CONJUGATED POLYUNSATURATED OXACYCLIC CARBENE COMPLEXES: SYNTHESIS, STRUCTURE, AND PROPERTIES

Helmut FISCHER[a1,*], Michael RÄDLER[a2], Alexander MOSBACHER[a3], Matthias DREXLER[a4], Eike HÜBNER[a5], Bernhard WEIBERT[a6], Jürgen HECK[b1], Christian WITTENBURG[b2] and Stefan STEFFENS[b3]

[a] *Universität Konstanz, Fachbereich Chemie, Fach M727, D-78457 Konstanz, Germany; e-mail: [1] helmut.fischer@uni-konstanz.de, [2] michael.raedler@gmx.de, [3] alexmosbacher@hotmail.com, [4] matthias.drexler@uni-konstanz.de, [5] chemie@eike-huebner.de, [6] bernhard.weibert@uni-konstanz.de*

[b] *Universität Hamburg, Institut für Anorganische und Angewandte Chemie, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany; e-mail: [1] juergen.heck@chemie.uni-hamburg.de, [2] wittenbg@chemie.uni-hamburg.de, [3] steffens-hamburg@t-online.de*

Received January 25, 2007
Accepted March 16, 2007

Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic synthesis and catalysis.

The reaction of $[(CO)_5M(thf)]$ with but-3-yn-1-ols in the presence of NEt_3 offers a convenient route to 2-oxacyclopentylidene complexes $[(CO)_5M{=}\overline{C{-}O{-}CH_2CH_2CH_2}]$ (M = Cr (**1a**), W (**1b**)) in yields up to 96%. Furthermore, the reaction of **1** with ω-(dimethylamino)-substituted enals, $Me_2N{-}(CH{=}CH)_n{-}C({=}O)H$, activated by Me_3SiCl/NEt_3 or $POCl_3/NEt_3$ gives via aldol condensation the unsaturated oxacyclic push-pull carbene complexes $[(CO)_5M{=}\overline{C{-}O{-}CH_2CH_2C}\{{=}CH{-}(CH{=}CH)_n{-}NMe_2\}]$ (n = 0 (**2**), 1 (**3**), 2 (**4**), 3 (**5**)). In **2**–**5**, the amino group acts as an electron-donor unit and the oxacyclic carbene pentacarbonyl moiety as an electron acceptor. The aminometallaenes **2**–**5** have been characterized spectroscopically, the chromium complexes **2a**–**5a** additionally by X-ray structure analysis. For some complexes, their nonlinear optical properties (second harmonic generation) have been studied and β values up to 58×10^{-30} esu have been determined. The results of DFT calculations on chromium complexes **2a**–**5a** show that on lengthening of the unsaturated chain the influence of the carbonyl-metal fragment on the polyunsaturated chain strongly decreases.

Keywords: Carbene complexes; Organometallic merocyanines; Solvatochromism; Nonlinear optics; X-ray diffraction; Chromium; Tungsten; Carbonyl complexes; DFT calculations.

Transition metal complexes containing metal–carbon double bonds $[M{=}C(sp^2)]$ are among the most powerful tools in modern organometallic chemistry and have found numerous applications in stoichiometric syn-

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 4, pp. 503–526

doi:10.1135/cccc20070503

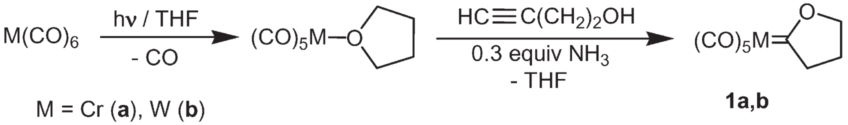
thesis as well as in catalysis[1,2]. Heteroatom-substituted Group 6 metal carbene complexes such as alkyl-, aryl-, alkenyl- and alkynyl(alkoxy)carbene complexes have proved to be very useful reagents in carbon–carbon and carbon–heteroatom forming reactions. The synthetic potential of alkyl(alkoxy)carbene complexes in part rests on the pronounced acidity of the C_α-bound hydrogen atoms[3]. The resulting deprotonated alkylcarbene complexes are reactive to electrophiles and thus can be used in carbon–carbon bond-forming reactions[4]. The introduction of an unsaturated carbon chain can make carbene complexes potentially useful candidates for the construction of one-dimensional molecular wires and for optoelectronic applications.

The discovery of nonlinear behavior in materials or molecules under the influence of a strong electric field such as that supplied by a laser beam has attracted considerable interest. For example, polarizable and noncentrosymmetric molecules are good candidates for second-order nonlinear activity. Large first hyperpolarizabilities have been observed in conjugated polyunsaturated organic or organometallic systems in which an electron-donating group D is connected with an electron-accepting group A through a π-system (push-pull molecules: D–π–A)[5]. Typical push-pull molecules can consist of different kinds of π-systems, donors D, and acceptors A. Amines and ferrocenes are the most popular donors due to their chemical and thermal stability and synthetic variability. The nature of the acceptor also plays an important role in determining the nonlinear optical behavior. Pentacarbonyl(carbene)metal units may act as very strong electron-withdrawing groups[6,7]. Enamino-substituted methoxycarbene pentacarbonyl complexes[6] and some other polyunsaturated alkenyl(amino)carbene pentacarbonyl complexes[7] have already been shown to exhibit considerable first hyperpolarizabilities.

In most alkenylcarbene complexes studied by X-ray structure analysis until now, the carbene and the olefin plane are (almost) perpendicularly oriented (torsion angle M=C–C=C: 60–80°). We now report on the synthesis, structure and spectroscopic properties of a series of (poly)enamino-substituted alkoxycarbene complexes (aminometallaenes) in which the metal–carbon and adjacent carbon–carbon double bonds are forced into coplanarity through incorporation into a rigid five-membered ring system thus allowing for a optimal interaction of both double bonds.

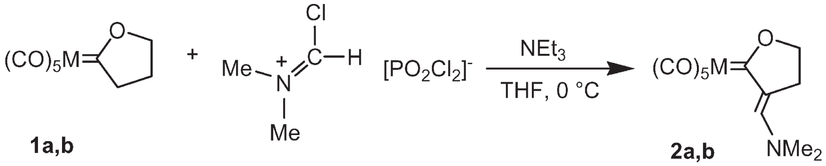
RESULTS

The starting oxacyclopentylidene complexes were prepared modifying a route published earlier[8]. Irradiation of hexacarbonyl chromium or hexacarbonyl tungsten in tetrahydrofuran generated pentacarbonyl(tetrahydrofuran)chromium and -tungsten. Subsequent reaction with 1.5 equivalents of but-3-yn-1-ol afforded, via cycloisomerization, the oxacyclopentylidene complexes **1a**, **1b** (Scheme 1) at room temperature within about 20 h. Addition of 0.3 equivalents of NEt_3 to the reaction mixture (after addition of butynol) accelerated the reaction and considerably increased the yields. The chromium complex **1a** was isolated in 93% and **1b** in 96% yields. Alternative routes to **1a**, **1b** involve reaction of pentacarbonyl[methoxy(methyl)-carbene]chromium with ethylene oxide[9], photolysis of $[M(CO)_6]$ in methanol or diethyl ether in the presence of but-3-yn-1-ol[8], reaction of pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium or -tungsten with but-3-yn-1-ol[10], or of $[M(CO)_6]$ with dilithiated oxetane and $(Me_3O)BF_4$[11]. However, all of these routes afford **1a**, **1b** in significantly lower yields.



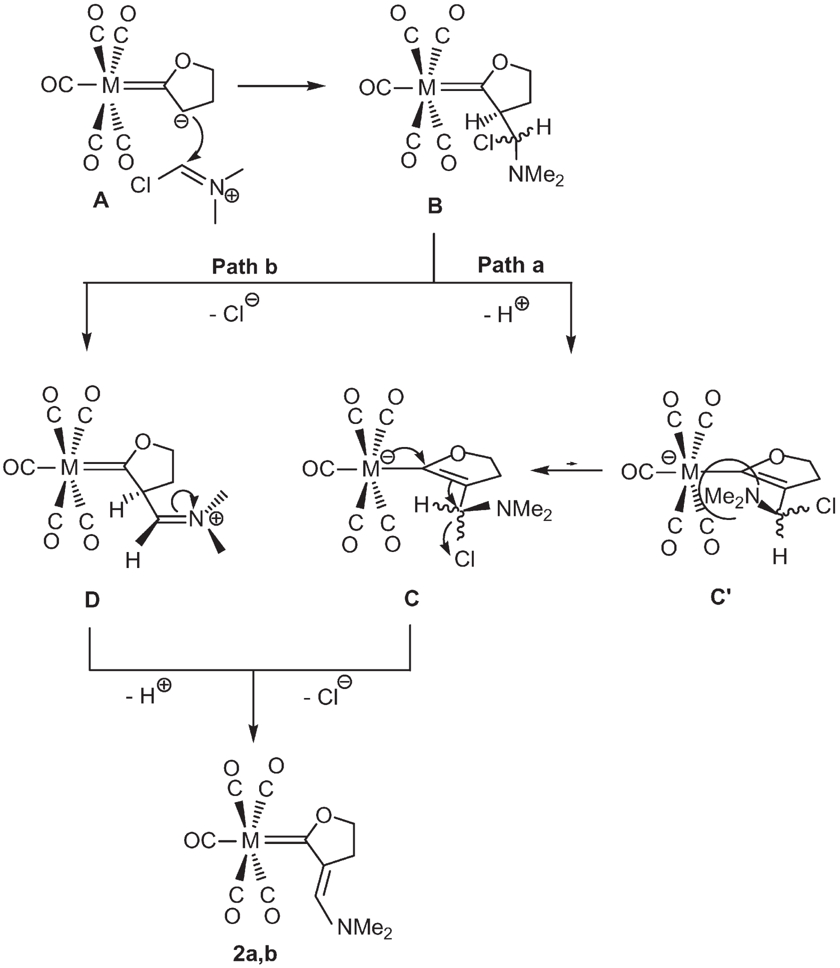
SCHEME 1

Reaction of **1a**, **1b** with the Vilsmeier–Haack compound (dimethylformamide activated with phosphorus oxychloride) and triethylamine in THF at 0 °C (Scheme 2) gave complexes **2a** and **2b** in excellent yields (**2a**: 91%, **2b**: 89%)[12]. 4-(Dimethylamino)-1-chromabutadiene (**2a**) has been obtained earlier by the reaction of **1a** with dimethylformamide dimethyl acetal, albeit in a lower yield (66.5%)[13]. The sequence of mixing the various components turned out to be an important factor in getting high yields. Complexes **1a**, **1b** had to be added to solution of the Vilsmeier–Haack compound before the addition of triethylamine.



