Organometallics **1996,** *15,* 1139−1145

Complexes with Diamino-Substituted Unsaturated C_3 and C_5 Ligands: First Group 6 Pentatetraenylidenes and New Allenylidene Complexes

Gerhard Roth and Helmut Fischer*

Fakultät für Chemie, Universität Konstanz, Postfach 5560 M727, D-78434 Konstanz, Germany

Received October 24, 1995[⊗]

Sequential reaction of $[(CO)_5M(THF)]$ (M = Cr (**1a**), W (**1b**)) with $Li[C{\equiv}CC(NMe_2)_3]$ and $BF_3{\cdot}OEt_2$ afforded the first diaminoallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(NMe_2)_2]$ (M = Cr (**2a**), W (**2b**)). These compounds are inert toward nucleophilic attack of $HNMe_2$ at room temperature. **2b** was characterized by an X-ray structural analysis. Treatment of **1** with the cumulogous acetylide $Li[C{\equiv}CC{\equiv}CC(NMe_2)_3]$ and then with $BF_3{\cdot}OEt_2$ produced the first group 6 pentatetraenylidene complexes, $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ (M = Cr (**3a**), W (**3b**)). The X-ray structural analysis of **3b** reveals a strong alternation of the CC bond lengths within the $(CO)_5MC_5$ unit. Although the compounds **3** are stable at room temperature, they quantitatively add $HNMe_2$ within 30 min to give the alkenyl(amino)allenylidene complexes $[(CO)_5M{=}C{=}C{=}C(NMe_2)C(H){=}C(NMe_2)_2]$ (M = Cr (**4a**), W (**4b**)). Complex **4b** was characterized by an X-ray structural analysis. **4b** is the first example of an open chain metal alkenylallenylidene with an *s-cis* conformation. The complexes **4** are comparable in stability and inertness toward nucleophiles such as amines to the metal diaminoallenylidenes **2**. The spectroscopic data and the X-ray structural analyses of **2b**, **3b**, and **4b** indicate that these heteroatom-substituted compounds are best described as hybrids of metallacumulene and strongly polarized alkynyl structures.

Introduction

Compounds containing unsaturated carbon chains σ-coordinated to transition metals recently 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 like $[ML_nC{\equiv}CXC{\equiv}C]_m$ (X = aryl) can exhibit both liquid crystalline[3] and nonlinear optical[4] properties similar to certain metal acetylides.[5] The catalytic potential of metallacumulenes has only recently been recognized. Ruthenium allenylidene complexes are active intermediates in the catalytic cyclization−reconstitutive addition of propargyl alcohols with allyl alcohols.[6]

Allenylidene complexes which have been known since 1976[7] may be regarded as "cumulogous" carbene complexes.[7a] Consequently, the electronic and geometrical characteristics (e.g. electrophilicity of the metal-bound carbon atom and of C_γ, structural features at the metal and at C_γ) and the guidelines for stabilizing allenylidene complexes should be similar to those of carbene complexes. Indeed, during the early years of metal allenylidene chemistry most substitution patterns known of carbene complexes have been verified. Monoheteroatom-stabilized allenylidene complexes as well as complexes with identical and different carbon substituents at the C_γ atom have been synthesized.[8] However, the first monocarbon-substituted complexes have been made accessible only recently.[9] Until now, diheteroatom-substituted allenylidene complexes have not been reported.[10] However, this type of metal allenylidenes can be expected to exhibit especially interesting physicochemical properties due to the strong dipolar characteristics of these compounds.

Furthermore, analogously substituted pentatetraenylidene complexes, which can be regarded as "cumulogous" allenylidene complexes, should possess even more exciting properties. The introduction of two additional atoms into the carbon chain of the unsaturated ligand provides not only a longer π-system for charge delocalization but also two additional potential reaction centers. Until now, only three pentatetraenylidene com-

---

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

[1] Recent reviews: (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem.* **1993**, *105*, 969; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (b) Lang, H. *Angew. Chem.* **1994**, *106*, 569; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.

[2] Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem.* **1994**, *106*, 1445; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.

[3] Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem.* **1991**, *103*, 370; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

[4] (a) *Inorganic Materials*; Bruce, D. W.; O'Hare, D., Eds.; Wiley: Chichester, U.K., 1992. (b) *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; ACS Symp. Ser. 572; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; American Chemical Society: Washington, DC, 1994.

[5] Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.

[6] Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.

[7] (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem.* **1976**, *88*, 683; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (b) Berke, H. *Angew. Chem.* **1976**, *88*, 684; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624.

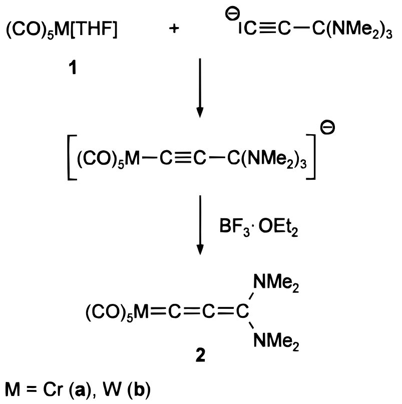
[8] Recent reviews: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39.

[9] Pirio, N.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18.

[10] Only the amino(silyl)allenylidene complexes $(CO)_5Cr{=}C{=}C{=}C(NR_2)SiMe_3$ (R = H, Me) have recently been isolated: Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051.

0276-7333/96/2315-1139$12.00/0

Scheme 1



plexes have been isolated.[11,12] All of them are diaryl-substituted.

Results and Discussion

Synthesis and Properties of the Diaminoallenylidene Complexes 2. The most straightforward route to diamino-substituted allenylidene complexes is first to introduce a complete C_3 skeleton into the coordination sphere of a metal−ligand fragment and then to abstract a preformed leaving group or molecule to form the unsaturated ligand. In the past, this general strategy has been used extensively for the preparation of *carbon*-substituted allenylidene complexes. Mostly propargyl alcohols and derivatives thereof have been employed as sources of the C_3 unit.[8]

This strategy could successfully be applied to the synthesis of diamino-stabilized metal allenylidenes. Pentacarbonyl(tetrahydrofuran)chromium (**1a**) and -tungsten (**1b**) rapidly reacted with deprotonated 3,3,3-tris(dimethylamino)prop-1-yne (Scheme 1). Subsequent abstraction of one dimethylamido group from the metalate intermediates $[(CO)_5MC{\equiv}CC(NMe_2)_3]^-$ (M = Cr, W) with BF_3 etherate directly afforded the bis(dimethylamino)allenylidene complexes **2a**,**b** in 64% and 67% yield, respectively. These were obtained as yellow crystalline compounds which are stable in air at room temperature. In contrast to non- and monoheteroatom-substituted allenylidene complexes[13,14] the compounds **2** did not react with amines by nucleophilic addition. When a solution of **2** and a 6-fold excess of $HNMe_2$ in THF was stirred for 1 week at room temperature, no reaction was detected by IR spectroscopy and by TLC.

