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Synthesis and Nonlinear Optical Properties of New Heptapentaenylidene Complexes: Study on the Second Harmonic Generation Efficiencies of Amino-Substituted Group 6 Cumulenylidenes

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Reaction of the ynamine $MeC{\equiv}CNEt_2$ with the pentatetraenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ (M = Cr (**3a**), W (**3b**)) at room temperature affords the new heptapentaenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NEt_2)C(Me){=}C(NMe_2)_2]$ (M = Cr (**5a**), W (**5b**)) in good yield. The spectroscopic data and the X-ray structural analysis of **5a** indicate that these amino-substituted metallacumulenes are best described as hybrids of a cumulene and several strongly polarized alkynyl structures. For **5a** and the related metallacumulenes $[(CO)_5M{=}C{=}C{=}C(NMe_2)_2]$ (M = Cr (**1a**), W (**1b**)), $[(CO)_5Cr{=}C{=}C{=}C(NEt_2)C(H){=}C(NMe_2)_2]$ (**2a**), and **3a**,**b** the molecular first hyperpolarizability β was determined by hyper-Rayleigh scattering experiments. The insertion of a *cumulated* C_2 unit into a metallacumulene quadruples β, while the insertion of a *conjugated* C_2 unit results in only slight enhancement of the second harmonic generation response. Substitution of tungsten for chromium has only a minor effect on β. All observed β values are reasonably high compared with those of other organometallic compounds.

Introduction

Organometallic compounds containing a linear unsaturated carbon chain recently have attracted considerable interest due to their physical and chemical properties. Carbon-bridged bimetallic π-conjugated complexes of the type $[L_nMC_mM'L'_{n'}]$ have been proposed[1] as a new class of one-dimensional molecular wires.[2] Rigid-rod polymers such as $[ML_nC{\equiv}CXC{\equiv}C]_m$ (X = aryl) can exhibit both liquid crystalline[3] and nonlinear optical[4] properties similar to those of certain metal acetylides.[5] Terminal metallacumulenes of the type $[L_nM{=}(C{=})_mCR_2]$ are of similar chemical and physicochemical interest.[6] Vinylidene complexes ($m = 1$)[7] and allenylidene complexes ($m = 2$)[8] have been known for quite a long time. Until now, no example of a butatrienylidene complex ($m = 3$) has been isolated.[9] However, in 1994 Dixneuf et al. achieved the synthesis of the first stable pentatetraenylidene complex ($m = 4$).[10] Since then, in addition to our own reports on the isolation of some group 6 pentatetraenylidenes[11] only two more notes about compounds of this type have appeared.[12]

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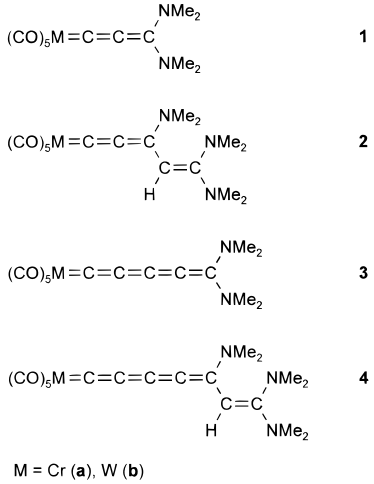


Figure 1. Known diamino- and amino–diaminoalkenyl-substituted group 6 metallacumulenes.

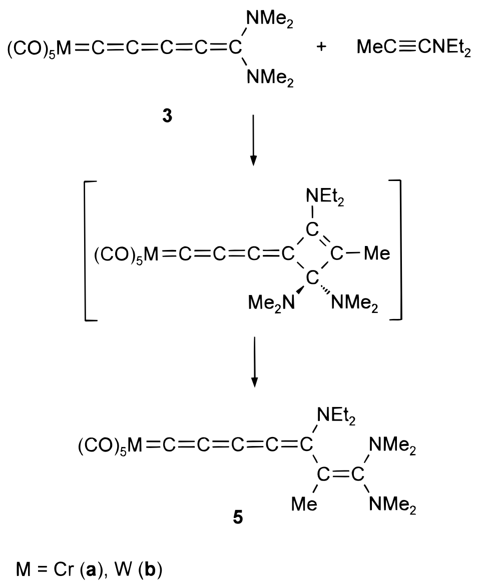
In view of their technological applications, materials displaying fast and intense nonlinear optical (NLO) responses are one important focus of interest.[13] Properly substituted metallacumulenes possess several promising intrinsic properties. Like other compounds with large second harmonic generation (SHG) efficiencies, metal cumulenylidenes are in a π-conjugated electron donor/acceptor arrangement. Dictated by structure, electronic interaction in these linear systems is obviously restricted to one dimension. Thus, strongly polarized amino-substituted cumulenylidene complexes such as compounds **1**–**4** (Figure 1) represent potential NLO materials. On the basis of results from organic NLO compounds[13,14] it is expected that the SHG efficiencies will depend on the length of the cumulenylidene ligand.