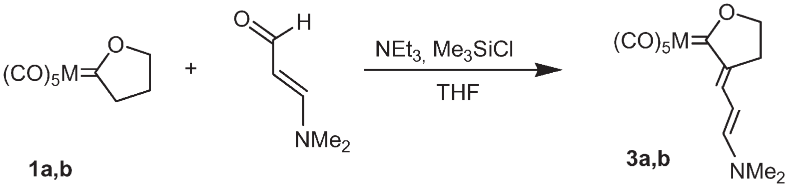
SCHEME 2

The formation of the condensation products **2a**, **2b** was highly selective. Only the *E* isomer with respect to the C=C bond was detected. A likely mechanism is depicted in Scheme 3. The reaction is presumably initiated by a nucleophilic attack of the metallate **A** (generated by deprotonation of **1a**, **1b** with NEt_3 at the C_α position) on the C atom of the chloriminium cation giving **B**. Subsequently, two paths are conceivable. The exocyclic double bond in **2a**, **2b** could be formed by deprotonation of C_α of **B** to give **C** followed by chloride elimination (path a). Alternatively, chloride elimination from **B** and subsequently deprotonation of the resulting complex **D** likewise affords **2a**, **2b** (path b). Based on the acidity of the C_α-bound hydrogen atoms in alkoxy(alkyl)carbene complexes path a is more likely. The stereoselectivity in the formation of **2a**, **2b** is then readily explained by unfavorable steric interactions between the NMe_2 group and the bulky $M(CO)_5$ fragment in rotamer **C′** (Scheme 3).



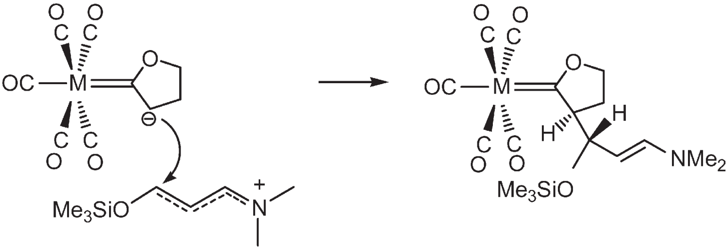
Scheme 3

The attempt to synthesize the next higher homologues, 3-[(dimethylamino)prop-2-enylidene]-2-oxacyclopentylidene complexes, by the methodology of Scheme 2 met with only limited success. It was not possible to isolate the product of the reaction of 3-(dimethylamino)acrylaldehyde with **1a**, **1b**, phosphorus oxychloride and triethylamine in pure form. However, when phosphorus oxychloride was replaced by trimethylsilyl chloride[14], the reaction giving **3a**, **3b** (Scheme 4) proceeded cleanly at room temperature. Chromatographic work-up of the reaction mixture then afforded orange-red crystals of **3a**, 3**b** in 85% (Cr) and 83% (W) yields. Again, the reactions proceeded highly selectively; only the *E*,*E* isomer was detected.



SCHEME 4

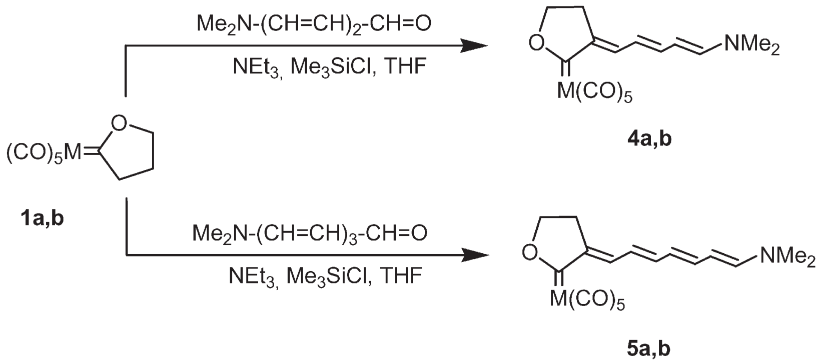
Very likely, the complexes **3a**, 3**b** are formed by a mechanism similar to that shown in Scheme 3 the initiating step being a nucleophilic attack of the metallate **A** at the carbonyl carbon atom of the aldehyde that is activated by the silyl group (Scheme 5).



SCHEME 5

An analogous procedure could be applied to the synthesis of complexes **4a**, **4b** and **5a**, **5b** (Scheme 6).

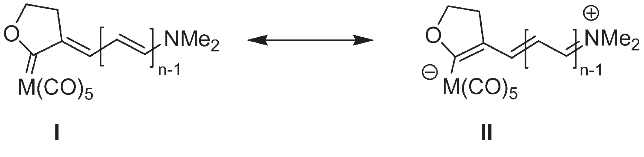
A further extension of the chain proved to be impossible. Attempts to synthesize a (dimethylamino)metalladodecahexaene from **1a**, **1b** with $Me_2N–(CH=CH)_4–CH=O$ were unsuccessful. On extending the chain in (dimethylamino)metallaoctatetraene **4a**, **4b** by another CH=CH unit (→ **5a**, **5b**) the yields dropped from 73 and 71 to 37 and 32%.



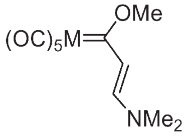
Scheme 6

All new complexes are readily soluble in polar organic solvents such as THF or CH_2Cl_2, the solubility in nonpolar solvents considerably decreasing in the series **1** > **2** > **3** > **4** > **5**. Complexes **5a**, **5b** are only very poorly soluble in pentane.

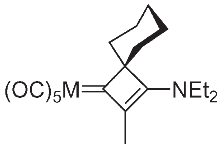
The IR spectra of the complexes **2**–**5** show the typical pentacarbonyl pattern in the region 1900–2100 cm^{-1} and additionally ν(CC) absorptions between 1650 and 1500 cm^{-1}. From the position of the ν(CO) A_1(*trans*) and E vibrations of **2**–**5** at very low energy compared with those of **1** it follows that the enamine substituents transfer considerable electron density to the metal center via the oxacyclic carbene ligand and strongly influence the bonding within the metal-carbene unit. Thus, the dipolar resonance form **II** (Scheme 7) significantly contributes to the overall bonding. The ν(CO) spectra of the aminometallaenes **2**–**5** are very similar to those of acyclic aminometallabutadiene complexes[15] **6** and cyclobutenylidene complexes[16] **7**.



Scheme 7



6



7

M = Cr (**a**), W (**b**)

Within the series **2**–**5** increasing chain length results in only a slight shift of the ν(CO) A_1(*trans*) and E absorptions indicating that a lengthening of the π-backbone only marginally reduces π-interaction of the NMe_2 donor with the $M(CO)_5$ fragment.

The conclusions drawn from the IR spectra are supported and refined by the NMR spectra. Compared with **1**, the signal of the carbene carbon in the ^{13}C NMR spectra is observed at a considerably higher field and changes only slightly on lengthening of the π-chain. As a consequence of π-interaction of the amino substituent with the olefin chain (resonance form **II**), the signal of the NMe_2 group in **2**–**5** is split into two singlets at low temperature. When increasing the temperature, the signals coalesce. From the coalescence temperature and the position of the signals at low temperature, the barrier $\Delta G^{\neq}$ to rotation around the N–C(sp^2) bond (Table I) is calculated to lie in the range 48.5–63.6 kJ/mol. In accord with the IR spectroscopic results the barrier is the lowest for complexes **5a**, **5b**, increasing only slightly with decreasing chain length.

The solid-state structures of chromium complexes **1a**–**5a** were additionally established by X-ray structure analysis (Figs 1–5, Tables II and V). The 2-oxacyclopentylidene ligand in **1a** (Fig. 1) adopts an envelope conformation, C8 lying 0.35 Å above the carbene plane formed by the atoms Cr1, C6, O6, C7, and C9 (torsion angle C6–O6–C9–C8 –14.2(2)°). The Cr1–C6 bond (2.019(2) Å) of **1a** is comparable to that in other, usually in position 3, substituted 2-oxacyclopentylidene complex (Cr1–C6: 1.980–2.055 Å)[17]. Within the error limit all Cr–CO distances are equal. In contrast to **1a**, the

TABLE I
Coalescence temperatures and rotational barriers of the aminometallaenes **2**–**5**

Complex	M	T_c, °C	$\Delta G^{\#}$, kJ/mol
2a	Cr	+9	61.0
3a	Cr	+32	61.2
4a	Cr	–6	53.3
5a	Cr	–29	48.5
2b	W	+18	63.6
3b	W	+38	62.5
4b	W	–1	54.3
5b	W	–26	49.2

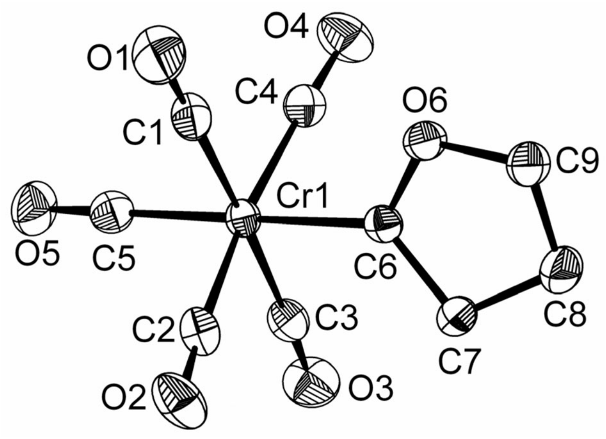


FIG. 1
Plot of complex **1a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)

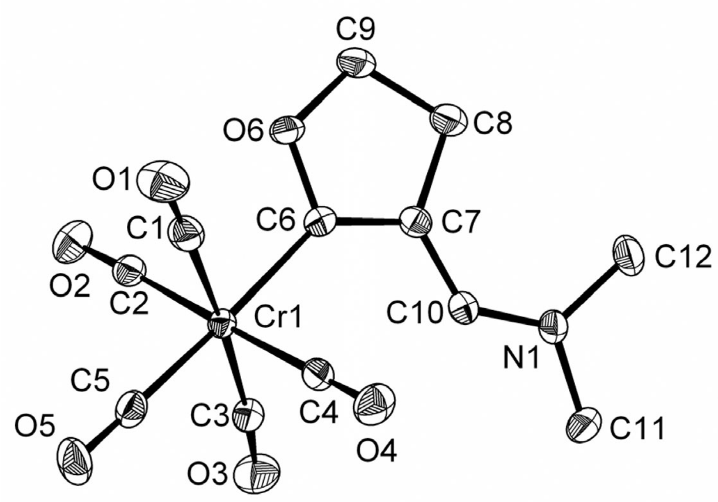


FIG. 2
Plot of complex **2a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)

Cr–C_{trans} distance in **2a**–**5a** is significantly shorter than the average of the Cr–C_{cis} distances. Such a *trans* influence agrees well with the expectations based on the IR data and emphasizes the pronounced enamine interaction with the $M(CO)_5$ fragment. The independence of the *trans* influence on the chain length within the error limit is likewise in accord with the conclusions drawn from the IR spectra. In contrast to **1a**, the oxacyclopentylidene ring in all aminometallaenes **2a**–**5a** is nearly planar the torsion angle C6–O6–C9–C8 varying only between –1.3(2)° (**5a**) and 2.3(6)° (**4a**).