From the positions of the E and the A_1(*trans*) ν(CO) absorptions of **2** at very low energy a considerable transfer of electron density from the $C_3(NMe_2)_2$ ligand to the metal can be deduced. These absorptions are similar to those of $[(CO)_5M{=}C{=}C{=}C(NMe_2)Ph]$,[7a] however, at significantly lower energy than those of dialkyl[15] and diarylallenylidene pentacarbonyl[16,17] complexes such as $[(CO)_5M{=}C{=}C{=}CPh_2]$ and $[(CO)_5M{=}C{=}C{=}C(C_6H_4NMe_2)_2]$. This indicates that the π-contribution of the second amino group is almost negligible.

In contrast to the ^{13}C NMR resonance of the metal-bound C_α atom in group 6 diarylallenylidenes at very low field ($\delta > 250$)[16] that of **2** is at rather high field (δ = 185.9 (**2a**), 173.0 (**2b**)). These spectroscopic results indicate that the dipolar resonance structures **B**−**E** (Scheme 2) significantly contribute to the stabilization of **2**.

The data for the X-ray structural analysis of **2b** (Figure 1; Tables 1, 4, and 5) support these conclusions. The CC distances within the MC_3 fragment differ markedly. The $C_\alpha-C_\beta$ bond length in **2b** (C(6)−C(7) = 1.205(11) Å) is one of the shortest ever found for metal allenylidenes. Conversely, the $C_\beta-C_\gamma$ distance (1.386(11) Å) is rather long (e.g. 1.348 Å for $=C{=}CPh_2$ in tetraphenylbutatriene[18]) and corresponds to the C(sp)−C(sp^2) bond in amino-substituted cumulenes like $S{=}C{=}C{=}C(NMePh)_2$ (1.380(3) Å[19a]) or $(NC)_2C{=}C{=}C{=}C(NMe_2)_2$ (1.397(2) Å[19b]). Both, the $C_\alpha-C_\beta$ as well as the $C_\beta-C_\gamma$ bond lengths are comparable to those reported for monoamino-stabilized allenylidene complexes.[7a,14b,20] This indicates that the influence of the "second" amino substituent on the alternation of the bond lengths in the $M-C_\alpha-C_\beta-C_\gamma$ chain is almost negligible. The amino nitrogen atoms in **2b** are planar coordinated (sum of angles at N(1)/N(1a): 359.3°). The C(8)−N bonds are short (1.348(6) Å) and compare well with those usually observed for C(sp^2)−N(sp^2) bonds in conjugated push−pull systems (e.g. 1.334(2) and 1.353(2) Å in $(NC)_2C{=}CHCH{=}C(NMe_2)_2$[19b]) indicating some double-bond character of these C−N bonds and emphasizing the importance of the polar mesomeric structures **D** and **E** (Scheme 2).

Surprisingly, the compounds **2** exhibit only one ^1H NMR resonance for the methyl groups. When a solution of **2b** in [D$_6$]acetone is cooled to −90 °C, there is neither splitting nor broadening of the signal. In contrast, two singlets for the Me substituents are observed for $[(CO)_5M{=}C{=}C{=}C(NMe_2)Ph]$.[7a] Obviously, the replacement of the Ph substituent in $[(CO)_5M{=}C{=}C{=}C(NMe_2)Ph]$ by a "second" NMe_2 group substantially lowers the barrier to rotation around the individual C−N bonds.

As expected from the polar resonance structures **B**−**E** (Scheme 2) the compounds **2** exhibit a significant negative solvatochromic effect. The UV/vis absorption at lowest energy shifts toward shorter wavelengths when unpolar or weakly polar solvents are replaced by more polar ones [e.g. $\Delta\tilde{\nu}$(toluene − DMF) = 2370 (**2a**), 2540 (**2b**) cm^{-1}].

Synthesis and Structure of the Diaminopentatetraenylidene Complexes 3. Interaction of the

---

[11] (a) Péron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497. (b) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.

[12] Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.*, in press.

[13] (a) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133. (b) Fischer, H.; Roth, G. *J. Organomet. Chem.* **1995**, *490*, 229. (c) Roth, G.; Fischer, H. *J. Organomet. Chem.*, in press.

[14] (a) Berke, H.; Huttner, G.; v. Seyerl, J. *Z. Naturforsch.* **1981**, *36b*, 1277. (b) Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556.

[15] (a) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36b*, 929. (b) Berke, H.; Härter, P.; Huttner, G.; v. Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317.

[16] Fischer, H.; Reindl, D.; Roth, G. *Z. Naturforsch.* **1994**, *49b*, 1207.

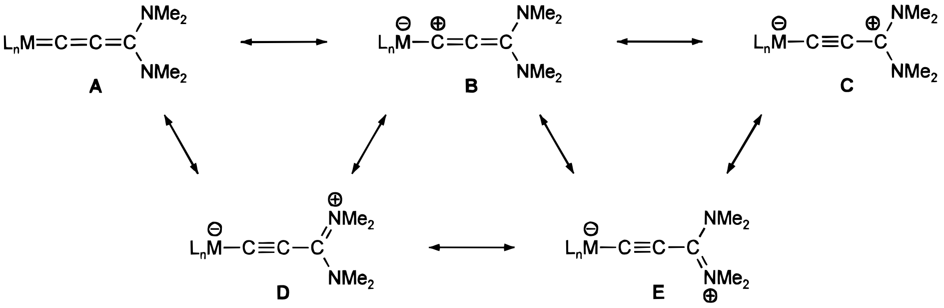
[17] Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 695.

[18] Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* **1975**, *97*, 5627.

[19] (a) Van Meerssche, M.; Germain, G.; Declercq, J. P.; Viehe, H. G.; Parmentier, M. *Acta Crystallogr.* **1977**, *B33*, 3871. (b) Tinant, B.; Declercq, J. P.; Bouvy, D.; Janousek, Z.; Viehe, H. G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 911.

[20] Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 3173.