Results and Discussion

Synthesis and Structure of Triaminoheptapentaenylidene Complexes 5. Recently, we reported on the high-yield syntheses of the allenylidene complexes **1** and **2** and the pentatetraenylidene complexes **3** (Figure 1).[11a] Unfortunately, efforts to isolate the cumulogous heptahexaenylidene complex $[(CO)_5W{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ have failed to date.[11b] This strongly electrophilic compound was quenched in situ with $HNMe_2$ to give the alkenyl-substituted pentatetraenylidene complex **4b** (Figure 1) in low yield. In this paper we report on an efficient alternative synthesis of heptapentaenylidene complexes similar to **4b**.

The electron-rich alkyne 1-(diethylamino)-1-propyne is known to insert into the M=C bond of carbene complexes $[L_nM{=}C(R^1)R^2]$, affording the alkenylcarbene complexes $[L_nM{=}C(NEt_2)C(Me){=}C(R^1)R^2]$.[15] A similar CC-coupling reaction has been observed on treatment of the diarylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(C_6H_4R\text{-}p)_2]$ (M = Cr, W; R = H, Me, OMe, NMe_2) with highly nucleophilic ynamines. In addition to cycloaddition of $MeC{\equiv}CNEt_2$ to the $C_\alpha{=}C_\beta$ bond of the allenylidene complexes the insertion of the C≡C into the $C_\beta{=}C_\gamma$ bond to form the alkenylallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(NEt_2)C(Me){=}C(C_6H_4R\text{-}p)_2]$ has also been found.[16] Therefore, an analogous enlargement of the π-system of the pentatetraenylidene complexes **3** via insertion of an alkyne C_2 unit seemed feasible.

Scheme 1



The reaction of the diamino-substituted pentatetraenylidene complexes **3a**,**b** with a small excess of the ynamine $MeC{\equiv}CNEt_2$ resulted in the formation of a single product in each case (Scheme 1). After the mixture was stirred for 2 days at room temperature, the chromatographic workup afforded orange **5a** and yellow **5b** in 65% and 61% yield, respectively. Both compounds are stable in air at room temperature.

The IR spectra of **5a**,**b** are similar to that of complex **4b**. For all of these compounds the E and A_1(trans) ν(CO) absorptions are at very low energy in comparison to nonheteroatom-substituted pentacarbonyl metallacumulenes,[17] indicating a considerable transfer of electron density from the cumulenylidene ligand to the metal center. Analogously to the pentatetraenylidene complexes **3a**,**b**,[11a] the new compounds **5a**,**b** show two IR absorptions for the cumulene system (ν(CCCCC) = 2000 w and 2149 w br cm^{-1} (**5a**), 2001 w and 2148 w br cm^{-1} (**5b**)). However, a splitting of the high-energy band as in the only other known heptapentaenylidene complex **4b** is not observed.[11b]

At 293 K the ^1H NMR spectra of **5a**,**b** show one set of broad signals for the NEt_2 substituent, one broad singlet for the two terminal NMe_2 groups, and one broad singlet

