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Heptahexaenylidene Complexes: Synthesis and Characterization of the First Complexes with an $M{=}C{=}C{=}C{=}C{=}C{=}C{=}CR_2$ Moiety ($M = Cr, W$)

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Silica-induced elimination of dimethylamide from $[(CO)_5M(C{\equiv}C)_3C(NMe_2)_3]^-$ [M = Cr (**4a**), W (**4b**)] affords the first isolated and characterized heptahexaenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ (**5a,b**). Complexes **4a,b** were generated by sequential reaction of $Me_3Si(C{\equiv}C)_3SiMe_3$ with LiMe·LiBr, $[(Me_2N)_3C]^+Cl^-$, LiBu, and $[(CO)_5M(thf)]$. Complex **5b** is inert in methanol, but adds dimethylamine across the C5=C6 bond to give $[(CO)_5W{=}C{=}C{=}C{=}C{=}C\{CH{=}C(NMe_2)_2\}NMe_2]$. The reaction of **5a,b** with LiMe·LiBr and SiO_2 generates the heptahexaenylidene complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C{=}C{=}C(Me)NMe_2]$ (**8a,b**). Trapping of **8b** with $HNMe_2$ yields pentatetraenylidene complex $[(CO)_5W{=}C{=}C{=}C{=}C{=}C\{CH{=}C(Me)NMe_2\}NMe_2]$.

Introduction

Organometallic compounds containing a linear unsaturated carbon chain are of considerable interest due to their unusual physical and chemical properties. Carbon-bridged bimetallic π-conjugated complexes of the type $[L_nMC_mM'L'_{n'}]$ have been proposed as a new class of one-dimensional molecular wires.[1] Rigid-rod polymers such as $[ML_nC{\equiv}CXC{\equiv}C]_m$ (X being an aromatic group) can exhibit both liquid crystalline[2] and nonlinear optical[3] properties similar to those of certain metal acetylides.[1,4]

Mononuclear metallacumulenes of the type $[L_nM{=}(C)_m{=}CR_2]$ are of similar chemical and physicochemical interest.[5] π-Conjugated $(C)_m$ moieties allow strong electronic communication between the metal−ligand fragment and terminal functional groups that can lead to fast and intense nonlinear optical (NLO) responses. Properly substituted metallacumulenes should possess several promising intrinsic properties since interaction in these linear systems is obviously restricted to one dimension. In recent years some vinylidene complexes ($m = 1$) and allenylidene complexes ($m = 2$) have also evolved into powerful catalysts.[6]

Mononuclear vinylidene complexes have been known since 1972,[7] allenylidene complexes since 1976.[8] The first examples of cationic bimetallic butatrienylidene complexes ($m = 3$), $[Cp^*(P{-}P)Fe{=}C{=}C{=}C{=}C(E)Fe(CO)_2Cp^*]^+X^-$ (P−P = dppe, dippe; E = H, Me; X = BF_4, CF_3SO_3) were isolated only in 1999.[9] The synthesis of the first neutral butatrienylidene complex, *trans*-$[Cl\{P(i\text{-}Pr)_3\}_2Ir{=}C{=}C{=}C{=}CPh_2]$, including its solid-state structure was reported in 2000.[10] Since then, a few other butatrienylidene complexes of iridium[11] and manganese[12] have been isolated or at least spectroscopically characterized in solution. Several cationic butatrienylidene complexes of ruthenium and iron were generated in solution by the groups of Selegue,[13] Bruce,[14] Winter,[15] Dixneuf,[16] and Lapinte.[17] Due to

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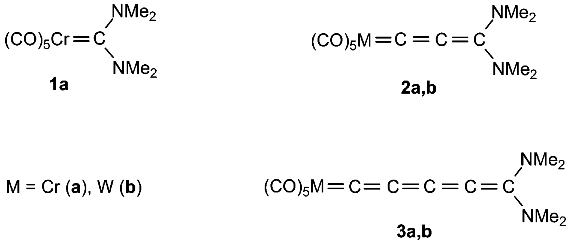
10.1021/om700386t CCC: $37.00

Chart 1



the very high reactivity of these complexes, they could be neither isolated nor spectroscopically detected and therefore were only trapped with nucleophiles.