Scheme 2



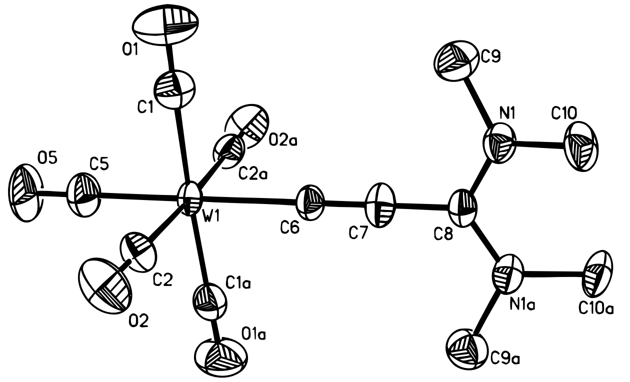


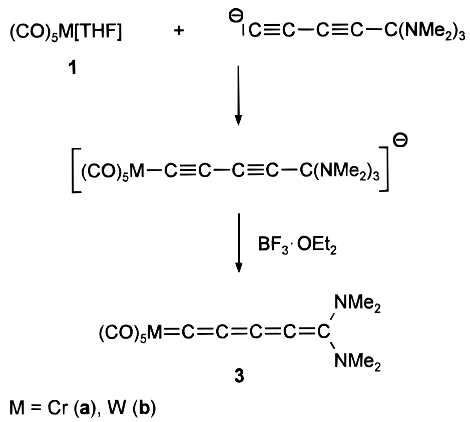
Figure 1. ORTEP plot of complex **2b** (ellipsoids drawn at 50% level, hydrogens omitted).

Table 1. Selected Bond Distances and Angles for 2b

Bond Distances (Å)			
W(1)−C(6)	2.185(8)	C(6)−C(7)	1.205(11)
C(7)−C(8)	1.386(11)	C(8)−N(1)	1.348(6)
N(1)−C(9)	1.468(7)	N(1)−C(10)	1.457(9)
Bond Angles (deg)			
C(7)−C(8)−N(1)	120.2(3)	N(1)−C(8)−N(1a)	119.5(7)
C(8)−N(1)−C(9)	120.1(5)	C(8)−N(1)−C(10)	125.3(5)
C(9)−N(1)−C(10)	113.9(5)		

lone pair at the nitrogen substituents with the MC_3 unit of the allenylidene pentacarbonyl complexes strongly polarizes the molecule and simultaneously enhances the thermal stability of these compounds. This stabilizing effect indicated that amino-substituted pentatetraenylidene pentacarbonyl complexes might also be isolable spezies. Pentatetraenylidene complexes are very rare. Until now, only three isolated examples are known. In 1990 Dixneuf et al. proposed $[(\eta^6\text{-}C_6Me_6)Cl(PMe_3)Ru{=}(C{=})_4CPh_2][PF_6]$ as an intermediate in the reaction of $[(\eta^6\text{-}C_6Me_6)Cl_2(PMe_3)Ru]$ with $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of $MeOH/NaPF_6$.[21] Finally in 1994, they succeeded in the isolation of $[(\eta^6\text{-}C_6Me_6)Cl(PMe_3)Ru{=}(C{=})_4C(C_6H_4NMe_2\text{-}p)_2][PF_6]$[11a] and $[Cl(dppe)_2Ru{=}(C{=})_4CPh_2][PF_6]$.[11b] In addition to these cationic ruthenium complexes, the synthesis of a neutral iridium complex, $[Cl(P^iPr_3)_2Ir{=}(C{=})_4CPh_2)]$,[12] has been reported recently. In each case, the C_5 unit of the pentatetraenylidenes was introduced into the coordination sphere of the metal by employing pentadiynyl ethers or alcohols of the type $R^1C{\equiv}CC{\equiv}CC(Aryl)_2OR^2$. All pentatetraenylidene complexes synthesized so far carry electron-donating coligands (PR_3, $\eta^6\text{-}C_6Me_6$) at the metal center.

Scheme 3



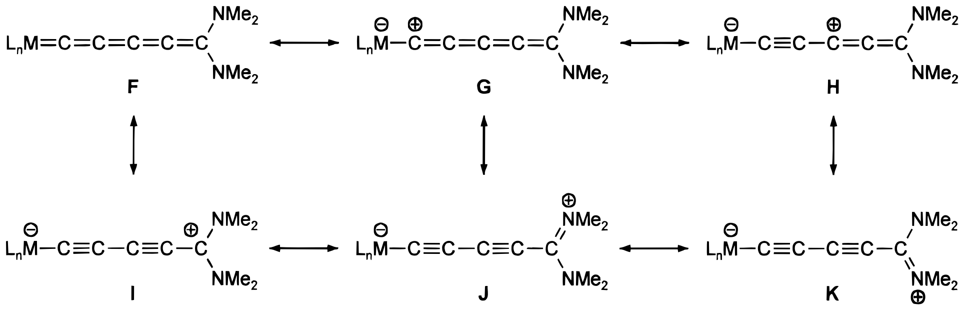
Similarly to the synthesis of the compounds **2**, $[(CO)_5Cr(THF)]$ (**1a**) and $[(CO)_5W(THF)]$ (**1b**) each were treated with lithium 5,5,5-tris(dimethylamino)penta-1,3-diynide generated *in situ* from butyllithium and $Me_3SiC{\equiv}CC{\equiv}CC(NMe_2)_3$ (Scheme 3). Rapid substitution of $[C{\equiv}CC{\equiv}CC(NMe_2)_3]^-$ for THF gave $[(CO)_5MC{\equiv}CC{\equiv}CC(NMe_2)_3]^-$ (M = Cr, W). These metalates were neither isolated nor spectroscopically characterized but immediately treated with $BF_3{\cdot}Et_2O$ to effect abstraction of one dimethylamido group. The resulting complexes **3** were finally obtained, after chromatography and recrystallization, in 36 and 42% yield, respectively. The orange crystalline compounds **3** which are stable in air at room temperature were characterized by spectroscopic means, and **3b** was characterized additionally by an X-ray structural analysis.