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for the alkenyl methyl protons. These observations indicate fast rotation around both the alkenyl C═C bond *and* the C−N bonds of **5**. When a CD_2Cl_2 solution of **5b** is cooled, the ═CMe and NEt_2 signals get sharper while the signal of the four NMe groups splits into two distinct singlets. On the basis of the rather small difference in chemical shifts of the new singlets (δ(233 K) 3.03 and 3.06) a hindered rotation around the alkenyl C═C bond seems more likely than a hindered rotation around the C(alkenyl)−N bonds at this temperature (for comparison: δ(NMe) 3.33 and 3.75 in $(CO)_5W{=}C{=}C{=}C(NMe_2)Ph$).[8a] Thus, from the coalescence of the two singlets at 291 K the free energy of activation to rotation around the alkenyl C═C bond of **5b** is calculated to be $\Delta G^{\ddagger} = 64 \pm 1$ kJ/mol. Further lowering of the temperature down to 183 K does not result in any additional coalescence phenomena. Nevertheless, near 280 K a second set of signals for **5b** emerges, indicating the existence of a minor conformational isomer at low temperature. The ratio of the second isomer increases with decreasing temperature, resulting in a 1:3 mixture at 233 K and below. On the basis of the nearly identical resonance patterns of the two isomers and the only slight differences of chemical shifts we tentatively assign an *s-cis* geometry for the heptapentaenylidene ligand of the minor isomer of **5b** and the thermodynamically more stable *s-trans* conformation for the major isomer.

The ^{13}C NMR resonances of the cumulene carbon atoms of **5a**,**b** are at rather high field. Shifts in the range of δ 55−102 reflect a strong mesomeric interaction of the amino substituents and the metal center, emphasizing the importance of alkynyl type resonance structures for **5a**,**b** (for comparison: δ(C(sp)) 103−166 in $Me_2C{=}C{=}C{=}C{=}C{=}C(H)SiEt_3$).[18] Surprisingly, the signal of the metal-bound C_α atom of complexes **5** (δ 175.3 (**5a**), 175.2 (**5b**)) is not influenced by the metal. The same observation has already been made for the alkenyl-substituted allenylidene complexes **2**.[11a] Usually, pentacarbonylmetal carbene[19] and allenylidene[17d,20] complexes show a significant high-field shift of the metal-bound carbons when tungsten is substituted for chromium. Consistent with the ^1H NMR data, two ^{13}C NMR singlets for the terminal NMe_2 groups are found for **5a**,**b**.

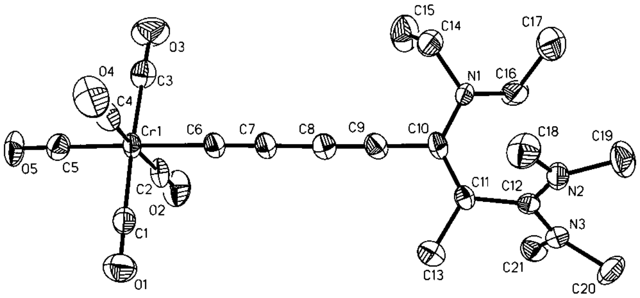

Figure 2. ORTEP drawing of complex **5a** (only one independent molecule shown, ellipsoids drawn at 50% level, hydrogens omitted).

Table 1. Selected Bond Lengths and Bond Angles for 5a (Two Independent Molecules)

	molecule 1	molecule 2		molecule 1	molecule 2
		Bond Lengths (Å)			
Cr1−C6	2.041(6)	2.043(6)	C6−C7	1.219(8)	1.220(9)
C7−C8	1.379(8)	1.389(9)	C8−C9	1.209(9)	1.179(9)
C9−C10	1.433(8)	1.449(9)	C10−C11	1.380(9)	1.377(9)
C11−C12	1.478(8)	1.458(8)	C10−N1	1.379(8)	1.381(8)
C12−N2	1.333(9)	1.339(9)	C12−N3	1.329(9)	1.328(8)
		Bond Angles (deg)			
Cr1−C6−C7	175.4(6)	177.0(6)	C6−C7−C8	177.1(7)	176.0(7)
C7−C8−C9	178.8(7)	177.2(7)	C8−C9−C10	180.0(10)	174.0(7)
C9−C10−C11	116.5(5)	117.4(6)	C10−C11−C12	123.2(5)	122.5(6)
C9−C10−N1	117.4(5)	116.2(5)	N1−C10−C11	126.1(5)	126.4(5)
C11−C12−N2	120.5(6)	118.5(6)	C11−C12−N3	118.0(6)	121.9(6)
N2−C12−N3	121.4(5)	119.6(5)			

