134 (C₉H₁₂N⁺, 100), 120 (C₈H₁₀N⁺, 75), 91 (C₇H₇⁺, 52), 77 (C₆H₅⁺, 30), 52 (Cr⁺, 8). IR (KBr): $\tilde{\nu}$ 2923, 2207, 1964, 1889, 1687, 1604, 1519, 1363, 945, 818, 661, 624 cm⁻¹. UV/vis (CHCl₃): λ_{\max} (ϵ) 344 (28 200), 378 (19 300) nm. Anal. Calcd for C₂₀H₁₅CrNO₄ (385.34): C, 62.34; H, 3.92; N, 3.63. Found: C, 61.89; H, 4.04; N, 3.49.³¹

General Procedure (GP 1) for the Cadiot–Chodkiewicz Coupling of Tricarbonyl(η^6 -ethynylbenzene)chromium(0) (1a**) with Bromoalkynes **2**.** A 0.150 g (0.63 mmol) portion of **1a** and 5 mg (70 μ mol) of hydroxylamine hydrochloride were suspended in 20 mL of degassed methanol. To this mixture was added a solution of 4 mg (40 μ mol) of copper(I) chloride in 3 mL of ethylamine under argon at room temperature. Then 0.63 mmol of the corresponding bromoalkyne **2** dissolved in 2 mL of *N,N*-dimethylformamide was added dropwise at room temperature to this suspension over a period of 2 min. This reaction mixture was stirred at room temperature under argon overnight. To the suspension was then added 20 mL of diethyl ether and 15 mL of water. The organic phase was separated, and the aqueous layer was extracted twice with 20 mL portions of ether. The combined organic phases were washed twice with 20 mL of brine. After these phases were dried over magnesium sulfate and filtered, the solvents were removed in a rotary evaporator to give the pure and crystalline butadiynes **3** (TLC). Further purification was achieved by recrystallization.

Cr(CO)₃(η^6 -C₆H₅)C≡CC≡C(*p*-C₆H₄)NO₂ (3a**).** According to GP 1 the reaction was carried out with 0.142 g (0.60 mmol) of bromo(4-nitrophenyl)acetylene (**2a**) to give 0.204 g (90%) of pure **3a** as orange-red crystals, mp 140 °C dec (dichloromethane/pentane). ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.77 (dd, *J* = 6.1 Hz, 2 H), 5.86 (t, *J* = 6.0 Hz, 1 H), 6.14 (d, *J* = 6.1 Hz, 2 H), 7.92 (d, *J* = 8.3 Hz, 2 H), 8.28 (d, *J* = 8.3 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 72.14 (C_{quat}), 77.12 (C_{quat}), 80.19 (C_{quat}), 81.03 (C_{quat}), 86.54 (C_{quat}), 93.30 (CH), 95.29 (CH), 98.46 (CH), 124.16 (CH), 126.85 (C_{quat}), 134.15 (CH), 147.93 (C_{quat}), 232.80 (C_{quat}, CO). MS (EI, 70 eV; *m/z* (%)): 383 (M⁺, 8), 327 (M⁺ – 2 CO, 5), 299 (M⁺ – 3 CO, 13), 247 (M⁺ – Cr(CO)₃, 60), 200 (M⁺ – Cr(CO)₃ – HNO₂, 29), 52 (Cr⁺, 100). IR (KBr): $\tilde{\nu}$ 2214, 1976, 1898, 1592, 1522, 1343, 852, 748, 667, 649, 614, 531 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 320 (27 700), 434 (6650) nm. Anal. Calcd for C₁₉H₉CrNO₅ (383.28): C, 59.54; H, 2.37; N, 3.65. Found: C, 59.08; H, 2.47; N, 4.09.³¹

Cr(CO)₃(η^6 -C₆H₅)C≡CC≡C(*p*-C₆H₄)N(CH₃)₂ (3b**).** According to GP 1 the reaction was carried out with 0.146 g (0.65 mmol) of (4-(dimethylamino)phenyl)bromoacetylene (**2b**) to give 0.238 g (96%) of pure **3b** as yellow platelets, mp 160 °C dec (diethyl ether/pentane). ¹H NMR ([D₆]DMSO, 300 MHz):

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(30) In analogy to ref 13a in boiling piperidine and subsequent base-mediated desilylation.

