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On the Way to Heptahexaenylidene Complexes: Trapping of an Intermediate with the Novel $M{=}C{=}C{=}C{=}C{=}C{=}C{=}CR_2$ Moiety

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Summary: Sequential treatment of the in situ generated heptatriyne $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ *with n-BuLi,* $(CO)_5W[THF]$*, and* $BF_3{\cdot}OEt_2$ *affords the first alkenyl-substituted pentatetraenylidene complex,* $(CO)_5W{=}C{=}C{=}C{=}C{=}C(NMe_2)C(H){=}C(NMe_2)_2$ *(**4**), via addition of dimethylamine to the* $C_\epsilon{=}C_\zeta$ *bond of the intermediate heptahexaenylidene complex* $(CO)_5W{=}C_\alpha{=}C_\beta{=}C_\gamma{=}C_\delta{=}C_\epsilon{=}C_\zeta{=}C_\eta(NMe_2)_2$*. In addition, the alkynyl(butatrienyl)carbene complex* $(CO)_5W{=}C(C{\equiv}CSiMe_3)C(Bu){=}C{=}C{=}C(NMe_2)_2$ *(**5**) is formed.*

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Introduction

Organometallic compounds containing a linear unsaturated carbon chain recently have attracted considerable interest due to their physical and chemical properties. Transition-metal complexes of this structural type have been proposed[1] as one-dimensional molecular wires[2] and exhibit both liquid crystalline[3] and nonlinear optical[4] properties. Bimetallic complexes with a "naked" σ-coordinated π-conjugated carbon bridge, $L_nMC_mM'L'_{n'}$, are well-known.[1,5] The maximum chain length ($m = 20$) achieved so far has been that in the homobinuclear complex $Cp^*(NO)(PPh_3)Re(C)_{20}Re(PPh_3)(NO)Cp^*$, recently synthesized by Gladysz et al.[6] Electrochemical studies show that both the terminal substituents of the carbon chain (i.e., the metal ligand fragments) and the number of carbon atoms in the chain strongly influence the properties of the system.[6,7]

Mononuclear cumulenylidene complexes, $L_nM({=}C)_mR_2$, are of similar chemical and physicochemical interest.[8] Complexes of this type are now known with carbon chain lengths up to $m = 5$.[9] Only in 1994 were the first pentatetraenylidene complexes ($m = 5$) synthesized and fully characterized.[9a,b] Complexes with $m > 5$ thus far have not been isolated or spectroscopically observed.

Results and Discussion

Recently we reported the synthesis of strongly dipolar dimethylamino-substituted allenylidene (**2**) and pentatetraenylidene complexes (**3**) by reaction of $(CO)_5M[THF]$ (M = Cr (**1a**), W (**1b**)) with lithiated tris(amino)methyl-substituted ethyne or butadiyne and subsequent abstraction of one dimethylamino group (Scheme 1).[9d]

The astonishing stability of **2** and **3** led to the assumption that pentacarbonyl complexes with even longer cumulenylidene ligands might also be stable and isolable species. The same methodology successfully used in the synthesis of **2** and **3** was used in the attempted synthesis of the heptahexaenylidene complex $(CO)_5W{=}C{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2$ (Scheme 2). Monodesilylation of the readily available triyne $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ with $MeLi{\cdot}LiBr$ and subsequent reaction with $(Me_2N)_3C^+Cl^-$ gave $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$, although in low yield.[10] Since we were not able to find a suitable method of purification for $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$, the heptatriyne was desilylated *in situ* with *n*-BuLi. The reaction mixture was then treated with $(CO)_5W[THF]$ and finally with $BF_3{\cdot}OEt_2$ to achieve abstraction of one dimethylamino group. After chromatographic workup, two crystalline products, **4** and **5** (Scheme 2), were isolated in low yield (5% for **4** and 7% for **5**, based on $(CO)_5W[THF]$). Both complexes, yellow **4** and red **5**, are stable in air at room temperature.