Most of the relevant IR and NMR spectroscopic data of **3** are similar to those of the complexes **2**. However, the ^{13}C NMR resonance of the C_α atom is at slightly higher field than that of **2** ($\Delta\delta = 11.8$ (**3a**) and 19.2 (**3b**) ppm). Obviously, insertion of a C_2 fragment into the MC_3 chain only marginally modifies the bonding situation. For **3** essentially six resonance structures (**F**−**K**) (Scheme 4) have to be taken into account. From the spectroscopic data it follows that the strongly dipolar ylidic structures **I**−**K** substantially contribute to the overall bonding situation which is confirmed by the X-ray structural analysis of **3b** (Figure 2; Tables 2, 4, and 6). As with **2b** the amino nitrogen atoms are nearly planar coordinated (sum of angles at N(1)/N(1a): 359.2°); the C(10)−N bonds (1.338(5) Å) are slightly shorter than the C(8)−N bonds in **2b**. In contrast to the published crystal structures of two diphenyl-substituted pentatetraenylidene complexes,[11b,12] the MC_5 chain in **3b** shows a marked alternation in bond lengths. The differences in CC bond lengths in the iridium complex[12] are small; those in the ruthenium compound[11b] are slightly more

---

[21] Romero, A.; Vegas, A.; Dixneuf, P. H. *Angew. Chem.* **1990**, *102*, 210; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 215.

Scheme 4



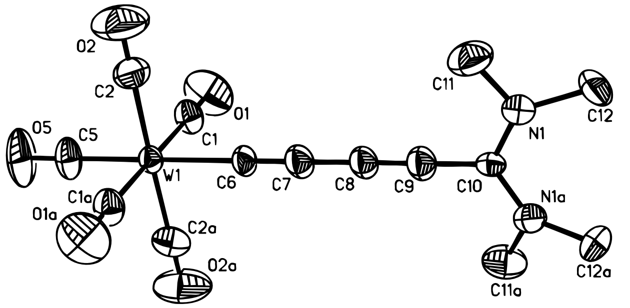


Figure 2. ORTEP plot of complex **3b** (ellipsoids drawn at 50% level, hydrogens omitted).

Table 2. Selected Bond Distances and Angles for 3b

Bond Distances (Å)			
W(1)−C(6)	2.144(6)	C(6)−C(7)	1.223(9)
C(7)−C(8)	1.361(9)	C(8)−C(9)	1.192(9)
C(9)−C(10)	1.399(9)	C(10)−N(1)	1.338(5)
N(1)−C(11)	1.450(6)	N(1)−C(12)	1.470(7)
Bond Angles (deg)			
C(9)−C(10)−N(1)	118.8(3)	N(1)−C(10)−N(1a)	122.4(6)
C(10)−N(1)−C(11)	120.3(4)	C(10)−N(1)−C(12)	123.8(4)
C(11)−N(1)−C(12)	115.1(4)		

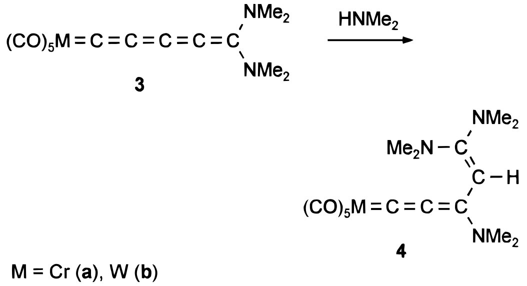
pronounced. However, even a comparison with the ruthenium compound is striking: $C_\alpha-C_\beta = 1.223(9)$ *vs* $1.25(1)$[11b] Å, $C_\beta-C_\gamma = 1.361(9)$ *vs* $1.30(1)$[11b] Å, $C_\gamma-C_\delta = 1.192(9)$ *vs* $1.24(1)$[11b] Å, $C_\delta-C_\epsilon = 1.399(9)$ *vs* $1.36(1)$[11b] Å.

In contrast to **2**, the ^{1}H NMR resonance of the $(NMe_2)_2$ singlet splits into two singlets when a solution of **3b** in [D$_6$]acetone is cooled to −90 °C. From the coalescence of these signals at −83 °C the free energy of activation to rotation around the C(sp^2)−N bond is calculated to be $\Delta G^\ddagger = 40 \pm 1$ kJ/mol. This indicates that the $(CO)_5WC_4$ fragment is a better π-acceptor than the $(CO)_5WC_2$ fragment.

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 positive and negative charge of the dipole. Therefore, a bathochromic shift of the MLCT absorption and an increase in the solvatochromic response is to be expected. These predictions are confirmed by the UV/vis spectra of **3**. Compared to **2** the absorption at lowest energy of **3** is at longer wavelengths ($\Delta\lambda$ depending on the solvent; e.g. for **2a**/**3a**, 52 nm in DMF and 102 nm in toluene) and the solvatochromic effect of **3** is more pronounced than that of **2** [$\Delta\tilde{\nu}$(toluene − DMF) = 3980 (**3a**), 3580 (**3b**) cm^{-1}].

Addition of HNMe$_2$ to the Pentatetraenylidene Complexes 3. On the basis of the various resonance structures (Scheme 4), a nucleophilic attack at $[(CO)_5M{=}C_\alpha{=}C_\beta{=}C_\gamma{=}C_\delta{=}C_\epsilon(NMe_2)_2]$ (**3**) is to be expected at either one or several of three different sites: at the metal-bound C_α, at C_γ, and at the terminal C_ϵ atom. The previously isolated[11b] or intermediary formed[11a,21,22,23] pentatetraenylideneruthenium complexes were found to usually add amines and alcohols across the $C_\gamma-C_\delta$ bond to give "functionalized" allenylidene complexes. Only in one case MeOH was observed to predominantly add across the $C_\alpha-C_\beta$ bond (in addition to $C_\gamma-C_\delta$ addition).[21,23]

Scheme 5



The reactivity of the new compounds **3** is similarly dominated by the electrophilicity of the central carbon atom of the chain (C_γ). Despite the strong π-electron donation of two amino substituents, the metal pentatetraenylidenes **3** quantitatively added $HNMe_2$ in THF at room temperature within 30 min (Scheme 5). Addition of the amine across the $C_\gamma-C_\delta$ bond was observed exclusively. After recrystallization the products, yellow crystalline alkenyl(amino)allenylidene complexes **4a**,**b** were isolated in 96% yield each. IR, ^{1}H NMR, and ^{13}C NMR spectra as well as stability and inertness toward nucleophiles of **4** were comparable to those of the diaminoallenylidene complexes **2**. When solutions of **4** in THF were treated with a 6-fold excess of $HNMe_2$ for 2 weeks at room temperature addition of further $HNMe_2$ was not observed.