(31) The deviation (–0.5 to 1%) of the calculated from the found percentages of carbon in the combustion analyses can be attributed to a small content (< 5%) of dichloromethane (solvent used for recrystallization) that cannot be removed even after 24 h of drying under dynamic vacuum (~10⁻⁴ mbar). In the proton NMR spectra a tiny peak at δ 5.3 is found. This seems to be reasonable also on the basis of an X-ray structure of a related complex where trichloromethane was incorporated nonstoichiometrically in the crystal lattice.^{8a}

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Table 4. Experimental Details on Synthesis of Alkenylated Arene Complexes 6

amt of complexed benzylphosphonate 4, mg (mmol)	amt of NaH, mg (mmol)	amt of aldehyde 5, mg (mmol)	amt of THF, mL	reacn time, h	yield of 6, mg (%)
504 (1.50)	40 (1.6)	161 (1.50), 5a	15	14	400 (84), ^a 6a
336 (1.00)	26 (1.0)	151 (1.00), 5b	10	14	220 (61), 6b
336 (1.00)	40 (1.6)	177 (1.00), 5c	25	19	343 (89), 6c
337 (1.00)	40 (1.6)	208 (1.02), 5d	25	22	279 (68), 6d
504 (1.50)	40 (1.6)	201 (1.49), 5e	15	15	482 (90), 6e
1001 (3.00)	80 (3.2)	530 (3.02), 5f	20	8	1000 (86), 6f
840 (2.50)	65 (2.6)	393 (2.50), 5g	25	8	750 (85), ^b 6g

^a Recrystallized from THF/pentane. ^b Recrystallized from diethyl ether/pentane.

δ 2.99 (s, 6 H), 5.77 (m, 3 H), 6.04 (m, 2 H), 6.72 (m, 2 H), 7.44 (m, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 39.74 (CH₃), 71.58 (C_{quat}), 74.17 (C_{quat}), 77.75 (C_{quat}), 85.06 (C_{quat}), 89.20 (C_{quat}), 93.75 (CH), 94.55 (CH), 97.94 (CH), 105.08 (C_{quat}), 111.99 (CH), 134.09 (CH), 151.20 (C_{quat}), 233.25 (C_{quat}, CO). MS (EI, 70 eV; *m/z* (%)): 381 (M⁺, 21), 325 (M⁺ - 2 CO, 17), 297 (M⁺ - 3 CO, 100), 245 (M⁺ - Cr(CO)₃, 19), 80 (Cr(CO)⁺, 5), 52 (Cr⁺, 21). IR (KBr): $\tilde{\nu}$ 2205, 1963, 1896, 1878, 1602, 1518, 1447, 1367, 1182, 1151, 813, 671, 654, 627, 614, 533 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 278 (12 600), 333 (28 800 sh), 347 (33 400), 410 (13 600 sh) nm. Anal. Calcd for C₂₁H₁₅CrNO₃ (381.35): C, 66.14; H, 3.96; N, 3.67. Found: C, 66.01; H, 4.28; N, 3.54.