NMR spectroscopic data, mass spectroscopic data, and elemental analysis confirm the constitution of **4** as a 1:1 adduct of $HNMe_2$ and the heptahexaenylidene complex $(CO)_5W{=}C{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2$ (**A**) (Scheme 3). It was not possible to either isolate or spectroscopically detect **A**. However, the intermediacy of **A** in the formation of **4** is plausible on the basis of the results obtained with the related pentatetraenylidene complex **3b**. Compound **3b** similarly adds $HNMe_2$ to give the (alkenylallenylidene)tungsten complex $(CO)_5W{=}C{=}C{=}C(NMe_2)C(H){=}C(NMe_2)_2$ (**6**).[9d] At present, it cannot be decided whether $HNMe_2$ addition to **A** proceeds in one step or in two steps by sequential attack of NMe_2^- and H^+. In contrast to **3b** and **A**, the bis(dimethylamino)allenylidene complex **2b** does not

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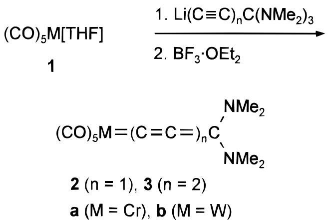
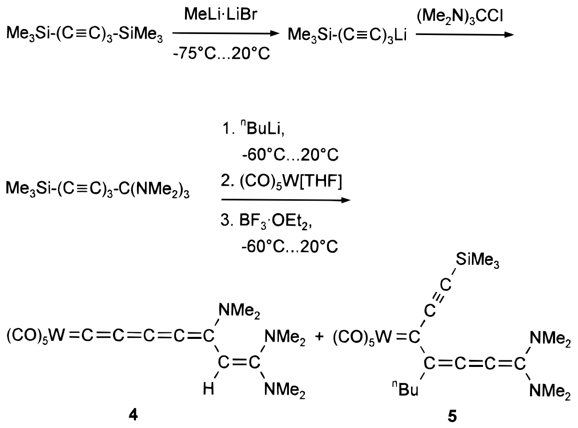
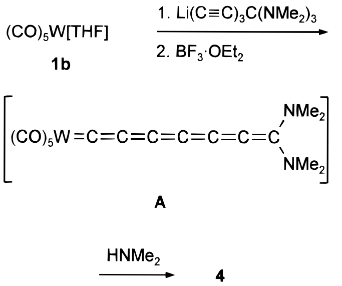
Scheme 1



Scheme 2



Scheme 3



add $HNMe_2$ within 1 week at room temperature when a 6-fold excess of the amine is used.[9d] Obviously, the electrophilicity of the complexes $(CO)_5W{=}(C{=}C{=})_nC(NMe_2)_2$ increases considerably with the number of C=C units in the carbon chain. In the tungsten cumulenylidene **A** ($n = 3$) the C_ϵ atom is the most electrophilic one (Scheme 3).

The structure of **4** as an (alkenylpentatetraenylidene)tungsten complex was established by ROESY NMR spectroscopy. The NOE observed in **4** between the alkenyl proton and the two alkenyl NMe_2 groups is comparable to that found for the alkenyl moiety in the (alkenylallenylidene)tungsten complex $(CO)_5W{=}C{=}C{=}C(NMe_2)C(H){=}C(NMe_2)_2$ (**6**), which has been characterized by an X-ray structural analysis.[9d]

Similar to **6**,[9d] the ^1H NMR spectrum of complex **4** in CD_2Cl_2 exhibits at room temperature only two signals (ratio 2:1) in addition to the resonance of the alkenyl proton: a sharp singlet at δ 3.06 for the four terminal NMe groups and a broad singlet at δ 3.15 for the pentatetraenylidene NMe_2 substituent. These observations indicate fast rotation around the $C{-}NMe_2$ bonds *and* around the alkenyl C=C bond. At −90 °C six resonances for the methyl groups are observed, which partially overlap. From the ^1H NMR spectra at different temperatures and the coalescence temperatures at −10, −53, and −65 °C, respectively, the activation barriers for the three dynamic processes can be estimated: $\Delta G^\ddagger = 53 \pm 1$ kJ/mol for the rotation around the $C_\epsilon{-}NMe_2$ bond, and $\Delta G^\ddagger = 47 \pm 1$ kJ/mol and $\Delta G^\ddagger = 43 \pm 1$ kJ/mol for equilibrating of the terminal NMe groups. From these results a strong mesomeric interaction between the terminal amino substituents and the metal center can be deduced. The importance of polar resonance structures for the description of the bonding situation in **4** is also emphasized by the 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. The solvent shift $\Delta\tilde{\nu}$(toluene−DMF) = 3290 cm^{-1} is slightly less pronounced than that of 3b[9d] ($\Delta\tilde{\nu}$(toluene−DMF) = 3580 cm^{-1}), in agreement with the smaller π-donor properties of $C(H){=}C(NMe_2)_2$ as compared to NMe_2.