TABLE II
Selected bond lengths (in Å) and angles (in °) for **1a**, **2a**, **3a**, **4a**, and **5a**

	1a	**2a**	**3a**	**4a**	**5a**
Bond lengths					
Cr–C_{trans} (av.)	1.908	1.906	1.907	1.906	1.902
Cr–C5	1.907(2)	1.868(2)	1.875(2)	1.879(6)	1.858(6)
Cr1–C6	2.019(2)	2.114(2)	2.088(2)	2.094(6)	2.087(5)
C6–O6	1.315(3)	1.358(2)	1.348(2)	1.342(7)	1.349(7)
C6–C7	1.505(3)	1.415(3)	1.420(2)	1.425(8)	1.430(8)
C7–C10		1.387(2)	1.384(2)	1.355(8)	1.375(7)
C10–N1		1.329(2)			
C10–C11			1.404(2)	1.422(8)	1.413(7)
C11–C12			1.384(3)	1.375(8)	1.374(8)
C12–N1			1.330(2)		
C12–C13				1.420(8)	1.411(7)
C13–C14				1.363(8)	1.374(8)
C14–N1				1.347(7)	
C14–C15					1.403(7)
C15–C16					1.378(8)
C16–N1					1.328(8)
Bond angles					
Cr1–C6–O6	122.33(15)	114.17(12)	116.94(12)	115.2(4)	115.1(4)
Cr1–C6–C7	129.33(15)	136.47(13)	134.13(13)	134.5(4)	136.2(4)
O6–C6–C7	108.34(17)	109.30(15)	108.88(15)	110.2(5)	108.6(4)

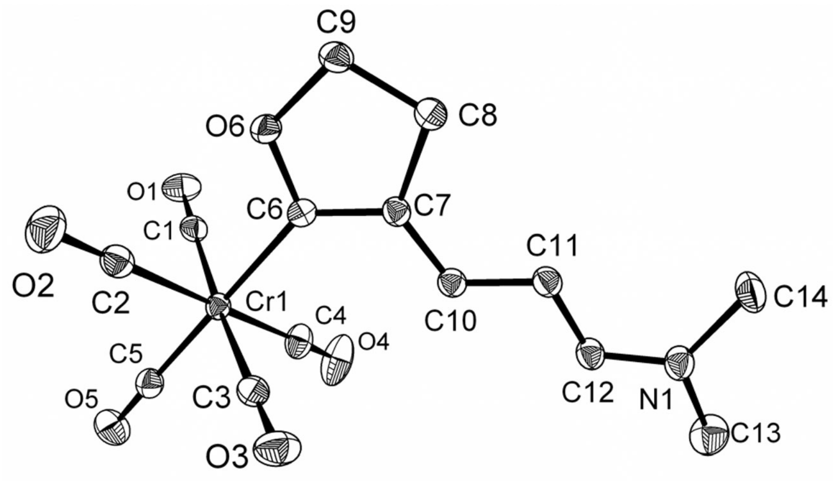


FIG. 3
Plot of complex **3a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)

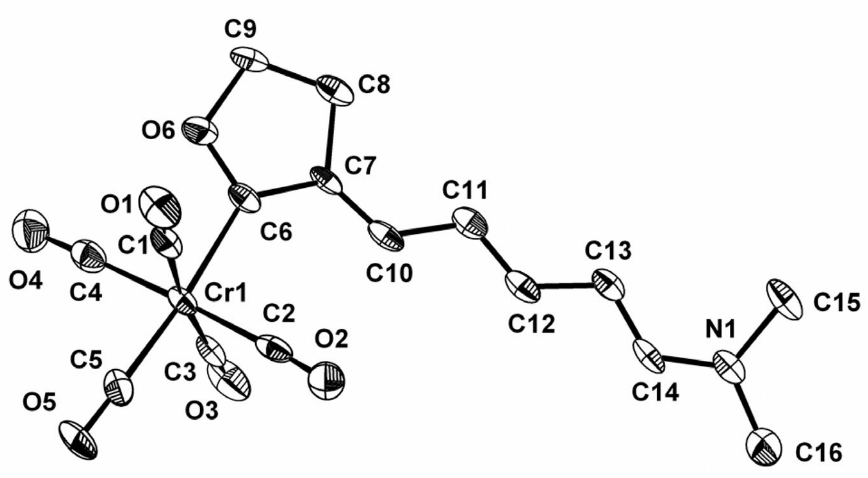


FIG. 4
Plot of complex **4a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)

The presence of an extended π-system in all aminometallaenes (see Scheme 7) is also evident from (i) the planarity of the ligand (the maximum distance from the plane formed by Cr1, C6 and both atoms of the terminal $C(sp^2)$–N bond in **2a**–**4a** is 0.144 Å, the plane in **5a** is slightly curved, the maximum distance of a carbon atom from the "plane" at the apex is 0.295 Å (C12)); (ii) the lengthening of the Cr–C6 bond when going from **1a** to **2a**–**5a** (see Table II); (iii) the very short $C(sp^2)$–$C(sp^2)$ distances within the chains (1.403–1.430 Å, for comparison, the mean $C(sp^2)$–$C(sp^2)$ distances are 1.478 Å (nonconjugated)[18] and 1.455 Å (conjugated)[18]); (iv) the rather long C=C distance in the chain (1.355–1.387 Å, for comparison, the mean C=C distance is 1.316 Å [18]) and (v) the short $C(sp^2)$–N bonds (1.328–1.347 Å, the mean $C(sp^2)$–N distance being 1.355 Å [18]).

These distances are nearly unaffected by the number of CH=CH spacers in the chain (Table II) thus once more confirming the strong electron delocalization from the terminally located dimethylamino group (sum of angles at nitrogen: 359.1–360°) through the polymethyne chain to the metal-carbonyl and the importance of the resonance form **II** for the overall bond description.

These conclusions are additionally supported by the electronic absorption spectra. As expected from the dipolar resonance form **II** (Scheme 7), all complexes **2**–**5** exhibit solvatochromism. The λ_{max} values in hexane, DMF,

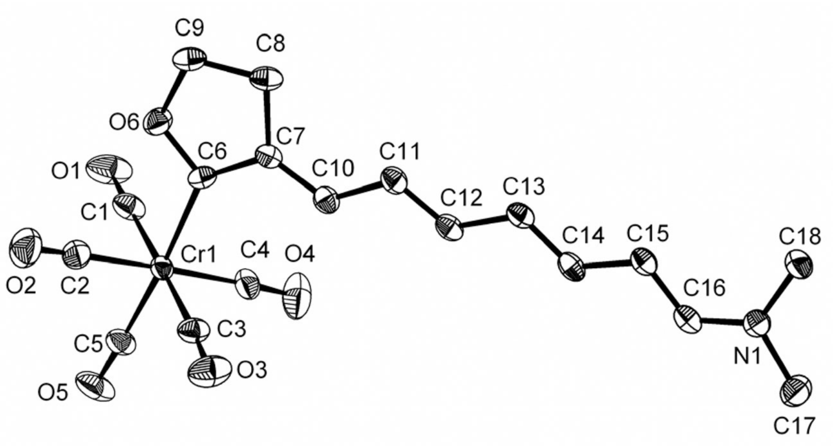


FIG. 5
Plot of complex **5a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)

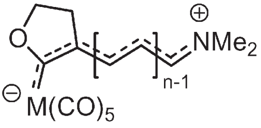
and CH_2Cl_2 are compiled in Table III. As in typical heteroatom-substituted carbene complexes, the electronic absorption at lowest energy is assigned to a metal-to-ligand charge transfer (MLCT) transition. Transformation of the 2-oxacyclopentylidene complexes **1a**, **1b** into the aminometallabutadienes **2a**, **2b** leads to a strong bathochromic shift of the absorption at lowest energy (Table III). Insertion of CH=CH units into the C(sp^2)–N bond causes further shifts of the MLCT band towards lower energies. However, the effect diminishes with increasing length of the π-conjugated system (Fig. 6). As expected on the basis of the dipolar nature of aminometallaenes **2**–**5**, complexes **2a**, **2b** exhibit a strong negative solvatochromic effect. Surprisingly, when extending the π-conjugated chain (**2** → **3** → **4** → **5**), the solvatochromism diminishes and then even reverses. Complexes **4** already show a small, **5** a strong positive solvatochromic effect (Table III). The influence of a lengthening of the π-conjugated system on the MLCT band is much more pronounced in polar than in nonpolar solvents and increases considerably in the series hexane, CH_2Cl_2, DMF. Furthermore, there is also a very strong hyperchromic effect leading to molar absorption coefficients of up to

TABLE III
Linear and nonlinear optical data for complexes **1**–**5**

Complex	M	Hexane λ_{max}, nm	DMF λ_{max}, nm	$\Delta\nu$ cm^{-1}	CH_2Cl_2 λ_{max}, nm	β	β_0
						10^{-30} esu	
1a	Cr	380	363	–1230			
2a	Cr	433	396	–2160	408	nd[a]	
3a	Cr	503	470	–1400	481	nd[a]	
4a	Cr	550	564	+450	560	26	10
5a	Cr	577	664	+2270	617	nd[a]	
1b	W	375	346	–2240			
2b	W	421	392	–1760	400	nd[a]	
3b	W	492	470	–950	476	18	10
4b	W	541	564	+750	563	58	42
5b	W	575	665	+2350	644	nd[a]	

[a] No signal detected in excess of the detection limit.