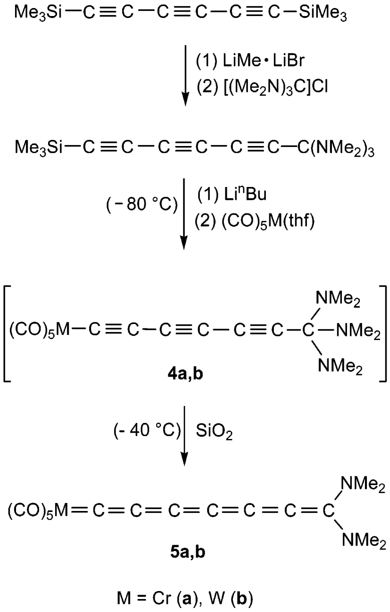
Like butatrienylidene complexes, pentatetraenylidene complexes ($m = 4$) are very rare. In 1994 Dixneuf et al. succeeded in preparing and isolating the first stable cationic pentatetraenylidene complexes: $[(C_6Me_6)Cl(PMe_3)Ru{=}(C)_4{=}CPh_2]PF_6$[18] and *trans*-$[Cl(dppe)_2Ru{=}(C)_4{=}CPh_2]PF_6$.[19] Two years later the first neutral pentatetraenylidene complex, *trans*-$[Cl\{P(i\text{-}Pr)_3\}_2Ir{=}(C)_4{=}CPh_2]$,[20] and three pentacarbonyl pentatetraenylidene complexes, $[(CO)_5M{=}(C)_4{=}C(NMe_2)R]$ ($M = W$, $R = NMe_2$, $CH{=}C(NMe_2)_2$; $M = Cr$, $R = NMe_2$; see also Chart 1, **3a,b**), were isolated.[21,22] Since then, the synthesis of only five additional pentatetraenylidene complexes of rhodium,[23] tungsten,[24] and rhenium[25] has been reported.

Complexes with $m > 4$ thus far have not been isolated or spectroscopically observed. A hexapentaenylideneruthenium complex ($m = 5$), $[\{Ru\}{=}(C)_5{=}C(H)SiMe_3]^+$ ($\{Ru\} = RuCl(dppe)_2$), has been proposed recently as an intermediate in the reaction of $[\{Ru\}(C{\equiv}C)_3SiMe_3]$ with $[\{Ru\}{=}(C)_2{=}CMe_2]^+$ to give a cationic C_9-bridged diruthenium complex.[26]

Attempts to isolate and characterize heptahexaenylidene complexes ($m = 6$) have likewise failed until now. The heptahexaenylidene complex $[(CO)_5W{=}(C)_6{=}C(NMe_2)_2]$ was very likely formed in the sequential reaction of the triyne $Me_3Si(C{\equiv}C)_3C(NMe_2)_3$ with LiMe·LiBr, $[(CO)_5W(thf)]$, and $BF_3{\cdot}OEt_2$ (see also Scheme 1), but could be neither isolated nor spectroscopically detected. Once formed, the putative heptahexaenylidene complex immediately added $HNMe_2$, generated in the course of the reactions as a byproduct, and an alkenyl-substituted pentatetraenylidene complex was obtained.[22]

Therefore, until now, mononuclear metallacumulenes, $[L_nM{=}(C)_m{=}CR_2]$, with up to only five carbon atoms in the chain ($m = 4$) have been prepared and fully characterized. As an example, the series of known bis(dimethylamino)-substituted cumulenylidene complexes of group 6b metals (**1a**[27] and **2a,b** and **3a,b**;[21] tungsten complex **1b** is still unknown) is depicted in Chart 1.

Scheme 1



We have now succeeded in the synthesis, isolation, and characterization of the first heptahexaenylidene complexes and report on their properties and on their reactivity.

Results

The methodology successfully employed in the synthesis of the pentatetraenylidene complexes $[(CO)_5M{=}(C)_4{=}C(NMe_2)_2]$ and in the earlier generation of $[(CO)_5W{=}(C)_6{=}C(NMe_2)_2]$ was modified for the synthesis of the heptahexaenylidene complexes. Monodesilylation of the triyne $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ with LiMe·LiBr and subsequent reaction with $[(Me_2N)_3C]^+Cl^-$ afforded $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ in low yield. After purification, the (trimethylsilyl)heptatriyne was desilylated at −60 °C with LiBu. When $[(CO)_5M(thf)]$ was added at −78 °C, the triynyl metalates **4a,b** were formed. Maintaining the low temperature in this reaction step is crucial as is the use of purified $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ in the previous step. At higher temperature, elimination of NMe_2^- from the terminal carbon atom and readdition at C5 occur. Chromatography of the reaction mixture containing **4a,b** at −40 °C on silica induces elimination of NMe_2^- which is adsorbed at the stationary phase. The heptahexaenylidene complexes **5a,b** (Scheme 1) are finally obtained as red microcrystalline solids in overall yields (five steps) of about 3%.

The new complexes are surprisingly stable at room temperature in the solid state. When heated, they start to decompose only at about 130 °C (Cr) or 145 °C (W). Solutions of **5a,b** in most common solvents are likewise stable for hours. Both complexes were characterized by spectroscopic means. Unfortunately, crystals suitable for an X-ray structure analysis could not be obtained. Both complexes crystallized in very thin needles only.