Cr(CO)₃(η^6 -C₆H₅)C \equiv CC \equiv C(η^5 -C₅H₄)Fe(η^5 -C₅H₅) (3c). According to GP1 the reaction was carried out with 0.182 g (0.63 mmol) of bromoethynylferrocene (**2c**) to give 0.272 g (97%) of pure **3c** as orange platelets, mp 171 °C dec (dichloromethane/pentane). ¹H NMR ([D₆]DMSO, 300 MHz): δ 4.28 (s, 5 H), 4.41 (m, 2 H), 4.66 (m, 2 H), 5.75 (m, 3 H), 6.03 (m, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 61.17 (C_{quat}), 69.37 (C_{quat}), 70.27 (C_{quat}), 70.32 (CH), 72.51 (CH), 74.03 (C_{quat}), 75.64 (C_{quat}), 84.03 (C_{quat}), 88.82 (C_{quat}), 93.69 (CH), 94.68 (CH), 98.05 (CH), 233.11 (C_{quat}, CO). MS (EI, 70 eV; *m/z* (%)): 446 (M⁺, 25), 362 (M⁺ - 3 CO, 100), 310 (M⁺ - Cr(CO)₃, 16), 306 (M⁺ - 3 CO - Fe, 5), 189 (M⁺ - Cr(CO)₃ - FeCp, 6), 121 (FeCp⁺, 10), 80 (Cr(CO)⁺, 13), 52 (Cr⁺, 69). IR (KBr): $\tilde{\nu}$ 2220, 1963, 1880, 1106, 1001, 823, 671, 654, 619, 532 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 305 (15 200 sh), 322 (16 900), 411 (6800) nm. Anal. Calcd for C₂₃H₁₄CrFeO₃ (446.21): C, 61.91; H, 3.16. Found: C, 61.50; H, 3.02.³¹

Horner-Emmons-Wadsworth Olefinations of Phosphonate Complexes (General Procedure, GP 2). To a degassed solution of 1 equiv of phosphonate complex 1 in THF was added 1.1 equiv of sodium hydride (95%) under argon. After the mixture was stirred for 10 min at room temperature, a solution of 1 equiv of the corresponding aldehyde in 2 mL of THF was added dropwise to the suspension. The reaction mixture was heated to reflux temperature for 12 h. After it was cooled, the reaction mixture was diluted with 20 mL of ether and filtered through a short plug of silica gel. The solvents were removed in vacuo to give the crude alkenylated arene complexes **2** as orange to deep red crystalline solids. Further purification was achieved by chromatography on silica gel (diethyl ether/pentane) and/or by recrystallization from dichloromethane/pentane. The experimental details and yields are summarized in Table 4.

(E)-Cr(CO)₃(η^6 -C₆H₅)CH=CH(4-C₅H₄N) (6a). Mp: 170–171 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.75 (t, *J* = 6.1 Hz, 1 H), 5.84 (dd, *J* = 6.2, 6.3 Hz, 2 H), 6.11 (d, *J* = 6.4 Hz, 2 H), 7.22 (d, *J* = 16.5 Hz, 1 H), 7.29 (d, *J* = 16.5 Hz, 1 H), 7.52 (m, AA'BB', *J* = 5.3 Hz, 2 H), 8.52 (m, AA'BB', *J* = 5.3 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 93.63 (CH), 94.43 (CH), 95.23 (CH), 105.83 (C_{quat}), 121.19 (CH), 128.38 (CH), 129.99 (CH), 143.23 (C_{quat}), 150.39 (CH), 234.04 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 317 (M⁺, 9), 261 (M⁺ - 2 CO, 4), 233 (M⁺ - 3 CO, 66), 181 (M⁺ - Cr(CO)₃, 10), 80 (CrCO⁺, 8), 52 (Cr⁺, 100). Anal. Calcd for C₁₆H₁₁CrNO₃ (317.27): C, 60.57; H, 3.49; N, 4.41. Found: C, 59.53; H, 3.50; N, 4.34.³¹

(E)-Cr(CO)₃(η^6 -C₆H₅)CH=CH(*p*-C₆H₄)NO₂ (6b). Mp: 180 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.75 (t, *J* = 6.2 Hz, 1 H), 5.88 (dd, *J* = 6.2, 6.4 Hz, 2 H), 6.13 (d, *J* = 6.4 Hz, 2 H), 7.21 (d, *J* = 16.4 Hz, 1 H), 7.43 (d, *J* = 16.4 Hz, 1 H), 7.83 (m, AA'BB', *J* = 8.6 Hz, 2 H), 8.26 (m, AA'BB', *J* = 8.6 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 93.67 (CH), 94.44 (CH), 95.19 (CH), 105.89 (C_{quat}), 124.32 (CH), 127.83 (CH), 128.64 (CH), 130.09 (CH), 142.83 (C_{quat}), 146.86 (C_{quat}), 234.04 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 361 (M⁺, 17), 305 (M⁺ - 2 CO, 9), 277 (M⁺ - 3 CO, 28), 225 (M⁺ - Cr(CO)₃, 75), 52 (Cr⁺, 100). IR (KBr): $\tilde{\nu}$ 1978, 1897, 1865, 1593, 1509, 1340, 873, 848, 837, 750, 669, 658, 626 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 321 nm (25 300), 451 (7200) nm. UV/vis (CHCl₃): λ_{\max} 317, 455 nm. Anal. Calcd for C₁₇H₁₁CrNO₅ (361.28): C, 56.52; H, 3.07; N, 3.88. Found: C, 56.22; H, 2.98; N, 3.85.