100 000 for **5**. It is well known that a meropolymethines (e.g. **III**) with equal contribution of both mesomeric structures (**I** and **II**, Scheme 7) have the longest-wavelength absorptions.



III

It has been established experimentally[19] that only those molecules exhibit a pronounced solvatochromic effect whose π-electron charge distribution (and, consequently, the dipole moment) in the electronic ground state considerably differs from that in the excited state. Therefore, the much stronger sensitivity of the MLCT absorption to chain extension in DMF than in hexane and the strong negative solvatochromic effect observed with **2** indicate that aminometalladecapentaenes **5** are more polyene-like (see **I**) than aminometallabutadienes **2**.

Aminometallaenes **2**–**5** are polar push-pull systems and are expected to exhibit nonlinear optical properties. Therefore, the complexes were subjected to hyper-Rayleigh scattering[20] (HRS) studies but as they absorb substantially in the area of 532 nm (*I*(2ω) when the incident light has a

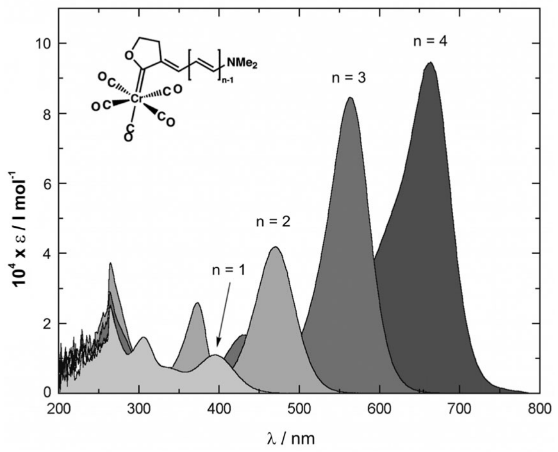
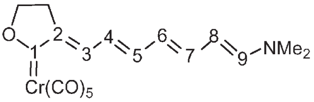


FIG. 6
UV-VIS spectra of complexes **2a**–**5a** in dimethylformamide

wavelength of $I(\omega)$ = 1064 nm), the stimulating laser light was shifted to 1500 nm. The experiments were carried out in CH_2Cl_2 as described earlier[21]. As a reference, Disperse Red 1 (DR 1, $\beta(CH_2Cl_2) = 70 \times 10^{-30}$ esu) was used. The first hyperpolarizability β beyond the detection threshold ($\beta_{limit} \sim 10 \times 10^{-30}$ esu) could only be obtained for complexes **3b** and **4a**/**4b** (Table III). All other complexes did not show any intensity in the HRS experiment. The β values of complex **4a** ($\beta = 26 \times 10^{-30}$ esu, $\beta_0 = 10 \times 10^{-30}$ esu) and **3b** ($\beta = 18 \times 10^{-30}$ esu, $\beta_0 = 10 \times 10^{-30}$ esu) are comparable to those of some (aminoallenylidene)pentacarbonylchromium complexes[22], e.g. $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$ ($\beta = 21 \times 10^{-30}$ esu, $\beta_0 = 9.5 \times 10^{-30}$ esu, in DMF[22a]). They are higher than those of $[(CO)_5Cr{=}C(OMe){-}CH{=}C(NMe_2)H]$ ($\beta = 16 \times 10^{-30}$ esu, $\beta_0 = 5 \times 10^{-30}$ esu)[6] or of the cyclobutenylidene complex **7** ($\beta_0 < 10 \times 10^{-30}$ esu)[16], but are considerably lower than those of some polyunsaturated pyrrolidino carbene complexes (($\beta = 50–350 \times 10^{-30}$ esu, $\beta_0 = 26–154 \times 10^{-30}$ esu, in CH_2Cl_2), in both cases the wavelength of the incident light being 1064 nm)[7]. For the heterodinuclear carbene complexes $[(CO)_5M{=}C(OMe)(CH{=}CH)_n\{(C_5H_4)FeCp\}]$ (M = W, Cr; n = 1–4) in which ferrocene is the donor element very high β values were reported ($\beta = 110 \times 10^{-30}$ to 2420×10^{-30} esu in acetonitrile, β_0 are not given, incident light 1064 nm)[23]; however, it has to be considered that their SHG-signals are in the area of the lowest-energy absorption band. This may cause very strong resonance effects which enhance the β values dramatically. The first hyperpolarizability more than doubles when a CH=CH unit is inserted into the chain of **3b** (**3b** → **4b**). It is also well known that when W and Cr complexes of equal conjugation length are employed, the tungsten complexes exhibit a higher effect of second harmonic generation. This is also confirmed by the β_0 values of **4a** and **4b**. The first hyperpolarizability β drops again when going from **4** to the aminometalladecapentaenes **5**. There is obviously an optimal chain length of the polyene backbone in aminometallaenes to achieve a high β value. Similar conclusions have been drawn for the investigation of organic donor–acceptor-substituted conjugated chromophores[24]. This result agrees well with the theoretical evaluation of the first static hyperpolarizability β_0 as a function of bond length alternation (BLA) of polyenes[24]. The maximum β_0 values have to be expected at a BLA between 4 and 5 pm for a donor–acceptor-substituted polyene compound (meropolymethine state). An increased delocalization of π-bonds reveals a smaller BLA and thus a smaller β_0 (polymethine state). The same occurs with increasing BLA (polyene state)[24d].

DFT calculations were carried out using Jaguar 5.5[25] on the LACVP* basis set (ECP basis set for chromium and tungsten, N31-G6* basis set for all other atoms) with the BP86 functional. The energy of the HOMO gradually increases in the series **2** < **3** < **4** < **5** whereas that of the LUMO decreases (Table IV). Since the influence of the chain extension on the LUMO energy is more pronounced than that on the HOMO energy, the HOMO–LUMO energy gap decreases in accord with the UV-VIS spectroscopic results. In **2**, the HOMO is completely centered on the acceptor pentacarbonylmetal moiety. However, increasing the length of the enamino substituent leads to enhanced delocalization of the HOMO onto the oxacyclic ligand and its unsaturated substituent (Table IV). Finally, in **5** the contribution of the ligand π-system exceeds that of the $M(CO)_5$ moiety. In contrast, the LUMO is ligand-centered (Table IV) and the contribution from $M(CO)_5$ is negligible. From the varying contribution of the ligand orbitals to the HOMO (Table IV) it follows that in **2** the lowest-energy band is pure MLCT absorp-

TABLE IV
Calculated energies of the HOMO and LUMO of **2a**–**5a** and breakdown of the orbital contributions from the CO ligands, metal and carbon atoms along the chain of the (dimethylamino)metallaenes to the HOMO and LUMO. Numbering scheme:



	E, eV	CO	Cr	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
						HOMO						
2a	–4.82	14.6	63.0	0.4	0.4	0.2						
3a	–4.69	14.7	63.0	0.4	0.4	0.1	0.0	0.0				
4a	–4.63	8.8	38.4	0.2	9.3	1.6	7.2	3.3	5.8	4.3		
5a	–4.55	4.2	26.1	0.4	10.6	0.8	9.3	2.4	7.9	4.6	6.6	5.4
						LUMO						
2a	–2.40	4.5	2.5	32.0	1.6	31.3						
3a	–2.78	2.9	3.1	22.0	4.8	23.2	0.5	20.5				
4a	–2.97	2.2	3.2	16.1	6.2	17.1	1.9	18.8	0.4	15.0		
5a	–3.10	1.9	3.1	12.6	6.7	13.2	3.2	15.4	0.8	15.0	0.5	11.5

tions and that a π→π* transition increasingly contributes to the absorption in the series **3**, **4**, **5**. The conclusion agrees well with the varying solvatochromic behavior of complexes **2**–**5** and readily explains the change from negative to positive solvatochromism when going from **2** to **5**.

All complexes **2**–**5** are thermally very stable, their decomposition point lying above 170 °C. Transforming **1** into aminometallaenes **2**–**5** strongly enhances the resistance to UV irradiation. Whereas UV irradiation ($\lambda >$ 300 nm) in THF transfers **1** within one hour into solvent-stabilized tetra-

TABLE V
Crystal data and refinement details for compounds **1a**, **2a**, **3a**, **4a**, and **5a**

	1a	**2a**	**3a**	**4a**	**5a**
M_r	262.14	317.22	343.25	369.29	395.33
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/n$	$Pna2_1$
a, Å	9.694(4)	19.785(14)	6.9963(18)	8.507(4)	17.166(11)
b, Å	10.262(4)	9.105(4)	14.101(5)	7.209(3)	10.5929(17)
c, Å	11.715(4)	15.772(7)	15.805(4)	27.95(3)	10.237(3)
α, °	90	90	90	90	90
β, °	112.69(3)	101.75(6)	90.954(13)	92.54(7)	90
γ, °	90	90	90	90	90
V, Å^3	1075.2(7)	2782(3)	1559.1(7)	1712.3(19)	1861.5(14)
Z	4	8	4	4	4
ρ_{calc}, g cm^{-3}	1.619	1.515	1.462	1.433	1.411
μ, mm^{-1}	1.072	0.845	0.760	0.698	0.647
$F(000)$	528	1296	704	760	816
$2\Theta_{max}$, °	53.98	54.00	54.00	50.84	54.00
Index ranges	$0 \le h \le 12$	$-23 \le h \le 25$	$-8 \le h \le 4$	$0 \le h \le 10$	$-21 \le h \le 21$
	$0 \le k \le 13$	$-11 \le k \le 11$	$-18 \le k \le 17$	$0 \le k \le 8$	$-13 \le k \le 13$
	$-14 \le l \le 13$	$-20 \le l \le 20$	$-20 \le l \le 20$	$-33 \le l \le 33$	$-13 \le l \le 13$
No. of data	2473	5869	4152	3246	5897
No. of unique data	2339	3038	3383	3003	3718
Parameters	145	181	199	217	236
$I > 2\sigma(I)$	0.0350	0.0306	0.0325	0.0714	0.0792
wR_2 (F^2), all data	0.0879	0.0734	0.0810	0.1704	0.1864
GOF on F^2	1.054	1.034	1.048	1.009	1.012

carbonyl oxacarbene species, complex **2** can be irradiated for several days at room temperature without any sigh of decomposition. The reason may be that the quantum yield of CO loss from carbene complexes such as $[(CO)_5M{=}C(X)R]$ (M = Cr, W; R = aromatic substituent; X = OR, NR_2) is fairly low (approximately 1% at 366 and 313 nm) and drops to less than 10^{-4} at 436 nm[26]. This has been explained by the inactivity in photodissociation of the MLCT transition and by the small activity of the ligand-field excitation due to its rapid radiationless decay to the lower MLCT state.