The structure of the new complexes **5** was additionally established by an X-ray structural analysis of **5a** (Figure 2, Table 1). **5a** crystallizes with two independent molecules in the unit cell. In the solid state **5a** reveals an *s-trans* conformation. The CrC_5 chain is almost linear. Within error limits the strongly alternating CC distances of the CrC_5 unit of **5a** are identical with those found for **3b**.[11a] Thus, the cumulenylidene bond lengths differ significantly from the rather balanced values observed for diaryl-substituted pentatetraenylidene complexes.[12] The nitrogen atoms of the ${=}C(NMe_2)_2$ moiety of **5a** are nearly trigonal planar coordinated (sum of angles: 359.5 and 359.8° for N(2), 359.7 and 359.6° for N(3)). The short C(ethenyl)−N distances indicate a strong double-bond character of these bonds due to π-interaction of the lone pair at nitrogen with the cumulene system. As a result, the ethenyl C═C bond is longer and the C_ϵ−C(ethenyl) bond is shorter than expected for $C(sp^2)-C(sp^2)$ double and single bonds in systems with negligible mesomeric effects, respectively (for comparison: C═C = 1.334(2) Å and C(H)−C(H) = 1.450(2) Å in $MeO_2CC(H){=}C(H)C(H){=}C(H)CO_2Me$].[21] However, these CC as well as the CN bonds of **5a** compare well with those found for organic push−pull systems such as $(NC)_2C{=}C(H)C(H){=}C(NMe_2)_2$ (C(H)═C(NMe$_2$)$_2$ = 1.416(2) Å, C(H)−C(H) = 1.366(2) Å).[22] The marked single-bond character of the ethenyl CC bond explains the deviation of the ethenyl N−C(ethenyl)−N plane from the pentatetraenylidene N−C_ϵ−C(ethenyl) plane of 63.1 and 56.6°, respectively. In contrast to the $={}C(NMe_2)_2$ moiety of **5a** the conformation of the NEt_2 nitrogen atom deviates slightly from planarity (sum of angles: 353.6 and 356.5° for N(1)), and the longer C_ϵ−N distance suggests less double-bond character. In summary, all structural data indicate a strong π-interaction in **5a** of the terminal NMe_2 substituents with the metal center. Therefore, complexes **5** are described best as hybrids of the cumulene form **A** and dipolar alkynyl forms such as **B**−**D** (Figure 3) with the ground state dominated by the mesomeric dipolar form.

As expected from the polar resonance structures **B**−**D** (Figure 3), the compounds **5** exhibit a strong negative solvatochromic effect. The UV/vis absorption at lowest energy shifts toward shorter wavelength when nonpolar or weakly polar solvents are replaced by more polar ones (Table 2). Usually, insertion of a C_2 unit into an MC_n chain (e.g., $MC_3 \rightarrow MC_5$) lowers the energy of the LUMO and increases the distance between the centers of

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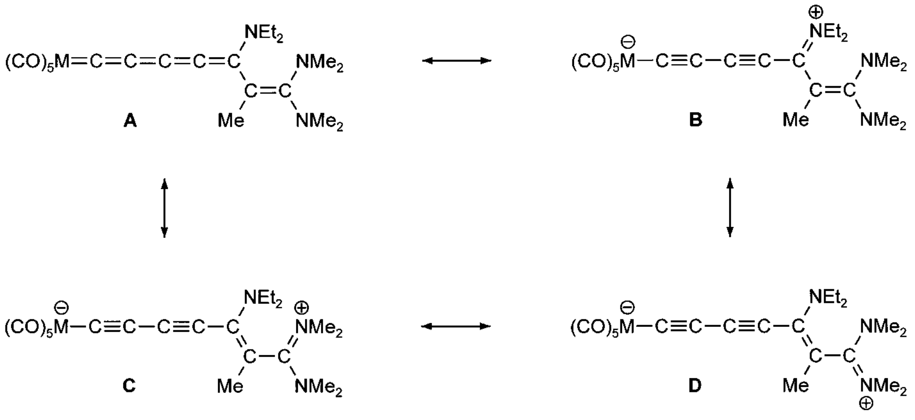

Figure 3. Canonical presentations for heptapentaenylidene complexes **5**.