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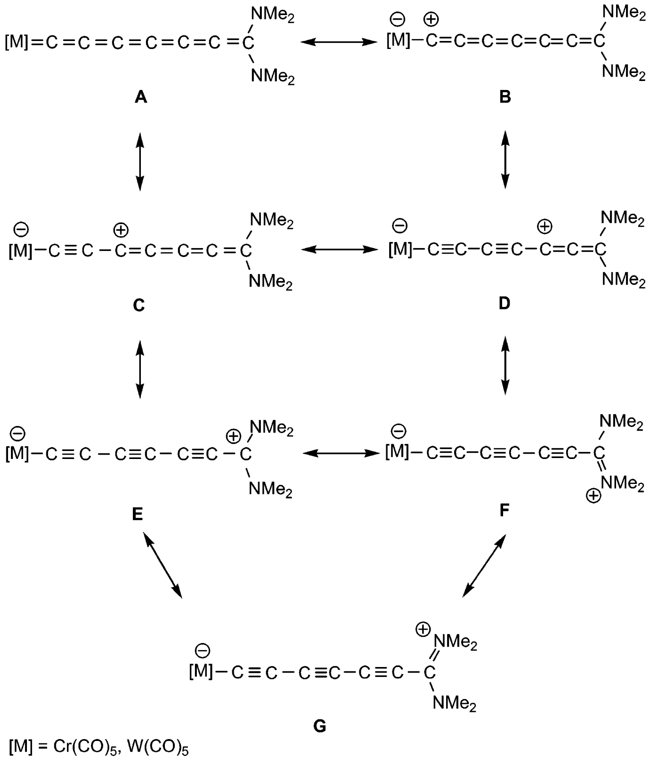
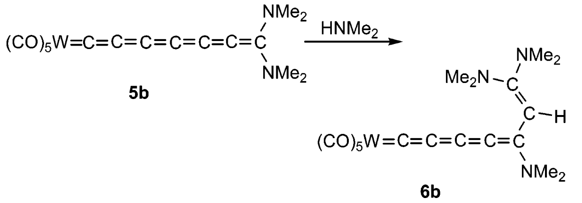
Scheme 2



Scheme 3



The IR spectra of **5a,b** show six absorptions in the range 1800−2200 cm^{-1}. Three of the absorptions exhibit the typical pattern of a C_{4v}-symmetric pentacarbonylmetal fragment and can be assigned to the ν(CO) vibrations. The remaining three absorptions (at 2158/2156, 2107, and 1956 cm^{-1}) can be assigned to ν(CC) modes. In contrast to two ν(CC) vibrations observed with pentatetraenylidene complexes **3a,b** (at 2140 and 1998/1999 cm^{-1}), three absorptions are to be expected for the C_7 fragment in **5a,b**. The ν(CO) absorptions are at rather low energy. They are at wavenumbers similar to those of **3a,b**[21] (for instance, ν(CO) = 2052, 1972, 1930, and 1902 cm^{-1} (**3a**) and 2047, 1927, and 1894 cm^{-1} (**5a**)), both A_1 absorptions being at even slightly lower energy. From the positions of these CO vibrations a very strong σ-donor property of the heptahexaenylidene ligand can be deduced. Its σ-donor/π-acceptor properties are similar to those of the bis(dimethylamino)pentatetraenylidene ligand. Therefore, for **5a,b** essentially seven resonance structures have to be taken into account (**A**−**G**, Scheme 2), the dipolar ylide structures **B**−**G** substantially contributing to the bonding situation.

In the ^{1}H NMR spectra of **5a,b** only one sharp resonance for the four *N*-Me groups is observed. At −80 °C, the signal broadens only slightly, indicating that the barrier to rotation around the C−N(Me)$_2$ bond is rather low. Analogously, in the ^{13}C NMR spectra only one Me resonance is observed in addition to peaks for the *cis*- and *trans*-carbonyl ligands and seven resonances for the C_7 moiety. On the basis of the W−C coupling constants, the resonances of the tungsten-bound carbon atom (C1) and the adjacent atom (C2) are easily assigned. The resonance of the terminal sp^2-hybridized carbon atom is readily identified by comparison of the spectrum with the spectra of the “shorter” cumulenylidene complexes [(CO)$_5$M=(C)$_n$=C(NMe$_2$)$_2$] (n = 2, 4).[21] The signals for the remaining carbon atoms were assigned with the aid of calculated NMR data (see the Experimental Section).

The absorption at lowest energy in the UV−vis spectra is assigned to a metal-to-ligand charge transfer (MLCT) band. Extension of an MC$_n$ chain by insertion of C$_2$ units (MC$_3$ → MC$_5$ → MC$_7$) lowers the energy of the LUMO and increases the distance between the centers of positive and negative charge of the dipole. A bathochromic shift of the MLCT absorption and an increase in the solvatochromism is to be expected. The UV−vis spectra are in accord with these expectations. Compared to those of **3a,b**, the absorptions at lowest energy of **5a,b** are at longer wavelengths (e.g., λ_{max} in CH$_2$Cl$_2$, 474 nm (**3a**), 550 nm (**5a**), 466 nm (**3b**), 537 nm (**5b**)). The shift depends on the solvent and decreases with increasing polarity of the solvent (e.g., ΔE(**3a** → **5a**) = 34.9 kJ/mol in CH$_2$Cl$_2$ and 31.3 kJ/mol in DMF). The negative solvatochromic effect of **5a,b** is more pronounced than that of **3a,b** (e.g., $\Delta\nu$(CH$_2$Cl$_2$ − DMF) = 2490 (**3a**) and 2780 (**5a**) cm^{-1}). This indicates a polar ground state and a less polar excited state and is in accord with the dipolar resonance forms **B**−**G** (Scheme 2).