Carbene complex **5** (Scheme 2) very likely is formed by substitution of the carbanion $[Me_3SiC{\equiv}CC^-{=}C(^nBu)C{\equiv}CC(NMe_2)_3]$ (generated *in situ* by addition of *n*-BuLi to $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$) for coordinated THF in $(CO)_5W[THF]$ via the most nucleophilic carbon atom (C-3) and subsequent abstraction of a dimethylamino group with $BF_3{\cdot}OEt_2$. Oligoynes are known to readily add nucleophiles such as organolithium compounds.[11] Obviously, *n*-BuLi addition to $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC(NMe_2)_3$ successfully competes with desilylation.

Compound **5** is a rare example of dicarbon-substituted open-chain $(CO)_5M$(carbene) complexes (M = Cr, Mo, W).[12] Moreover, until now only one other butatrienyl carbene complex has been reported, the heteroatom-substituted compound $[(\eta^6\text{-}C_6Me_6)Cl(PMe_3)Ru{=}C(OMe)\text{-}C(H){=}C{=}C{=}CPh_2][PF_6]$.[13] The surprisingly high stability of **5** may be explained by strong mesomeric interaction between the amino groups and the metal center. As a consequence, the resonance of the carbene carbon of **5** in the ^{13}C NMR spectrum appears at unusually high field (δ 192.0) despite the lack of a heteroatom substituent (e.g., δ 357.9 for $(CO)_5W{=}CPh_2$).[12b] The results of an X-ray structural analysis of **5** support this conclusion (Figure 1) by (a) the alternating C=C bond lengths of the almost linear butatrienyl substituent, (b) the planar coordination of the nitrogen atoms (sum of angles at N(1) 358.7° and at N(2) 359.1°), the rather short C−N bond lengths (C(10)−N(1) = 1.330(7) Å, C(10)−N(2) = 1.327(7) Å) and C(6)−C(7) distance (1.374(7) Å), and (c) the unusually long W(1)−C(6) bond (2.272(5) Å) as compared to other nonheteroatom-stabilized carbene complexes (e.g., 2.13(2) and 2.15(2) Å in $(CO)_5W{=}CPh_2$).[12c] The slight deviation from coplanarity of the two dimethylamino groups is presumably due to steric repulsion.

At room temperature only one resonance in the ^1H NMR spectrum of **5** (δ 3.44) for the four NMe groups is observed. This indicates fast rotation around the $C{-}NMe_2$ *and* the butatrienyl C=C bonds. From the appearance of two singlets at −95 °C (ratio 1:1) we

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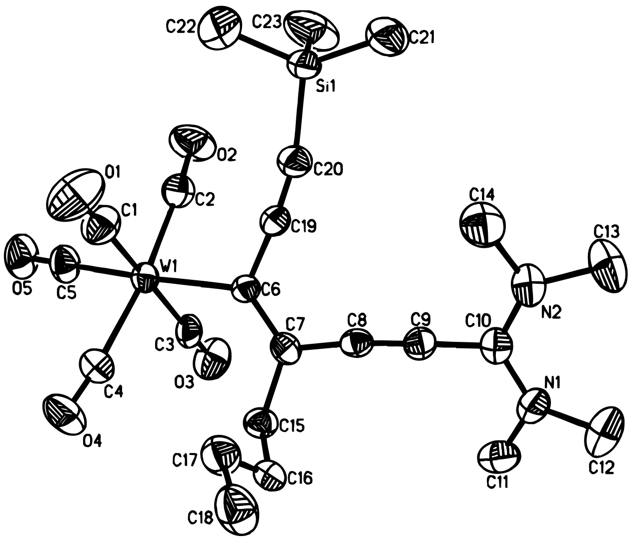