Structural Properties of the Alkenylallenylidene Complexes 4. The X-ray structural analysis of **4b** (Figure 3; Tables 3, 4, and 7) reveals an unusual *s-cis* conformation in the crystalline state. π-interaction between the $(CO)_5WC_\alpha C_\beta C_\gamma$ fragment and both substituents at the C_γ atom (the amino group N(1), C(11), C(12) and the (dimethylamino)alkenyl substituent) is indicated (a) by the short $C_\alpha-C_\beta$ and the long $C_\beta-C_\gamma$ bond

---

(22) (a) Romero, A.; Péron, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1410. (b) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. . *J. Chem. Soc., Chem. Commun.* **1991**, 980. (c) Wolinska, A.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1991**, *420*, 217. (d) Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem.* **1992**, *104*, 664; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 651.

(23) Péron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319.

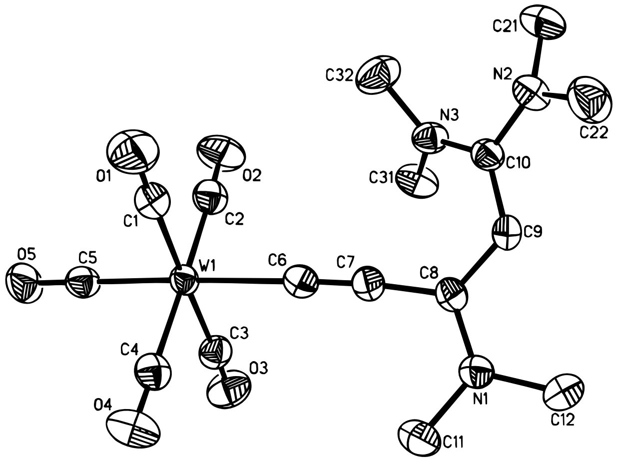


Figure 3. ORTEP plot of complex **4b** (ellipsoids drawn at 50% level, hydrogens omitted).

Table 3. Selected Bond Distances and Angles for 4b

Bond Distances (Å)			
W(1)−C(6)	2.178(5)	C(6)−C(7)	1.216(7)
C(7)−C(8)	1.427(6)	C(8)−N(1)	1.360(6)
N(1)−C(11)	1.440(7)	N(1)−C(12)	1.450(7)
C(8)−C(9)	1.393(7)	C(9)−C(10)	1.407(7)
C(10)−N(2)	1.350(6)	C(10)−N(3)	1.351(6)
N(2)−C(21)	1.451(7)	N(2)−C(22)	1.468(7)
N(3)−C(31)	1.461(6)	N(3)−C(32)	1.449(7)
Bond Angles (deg)			
W(1)−C(6)−C(7)	178.8(4)	C(6)−C(7)−C(8)	172.8(5)
C(7)−C(8)−N(1)	116.0(4)	C(8)−N(1)−C(11)	122.5(4)
C(8)−N(1)−C(12)	120.8(4)	C(11)−N(1)−C(12)	115.8(4)
C(7)−C(8)−C(9)	123.1(4)	C(8)−C(9)−C(10)	125.4(4)
N(1)−C(8)−C(9)	120.9(4)	C(9)−C(10)−N(2)	119.9(4)
C(9)−C(10)−N(3)	123.3(4)	N(2)−C(10)−N(3)	116.8(4)
C(10)−N(2)−C(21)	122.3(4)	C(10)−N(2)−C(22)	121.1(4)
C(21)−N(2)−C(22)	115.0(4)	C(10)−N(3)−C(31)	122.6(4)
C(10)−N(3)−C(32)	121.8(4)	C(31)−N(3)−C(32)	115.6(4)

Table 4. Crystallographic Data for 2b, 3b, and 4b

	compound		
	2b	**3b**	**4b**
empirical formula	$C_{12}H_{12}N_2O_5W$	$C_{14}H_{12}N_2O_5W$	$C_{16}H_{19}N_3O_5W$
fw	448.1	472.1	517.2
cryst size, mm^3	0.3 × 0.3 × 0.3	0.5 × 0.5 × 0.5	0.3 × 0.3 × 0.3
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/n$
a, Å	13.125(7)	12.464(3)	13.146(3)
b, Å	13.008(7)	15.427(4)	9.754(2)
c, Å	9.926(6)	10.352(3)	14.698(3)
β, deg	119.44(4)	122.75(2)	96.23(2)
V, Å^3	1475.9(14)	1674.0(9)	1873.4(7)
Z	4	4	4
d_{calcd}, g cm^{-3}	2.017	1.873	1.834
temp, K	246	243	246
μ, mm^{-1}	8.013	7.069	6.326
min/max transm	0.1705/0.2359	0.1857/0.2294	0.0744/0.1182
indepdt reflns	1615	1832	4093
obsd reflns ($F > 4\sigma(F)$)	1525	1718	3336
params refined	94	104	226
R	0.032	0.025	0.027
R_w	0.039	0.029	0.029
largest diff peak/hole, e Å^{-3}	+0.99/−3.07	+1.19/−1.64	+0.67/−0.81

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for 2b

atom	x/a	y/b	z/c	U(eq)[a]
W(1)	0	0.3518(1)	0.2500	0.028(1)
C(1)	−0.1148(6)	0.3478(5)	0.0179(9)	0.043(3)
O(1)	−0.1784(6)	0.3452(5)	−0.1122(7)	0.075(3)
C(2)	0.1343(6)	0.3564(4)	0.2010(8)	0.038(3)
O(2)	0.2094(6)	0.3619(4)	0.1754(8)	0.064(3)
C(5)	0	0.5066(8)	0.2500	0.050(5)
O(5)	0	0.5946(5)	0.2500	0.076(5)
C(6)	0	0.1839(6)	0.2500	0.031(3)
C(7)	0	0.0912(6)	0.2500	0.038(4)
C(8)	0	−0.0154(6)	0.2500	0.031(3)
N(1)	−0.0680(5)	−0.0676(3)	0.1185(6)	0.034(2)
C(9)	−0.1632(6)	−0.0146(6)	−0.0146(8)	0.049(3)
C(10)	−0.0456(7)	−0.1714(5)	0.0845(8)	0.045(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for 3b