Reactions with Nucleophiles. Complex **5b** readily adds HNMe$_2$ across the C5=C6 bond to give the pentatetraenylidene complex **6b** (Scheme 3) presumably by an initial nucleophilic addition of the amine to C5 of the heptahexaenylidene ligand. Complex **6b** was identified by comparison of its spectral data with those published earlier.[22] The formation of **6b** by reaction of **5b** with HNMe$_2$ confirms our previous suggestion that **5b** is an intermediate in the synthesis of **6b** from [(CO)$_5$W(thf)], Li[C≡CC≡CC≡CC(NMe$_2$)$_3$], and BF$_3$·OEt$_2$.[22]

Contrary to HNMe$_2$, methanol does not react with **5b** at room temperature. When dissolved in methanol for 90 min, complex **5b** was recovered nearly quantitatively. In contrast, most pentatetraenylideneruthenium complexes were found to add alkanols either across the C1=C2 bond to form alkoxycarbene complexes[28] or across C3=C4 to give alkenyl(alkoxy)allenylidene complexes.[18,19,29]

Contrary to the observed nucleophilic addition of HNMe$_2$ at C5 of **5b**,[22] carbanions add at the terminal (C7) atom of the chain. Addition of 5 equiv of LiMe·LiBr at −78 °C to violet solutions of **5a,b** in THF led to rapid formation of the yellow triynyl metalates **7a,b** (Scheme 4). Complexes **7a,b** turned out to be unstable and could not be isolated; however, they could be characterized IR spectroscopically (ν(CO) = 2049, 1922, and 1878 cm^{-1} (**7a**) and 2055, 1916, and 1876 cm^{-1} (**7b**); ν(CC) = 2119 and 1992 cm^{-1} (**7a**) and 2121 and 1992 cm^{-1} (**7b**); in both cases the third band was too weak to be detected). Rapid chromatography of **7b** on silica at −70 °C gave a blue solution, its color being presumably due to the heptahexaenylidene complex **8b** (Scheme 4). Complex **8b** (ν(CO) = 2049, 1922, and 1878 cm^{-1}; ν(CC) = 2119 and 1992 cm^{-1}) was

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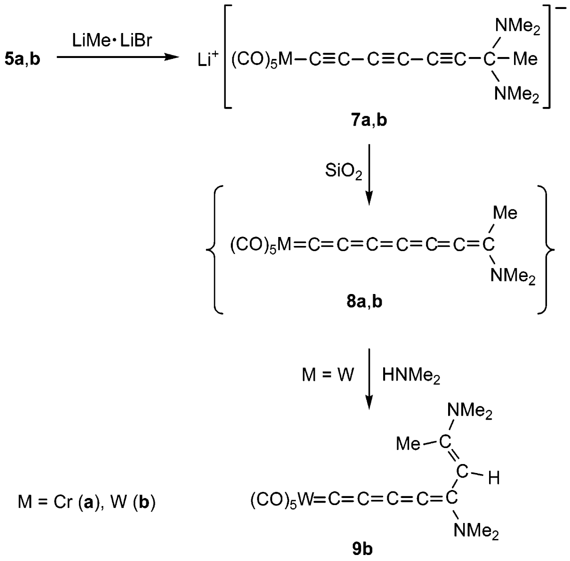
Scheme 4



unstable and rapidly decomposed on removal of the solvent. However, **8b** could be trapped by addition of $HNMe_2$ to the blue solutions. The product, pentatetraenylidene complex **9b** (Scheme 4), formed by addition of the amine across the C5═C6 bond, was isolated and characterized by IR and NMR spectroscopy.

The ν(CO) and ν(CC) absorptions of **9b** are similar to those of the related pentatetraenylidene complexes **6b**[22] and $[(CO)_5W{=}C{=}C{=}C{=}C{=}C(NEt_2)(CMe{=}C\{NMe_2\}_2)]$.[21] The ^{1}H NMR spectrum in d_6-acetone at −60 °C shows a singlet at $\delta = 5.31$ (relative intensity 1) and five additional singlets for the various Me groups in the range 2.6−3.5 (relative intensity 3 each). On warming the solution to room temperature, the two *N*-methyl resonances assigned to the terminal NMe_2 group coalesce and the other two *N*-methyl resonances broaden. These observations indicate a lower barrier to rotation around the terminal $C-NMe_2$ bond and a lower π-contribution from the $C(Me)NMe_2$ amino group to the stabilization of the complex. The *trans* arrangement of the NMe_2 group and the C_5 chain at the olefin bond follows from the similarity of the resonances with those of similarly substituted allenylidene complexes[30] whose structure assignments were established by ROESY NMR experiments and by X-ray structure analyses. The ^{13}C NMR spectroscopic data likewise confirmed the proposed constitution of **9b**. Analogously to the ^{1}H NMR spectrum at room temperature, the terminal NMe_2 group gives rise to only one signal in the ^{13}C NMR spectrum.