Figure 1. ORTEP drawing of complex **5** (ellipsoids drawn at 50% level, hydrogens omitted). Selected bond lengths (Å) and angles (deg): C(7)−C(8), 1.413(8); C(8)−C(9), 1.205(8); C(9)−C(10), 1.423(8); C(7)−C(8)−C(9), 174.0(6); C(8)−C(9)−C(10), 178.2(6).

conclude that one of these dynamic processes is still fast at this temperature ($\Delta G^{\ddagger}_{189} = 40 \pm 1$ kJ/mol for the other one).

Until now, it has not been possible to isolate the heptahexaenylidene complex $(CO)_5W{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2$ due to the rapid trapping of the complex with dimethylamine. Efforts to avoid the in situ trapping and to increase the yield by varying reaction conditions and/or modification of the substitution pattern are presently under way.

Experimental Section

General Considerations. 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, Et_2O, THF). The reported yields refer to analytically pure substances. Instrumentation: ^1H NMR, ^{13}C NMR, and ROESY, Bruker DRX 600 spectrometer (chemical shifts are relative to TMS); IR, Biorad FTS 60; MS, Finnigan MAT 312; UV/vis, Hewlett-Packard diode array spectrophotometer 8452A; elemental analysis, Heraeus CHN-O-RAPID. Alumina for column chromatography (Al_2O_3 neutral, Fluka) was used without modification.

Preparation of 4 and 5. The colorless solution of 5.00 mmol (1.10 g) of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne[10] in 20 mL of THF was treated at −75 °C with a 5.00 mmol amount of MeLi·LiBr (3.33 mL of a 1.5 M solution in Et_2O) and stirred for 5 h with warming to room temperature. The color of the solution gradually changed from yellow-orange to reddish brown and finally to violet. Additionally, formation of some precipitate was observed. Then, 5.00 mmol (0.90 g) of $(Me_2N)_3CCl$[14] was added and stirring was continued for 18 h at room temperature. The solvent of the resulting green-blue suspension was evaporated in vacuo and the residue extracted with 150 mL of pentane. The extract was filtered through a 10 cm layer of Celite. Removal of pentane afforded a dark brown residue. Then, 30 mL of THF was added at −60 °C and the mixture treated with a 5.00 mmol amount of *n*-BuLi (3.13 mL of a 1.6 M solution in hexane). After this mixture was stirred for 15 min at −60 °C and for 1 h at room temperature, 5.00 mmol of $(CO)_5W[THF]$[15] (50 mL of a 0.1 M solution in THF) was added. The resulting yellow-brown mixture was stirred for 10 min and then treated at −60 °C with 4.00 mmol (0.50 mL) of $BF_3{\cdot}OEt_2$. After addition of the etherate stirring was continued for 10 min at −60 °C and 30 min at room temperature. Then, the red-brown mixture was transferred to the top of a frit filled with a 15 cm layer of Al_2O_3. Elution with ca. 200 mL of THF/CH_2Cl_2 (1:1) gave a red solution. The solvent was evaporated in vacuo, and the residue was chromatographed at room temperature with Et_2O/CH_2Cl_2 (ratio decreasing from 9:1 to 4:6) on neutral Al_2O_3. First a pale yellow band ($W(CO)_6$ and $(CO)_5W[NHMe_2]$) and then a bright yellow band containing **4** (0.13 g, 5% based on $(CO)_5W[THF]$) were eluted. The yellow band was directly followed by a red band, which contained **5** (0.22 g, 7% based on $(CO)_5W[THF]$).