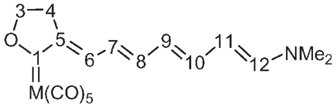
In summary, complexes **2**–**5** constitute a series of conjugated unsaturated complexes with a dimethylamino donor at one terminus of the chain and a pentacarbonyl 2-oxacyclopentylidene metal fragment at the other end. Lengthening of the unsaturated chain significantly changes the character of the HOMO from a purely $M(CO)_5$-localized orbital to an orbital with contribution from the pentacarbonylmetal and the unsaturated chain. Whereas in **2**, the $M(CO)_5$ group constitutes the acceptor in **5** the pentacarbonyl(2-oxacyclopentylidene)metal fragment has to be regarded as the acceptor moiety. The increasing contribution of a $\pi \rightarrow \pi^*$ type transition to the absorption at longest wavelength cancels the effect of the metal-to-ligand charge transfer transition. As a consequence, the first hyperpolarizability increases from **3** to **4** and then drops again.

EXPERIMENTAL

5-(Dimethylamino)penta-2,4-dienal[27], 7-(dimethylamino)hepta-2,4,6-trienal[28], and 9-(dimethylamino)nona-2,4,6,8-tetraenal[29] were synthesized according to literature procedures. All other chemicals were used as received from commercial suppliers.

All operations were performed in an inert gas atmosphere (nitrogen or argon) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, Et_2O, pentane, hexane) and sodium (THF). The silica gel used for chromatography (Baker, silica for flash chromatography) was nitrogen-saturated. The reported yields refer to analytically pure compounds and are not optimized. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with Varian Inova 400, Bruker AC 250, Bruker WM 250, or Bruker DRX 600 spectrometers at ambient temperature. Chemical shifts (δ, ppm) are relative to the tetramethylsilane peak (^1H) or $CDCl_3$ (^{13}C). Coupling constants, *J*, are in Hz. IR spectra (ν, cm^{-1}) were recorded on a Biorad FTS 60. UV-VIS spectra were recorded on a Hewlett–Packard diode array spectrophotometer 8453; mass spectra on a Finnigan MAT 312 at 70 eV; elemental analyses on a Heraeus CHN-O-Rapid.

General numbering scheme for the assignment of the ^{13}C resonances:



Pentacarbonyl(1-oxacyclopentan-2-ylidene)chromium (**1a**)[8] and Pentacarbonyl(1-oxacyclopentan-2-ylidene)tungsten (**1b**)

20 mmol of [M(CO)$_6$] (M = Cr, 4.4 g; M = W, 7.04 g) in ca. 200 ml of THF were transformed into the corresponding [(CO)$_5$M(thf)] complex by irradiation. The progress of the reaction was checked by IR spectroscopy. Subsequently, a solution of 1.40 g (20 mmol) of but-3-yn-1-ol in ca. 5 ml of THF and then 1 ml of triethylamine were added. The solution was stirred for about 1 h. When the IR spectrum of the solution did not exhibit absorptions due to [(CO)$_5$M(thf)] any longer, the solvent was almost completely removed in vacuo. Then 20 ml of silica were added to the residue and the solvent was removed completely. Chromatography at –30 °C on silica with mixture of pentane/diethyl ether and removal of the solvent gave a yellow crystalline solid. Recrystallization from pentane finally afforded yellow crystals.

1a: Yield 6.10 g (23.3 mmol, 93%). M.p. 63 °C. IR (pentane): ν(CO) 2067 m, 1988 w, 1964 s, 1949 vs. ^{1}H NMR (250 MHz): 1.94 (quint, 2 H, $^3J_{HH}$ = 7.8, H4); 3.65 (t, 2 H, $^3J_{HH}$ = 7.9, H5); 4.92 (t, 2 H, $^3J_{HH}$ = 7.8, H3). ^{13}C NMR (63 MHz): 21.0 (C4), 60.6 (C5), 85.4 (C3), 216.4 (*cis*-CO), 223.3 (*trans*-CO), 342.3 (C1). UV-VIS, λ_{max} (log ε): 363 (3.842) [DMF]; 380 (3.960) [hexane]. EI-MS (20 °C), *m/z* (%): 262 (50) [M$^+$], 234 (24) [(M – CO)$^+$], 206 (29) [(M – 2 CO)$^+$], 192 (8) [(Cr(CO)$_5$)$^+$], 178 (33) [(M – 3 CO)$^+$], 164 (15) [(Cr(CO)$_4$)$^+$], 150 (56) [(M – 4 CO)$^+$], 136 (23) [(Cr(CO)$_3$)$^+$], 122 (100) [(M – 5 CO)$^+$], 108 (35) [(Cr(CO)$_2$)$^+$], 94 (46) [(M – 6 CO)$^+$]. For $C_9H_6CrO_6$ (262.1) calculated: 41.24% C, 2.31% H; found: 41.09% C, 2.35% H.

1b: Yield 7.56 g (19.2 mmol, 96%). M.p. 61 °C. IR (pentane): ν(CO) 2074 m, 1984 w, 1958 s, 1945 vs. ^{1}H NMR (250 MHz): 1.95 (quint, 2 H, $^3J_{HH}$ = 7.8, H4); 3.41 (t, 2 H, $^3J_{HH}$ = 7.9, H5); 4.89 (t, 2 H, $^3J_{HH}$ = 7.8, H3). ^{13}C NMR (63 MHz): 21.7 (C4), 63.6 ($^2J_{WC}$ = 12.2, C5), 85.8 (C3), 197.3 ($^1J_{WC}$ = 126.9, *cis*-CO), 204.3 ($^1J_{WC}$ = 121.4, *trans*-CO), 314.6 ($^1J_{WC}$ = 100.2, C1). UV-VIS, λ_{max} (log ε): 346 (4.167) [DMF]; 375 (4.080) [hexane]. EI-MS (40 °C), *m/z* (%): 394 (56) [M$^+$], 366 (17) [(M – CO)$^+$], 338 (10) [(M – 2 CO)$^+$], 324 (18) [(W(CO)$_5$)$^+$], 310 (77) ((M – 3 CO)$^+$], 296 (32) [(W(CO)$_4$)$^+$], 282 (100) [(M – 4 CO)$^+$], 268 (39) [(W(CO)$_3$)$^+$], 254 (82) [(M – 5 CO)$^+$], 240 (35) [(W(CO)$_2$)$^+$], 226 (60) [(M – 6 CO)$^+$], 212 (39) [(W(CO))$^+$], 184 (25) [W$^+$]. For $C_9H_6O_6W$ (394.0) calculated: 27.44% C, 1.53% H; found: 27.36% C, 1.55% H.

Pentacarbonyl{(*E*)-3-[(dimethylamino)methylidene]-1-oxacyclopentan-2-ylidene}chromium (**2a**) and Pentacarbonyl{(*E*)-3-[(dimethylamino)methylidene]-1-oxacyclopentan-2-ylidene}tungsten (**2b**)

1.5 ml of phosphorus oxychloride was slowly added at 0 °C to a solution of 1.5 ml dimethylformamide in 20 ml of THF. The solution was stirred for 30 min. Then 4 mmol of **1a**, **1b** (1.05 g of **1a**, 1.58 g of **1b**) were added. The solution was vigorously stirred. When **1a**, **1b** completely dissolved, 10 ml of triethylamine were added. The solution immediately turned red. After stirring for another 20 min, 20 ml of silica were added and the solvent was removed in vacuo. The residue was chromatographed at –30 °C on silica. With pentane/CH_2Cl_2 a yellow band was eluted. Removal of the solvent gave **2a**, **2b** as yellow crystalline solids.

2a: Yield 1.15 g (3.63 mmol, 91%). M.p. 116–117 °C. IR (hexane): ν(CO) 2055 m, 1979 m, 1939 vs, 1921 s; ν(CC) 1621 m; (THF): ν(CO) 2051 m, 1969 w, 1926 vs, 1917 sh; ν(CC) 1622 m. ^{1}H NMR (400 MHz): 2.88 (t, 2 H, $^3J_{HH}$ = 8.6, H4); 3.29 (s, 6 H, CH_3); 4.67 (t, 2 H, $^3J_{HH}$ = 8.7, H3); 7.95 (s, 1 H, H6). ^{13}C NMR (100 MHz): 26.2 (C4), 38.4 and 47.7 (br, CH_3), 78.2 (C3), 125.5 (C5), 162.2 (C6), 219.1 (*cis*-CO), 223.7 (*trans*-CO), 285.8 (C1). UV-VIS, λ_{max} (log ε):

396 (4.029) [DMF]; 433 (3.857) [hexane]; 408 (4.021) [CH_2Cl_2]. EI-MS (90 °C), *m/z* (%): 317 (14) [M^+], 289 (5), [$(M - CO)^+$], 261 (5) [$(M - 2\ CO)^+$], 233 (5) [$(M - 3\ CO)^+$], 205 (14) [$(M - 4\ CO)^+$], 177 (100) [$(M - 5\ CO)^+$], 149 (11) [$(M - 6\ CO)^+$], 121 (10) [$(C_4H_7CrN)^+$], 109 (8) [$(C_3H_7CrN)^+$], 80 (8) [$(Cr(CO)^+$], 52 (51) [Cr^+]. For $C_{12}H_{12}CrNO_6$ (317.2) calculated: 45.44% C, 3.50% H, 4.42% N; found: 45.27% C, 3.54% H, 4.39% N.