The MLCT absorption of **9b** in the UV−vis spectra is observed, as expected, at higher energy when compared with that of the heptahexaenylidene complex **5b**. Replacing one NMe_2 group in the bis(dimethylamino)pentatetraenylidene complex **3b** by $CH{=}C(Me)NMe_2$ gives rise to a bathochromic shift of the MLCT absorptions, whereas displacement by $CH{=}C(NMe_2)_2$ leads to a hypsochromic shift.[22]

When a solution of **5b** was treated with LiMe·LiBr and subsequently with silica, the color of the solution changed from red-violet to yellow to blue. A similar color change was observed when LiMe·LiBr was replaced by LiPh and LiBu, indicating that the corresponding heptahexaenylidene complexes $[(CO)_5W{=}(C)_6{=}C(R)NMe_2]$ (R = Ph, Bu) had been formed. Both complexes have not been isolated in a pure form. However, in accord with the assumption, the IR spectra were similar to those of **5a,b** albeit the "third" $\nu(C_7)$ at about 1956 cm^{-1} was missing presumably due to its low intensity.

Discussion

By modification of the procedure published earlier by us,[22] very careful control of the reaction conditions and using silica instead of $BF_3{\cdot}OEt_2$ in the abstraction of one dimethylamino group from the triynyl metalates **4a,b**, it was possible to prepare and isolate the first heptahexaenylidene complexes albeit in only low overall yield. The thermal stability of the complexes in the homologous series $[(CO)_5M{=}(C)_n{=}C(NMe_2)_2]$, containing an odd number of carbon atoms in the chain, only slightly decreases on going from carbene ($n = 0$) via allenylidene ($n = 2$) and pentatetraenylidene ($n = 4$) to heptahexaenylidene ($n = 6$) complexes. From these observations we conclude that complexes with an even longer chain of carbon atoms ($n = 8$ or 10) should be thermally stable once a suitable synthesis has been developed. However, replacing one of the two strong π-donors NMe_2 by an alkyl or aryl substituent significantly reduces the thermal stability as has already been observed with the corresponding allenylidene complexes.[31] The high thermal stability of **5a,b** is in accord with predictions based on calculated M−C(cumulenylidene) bond dissociation energies of $[(CO)_5Cr{=}(C)_n{=}CR_2]$ complexes ($n = 1-8$).[32] In contrast to the thermal stability, the nucleophilicity of these metallacumulenes considerably increases when the carbon chain is lengthened, thus causing enhanced problems in handling the compounds.

In the series of $[(CO)_5M{=}(C{=}C)_x{=}C(NMe_2)_2]$ complexes ($x = 1$ (**2**), 2 (**3**), 3 (**5**)) the σ-donor/π-acceptor properties of the cumulenylidene ligand are almost independent of the number of carbon atoms n separating the donor group $C(NMe_2)_2$ and the acceptor fragment $(CO)_5M$. The ν(CO) absorptions of all complexes are nearly identical. These undiminished strong donor properties are presumably a major factor responsible for the high thermal stability since the decomposition of most carbonyl complexes is initiated by M−CO dissociation.

In agreement with the IR spectra the resonances of the carbonyl carbon atoms of **2**, **3**, and **5** are almost unaffected by the length of the cumulenylidene ligand. The metal-bound C1 atom of the cumulenylidene ligand only slightly shifts to higher field with increasing n, indicating that insertion of one or two C_2 fragments into the MC_3 chain of allenylidene complexes barely modifies the bonding situation.

The barrier to rotation around the $C-NMe_2$ bond in **5a,b** is significantly lower than that in the pentatetraenylidene complex **3b** ($\Delta G^{\ddagger} = 40 \pm 1$ kJ/mol)[21] but higher than in the allenylidene complex **2b**.[21] Obviously, the importance of π-donation from the amino groups in **5b** (Scheme 2, resonance forms **F** and **G**) is intermediate between that of the complexes with $n = 2$ and 4.

DFT calculations[32] indicate that, on lengthening the chain by C_2 units, the energy of the LUMO decreases whereas the energy of the HOMO remains essentially unaffected. As a consequence, the absorption at longest wavelength shifts toward lower energy (Figure 1). However, the magnitude diminishes with increasing length of the chain (e.g., in CH_2Cl_2, $\Delta\lambda_{max} = 4200$ cm^{-1} for **2a** → **3a** and 3000 cm^{-1} for **3a** → **5a**).

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(30) (a) Dede, M. Ph.D. Thesis, Universität Konstanz, 2004. (b) Manuscript in preparation.

(31) See, e.g.: Fischer, H.; Szesni, N. *Coord. Chem. Rev.* **2004**, *248*, 1659.