Characterization of 4: yellow powder, mp 135 °C dec. IR (CH_2Cl_2): ν(CO) 2060 w, 1965 vw, 1919 vs, 1886 m cm^{-1}; ν(CCCCC) 2161 and 2145 w br superimposed, 2003 w cm^{-1}. ^1H NMR (CD_2Cl_2, 293 K): δ 3.06 (s, 12H, $=C[N(CH_3)_2]_2$), 3.15 (s br, 6H, $N(CH_3)_2$), 4.45 (s, 1H, =CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 41.5 (br, $N(CH_3)_2$), 42.2 ($=C[N(CH_3)_2]_2$), 87.4 (=CH), 56.0, 92.7, 93.8, 142.9, 149.8 (C_β, C_γ, C_δ, C_ϵ, $=C[N(CH_3)_2]_2$), 170.4 (C_α), 198.3 (*cis*-CO, $J_{WC} = 124.6$ Hz), 201.0 (*trans*-CO). UV/vis (λ_{max}, nm (log ϵ)): 482 (4.074) [toluene]; 464 (4.163) [$CHCl_3$]; 442 (4.163) [CH_2Cl_2]; 436 (4.082) [EtOH]; 416 (4.139) [DMF]. MS (FAB, 3-nitrobenzyl alcohol matrix; *m/z*): 541 [M^+, ^{184}W], isotopic pattern of signal in agreement with theory. Anal. Calcd for $C_{18}H_{19}N_3O_5W$ (541.2): C, 39.95; H, 3.54; N, 7.76. Found: C, 39.83; H, 3.53; N, 7.76.

Characterization of 5: red crystals, mp 135 °C dec. IR (CH_2Cl_2): ν(CO) 2046 m, 1958 vw, 1911 vs, 1871 m cm^{-1}; ν(CC, CCCC) 2150 w sh br, 2136 w br cm^{-1}. ^1H NMR (CD_2Cl_2, 293 K): δ 0.18 (s and d, $^2J_{SiH} = 6.9$ Hz, 9H, $Si(CH_3)_3$), 0.94 (t, 7.2 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.38−1.48 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.51−1.61 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.64−2.71 (m, 2H, $CH_2CH_2CH_2CH_3$), 3.29 (s, 12H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 0.5 ($Si(CH_3)_3$, $J_{SiC} = 55.6$ Hz), 14.3 ($CH_2CH_2CH_2CH_3$), 22.9 ($CH_2CH_2CH_2CH_3$), 32.4 ($CH_2CH_2CH_2CH_3$), 41.6 ($CH_2CH_2CH_2CH_3$), 43.9 ($N(CH_3)_2$), 80.8, 118.1, 118.5, 119.0, 133.2 (C≡C, $C{=}C{=}C{=}C[N(CH_3)_2]_2$), 156.2 ($=C[N(CH_3)_2]_2$), 192.0 (C(carbene), $J_{WC} = 73.0$ Hz), 201.7 (*cis*-CO, $J_{WC} = 127.5$ Hz), 207.2 (*trans*-CO, $J_{WC} = 135.1$ Hz). Anal. Calcd for $C_{23}H_{30}N_2O_5SiW$ (626.4): C, 44.10; H, 4.83; N, 4.47. Found: C, 43.87; H, 4.93; N, 4.60.

Crystal data for 5: $C_{23}H_{30}N_2O_5SiW$, $M_r = 626.4$, monoclinic, space group $P2_1/n$, $a = 12.786(4)$ Å, $b = 15.237(6)$ Å, $c = 13.686(6)$ Å, $\beta = 93.35(3)°$, $V = 2662(2)$ Å^3, $Z = 4$, $d_c = 1.563$ g cm^{-3}, $F(000) = 1240$, $\mu = 4.508$ mm^{-1}, R (R_w) = 0.035 (0.035) for 4197 observed reflections ($F > 4.0\sigma(F)$), largest difference peak/hole +1.12/−0.61 e Å^{-3}. All crystal data were collected on a Siemens R3m/V diffractometer at −36 °C (Wyckoff scan, $4° < 2\theta < 54°$) with a graphite monochromator (Mo Kα, $\lambda = 0.710\,73$ Å). A semiempirical absorption correction was employed (ψ scans with 10 reflections, min/max transmission 0.1888/0.2490). 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. The two central butyl carbon atoms (C(16) and C(17)) are disordered. These were refined in two positions with different occupancy factors each (2:3). Figure 1 shows the major positions.

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Supporting Information Available: Figures giving ROESY spectra of **4** and **6** and tables of crystal data and refinement details, complete positional and thermal parameters, and bond distances and angles for **5** (18 pages). Ordering information is given on any current masthead page.

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