2b: Yield 1.65 g (3.67 mmol, 92%). M.p. 126–127 °C. IR (hexane): ν(CO) 2063 m, 1974 m, 1935 vs, 1918 s, 1899 sh; ν(CC) 1622 m; (THF): ν(CO) 2059 m, 1967 w, 1922 vs, 1915 sh, 1899 s; ν(CC) 1624 m. ^1H NMR (400 MHz): 2.91 (td, $^3J_{HH}$ = 8.8, 2 H, H4); 3.28 (s, 6 H, CH_3); 4.68 (t, $^3J_{HH}$ = 8.8, 2 H, H3); 7.95 (s, 1 H, H6). ^{13}C NMR (100 MHz): 25.7 (C4), 38.5 and 47.7 (br, CH_3), 78.6 (C3), 126.0 ($^2J_{WC}$ = 9.4, C5), 164.0 (C6), 199.3 ($^1J_{WC}$ = 126.6, *cis*-CO), 203.6 ($^1J_{WC}$ = 130.9, *trans*-CO), 265.2 ($^1J_{WC}$ = 93.1, C1). UV-VIS, λ_{max} (log ε): 392 (4.077), 354 (4.082) [DMF]; 421 (4.086) [hexane]; 400 (4.085) [CH_2C1_2]. EI-MS (120°C), *m/z* (%): 449 (42) [M^+], 421 (6) [$(M - CO)^+$], 393 (35) [$(M - 2\ CO)^+$], 391 (30) [$(M - CO - 2\ CH_3)^+$], 365 (91) [$(M - 3\ CO)^+$], 363 (100) [$(M - 2\ CO - 2\ CH_3)^+$], 337 (51) [$(M - 4\ CO)^+$), 335 (52) [$(M - 3\ CO - 2\ CH_3)^+$] 309 (38) [$(M - 5\ CO)^+$], 307 (51) [$(M - 4\ CO - 2\ CH_3)^+$], 281 (33) [$(M - 6\ CO)^+$], 279 (35) [$(M - 5\ CO - 2\ CH_3)^+$], 251 (23) [$(C_4H_7NW)^+$], 153 (21) [$(C_8H_{11}NO_2)^+$]. For $C_{12}H_{12}NO_6W$ (449.1) calculated: 32.10% C, 2.47% H, 3.12% N; found: 32.09% C, 2.50% H, 3.27% N.

Preparation of Complexes **3a**, **3b**, **4a**, **4b** and **5a**, **5b**

A Schlenk tube was charged with 4 mmol of **1a**, **1b** (1.05 g of **1a**, 1.58 g of **1b**) and the corresponding dimethylamino-substituted unsaturated aldehyde (3.8 mmol of 3-(dimethylamino)propenal, 3 mmol of 5-(dimethylamino)penta-2,4-dienal or 2.7 mmol of 7-(dimethylamino)hepta-2,4,6-trienal). Then, 10 ml of THF, 10 ml of NEt_3, and 2 ml of Me_3SiCl were added. The mixture was stirred at ambient temperature. The color of the solution changed from yellow to orange-red (**3a**, **3b**), dark violet (**4a**, **4b**) or dark blue (**5a**, **5b**). The progress of the reaction was checked by IR spectroscopy following the ν(CO) absorptions; it was complete after ca. 1 h (**3a**, **3b** and **4a**, **4b**) or 1 day (**5a**, **5b**). After addition of 20 ml of silica, the solvent was removed in vacuo. Chromatography over a 15-cm layer of silica at –30 °C with pentane/CH_2Cl_2, elution of the orange (**3a**, **3b**), dark violet (**4a**, **4b**) or dark blue band (**5a**, **5b**) and removal of the solvent gave crystals of **3a**, **3b** or **4a**, **4b**, or **5a**, **5b**. The yields given were relative to the starting dimethylamino-substituted unsaturated aldehydes which were used in insufficient amounts.

Pentacarbonyl{(*E*)-3-[(*E*)-3-(dimethylamino)prop-2-enylidene]-1-oxacyclopentan-2-ylidene}chromium (**3a**)
and
Pentacarbonyl{(*E*)-3-[(*E*)-3-(dimethylamino)prop-2-enylidene]-1-oxacyclopentan-2-ylidene}tungsten (**3b**)

3a: Yield 1.14 g (3.31 mmol, 87%). M.p. 174–175 °C (dec.). IR (hexane): ν(CO) 2053 m, 2048 sh, 1978 w, 1941 vs, 1931 s; ν(CC) 1620 w, 1587 m; (THF): ν(CO) 2048 m, 1968 w, 1925 vs, 1904 s; ν(CC) 1646 sh, 1625 m, 1571 m. ^1H NMR (400 MHz): 2.57 (td, 2 H, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 1.8, H4); 3.00 (br, 3 H, CH_3); 3.20 (br, 3 H, $N(CH_3)_2$); 4.72 (t, 2 H, $^3J_{HH}$ = 8.5, H3); 5.15 (t, 1 H, $^3J_{HH}$ = 12.2, H7); 7.15 (d, 1 H, $^3J_{HH}$ = 12.2, H8); 7.83 (dt, 1 H, $^3J_{HH}$ = 12.1, $^4J_{HH}$ = 1.8, H6). ^{13}C NMR (100 MHz): 26.1 (C4), (N-CH_3) not detected, 78.8 (C3), 98.9 (C7), 140.0 (C5), 155.0 and 156.3 (C6 and C8), 219.0 (*cis*-CO), 224.4 (*trans*-CO), 291.9 (C1).

UV-VIS, λ_{max} (log ε): 470 (4.621) [DMF]; 503 (4.217) [hexane]; 481 (4.477) [CH_2C1_2]. EI-MS (170 °C), *m/z* (%): 343 (6) [M^+], 315 (10) [$(M - CO)^+$], 287 (1) [$(M - 2\ CO)^+$], 259 (2) [$(M - 3\ CO)^+$], 231 (7) [$(M - 4\ CO)^+$], 203 (42) [$(M - 5\ CO)^+$], 95 (100) [$(C_6H_9N)^+$], 80 (20) [$(Cr(CO))^+$]. For $C_{14}H_{13}CrNO_6$ (343.3) calculated: 48.99% C, 3.82% H, 4.08% N; found: 49.25% C, 3.92% H, 4.31% N.

3b: Yield 1.51 g (3.18 mmol, 84%). M.p. 192 °C (dec.). IR (hexane): ν(CO) 2061 m, 2056 sh, 1973 w, 1936 vs, 1927 s; ν(CC) 1620 w, 1586 mw; (THF): ν(CO) 2057 m, 1965 w, 1921 vs, 1900 s; ν(CC) 1625 mw, 1570 m. ^1H NMR (400 MHz): 2.61 (td, 2 H, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 1.7, H4); 2.99 (br, 3 H, CH_3); 3.22 (br, 3 H, CH_3); 4.71 (t, 2 H, $^3J_{HH}$ = 8.6, H3); 5.18 (t, 1 H, $^3J_{HH}$ = 12.2, H7); 7.19 (d, 1 H, $^3J_{HH}$ = 12.1, H8); 7.82 (dt, 1 H, $^3J_{HH}$ = 12.3, $^4J_{HH}$ = 1.8, H6). ^{13}C NMR (100 MHz): 25.7 (C4), 37.6 and 45.6 (CH_3), 79.1 (C3), 99.29 (C7), 141.4 ($^2J_{WC}$ = 10.1, C5), 156.9 and 157.0 (C6 and C8), 199.2 ($^1J_{WC}$ = 126.8, *cis*-CO), 204.4 ($^1J_{WC}$ = 129.5, *trans*-CO), 269.0 ($^1J_{WC}$ = 92.6, C1). UV-VIS, λ_{max} (log ε): 470 (4.711) [DMF]; 492 (4.288) [hexane]; 476 (4.595) [CH_2C1_2]. EI-MS (180 °C), *m/z* (%): 475 (32.5) [M^+], 419 (17.9) [$(M - 2\ CO)^+$], 391 (23.5) [$(M - 3\ CO)^+$], 389 (28.5) [$(M - 2\ CO - 2\ CH_3)^+$], 363 (27.8) [$(M - 4\ CO)^+$], 361 (38.0) [$(M - 3\ CO - 2\ CH_3)^+$], 335 (91.4) [$(M - 5\ CO)^+$], 333 (100) [$(M - 4\ CO - 2\ CH_3)^+$] 305 (37.6) [$(M - 5\ CO - 2\ CH_3)^+$), 167 (30) [$(C_9H_{13}NO_2)^+$], 151 (26) [$(C_9H_{13}NO)^+$]. For $C_{14}H_{13}NO_6W$ (475.1) calculated: 35.39% C, 2.76% H, 2.95% N; found: 35.42% C, 2.78% H, 3.14% N.

Pentacarbonyl{(*E*)-3-[(*E*,*E*)-5-(dimethylamino)penta-2,4-dienylidene]-1-oxacyclopentan-2-ylidene}chromium (**4a**)
and
Pentacarbonyl{(*E*)-3-[(*E*,*E*)-5-(dimethylamino)penta-2,4-dienylidene]-1-oxacyclopentan-2-ylidene}tungsten (**4b**)

4a: Yield 0.81 g (2.19 mmol, 73%). M.p. 175–176 °C (dec.). IR (THF): ν(CO) 2049 m, 1970 w, 1928 vs, 1910 s; ν(CC) 1633 w, 1580 w, 1540 s. ^1H NMR (400 MHz): 2.64 (td, 2 H, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1.9, H4); 3.00 (s, 6 H, CH_3); 4.74 (t, 2 H, $^3J_{HH}$ = 8.4, H3); 5.38 (t, 1 H, $^3J_{HH}$ = 12.1, H9); 6.02 (t, 1 H, $^3J_{HH}$ = 12.2, 13.6, H7); 6.86 (d, 1 H, $^3J_{HH}$ = 12.4, H10); 7.05 (t, 1 H, $^3J_{HH}$ = 11.8, 13.6, H8); 7.77 (d, 1 H, $^3J_{HH}$ = 12.1, $^4J_{HH}$ = 2.0, H6). ^{13}C NMR (150 MHz): 25.9 (C4), (N-CH_3) not detected, 79.4 (C3), 100.8 (C9), 118.0 (C7), 142.8 (C5), 152.6 (C8), 152.63 (C10), 153.8 (C6), 218.7 (*cis*-CO), 224.7 (*trans*-CO), 297.6 (C1). UV-VIS, λ_{max} (log ε): 564 (4.927), 433 (4.225) [DMF]; 550 (4.386), 438 (4.589) [hexane]; 560 (4.726), 441 (4.483) [CH_2C1_2]. EI-MS (160 °C), *m/z* (%): 369 (19) [M^+], 341 (3) [$(M - CO)^+$], 313 (7) [$(M - 2\ CO)^+$], 285 (6) [$(M - 3\ CO)^+$], 258 (23) [$(M - 4\ CO)^+$], 229 (56) [$(M - 5\ CO)^+$], 186 (46) [$(C_9H_{10}CrO)^+$], 95 (66) [$(C_6H_9N)^+$]. For $C_{16}H_{15}CrNO_6$ (369.3) calculated: 52.04% C, 4.09% H, 3.79% N; found: 51.82% C, 3.88% H, 3.82% N.