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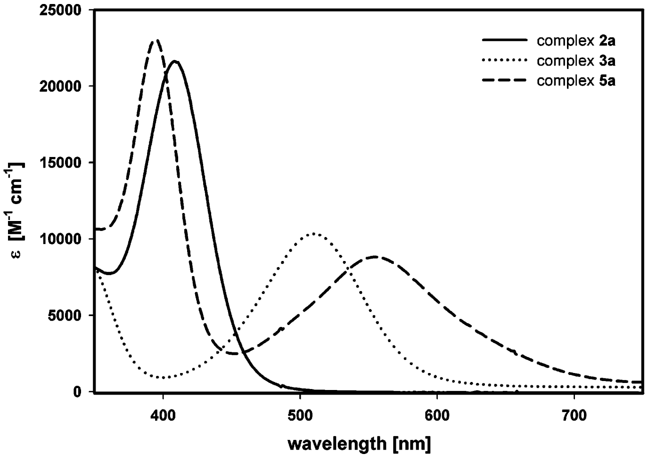

Figure 1. UV−vis spectra of complexes **2a**, **3a**, and **5a** in toluene.

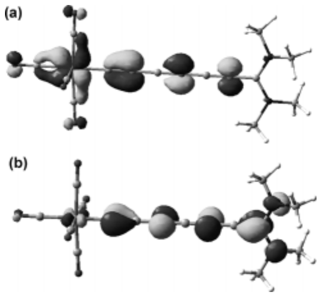

Figure 2. Orbital contributions to the HOMO (a) and LUMO (b) of complex **5a**.

The analysis[32,33] of the electronic structure of $[L_mM{=}(C)_n{=}CR_2]$ shows that, in cumulenylidene complexes with an odd number of carbon atoms, $[L_mM{=}(C{=}C)_x{=}CR_2]$, the LUMO is oriented perpendicularly to the ligand plane and is mostly localized on the odd carbon atoms C1, C3, C5, ... (for the LUMO of **5a** see Figure 2; for a breakdown of the orbital contributions of chromium and the carbon atoms along the chain to the HOMO and LUMO of **5a** and **8a** see the Supporting Information). The HOMO is an in-plane orbital and is mostly localized on the even carbon atoms. The calculations also reveal that the contributions from the odd carbon atoms to the LUMO slightly increase along the chain but vary only minimally.

In agreement with these calculations pentatetraenylidene complexes were found to add *O*-nucleophiles to either C1[28] or (mostly) C3.[18,19,29] *N*-Nucleophiles were observed to exclusively add to C3 to form alkenyl(amino)allenylidene complexes.[18,19,21,22,28b,29a] Insertion of an ynamine into the C4═C5 bond affords a heptapenta-1,2,3,4,6-enylidene complex. The reaction was suggested to proceed by an initial nucleophilic attack at the terminal (C5) atom.[24]

As with pentatetraenylidene complexes, $HNMe_2$ was found to initially add to the third to last carbon atom of the chain (C3 in **3** and C5 in **5**). A nucleophilic addition to either C1 or C3 has so far not been observed. Analogously to [bis(dimethylamino)allenylidene]- and [bis(dimethylamino)pentatetraenylidene]-pentacarbonylchromium and -tungsten, and to the cationic pentatetraenylidene complex $[(C_6Me_6)Cl(PMe_3)Ru{=}C{=}C{=}C{=}C{=}C(C_6H_4NMe_2\text{-}4)_2]PF_6$,[18] bis(dimethylamino)heptahexaenylidene complexes **5a,b** did not react with methanol despite their high electrophilicity. The addition of carbon nucleophiles to the terminal carbon atom of the chain also has precedence. Bis(dimethylamino)allenylidene pentacarbonyl complexes react with lithium alkyl and aryl compounds by addition of the carbanion to the C3 atom to give alkynyl metalates.[31] Addition of carbon nucleophiles to C7 of **5a,b** and subsequent amide elimination give (dimethylamino)(organyl)heptahexaenylidene complexes, thus constituting a simple substitution approach to N/C-substituted heptahexaenylidene complexes. An alternative method for modifying heptahexaenylidene complexes is probably the insertion of ynamines into the C6═C7 bond, affording alkenyl(amino)heptahexaenylidene complexes. The feasibility of this route has already been demonstrated by the example of allenylidene and pentatetraenylidene pentacarbonyl complexes.[24,31]

Experimental Section

All operations were performed in a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, pentane) and sodium/diphenylketyl (THF, Et_2O). The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitrogen-saturated. The yields reported were not optimized. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250, Bruker WM 250, or Bruker DRX 600 spectrometer at room temperature unless mentioned otherwise. Chemical shifts are reported relative to the residual solvent peaks. IR spectra were recorded on a Biorad FTS 60. MS measurements were carried out on a Finnigan MAT 312 instrument. The UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

The following compounds were prepared according to literature procedures: the complexes $[CO)_5M(thf)]$,[34] 1,6-bis(trimethylsilyl)-hexa-1,3,5-triyne,[35] and tris(dimethylamino)carbenium chloride.[36] All other chemicals were used as obtained from commercial suppliers.