Table 2. UV/Vis Data for Complexes 1−3[11a] **and 5 and Quadratic Hyperpolarizabilities for Complexes 1a,b, 2a, 3a,b, and 5a**

compd	λ_{max} (nm) DMF	toluene	$\Delta\tilde{\nu}$ (cm^{-1})	β (10^{-30} esu),[a] DMF	β_0 (10^{-30} esu),[b] DMF
1a	372	408	2372	21	9.5
1b	368	406	2543	25	11
2a	388	426	2299	22	9
2b	374	420	2928		
3a	424	510	3977	100	31
3b	424	500	3585	102	31
5a	418	496	3762	125	40
5b	414	486	3578		

[a] All values ±10%. [b] HRS experimental data corrected for resonance enhancement using the two-level model with $\beta_0 = \beta[1 - (\lambda_{max}/1064)^2][1 - (2\lambda_{max}/1064)^2]$.[25b]

positive and negative charge of the dipole. This is confirmed by the complexes **5**. A bathochromic shift of the MLCT absorption and an increase in the solvatochromic response are observed in comparison to the pentatrienylidene complexes **2** (Table 2). However, with respect to the pentatetraenylidene complexes **3**, instead of bathochromic a slight hypsochromic shift and almost no change in the solvatochromic response is found (Table 2). Obviously, the chain length *and* the conformational features influence the shift of λ_{max} in the metallacumulenes **1**−**5**.

All spectroscopic and analytical data of **5a**,**b** confirm the structure as heptapentaenylidene complexes. On the synthesis of complexes **5**, intermediates were not detectable. However, the formation of these compounds can be rationalized by a two-step mechanism. Very likely, the first step involves the formal cycloaddition of $MeC{\equiv}CNEt_2$ to the $C_\delta{=}C_\epsilon$ bond of **3a**,**b** via a nucleophilic attack of the ynamine C_β carbon atom at the electrophilic pentatetraenylidene C_ϵ atom (Scheme 1). In the succeeding step a cycloreversion of the unobserved intermediate affords the isolated complexes **5**. Obviously, no irreversible interaction of the nucleophile with the two other electrophilic pentatetraenylidene carbon atoms (C_α and C_γ) takes place.

Second Harmonic Generation Efficiencies of 1a,b, 2a, 3a,b, and 5a. It has been discussed earlier that a strong solvatochromic effect may be accompanied by a significant NLO response.[23] Therefore, we determined the first molecular hyperpolarizabilities β of the metallacumulenes **1a**,**b**, **2a**, **3a**,**b**, and **5a** by the hyper-Rayleigh scattering (HRS) method with a Nd:YAG laser (λ = 1064 nm). The intensity of the scattered energy doubled light (λ = 532 nm) was measured as a function of the metallacumulene concentration in DMF. As a reference *p*-nitroaniline [β(DMF) = 30 × 10^{-30} esu] was used.[24] The obtained β values for **1a**,**b**, **2a**, **3a**,**b**, and **5a** are summarized in Table 2. To eliminate fluorescence contributions to the observed SHG signal at λ = 532 nm, additional intensity measurements were performed at λ = 650, 600, 560, and 500 nm. For **3a**,**b** and **5a** an additional broad signal with a maximum around λ = 600 nm could be recorded, the intensity of which is less than one-third of the intensity of the SHG signal at λ = 532 nm and drops distinctly on going to smaller wavelengths. Therefore, this signal intensity was neglected for the calculation of the first hyperpolarizability β of **3a**,**b** and **5a**. Using the two-level model from β, the frequency of the absorption at lowest energy, and the frequency of the incident laser beam the static hyperpolarizability β_0 was calculated (Table 2).[25]

From the results of the HRS experiments with **1a**,**b**, **2a**, **3a**,**b**, and **5a** it follows that also for metallacumulenes β strongly depends on the chain length of the chromophore, i.e., the cumulenylidene ligand. The insertion of a C_2 unit into the cumulenylidene ligand (i.e., **1a** → **3a**, **2a** → **5a**, and **1b** → **3b**) approximately quadruples the β and β_0 values. In contrast, the insertion of a conjugated C_2 unit into a terminal C−N bond (i.e., **1a** → **2a** and **3a** → **5a**) enhances the SHG efficiency only slightly. Consequently, pentatetraenylidene complexes show a quadrupled SHG response relative to alkenyl-substituted allenylidene complexes (cf. **2a** → **3a**). From these observations it can be deduced that the SHG potential of a cumulated C_n bridge obviously surpasses by far that of a conjugated cumulenic C_n chain. In contrast to the results of others,[26] the substitution of tungsten for chromium (i.e., **1a** → **1b** and **3a** → **3b**) only leads to a very slight enhancement of the β value, although the $(CO)_5W$