4b: Yield 1.07 g (2.13 mmol, 71%). M.p. 174 °C (dec.). IR (THF): ν(CO) 2056 m, 1967 w, 1923 vs, 1905 sh; ν(CC) 1639 m, 1580 w, 1539 s. ^1H NMR (250 MHz): 2.68 (td, 2 H, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.9, H4); 3.01 (s, 6 H, CH_3); 4.72 (t, 2 H, $^3J_{HH}$ = 8.4, H3); 5.40 (t, 1 H, $^3J_{HH}$ = 12.1, H9); 6.02 (t, 1 H, $^3J_{HH}$ = 12.4, 13.4, H7); 6.86 (d, 1 H, $^3J_{HH}$ = 12.4, H10); 7.10 (t, 1 H, $^3J_{HH}$ = 12.0, 13.4, H8); 7.77 (dt, 1 H, $^3J_{HH}$ = 12.2, $^4J_{HH}$ = 1.9, H6). ^{13}C NMR (150 MHz): 25.5 (C4), (N-CH_3) not detected, 97.7 (C3), 101.1 (C9), 118.1 (C7), 144.5 (C5), 153.2 (C10), 153.4 (C8), 155.7 (C6), 198.9 ($^1J_{WC}$ = 126.9, *cis*-CO), 204.6 (*trans*-CO), 273.8 (C1). UV-VIS, λ_{max} (log ε): 564 (4.964), 411 (4.021) [DMF]; 541 (4.502), 430 (4.467) [hexane]; 563 (4.831), 427 (4.293) [CH_2C1_2]. EI-MS (190 °C), *m/z* (%): 501 (32) [M^+], 445 (18) [$(M - 2\ CO)^+$], 417 (10) [(M –

3 CO)$^+$], 389 (21) [(M – 4 CO)$^+$], 387 (20) [(M – 3 CO – 2 CH_3)$^+$], 361 (57) [(M – 5 CO)$^+$], 359 (68) [(M – 4 CO – 2 CH_3)$^+$], 331 (37) [(M – 5 CO – 2 CH_3)$^+$], 296 (52) [($W(CO)_4$)$^+$], 268 (100) [($W(CO)_3$)$^+$], 240 (43) [($W(CO)_2$)$^+$], 212 (53) [(W(CO))$^+$]. For $C_{16}H_{15}NO_6W$ (501.2) calculated: 38.35% C, 3.02% H, 2.79% N; found: 38.25% C, 3.05% H, 2.80% N.

Pentacarbonyl{(*E*)-3-[(*E*,*E*,*E*)-7-dimethylamino)hepta-2,4,6-trienylidene]-1-oxacyclopentan-2-ylidene}chromium (**5a**)
and
Pentacarbonyl{(*E*)-3-[(*E*,*E*,*E*)-7-dimethylamino)hepta-2,4,6-trienylidene]-1-oxacyclopentan-2-ylidene}tungsten (**5b**)

5a: Yield 0.29 g (0.73 mmol, 37%). M.p. 173 °C (dec.). IR (THF): ν(CO) 2049 m, 1973 vw, 1932 vs, 1914 sh; ν(CC) 1630 m, 1580 w, 1526 m. ^{1}H NMR (400 MHz): 2.68 (td, 2 H, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.8, H4); 2.93 (s, 6 H, $N(CH_3)_2$); 4.77 (t, 2 H, $^3J_{HH}$ = 8.2, H3); 5.23 (t, 1 H, $^3J_{HH}$ = 12.0, H11); 6.12 (t, 2 H, $^3J_{HH}$ = 12.9, H7 and H9); 6.65 (d, 1 H, $^3J_{HH}$ = 12.7, H12); 6.70 (dd, 1 H, $^3J_{HH}$ = 14.0, 11.5, H10); 7.02 (dd, 1 H, $^3J_{HH}$ = 13.8, 11.8, H8); 7.75 (dt, 1 H, $^3J_{HH}$ = 12.0, $^4J_{HH}$ = 1.9, H6). ^{13}C NMR (150 MHz): 25.7 (C4), 40.8 (br, $N(CH_3)_2$), 80.0 (C5), 100.1 (C11), 121.0 (C9), 122.3 (C7), 145.3 (C3), 149.8 (C12), 151.0 (C8), 151.9 (C6), 218.4 (*cis*-CO), 224.7 (*trans*-CO), 303.0 (C1). UV-VIS, λ_{max} (log ε): 664 (4.976), 487 (4.121), 396 (3.786) [DMF]; 577 (4.528), 491 (4.581), 376 (3.929) [hexane]. EI-MS (150 °C), *m/z* (%): 395 (70) [M$^+$], 339 (24) [(M – 2 CO)$^+$], 311 (16) [(M – 3 CO)$^+$], 283 (71) [(M – 4 CO)$^+$], 255 (90) [(M – 5 CO)$^+$], 229 (65) [(M – 5 CO – C_2H_2)$^+$], 136 (32) [($Cr(CO)_3$)$^+$], 135 (100) [($(CH)_7N(CH_3)_2$)$^+$], 109 (69) [($(CH)_5N(CH_3)_2$)$^+$], 108 (14) [($Cr(CO)_2$)$^+$], 95 (73) [(C_6H_9N)$^+$], 80.0 (34). For $C_{18}H_{17}CrNO_6$ (395.3) calculated: 54.69% C, 4.33% H, 3.54% N; found: 54.50% C,; 4.24 H, 3.34% N.

5b: Yield 0.34 g (0.64 mmol, 32%). M.p. 168 °C (dec.). IR (THF): ν(CO) 2057 m, 1969 w, 1926 vs, 1909 sh; ν(CC) 1629 w, 1558 w, 1521 s. ^{1}H NMR (400 MHz): 2.74 (td, 2 H, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.7, H4); 2.93 (s, 6 H, $N(CH_3)_2$); 4.75 (t, 2 H, $^3J_{HH}$ = 8.3, H3); 5.24 (t, 1 H, $^3J_{HH}$ = 12.0, H11); 6.10 (dd, 1 H, $^3J_{HH}$ = 13.0, H7); 6.11 (t, 1 H, $^3J_{HH}$ = 13.8, 11.8, H9); 6.69 (d, 1 H, $^3J_{HH}$ = 12.6, H12); 6.76 (dd, 1 H, $^3J_{HH}$ = 13.8, 11.6, H10); 7.07 (dd, 1 H, $^3J_{HH}$ = 13.6, 12.0, H8); 7.75 (d, 1 H, $^3J_{HH}$ = 12.2, $^4J_{HH}$ = 2.0, H6). ^{13}C NMR (150 MHz): 25.4 (C4), 40.9 (br, $N(CH_3)_2$), 80.4 (C5), 100.3 (C11), 121.1 (C9), 122.3 (C7), 146.9 (C10), 147.3 (C3), 150.3 (C12), 151.6 (C8), 153.9 (C6), 198.6 ($^1J_{WC}$ = 126.9, *cis*-CO), 204.6 ($^1J_{WC}$ = 127.1, *trans*-CO), 278.5 ($^1J_{WC}$ = 96.2, C1). UV-VIS, λ_{max} (log ε): 665 (5.013), 455 (3.868), 396 (3.860) [DMF]; 575 (4.477), 480 (4.307), 352 (3.809) [hexane]. EI-MS (180 °C), *m/z* (%): 527 (55.7) [M$^+$], 443 (36.3) [(M – 3 CO)$^+$], 415 (18) [(M – 4 CO)$^+$], 387 (86.3) [(M – 5 CO)$^+$], 385 (100) [(M – 4 CO – 2 CH_3)$^+$], 35933.0 (26.8) [(M – 6 CO)$^+$], 352 (59.6) [($W(CO)_6$)$^+$], 296 (49.5) [($W(CO)_4$)$^+$], 268 (64.0) [($W(CO)_3$)$^+$], 240 (46.9) [($W(CO)_2$)$^+$], 212 (49.1) [(W(CO))$^+$], 203 (29.8) [($C_{13}H_{17}NO$)$^+$]. For $C_{18}H_{17}NO_6W$ (527.2) calculated: 41.01% C, 3.25% H, 2.66% N; found: 40.73% C, 3.12% H, 2.55% N.

X-ray Structural Analysis of **1a**, **2a**, **3a**, **4a**, and **5a**

Single crystals suitable for X-ray structural analysis were obtained by slow diffusion of hexane into solutions of the complexes in CH_2Cl_2 at room temperature. The crystals of **5a** were orthorhombic, the crystals of all other complexes were monoclinic. The measurements were performed with a crystal mounted on a glass fiber in a Siemens P4 diffractometer (graphite monochromatizer, MoKα radiation, λ = 0.71073 Å) at 188(2) K. For data collection, the Wykoff technique was used. For complexes **2a** and **3a** a semiempirical absorption correction (ψ-scan with 12 reflections) was performed. The structures were solved by direct methods using the SHELX97 program package[30]. The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as 'riding model'. All other atoms were refined anisotropically.

CCDC 634306 (**1a**), 634307 (**2a**), 634308 (**3a**), 634309 (**4a**), and 634310 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

DFT Calculations

All DFT calculations of the chromium complexes **2b**, **3b**, **4b**, and **5b** were performed using JAGUAR[25] (version 5.5.016) running on Linux 2.4.20–28.7 smp on six Athlon MP 2400+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. Known X-ray structures were used as initial geometries for a geometry optimization using the LACVP* basis set (ECP basis set for Cr and W, N31G6* basis set for all other atoms) and the BP86 density functional. The structures were shown to be ground-state structures since no large imaginary frequencies were obtained after calculation of the second derivative. The breakdown of molecular orbital contributions were obtained using the AOMix[31] program package.