[7,7-Bis(dimethylamino)heptahexa-1,2,3,4,5,6-enylidene]pentacarbonylchromium (5a). At −78 °C 5.4 mmol of LiMe·LiBr (3.4 mL of a 1.6 M solution in Et_2O) was added to a solution of 1.18 g (5.40 mmol) of $(CH_3)_3SiC{\equiv}CC{\equiv}CC{\equiv}CSi(CH_3)_3$ in 50 mL of THF. The color of the solution changed from slightly yellow to red. The solution was stirred for 90 min. Then 0.97 g (5.4 mmol) of $[((CH_3)_2N)_3C]Cl$ was added. Stirring was continued for 90 min at −78 °C and then for 12 h at room temperature. The solvent was removed in vacuo. The residue was extracted with 150 mL of pentane, and a clear red solution was obtained. The solvent was again removed in vacuo. The resulting black residue was dissolved in 60 mL of THF, and 5.4 mmol of Li^nBu (3.4 mL of a 1.6 M solution in hexane) was added at −60 °C. The solution was stirred for 30 min at −60 °C and for 75 min at room temperature and then cooled to −78 °C. A solution of 6.00 mmol of $[(CO)_5Cr(THF)]$ (60.0 mL of a 0.1 M solution in THF) was added. After 10 min the solution was placed at −40 °C on top of a 3 cm layer of silica wetted with 50 mL of CH_2Cl_2. Elution with 450 mL of CH_2Cl_2 gave a deep violet solution (the first 230 mL of the eluant was discarded!). The solvent was removed in vacuo, and the residue was chromatographed at −40 °C on neutral Al_2O_3 with pentane/CH_2Cl_2 (ratio decreasing from 1:1 to 0:1). The red band containing complex **5a** was eluted with CH_2Cl_2. Removal of the solvent gave a red solid. Yield: 50 mg (2.5% based on the hexatriyne). Mp: >130 °C dec. IR (THF): ν(CO) 2047 m, 1933 vs, 1900 s cm^{-1}; ν(CC) 2156 w, 2107 m, 1956 m cm^{-1}. ^1H NMR (d_6-acetone,

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250 MHz): δ 3.41 (s, 12H, $N(CH_3)_2$). ^{13}C NMR (d_6-acetone, 62.5 MHz): δ 43.7 ($N(CH_3)_2$), 43.9 (C6), 55.6 (C4), 82.9 (C3), 96.6 (C5), 97.6 (C2), 153.5 (C7), 167.5 (C1), 219.0 (*cis*-CO), 221.0 (*trans*-CO). UV−vis: λ_{max} (log ε) 555 (3.945) [toluene], 550 (4.235) [CH_2Cl_2], 518 (4.177) [EtOH], 477 (4.090) [DMF]. MS (FAB, NBA): *m*/*z* (rel intens) 364 (32) [M^+], 336 (8) [$(M - CO)^+$], 308 (24) [$(M - 2CO)^+$], 280 (14) [$(M - 3CO)^+$], 252 (37) [$(M - 4CO)^+$], 224 (22) [$(M - 5CO)^+$], 173 (35) [$(M - 5CO - Cr + H^+)^+$]. Anal. Calcd for $C_{16}H_{12}CrN_2O_5$ (364.3): C, 52.76; N, 3.32; H, 7.69. Found: C, 52.00; H, 3.94; N, 7.15.

[7,7-Bis(dimethylamino)heptahexa-1,2,3,4,5,6-enylidene]pentacarbonyltungsten (5b). The synthesis of **5b** from 1.11 g (5.10 mmol) of $(CH_3)_3SiC{\equiv}CC{\equiv}CC{\equiv}CSi(CH_3)_3$ in 50 mL of THF, 5.1 mmol of LiMe•LiBr (3.2 mL of a 1.6 M solution in Et_2O), 0.92 g (5.1 mmol) of $[((CH_3)_2N)_3C]Cl$, 5.1 mmol of Li^nBu (3.2 mL of a 1.6 M solution in hexane), and 5.30 mmol of $[(CO)_5W(THF)]$ (53.0 mL of a 0.1 M solution in THF) was carried out with minor deviations analogously to that of **5a**. Instead of 150 mL of pentane, 200 mL was used for the extraction of $(CH_3)_3SiC{\equiv}CC{\equiv}CC{\equiv}C[N(CH_3)_3]$, and the final reaction mixture was eluted with 600 mL of CH_2Cl_2 instead of 450 mL. Yield: 70 mg (2.8% based on the hexatriyne). Mp: > 145 °C dec. IR (THF): ν(CO) 2052 m, 1927 vs, 1894 m cm^{-1}; ν(CC) 2158 w, 2107 m, 1956 m cm^{-1}. ^1H NMR (d_6-acetone, 250 MHz): δ 3.42 (s, 12H, $N(CH_3)_2$). ^{13}C NMR (d_6-acetone, 62.5 MHz): δ 43.7 ($N(CH_3)_2$), 46.6 (C6), 56.9 (C4), 83.0 (C3), 96.7 (C5), 95.8 (C2, $^2J_{WC} = 25.2$ Hz), 146.7 (C1, $^2J_{WC} = 103.2$ Hz), 153.4 (C7), 198.1 (*cis*-CO, $^1J_{WC} = 109.0$ Hz), 199.9 (*trans*-CO, $^1J_{WC} = 114.0$ Hz). UV−vis: λ_{max} (log ε) 541 (3.753) [toluene], 537 (4.205) [CH_2Cl_2], 507 (4.088) [EtOH], 470 (4.035) [DMF]. MS (FAB, NBA): *m*/*z* (rel intens) 496 (22) [M^+], 468 (20) [$(M - CO)^+$], 440 (13) [$(M - 2CO)^+$]. Anal. Calcd for $C_{16}H_{12}N_2O_5W$ (496.1): C, 38.73; H, 2.44; N, 5.65. Found: C, 39.96; H, 3.11; N, 5.35.