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moiety was expected to be a considerably stronger Lewis acid than the $(CO)_5Cr$ unit, as deduced from the relative M−CO bond strengths (108 kJ/mol for M = Cr, 178 kJ/mol for M = W).[27]

The β and β_0 values of **1a**,**b**, **2a**, **3a**,**b**, and **5a** are reasonably high compared to those of the reference system *p*-nitroaniline[24] or of other organic and organometallic compounds with a comparable length of the chromophore.[13,14] To our knowledge, the molecular SHG properties of only one other terminal metallacumulene has been examined so far.[28] For the cationic allenylidene complex $[Cp(PPh_3)_2Ru{=}C{=}C{=}CR_2]^+$ (CR_2 = 2,7-dimethyl-4,5-benzocycloheptatrienylidene) a β_0 value of 19×10^{-30} esu has been reported.[29] However, since this compound shows a significant absorption at the frequency of the HRS light (λ = 532 nm), the two-level model does not hold and the β_0 value has to be regarded as rather unreliable.[29] In addition, it has to be noted that for several related alkenyl-substituted Fischer carbene complexes β_0 values between 5×10^{-30} and 12×10^{-30} esu have been found.[26a,30] All of these values are in good agreement with our results (Table 2). The most relevant comparison with metal acetylide complexes on optical transparency grounds is to a series of gold(I)[31] and nickel(II)[32] acetylides, which have a λ_{max} value similar to that of the cumulenylidene complexes discussed here. The highest observed β values of the nickel complexes[32] are indeed larger than those reported here. However, the dipole length (distance between the metal center and the terminal group of the carbon bridge) is by far longer in the nickel complexes than in the cumulenylidene complexes **3a** and **3b**. This indicates that the cumulenylidene species are very effective NLO chromophores, which induces us to investigate the synthesis and NLO properties of even more extended cumulenylidene systems.

Concluding Remarks

The heptapentaenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NEt_2)C(Me){=}C(NMe_2)_2]$ are accessible in high yield by formal insertion of the electron-rich alkyne $MeC{\equiv}CNEt_2$ into the terminal C=C bond of the pentatetraenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ (M = Cr, W). In contrast to diarylallenylidene complexes, in the first reaction step a site-specific attack of the nucleophilic C_β carbon atom of the ynamine at the terminal pentatetraenylidene C_ϵ atom is observed. As discussed for allenylidene complexes,[33] the reactions of metal pentatetraenylidenes with nucleophiles can be assumed to be orbital-controlled. While the soft nucleophile $MeC{\equiv}CNEt_2$ only attacks the pentatetraenylidene C_ϵ carbon atom, hard nucleophiles such as amines or alcohols predominantly add to the central pentatetraenylidene carbon C_γ.[10,11a,12a,34,35] Only in one case has an additional attack of MeOH at the metal-bound carbon C_α of an in situ generated cationic ruthenium pentatetraenylidene complex been observed.[35]

The heptapentaenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NEt_2)C(Me){=}C(NMe_2)_2]$ (M = Cr, W) as well as other amino-substituted metallacumulenes of the types $[(CO)_5M{=}(C{=}C{=})_nC(NMe_2)_2]$ and $[(CO)_5M{=}C{=}C{=}C(NMe_2)C(H){=}C(NMe_2)_2]$ (M = Cr, W; n = 1, 2) show significant second-order NLO properties. The SHG efficiencies clearly depend on the chain length of the cumulenylidene ligand. Probably due to the conformational flexibility, the insertion of a *conjugated* C_2 unit only slightly enhances the SHG response, while the insertion of a *cumulated* C_2 unit into the strictly linear chromophore quadruples the molecular first hyperpolarizability β. All β values reported in this paper are reasonably high in comparison to those of other organometallic systems. Nevertheless, we were not able to achieve the results obtained by others with nickel(II)[32] or ruthenium(II)[36] acetylide complexes (e.g., β(THF) = 468×10^{-30} esu for $[Cp(PPh_3)_2RuC{\equiv}CC_6H_4NO_2\text{-}p]$). However, neutral metallacumulenes of the type $[(CO)_5M{=}(C{=}C{=})_nC(NMe_2)R]$ (M = Cr, W; R = NMe_2, $C(H){=}C(NMe_2)_2$, $C(Me){=}C(NMe_2)_2$; n = 1, 2) offer interesting advantages. First, the complexes are transparent at the frequency of the scattered SHG light. Thus, problems with resonance effects by absorption are unlikely. Second, these metallacumulenes are soluble in most organic solvents. Apparently, for all of these complexes the dipolar mesomeric form is favored in highly polar solvents, as demonstrated by the observed negative solvatochromism.[11] This leads to a certain bond length alternation (BLA). However, nonpolar solvents may promote the cumulenic mesomeric form, which can call forth another BLA. This will give us the opportunity to determine β values as a function of the solvent polarity over a wide range. Future examinations will focus on both the synthesis of complexes with longer cumulated ligands and the determination of the NLO responses of the SHG-active compounds discussed here in solvents of different polarity.