HRS Measurements of the First Hyperpolarizabilities of **2a**, **2b**–**5a**, **5b**

The measurements at a wavelength of 1500 nm were carried out as described in ref.[32]. Instead of the third harmonic (355 nm) generated by an Nd:YAG laser with a wavelength of 1064 nm, the optical parametric oscillator (OPO)[33] in use was pumped with the second harmonic (532 nm). The signal intensity at 824 nm and the fundamental at 532 nm were removed from the Idler using dichroic mirrors (HR 650–850 and HR 532), green light and a silicon filter (transparent >1000 nm). An additional Glan–Taylor polarizer ensured the vertical polarization of the beam in the measurement cell. Measurements were performed with 10^{-4}–10^{-6} M solutions. The validity of Beer law was confirmed by UV-VIS measurements of samples with corresponding concentrations. Disperse Red 1 (DR 1) was used as an external standard with a value of β_{1500}(DR 1) = 70×10^{-30} esu. This value was obtained by comparing the slopes of the reference in CH_2Cl_2 and $CHCl_3$ to obtain the ratio of β_{solute}[34]. Using the value $\beta(CHCl_3) = 80 \times 10^{-30}$ esu[35], the hyperpolarizability of DR 1 in CH_2Cl_2 is estimated to be 70×10^{-30} esu. The effect of the refractive indices of the solvents was corrected using the simple Lorentz local field[36].

REFERENCES

1. Selected recent reviews: a) Barluenga J., Fernández-Rodriguez M. A., Aguilar E.: *J. Organomet. Chem.* **2005**, *690*, 539; b) Dötz K. H. (Ed.): *Metal Carbenes in Organic Synthesis* in *Topics in Organometallic Chemistry*. Springer, Berlin 2004; c) Herndon J. W.: *Tetrahedron* **2000**, *56*, 1257; d) Dörwald F. Z.: *Metal Carbenes in Organic Synthesis*. Wiley-VCH, Weinheim 1999.
2. Selected recent reviews: a) Grubbs R. H.: *Angew. Chem.* **2006**, *118*, 3845; *Angew. Chem., Int. Ed.* **2006**, *45*, 3760; b) Schrock R. R.: *Angew. Chem.* **2006**, *118*, 3832; *Angew. Chem.,*

Int. Ed. **2006**, *45*, 3748; c) Fürstner A.: *Angew. Chem.* **2000**, *112*, 3140; *Angew. Chem., Int. Ed.* **2000**, *39*, 3012.

3. a) Kreiter C. G.: *Angew. Chem.* **1968**, *80*, 402; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390; b) Casey C. P., Anderson R. L.: *J. Am. Chem. Soc.* **1974**, *96*, 1230.
4. See, e.g.: a) Casey C. P., Brunsvold W. R., Scheck, D. M.: *Inorg. Chem.* **1977**, *16*, 3059, and references therein; b) Hegedus L. S.: *Transition Metals in the Synthesis od Complex Organic Molecules*. University Science Books, San Francisco 1994.
5. For some recent reviews, see: a) Whittall I. R., McDonagh A. M., Humphrey M. G., Samoc M.: *Adv. Organomet. Chem.* **1998**, *42*, 291; b) Whittall I. R., McDonagh A. M., Humphrey M. G., Samoc M.: *Adv. Organomet. Chem.* **1998**, *43*, 349; c) Cifuentes M. P., Humphrey M. G.: *J. Organomet. Chem.* **2004**, *689*, 3968.
6. Maiorana S., Papagni A., Licandro E., Hellier P., Persoons A., Clays K., Houbrechts S., Porzio W.: *Gazz. Chim. Ital.* **1995**, *125*, 377.
7. Licandro E., Maiorana S., Papagni A., Hellier P., Capella L., Persoons A., Houbrechts S.: *J. Organomet. Chem.* **1999**, *583*, 111.
8. a) Parlier A., Rudler H.: *J. Chem. Soc., Chem. Commun.* **1986**, 514; b) Dötz K. H., Sturm W., Alt H. G.: *Organometallics* **1987**, *6*, 1424.
9. a) Casey C. P., Anderson R. L.: *J. Organomet. Chem.* **1974**, *73*, C28; b) Lattuada L., Licandro E., Maiorana S., Molinari H., Papagni A.: *Organometallics* **1991**, *10*, 807.
10. Segundo A., Moretó J. M., Vinas J. M., Ricart S., Molins E.: *Organometallics* **1994**, *13*, 2467.
11. Licandro E., Maiorana S., Papagni A., Zanotti-Gerosa A.: *J. Chem. Soc., Chem. Commun.* **1992**, 1623.
12. For the first report on condensation of carbonyl compounds with alkylcarbene complexes in the presence of $POCl_3/NEt_3$ see: Aumann R., Heinen H.: *Chem. Ber.* **1990**, *123*, 611.
13. Baldoli C., Lattuada L., Licandro E., Maiorana S., Papagni A.: *Organometallics* **1993**, *12*, 2994.
14. For the condensation of reactive aldehydes with pentacarbonyl[ethoxy(methyl)carbene]-chromium in the presence of NEt_3/Me_3SiCl see: Aumann R., Heinen H.: *Chem. Ber.* **1987**, *120*, 537.
15. Maiorana S., Licandro E., Lattuada L., Papagni A., Villa A. C., Guastini C.: *J. Chem. Soc., Chem. Commun.* **1988**, 1092.
16. Fischer H., Podschadly O., Roth G., Herminghaus S., Klewitz S., Heck J., Houbrechts S., Meyer T.: *J. Organomet. Chem.* **1997**, *541*, 321.
17. a) Schmidt B., Kocienski P., Reid G.: *Tetrahedron* **1996**, *52*, 1617; b) Dötz K.-H., Haase W.-C., Klumpe M., Nieger M.: *Chem. Commun.* **1997**, 1217; c) Barluenga J., Aznar F., Barluenga S., Garcia-Granda S., Alvarez-Rua C.: *Synlett* **1997**, 1040; d) Weyershausen B., Nieger M., Dötz K.-H.: *Organometallics* **1998**, *17*, 1602; e) Weyershausen B., Nieger M., Dötz K.-H.: *J. Org. Chem.* **1999**, *64*, 4206; f) Dötz K.-H., Koch A. W., Weyershausen B., Hupfer H., Nieger M.: *Tetrahedron* **2000**, *56*, 4925.
18. Allen F. H., Kennard O., Watson D. G., Brammer L., Orpen A. G., Tayler R.: *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
19. Reichardt C.: *Solvents and Solvent Effects in Organic Chemistry*. Wiley-VCH, Weinheim 2003.
20. a) Clays K., Persoons A.: *Phys. Rev. Lett.* **1991**, *66*, 2980; b) Hendrickx E., Clays K., Persoons A., Dehu C., Brédas J. L.: *J. Am. Chem. Soc.* **1995**, *117*, 3547.

21. Farrel T., Manning A. R., Mitchell G., Heck J., Meyer-Friedrichsen T., Malessa M., Wittenburg C., Prosenc M. H., Cunningham D., McArdle P.: *Eur. J. Inorg. Chem.* **2002**, 1677.
22. a) Roth G., Fischer H., Meyer-Friedrichsen T., Heck J., Houbrechts S., Persoons A.: *Organometallics* **1998**, *17*, 1511; b) Szesni N., Drexler M., Maurer J., Winter R. F., de Montigny F., Lapinte C., Steffens S., Heck J., Weibert B., Fischer H.: *Organometallics* **2006**, *25*, 5774.
23. Jayaprakash K. N., Ray P. C., Matsuoka I., Bhadbhade M. M., Puranik V. G., Das P. K., Nishihara H., Sarkar A.: *Organometallics* **1999**, *18*, 3851.
24. See, e.g.: a) Marder S. R., Gordon C. B., Tiemann B. G., Cheng L.-T.: *J. Am. Chem. Soc.* **1993**, *115*, 3006; b) Marder S. R., Risser S. M., Beratan D. N.: *J. Am. Chem. Soc.* **1993**, *115*, 7719; c) Marder S. R., Bourhill G., Brédas J.-L., Cheng L.-T., Meyers F., Perry J. W., Tiemann B. G.: *J. Am. Chem. Soc.* **1994**, *116*, 2619; d) Marder S. R., Gorman C. B.: *Chem. Mater.* **1995**, *7*, 215.
25. *JAGUAR 5.5*. Schrödinger, LLC, Portland (OR) 2003.
26. a) Foley H. C., Strubinger L. M., Targos T. S., Geoffroy G. L. J.: *J. Am. Chem. Soc.* **1983**, *105*, 3064; b) Pourreau D. B., Geoffroy G. L.: *Adv. Organomet. Chem.* **1985**, *24*, 249.
27. Raap J., Nieuwenhuis S., Creemers A., Hexspoor S., Kragl U., Lugtenburg J.: *Eur. J. Org. Chem.* **1999**, 2609.
28. Friedli A. C., Yang E., Marder S. R.: *Tetrahedron* **1997**, *53*, 2717.
29. Makin S. M., Shavrygina O. A., Berezhnaya M. I., Kirillova G. V.: *Zh. Org. Khim.* **1971**, *8*, 674; *J. Gen. Chem. U.S.S.R.* **1971**, *8*, 682.
30. Sheldrick G. M.: *SHELX97, Program for Crystal Structure Analysis*. University of Göttingen, Göttingen 1997.
31. a) Gorelsky S. I.: *AOMix Program*, http://www.sg-chem.net/; b) Gorelsky S. I., Lever A. B. P.: *J. Organomet. Chem.* **2001**, *635*, 187.
32. Stadler S., Dietrich G., Bourhill G., Bräuchle C., Pawlik A., Grahn W.: *Chem. Phys. Lett.* **1995**, *247*, 271.
33. Paralite Optical Parametrical Oscillator, LAS GmbH.
34. Kodaira T., Watanabe A., Ito O., Matsuda M., Clays K., Persoons A.: *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3039.
35. Lambert C., Nöll G., Schmälzlin E., Meerholz K., Bräuchle C.: *Chem. Eur. J.* **1998**, *4*, 2129.
36. Lambert C., Gaschler W., Schmälzlin E., Meerholz K., Bräuchle C.: *J. Chem. Soc., Perkin Trans. 2* **1999**, 577.