Pentacarbonyl[5-(dimethylamino)-5-[2-(dimethylamino)-2-methylethenyl]-1,2,3,4-pentatetraenylidene]tungsten (9b). Addition of 0.21 mL of a solution of MeLi•LiBr (1.6 M in Et_2O, 0.34 mol) to a solution of 17 mg (34 μmol) of **5b** in 25 mL of THF led to a quick color change from violet to yellow-brown. The solution was placed on top of a 2 cm layer of silica cooled to −70 °C. Elution with 350 mL of CH_2Cl_2 (−70 °C) gave a deep-blue solution. When 2.9 mL of $HNMe_2$ was added, the color of the solution rapidly changed to yellow. The solution was placed on top of a 10 cm layer of silica cooled to −70 °C. With 450 mL of CH_2Cl_2 (again at −70 °C) a yellow solution was eluted. The solvent was removed in vacuo. The residue was chromatographed at −30 °C on silica with pentane/CH_2Cl_2 mixtures of gradually increasing polarity. The orange band containing **9b** was collected. Removal of the solvent gave **9b** in the form of a red film. Yield: ∼10 mg (57% based on **5b**). IR (THF): ν(CO) 2058 m, 1963 vw, 1922 vs, 1890 m cm^{-1}; ν(CC) 2139 m, 2001 m cm^{-1}. ^1H NMR (d_6-acetone, 250 MHz): δ 2.64 (s, 3H, CCH_3), 3.30, 3.40 (2s, br, 2 × 3H, C5-$N(CH_3)_2$), 3.34 (s, br, 6H, $CH{=}CN(CH_3)_2$), 5.35 (s, 1H, $-CH{=}$). ^1H NMR (d_6-acetone, −60 °C, 250 MHz): δ 2.61 (s, 3H, CCH_3), 3.29, 3.40 (2s, 2 × 3H, C5-$N(CH_3)_2$), 3.24, 3.45 (2s, 2 × 3H, $CH{=}CN(CH_3)_2$), 5.31 (s, 1H, $-CH{=}$). ^{13}C NMR (d_6-acetone, 150 MHz): δ 18.6 (CCH_3), 42.3 (C5-$N(CH_3)_2$), 41.3, 43.4 ($CH{=}CN(CH_3)_2$), 56.9 (C4), 94.9 (C2, $^2J_{WC} = 25.0$ Hz), 96.0 ($-CH{=}$), 99.8 (C3), 146.7 (C1, $^1J_{WC} = 100.9$ Hz), 151.6 (C5), 169.5 ($CH{=}C$), 198.7 (*cis*-CO, $^1J_{WC} = 124.2$ Hz), 201.1 (*trans*-CO, $^1J_{WC}$ 131.6 Hz). UV−vis: λ_{max} (log ε) 526 (4.010) [toluene], 477 (4.241) [CH_2Cl_2], 467 (4.216) [EtOH], 441 (qual) [DMF]. MS (FAB, NBA): *m*/*z* (rel intens) 512 (15) [M^+], 484 (13) [$(M - CO)^+$], 456 (10) [$(M - 2CO)^+$], 154 (100) [$(NBA + H^+)^+$]. Molecular weight: 512.2.

Computational Details. All ab initio calculations were performed using Jaguar[37a] (version 5.5.016) running on Linux-2.4.20-28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf cluster) parallelized with MPICH 1.2.4. Initial structures were obtained by MM+ optimization using Hyperchem.[38] Geometries were optimized using the LACVP* basis set (ECP for Cr and W, N31G6* for all other atoms) and the BP86 density functional. NMR shielding tensors were calculated at the same level of theory with Jaguar 6.0[37b] at the University of Erlangen-Nürnberg. Chemical shifts were obtained in reference to calculated tetramethylsilane.

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Supporting Information Available: Tables giving the calculated Cartesian coordinates, bond distances, bond angles, and energies of complexes **5a** and **8a** and breakdown of the orbital contributions of the metal and the carbon atoms along the chain to the HOMO and LUMO of these complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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