atom	x/a	y/b	z/c	U(eq)[a]
W(1)	0	0.1132(1)	0.2500	0.031(1)
C(1)	0.1551(5)	0.1138(3)	0.2351(7)	0.047(2)
O(1)	0.2411(6)	0.1136(4)	0.2222(9)	0.103(4)
C(2)	−0.1139(6)	0.1150(4)	0.0178(6)	0.055(3)
O(2)	−0.1795(6)	0.1163(4)	−0.1125(5)	0.106(3)
C(5)	0	−0.0149(5)	0.2500	0.054(4)
O(5)	0	−0.0914(4)	0.2500	0.096(6)
C(6)	0	0.2522(4)	0.2500	0.038(3)
C(7)	0	0.3315(4)	0.2500	0.047(3)
C(8)	0	0.4198(4)	0.2500	0.042(3)
C(9)	0	0.4970(4)	0.2500	0.044(3)
C(10)	0	0.5877(4)	0.2500	0.030(2)
N(1)	−0.0643(4)	0.6295(2)	0.1154(4)	0.039(2)
C(11)	−0.1586(6)	0.5841(5)	−0.0229(6)	0.064(3)
C(12)	−0.0312(6)	0.7167(3)	0.0908(7)	0.061(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 7. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for 4b

atom	x/a	y/b	z/c	U(eq)[a]
W(1)	0.1154(1)	0.0286(1)	0.2199(1)	0.030(1)
C(1)	0.0093(4)	0.0851(6)	0.1162(3)	0.041(2)
O(1)	−0.0504(3)	0.1179(5)	0.0585(3)	0.067(2)
C(2)	0.1002(4)	0.2171(6)	0.2767(4)	0.043(2)
O(2)	0.0932(3)	0.3249(4)	0.3055(3)	0.064(2)
C(3)	0.2223(4)	−0.0278(5)	0.3271(3)	0.039(1)
O(3)	0.2825(3)	−0.0586(4)	0.3833(3)	0.059(1)
C(4)	0.1327(3)	−0.1575(6)	0.1604(3)	0.037(2)
O(4)	0.1446(3)	−0.2617(4)	0.1280(3)	0.058(1)
C(5)	0.2289(3)	0.0986(5)	0.1528(3)	0.038(2)
O(5)	0.2933(3)	0.1378(4)	0.1116(3)	0.059(1)
C(6)	−0.0070(3)	−0.0551(5)	0.2918(3)	0.033(1)
C(7)	−0.0741(3)	−0.1037(5)	0.3327(3)	0.033(1)
C(8)	−0.1428(3)	−0.1680(5)	0.3882(3)	0.030(1)
C(9)	−0.2261(3)	−0.1006(5)	0.4188(3)	0.036(2)
C(10)	−0.2523(3)	0.0376(5)	0.4016(3)	0.032(1)
N(1)	−0.1237(3)	−0.3020(4)	0.4091(3)	0.037(1)
C(11)	−0.0510(4)	−0.3823(6)	0.3653(4)	0.048(2)
C(12)	−0.1888(5)	−0.3778(6)	0.4648(4)	0.056(2)
N(2)	−0.3515(3)	0.0759(4)	0.3920(3)	0.039(1)
C(21)	−0.3843(4)	0.2105(6)	0.4189(4)	0.053(2)
C(22)	−0.4338(4)	−0.0256(6)	0.3748(4)	0.055(2)
N(3)	−0.1823(3)	0.1376(4)	0.3955(3)	0.036(1)
C(31)	−0.0861(4)	0.1433(6)	0.4555(3)	0.046(2)
C(32)	−0.1963(4)	0.2437(6)	0.3263(4)	0.058(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

and (b) by the short distances between C_γ and its nitrogen substituents. The allenylidene plane formed by the atoms C(7), C(8), N(1), and C(9) and the alkenyl moiety of **4b** are almost coplanar (torsion angle C(7)−C(8)−C(9)−C(10) = 1.6(7)°). The single bond C(8)−C(9) (1.393(7) Å) is unusually short compared to a conjugated C(sp^2)−C(sp^2) single bond (1.455 Å[24]) and rather resembles that found for push−pull systems like $(NC)_2C{=}CHCH{=}C(NMe_2)_2$ (1.366(2) Å[19b]). The double bond C(9)−C(10) (1.407(7) Å) is very long compared to a conjugated C(sp^2)=C(sp^2) double bond (1.330 Å[24]) and is comparable to that of organic push−pull systems (e.g. 1.416(2) Å in $(NC)_2C{=}CHCH{=}C(NMe_2)_2$[19b]). These distances support the conclusion of a strong mesomeric interaction between the (dimethylamino)alkenyl substituent and C_γ. All nitrogen atoms are nearly planar coordinated (sum of angles: at N(1), 359.1°; at N(2), 358.4°; at N(3), 360.0°). Within error limits all $C(sp^2){-}N$ distances are equal in length. The CC bond lengths within the almost linear W−C(6)−C(7)−C(8) chain (W(1)−C(6)−C(7) = 178.8(4)°, C(6)−C(7)−C(8) = 172.8(5)°) of **4b** strongly alternate (C(6)−C(7) = 1.216(7) Å, C(7)−C(8) = 1.427(6) Å) and resemble those found in **2b**. Thus, comparable to **2b** dipolar resonance structures considerably contribute to the stabilization of **4b** and explain the inertness of the compounds **4** toward $HNMe_2$ addition analogous to the complexes **2** but in contrast to "simple" monoamino-substituted allenylidenes.[14b]

Concluding Remarks

These results demonstrate that $L_nM{=}C{=}C{=}C{=}C{=}CR_2$ complexes with electron-poor group 6 metal−ligand fragments instead of L_nM moieties with electron-donating ligands L are isolable compounds. Despite their astonishing stability, the reactivity of the new complexes $[(CO)_5M{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ is comparable to that of already known more labile (and mostly not isolable) pentatetraenylidene complexes. Insertion of a C_2 unit into the MC_3 chain of the diaminoallenylidene complexes $[(CO)_5M{=}C{=}C{=}C(NMe_2)_2]$ reduces the stability of the compounds only to a minor degree (if at all). This fact supports the assumption that pentacarbonyl complexes with even longer carbon chains might also be stable und isolable species. Efforts to prepare examples are in progress. The facile polarizability of the new complexes with linear unsaturated carbon ligands indicates interesting physicochemical properties. Investigations to determine the second-order nonlinear optical properties response are presently under way.

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, Et_2O, THF). The reported yields refer to analytically pure substances. Melting points are uncorrected. Instrumentation: ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC 250, Bruker WM 250, and Jeol JNX400 spectrometers. Chemical shifts are relative to TMS. Other analyses: IR, Biorad FTS 60; MS, Finnigan MAT 312; elemental analysis, Heraeus CHN-O-RAPID. Alumina used for column chromatography (Al_2O_3 neutral, Fluka) was used without modification.