Experimental Section

All operations were performed under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) and sodium/benzophenone (pentane, THF). The reported yields refer to analytically pure substances. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC 250, JEOL JNX400, and Bruker DRX 600 spectrometers.

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Chemical shifts are relative to TMS. Other analyses: IR Biorad FTS 60; MS Finnigan MAT 312; elemental analysis Heraeus CHN-O-RAPID. Silica used for column chromatography (silica for flash chromatography, J. T. Baker) was dried in vacuo for 8 h before use.

Preparation of the Complexes 5. At room temperature 3.50 mmol (0.39 g) of 1-(diethylamino)-1-propyne[37] was added to a solution of 2.00 mmol (0.68 g (**3a**), 0.94 g (**3b**)) of the pentatetraenylidene complex **3**[11a] in 50 mL of CH_2Cl_2. After the mixture was stirred for 2 days, the solvent of the yellow-orange reaction mixture was evaporated in vacuo and the residue chromatographed at room temperature on silica. First, with THF/CH_2Cl_2 (9:1) a short brown-yellow band ($[M(CO)_6]$, M = Cr, W) was eluted. Then, with THF/CH_2Cl_2 (increasing polarity from 9:1 to 1:1) a long orange band containing **5a** or **5b** was eluted.

[5-(Diethylamino)-7,7-bis(dimethylamino)-6-methyl-1,2,3,4,6-heptapentaenylidene]pentacarbonylchromium (5a): 0.59 g (65% based on **3a**) of orange crystals from pentane/CH_2Cl_2 (4:5), mp 135 °C dec. IR (CH_2Cl_2): ν(CO) 2053 w, 1968 vw, 1922 vs, 1887 m; ν(CCCCC) 2149 w br, 2000 w cm^{-1}. ^1H NMR (CD_2Cl_2, 293 K): δ 1.10 (t, $^3J_{H,H}$ = 7 Hz, 6 H, $N(CH_2C\mathit{H}_3)_2$); 1.75 (s br, 3 H, $=CCH_3$); 3.02 (s br, 12 H, $N(CH_3)_2$); 3.28 (q, $^3J_{H,H}$ = 7 Hz, 4 H, $N(C\mathit{H}_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 14.7 ($N(CH_2\mathit{C}H_3)_2$); 17.3 ($=C\mathit{C}H_3$); 42.1, 43.1 ($N(CH_3)_2$); 46.9 ($N(\mathit{C}H_2CH_3)_2$); 55.8, 87.3, 94.7, 102.2, (C_β, C_γ, C_δ, $=\mathit{C}CH_3$); 147.0, 154.0 (C_ϵ, $=\mathit{C}[N(CH_3)_2]_2$); 175.3 (C_α); 219.3 (*cis*-CO); 222.1 (*trans*-CO). UV/vis: λ_{max} (log ϵ) 496 (3.786) [toluene]; 474 (4.035) [$CHCl_3$]; 452 (4.111) [CH_2Cl_2]; 438 (3.848) [EtOH]; 418 (4.181) [DMF]. Anal. Calcd for $C_{21}H_{25}CrN_3O_5$ (451.4): C, 55.87; H, 5.58; N, 9.31. Found: C, 55.66; H, 5.62; N, 9.17.