(E,E)-Cr(CO)₃(η^6 -C₆H₅)CH=CHCH=CH(*p*-C₆H₄)NO₂ (6c). Mp: 166 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.69 (m, 1 H), 5.79 (m, 2 H), 6.03 (d, *J* = 5.8 Hz, 2 H), 6.50 (d, *J* = 15.3 Hz, 1 H), 6.86 (d, *J* = 15.4 Hz, 1 H), 7.12 (m, 1 H), 7.27 (m, 1 H), 7.76 (m, AA'BB', *J* = 8.1 Hz, 2 H), 8.18 (m, AA'BB', *J* = 8.1 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 93.49 (CH), 94.30 (CH), 95.14 (CH), 106.51 (C_{quat}), 124.21 (CH), 127.59 (CH), 131.27 (CH), 131.92 (CH), 132.29 (CH), 133.11 (CH), 143.63 (C_{quat}), 146.50 (C_{quat}), 234.16 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 387 (M⁺, 11), 331 (M⁺ - 2 CO, 6), 303 (M⁺ - 3 CO, 14), 251 (M⁺ - Cr(CO)₃, 100), 52 (Cr⁺, 56). IR (KBr): $\tilde{\nu}$ 1969, 1885, 1859, 1589, 1515, 1336, 989, 856, 747, 659, 630 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 290 (sh, 16 200), 351 (26 200), 451 (11 100) nm. UV/vis (CHCl₃): λ_{\max} 339, 457 nm. Anal. Calcd for C₁₉H₁₃CrNO₅ (387.32): C, 58.92; H, 3.38; N, 3.62. Found: C, 58.90; H, 3.30; N, 3.63.

(E,E,E)-Cr(CO)₃(η^6 -C₆H₅)CH=CHCH=CHCH=CH(*p*-C₆H₄)NO₂ (6d). Mp: 168 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.66 (t, *J* = 6.3 Hz, 1 H), 5.80 (dd, *J* = 6.2, 6.4 Hz, 2 H), 5.99 (d, *J* = 6.5 Hz, 2 H), 6.40 (d, *J* = 15.5 Hz, 1 H), 6.65 (m, *J* = 15.3, 9.6 Hz, 2 H), 6.84 (d, *J* = 15.6 Hz, 1 H), 7.07 (m, *J* = 15.4, 9.6 Hz, 1 H), 7.30 (m, *J* = 15.2, 9.7 Hz, 1 H), 7.73 (m, AA'BB', *J* = 8.6 Hz, 2 H), 8.18 (m, AA'BB', *J* = 8.6 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 93.20 (CH), 93.97 (CH), 95.39 (CH), 107.29 (C_{quat}), 124.24 (CH), 127.43 (CH), 130.36 (CH), 131.45 (CH), 131.60 (CH), 133.92 (CH), 135.17 (CH), 135.48 (CH), 144.01 (C_{quat}), 146.30 (C_{quat}), 234.66 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 413 (M⁺, 5), 357 (M⁺ - 2 CO, 1), 329 (M⁺ - 3 CO, 4), 277 (M⁺ - Cr(CO)₃, 100), 52 (Cr⁺, 36). IR (KBr): $\tilde{\nu}$ 1957, 1918, 1889, 1865, 1581, 1514, 1336, 999, 867, 825, 747, 657, 630 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 312 (19 600 sh), 384 (33 600), 448 (20 100 sh) nm. UV/vis (CHCl₃): λ_{\max} 377, 453 nm. Anal. Calcd for C₂₁H₁₅CrNO₅ (413.35): C, 61.02; H, 3.66; N, 3.39. Found: C, 60.67; H, 3.72; N, 3.34.³¹