Preparation of Complexes 2: A 5.00 mmol amount of *n*-BuLi (3.13 mL of a 1.6 M solution in hexane) was added at −80 °C to a solution of 5.00 mmol (0.85 g) of $HC{\equiv}CC(NMe_2)_3$[25] in 30 mL of THF. After the mixture was stirred for 5 min at −80 °C and then for 30 min at room temperature 5.00 mmol (50 mL of a 0.1 M solution in THF[16]) of $[(CO)_5M(THF)]$ (**1**) was added. Within 30 min the light orange solution turned brown. A 5.00 mmol (0.62 mL) amount of $BF_3{\cdot}OEt_2$ was added. The color of the solution changed immediately to dark red. After 20 min the solution 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 an orange-yellow solution. The solvent was evaporated in vacuo, and the residue was chromatographed at room temperature with THF/CH_2Cl_2 (9:1) on neutral Al_2O_3. First a short pale yellow band ($M(CO)_6$) and then the light orange solution containing **2** were eluted.

(3,3-Bis(dimethylamino)-1,2-propadienylidene)(pentacarbonyl)chromium (2a): 1.02 g (64% based on **1a**) of yellow crystals from pentane/CH_2Cl_2 (3:2), mp 157 °C, dec. IR (THF): ν(CO) 2078 w, 1929 vs, 1903 m; ν(CCC) 2014 m cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 3.21 (s, NMe_2). $^{13}C\{^1H\}$ NMR ([D_6]acetone, 293 K): δ 42.9 (NMe_2); 106.5 (C_β); 151.7 (C_γ); 185.9 (C_α); 219.5 (*cis*-CO); 223.3 (*trans*-CO). UV/vis: λ_{max} (log ϵ) 408 (4.208) [toluene]; 394 (4.164) [CH_2Cl_2]; 390 (4.111) [EtOH]; 372 (4.072) [DMF]. MS (70 eV) [*m/z* (%)]: 316 (8) [M^+], 204 (15) [$(M - 4CO)^+$], 176 (100) [$(M - 5CO)^+$], 117 (16) [$(CrCCCNMe)^+$]. Anal. Calcd for $C_{12}H_{12}CrN_2O_5$ (316.2): C, 45.58; H, 3.82; N, 8.86. Found: C, 45.46; H, 3.84; N, 8.84.

(3,3-Bis(dimethylamino)-1,2-propadienylidene)(pentacarbonyl)tungsten (2b): 1.51 g (67% based on **1b**) of yellow crystals from pentane/CH_2Cl_2 (7:6), mp 160 °C, dec. IR (THF): ν(CO) 2082 vw, 1923 vs, 1897 m; ν(CCC) 2018 m cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 3.21 (s, NMe_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 42.9 (NMe_2); 105.0 (C_β, $^2J_{(W,C)} = 24.7$ Hz); 152.4 (C_γ, $^3J_{(W,C)}$ not found); 173.0 (C_α, $^1J_{(W,C)} = 101.1$ Hz); 197.9 (*cis*-CO, $^1J_{(W,C)} = 124.7$ Hz); 202.3 (*trans*-CO, $^1J_{(W,C)} = 133.2$ Hz). UV/vis: λ_{max} (log ϵ) 406 (4.091) [toluene]; 394 (4.155) [CH_2Cl_2]; 388 (4.096) [EtOH]; 368 (4.089) [DMF]. MS (70 eV) [*m/z* (%)]: 448 (32) [M^+], 420 (23) [$(M - CO)^+$], 392 (46) [$(M - 2CO)^+$], 336 (36) [$(M - 4CO)^+$], 308 (100) [$(M - 5CO)^+$], 249 (28) [$(WCCCNMe)^+$]. Anal. Calcd for $C_{12}H_{12}N_2O_5W$ (448.1): C, 32.17; H, 2.70; N, 6.25. Found: C, 32.21; H, 2.79; N, 6.16.

Preparation of Complexes 3. At −80 °C 5.00 mmol of $MeLi{\cdot}LiBr$ (3.33 mL of a 1.5 M solution in Et_2O) was added to a solution of 5.00 mmol (0.97 g) of $Me_3SiCCCCSiMe_3$[26] in 20 mL of THF. The mixture was warmed to 15 °C within 5 h and then stirred for 1 h at room temperature. A 5.00 mmol (0.90 g) amount of $(Me_2N)_3CCl$[27] was added, and stirring was continued for 18 h. The solvent was evaporated in vacuo. The residue was extracted with 100 mL of pentane. Removal of the pentane in vacuo afforded a slightly colored mass which was dissolved in 30 mL of THF. The solution was cooled to −60 °C, and 5.00 mmol of *n*-BuLi (3.13 mL of a 1.6 M solution in hexane) was added. After the solution was stirred for 30 min at −60 °C and an additional 1 h at room temperature, 5.00 mmol of $[(CO)_5M(THF)]$ (50 mL of a 0.1 M solution in THF[16]) was added. Within 20 min the resulting light orange solution turned brown. When 5.00 mmol (0.62 mL) of $BF_3{\cdot}OEt_2$ was added, the color of the solution immediately changed to dark red. After 20 min the solution was transferred to the top of a frit filled with a 15-cm layer of Al_2O_3. Elution with ca. 300 mL of THF/CH_2Cl_2 (1:1) gave a red-orange solution. The solvent was evaporated in vacuo. The residue was chromatographed at room temperature with THF/CH_2Cl_2 (8:2) on neutral Al_2O_3. First a short pale yellow ($M(CO)_6$) and then a red-orange band containing **3** were eluted.

(5,5-Bis(dimethylamino)-1,2,3,4-pentatetraenylidene)(pentacarbonyl)chromium (3a): 0.71 g (42% based on **1a**) of orange crystals from pentane/CH_2Cl_2 (2:5), mp 120 °C, dec. IR (THF): ν(CO) 2052 w, 1972 vw, 1930 vs, 1902 m; ν(CCCCC) 2140 w br, 1998 w cm^{-1}. ^1H NMR ([D_6]acetone, 293 K): δ 3.35 (s, NMe_2). $^{13}C\{^1H\}$ NMR ([D_6]acetone, 293 K): δ 43.4 (NMe_2); 49.6, 95.7, 99.5 (C_β, C_γ, C_δ); 155.0 ($={C}(NMe_2)_2$); 174.1 (C_α); 219.2 (*cis*-CO); 221.8 (*trans*-CO). UV/vis: λ_{max} (log ϵ) 510 (4.238) [toluene]; 474 (4.262) [CH_2Cl_2]; 456 (4.260) [EtOH]; 424 (4.230) [DMF]. Anal. Calcd for $C_{14}H_{12}CrN_2O_5$ (340.3): C, 49.42; H, 3.55; N, 8.23. Found: C, 49.43; H, 3.63; N, 8.16.