[5-(Diethylamino)-7,7-bis(dimethylamino)-6-methyl-1,2,3,4,6-heptapentaenylidene]pentacarbonyltungsten (5b): 0.71 g (61% based on **3b**) of a yellow powder from pentane/CH_2Cl_2 (5:3), mp 135 °C dec. IR (CH_2Cl_2): ν(CO) 2059 w, 1964 vw, 1917 vs, 1882 m; ν(CCCCC) 2148 w br, 2001 w cm^{-1}. ^1H NMR (CD_2Cl_2, 293 K): δ 1.18 (t, $^3J_{H,H}$ = 7 Hz, 6 H, $N(CH_2C\mathit{H}_3)_2$); 1.82 (s br, 3 H, $=CCH_3$); 3.09 (s br, 12 H, $N(CH_3)_2$); 3.35 (q, $^3J_{H,H}$ = 7 Hz, 4 H, $N(C\mathit{H}_2CH_3)_2$). ^1H NMR (CD_2Cl_2, 233 K, major/minor isomer): δ 1.13/1.15 (t, $^3J_{H,H}$ = 7.0/7.1 Hz, $N(CH_2C\mathit{H}_3)_2$); 1.75/1.90 (s, $=CCH_3$); 3.03 and 3.06/2.90 and 3.00 (2 s, $N(CH_3)_2$); 3.33/3.21 (q, $^3J_{H,H}$ = 7.0/7.1 Hz, 4 H, $N(C\mathit{H}_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 14.8 ($N(CH_2\mathit{C}H_3)_2$); 17.4 ($=C\mathit{C}H_3$); 42.2, 43.2 ($N(CH_3)_2$); 47.0 ($N(\mathit{C}H_2CH_3)_2$); 58.3, 87.4, 93.9, 102.5 (C_β, C_γ, C_δ, $=\mathit{C}CH_3$); 136.4, 146.7 (C_ϵ, $=\mathit{C}[N(CH_3)_2]_2$); 175.2 (C_α); 198.5 (*cis*-CO, $^1J_{WC}$ = 124.5 Hz); 201.1 (*trans*-CO, $^1J_{WC}$ = 131.8 Hz). UV/vis: λ_{max} (log ϵ) 486 (3.824) [toluene]; 464 (4.072) [$CHCl_3$]; 446 (4.117) [CH_2Cl_2]; 432 (3.936) [EtOH]; 414 (4.191) [DMF]. Anal. Calcd for $C_{21}H_{25}N_3O_5W$ (583.3): C, 43.24; H, 4.32; N, 7.05. Found: C, 43.19; H, 4.24; N, 7.20.

X-ray Structural Analysis of 5a. $C_{21}H_{25}CrN_3O_5$, M_r = 451.4, monoclinic, space group $P2_1/c$, a = 15.940(2) Å, b = 9.432(1) Å, c = 30.905(3) Å, β = 90.13(1)°, V = 4645(1) Å^3, Z = 8, d_c = 1.291 g cm^{-3}, $F(000)$ = 1888, μ = 0.512 mm^{-1}, R (R_w) = 0.070 (0.063) for 4325 observed reflections ($F > 4.0\sigma(F)$), largest difference peak/hole +0.52/−0.43 e Å^{-3}. A single crystal was grown by diffusion of pentane into a pentane/CH_2Cl_2 (4:5) solution and mounted in a glass capillary. All crystal data were collected on a Siemens P4 diffractometer at −29 °C (Wyckoff scan, $4° < 2\theta < 54°$) with a graphite monochromator (Mo Kα, λ = 0.710 73 Å). The structure was solved with Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS). The positions of the hydrogen atoms were calculated in ideal geometry (d_{CH} = 0.960 Å) and refined in the "riding model". All other atoms were refined anisotropically. **5a** crystallizes with two independent molecules in the unit cell. Figure 2 shows molecule 1.

Hyper-Rayleigh Scattering Experiments with 1a,b, 2a, 3a,b, and 5a. The incident beam generated by a Nd:YAG laser (Q-switched Coherent Infinity 40-100, 1064 nm, 3.5 ns, 20 Hz) was focused into a cylindrical cell (7 mL) containing the sample. All measurements were performed in DMF using *p*-nitroaniline (β(DMF) = 30 × 10^{-30} esu) as a reference. Sample concentrations were varied in the range of 0.1−6.3 mM. Further details of the experimental setup and procedure can be found elsewhere.[38]

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Supporting Information Available: Figures giving additional views and tables of crystal data and refinement details, positional and thermal parameters, and bond distances and angles for compound **5a** (16 pages). Ordering information is given on any current masthead page. enylidenes show significant second harmonic generation efficiencies. The quadratic hyperpolarizabilities are approximately quadrupled by insertion of a cumulated C_2 unit into the cumulenylidene ligand, while insertion of a conjugated C_2 unit only slightly enhances the β values.

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