(E)-Cr(CO)₃(η^6 -C₆H₅)CH=CH(*p*-C₆H₄)N(CH₃)₂ (6e). Mp: 172 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 2.94 (s, 6 H), 5.58 (t, *J* = 6.2 Hz, 1 H), 5.85 (dd, *J* = 6.2, 6.4 Hz, 2 H), 5.98 (d, *J* = 6.4 Hz, 2 H), 6.61 (d, *J* = 16.3 Hz, 1 H), 6.72 (m, AA'BB', *J* = 8.6 Hz, 2 H), 7.16 (d, *J* = 16.3 Hz, 1 H), 7.39 (m, AA'BB', *J* = 8.6 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 40.04 (CH₃), 92.07 (CH), 92.83 (CH), 96.17 (CH), 110.65 (C_{quat}), 112.25 (CH), 119.26 (CH), 123.65 (C_{quat}), 128.30 (CH), 132.04

(CH), 150.73 (C_{quat}), 234.73 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 359 (M⁺, 17), 303 (M⁺ - 2 CO, 10), 275 (M⁺ - 3 CO, 100), 223 (M⁺ - Cr(CO)₃, 19), 52 (Cr⁺, 37). IR (KBr): $\tilde{\nu}$ 1956, 1899, 1603, 1529, 1364, 963, 811, 674, 660, 631 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 337 (25 300 sh), 362 (26 700), 413 (13 000 sh) nm. UV/vis (CHCl₃): λ_{\max} 360, 418 nm. Anal. Calcd for C₁₉H₁₇CrNO₃ (359.35): C, 63.51; H, 4.77; N, 3.90. Found: C, 63.27; H, 4.88; N, 3.90.

(E,E)-Cr(CO)₃(η^6 -C₆H₅)CH=CHCH=CH(*p*-C₆H₄)N(CH₃)₂ (6f). Mp: 174 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 2.92 (s, 6 H), 5.60 (m, 1 H), 5.80 (m, 2 H), 5.94 (m, 2 H), 6.21 (d, *J* = 15.2 Hz, 1 H), 6.69 (m, *J* = 10.3, 15.4 Hz, AA'BB', *J* = 7.9 Hz, 4 H), 7.03 (dd, *J* = 10.3, 15.2 Hz, 1 H), 7.34 (m, AA'BB', *J* = 7.9 Hz, 2 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 39.98 (CH₃), 92.48 (CH), 93.31 (CH), 95.77 (CH), 109.32 (C_{quat}), 112.33 (CH), 123.56 (CH), 124.53 (C_{quat}), 125.50 (CH), 128.04 (CH), 133.29 (CH), 135.91 (CH), 150.45 (C_{quat}), 234.57 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 385 (M⁺, 26), 329 (M⁺ - 2 CO, 4), 301 (M⁺ - 3 CO, 100), 249 (M⁺ - Cr(CO)₃, 50), 52 (Cr⁺, 50). IR (KBr): $\tilde{\nu}$ 1959, 1885, 1601, 1521, 1359, 987, 833, 752, 693, 673, 659, 631 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) = 337 nm (15 900 sh), 388 (29 300), 428 (22 300 sh). UV/vis (CHCl₃) λ_{\max} 383, 438 nm. Anal. Calcd for C₂₁H₁₉CrNO₃ (385.35): C, 65.45; H, 4.97; N, 3.63. Found: C, 65.79; H, 4.97; N, 3.58.

(E)-Cr(CO)₃(η^6 -C₆H₅)CH=CH[2-(5-C₄H₂S)NO₂] (6g). Mp: 158–159 °C dec. ¹H NMR ([D₆]DMSO, 300 MHz): δ 5.79 (t, *J* = 6.0 Hz, 1 H), 5.86 (dd, *J* = 6.0, 6.6 Hz, 2 H), 6.11 (d, *J* = 6.6 Hz, 2 H), 7.10 (d, *J* = 16.2 Hz, 1 H), 7.35 (d, *J* = 3.9 Hz, 1 H), 7.53 (d, *J* = 16.2 Hz, 1 H), 8.10 (d, *J* = 3.9 Hz, 1 H). ¹³C NMR ([D₆]DMSO, 75 MHz): δ 89.69 (C_{quat}), 93.57 (CH), 94.44 (CH), 94.69 (CH), 122.32 (CH), 126.83 (CH), 130.40 (CH), 131.65 (C_{quat}), 131.20 (CH), 148.80 (C_{quat}), 234.02 (C_{quat}, CO). MS (CI, 70 eV; *m/z* (%)): 367 (M⁺, 51), 311 (M⁺ - 2 CO, 20), 283 (M⁺ - 3 CO, 20), 235 (M⁺ - 3 CO - SO, 47), 231 (M⁺ - Cr(CO)₃, 15), 198 (C₃H₂Cr(CO)₃⁺, 100), 52 (Cr⁺, 93). IR (KBr): $\tilde{\nu}$ 1967, 1889, 1866, 1624, 1491, 1427, 1329, 945, 812, 733, 656, 629 cm⁻¹. UV/vis (DMSO): λ_{\max} (ϵ) 357 (22 900), 485 (8600) nm. UV/vis (CHCl₃): λ_{\max} 356, 488 nm. Anal. Calcd for C₁₅H₉CrNO₅S (367.29): C, 49.05; H, 2.47; N, 3.81; S, 8.71. Found: C, 48.03; H, 2.60; N, 3.66; S, 8.74.³¹

HRS Measurements of the Hyperpolarizabilities of the Complexes 1, 3, and 6. The HRS experiments were carried out in chloroform. The HRS cell consisted of a 12 cm glass tube of 1 cm diameter filled with the solution under investigation. A tuneable optical parametric oscillator (OPO) based HRS apparatus was used for the measurements at 1500

nm.³² To determine the β -values, the external reference method was used. Here, the intensity of the second harmonic $I(2\omega)$ is measured for a dilution series of the chromophore under investigation and for a reference chromophore with a known hyperpolarizability in the same solvent. Both are plotted as a function of chromophore number density N and, in the absence of absorption, the ratio of the two slopes is directly proportional to ratio of the orientational averages of the square of the first hyperpolarizabilities:

$$\frac{\text{slope}_{\text{sample}}}{\text{slope}_{\text{reference}}} = \frac{dI(2\omega)_{\text{sample}}/dN_{\text{sample}}}{dI(2\omega)_{\text{reference}}/dN_{\text{reference}}} = \frac{\langle\beta_{\text{HRS}}^2\rangle_{\text{sample}}}{\langle\beta_{\text{HRS}}^2\rangle_{\text{reference}}} \quad (1)$$

Chromophores with a CT along the molecule axis can be assumed to be rodlike, and all β tensor elements except β_{333} can be neglected. In this case the relation between β_{333} and the orientational averages is given by eq 2:

$$\langle\beta_{\text{HRS}}^2\rangle = \frac{6}{35} \beta_{333}^2 \quad (2)$$

As a reference chromophore, *p*-dimethylamino cinnamic aldehyde ($\beta_{333} = 35 \times 10^{-30}$ esu at 1500 nm in chloroform) was used.³³ A more detailed description of the HRS experiment and the data evaluation can be found in ref 31.

Acknowledgment. The financial support of the Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, FORMAT, and the Dr.-Otto-Röhm Gedächtnisstiftung is gratefully acknowledged. We wish to express our appreciation to Prof. H. Mayr for his generous support. We heartily thank Ms. Brigitte Jancker for recording the fluorescence spectra, Ms. S. Foro and Prof. Dr. H. J. Lindner, Technical University of Darmstadt, for performing the X-ray crystal structure analyses, and Ms. Diana Angebrandt for experimental assistance.

Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **6a,e**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM9904551

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