(5,5-Bis(dimethylamino)-1,2,3,4-pentatetraenylidene)(pentacarbonyl)tungsten (3b): 0.86 g (36% based on **1b**) of

---

[24] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[25] Kantlehner, W.; Speh, P.; Lehmann, H.; Bräuner, H.-J.; Haug, E.; Mergen, W. W. *Chem.-Ztg.* **1990**, *114*, 176.

[26] Corey, E. J.; Albright, J. O. *J. Org. Chem.* **1983**, *48*, 2114.

[27] Kantlehner, W.; Haug, E.; Mergen, W. W. *Synthesis* **1983**, 904.

orange crystals from pentane/CH_2Cl_2 (2:5), mp 150 °C, dec. IR (THF): ν(CO) 2058 w, 1964 vw, 1925 vs, 1896 m; ν(CCCCC) 2140 w br, 1999 w cm^{-1}. ^{1}H NMR ([D$_6$]acetone, 293 K): δ 3.36 (s, NMe_2) [2 s at 183 K: δ 3.34, 3.42]. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 293 K): δ 43.5 (NMe_2); 52.1, 99.5 (C_γ, C_δ); 94.6 (C_β, $^2J_{(W,C)}$ = 25.6 Hz); 153.8 (C_α, $^1J_{(W,C)}$ = 102.6 Hz); 154.8 (=*C*(NMe_2)$_2$); 198.3 (*cis*-CO, $^1J_{(W,C)}$ = 124.6 Hz); 200.7 (*trans*-CO, $^1J_{(W,C)}$ = 133.1 Hz). UV/vis: λ_{max} (log ϵ) 500 (4.342) [toluene]; 466 (4.338) [CH_2Cl_2]; 450 (4.229) [EtOH]; 424 (4.159) [DMF]. Anal. Calcd for $C_{14}H_{12}N_2O_5W$ (472.1): C, 35.62; H, 2.56; N, 5.93. Found: C, 35.68; H, 2.61; N, 5.92.

Preparation of Complexes 4. A solution of 1.00 mmol (0.34 g of **3a**, 0.47 g of **3b**) of the pentatetraenylidene complexes **3** and of 2.00 mmol (0.25 mL of a 40% aqueous solution) of $HNMe_2$ in 30 mL of THF was stirred at room temperature. The color of the reaction mixture changed from red-orange to yellow. After 30 min the reaction was complete as indicated by IR spectroscopy and TLC. The formation of complexes apart from **4** could not be detected. Removal of the solvent at room temperature in vacuo and recrystallization of the residue afforded **4a**,**b** each as yellow crystals.

[3-[2′,2′-Bis(dimethylamino)ethenyl]-3-(dimethylamino)-1,2-propadienylidene](pentacarbonyl)chromium (4a): 0.74 g (96% based on **3a**) of yellow crystals from pentane/CH_2Cl_2 (7:3), mp 135−138 °C. IR (Et_2O): ν(CO) 2075 w, 1923 vs, 1898 m; ν(CCC) 2020 m cm^{-1}. ^{1}H NMR ([D$_6$]acetone, 293 K): δ 3.09 (s, 12 H, =C(NMe_2)$_2$); 3.23 (br s, 6 H, C_γ-NMe_2); 4.45 (s, 1 H, =CH). ^{13}C{^{1}H} NMR ([D$_6$]acetone, 293 K): δ 40.8 (br, C_γ-N*Me$_2$*); 41.8 (=C(N*Me$_2$*)$_2$); 84.2 (=CH); 110.6 (C_β); 150.1, 162.4 (=*C*(NMe_2)$_2$, C_γ); 170.9 (C_α); 220.5 (*cis*-CO); 223.8 (*trans*-CO). Anal. Calcd for $C_{16}H_{19}CrN_3O_5$ (385.3): C, 49.87; H, 4.97; N, 10.90. Found: C, 49.55; H, 4.91; N, 10.71.

[3-[2′,2′-Bis(dimethylamino)ethenyl]-3-(dimethylamino)-1,2-propadienylidene](pentacarbonyl)tungsten (4b): 0.99 g (96% based on **3b**) of yellow crystals from pentane/CH_2Cl_2 (5:3), mp 144−145 °C. IR (Et_2O): ν(CO) 2079 w, 1918 vs, 1894 m; ν(CCC) 2025 m cm^{-1}. ^{1}H NMR (CD_2Cl_2, 293 K): δ 3.03 (s, 12 H, =C(NMe_2)$_2$); 3.19 (br s, 6 H, C_γ-NMe_2); 4.27 (s, 1 H, =CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): δ 40.9 (br, C_γ-N*Me$_2$*); 41.9 (=C(N*Me$_2$*)$_2$); 84.1 (=CH); 108.3 (C_β); 148.3, 150.1 (=*C*(NMe_2)$_2$, C_γ); 170.3 (C_α); 198.9 (*cis*-CO, $^1J_{(W,C)}$ = 123.1 Hz); 202.7 (*trans*-CO, $^1J_{(W,C)}$ not found). Anal. Calcd for $C_{16}H_{19}N_3O_5W$ (517.2): C, 37.16; H, 3.70; N, 8.12. Found: C, 37.25; H, 3.73; N, 8.08.

X-ray Structural Analyses of 2b, 3b, and 4b. Single crystals were grown from pentane/CH_2Cl_2 and mounted in a glass capillary. All crystal data were collected on a Siemens R3m/V diffractometer (Wyckoff scan, $4° < 2\theta < 54°$) with graphite monochromator (Mo Kα, λ = 0.710 73 Å). Semiempirical absorption corrections were employed (ψ-scans with 10 reflections). The structures were solved with Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS). The structures of **2b** and **3b** can also be solved in space group *Cc*, but refinement diverges at an early stage. In the unit cell of **2b** and **3b** the molecules lie on symmetry axes. The comparably big largest difference hole (−3.07 eÅ^{-3}) in the structure of **2b** has its position near the heavy atom and may be explained with an imperfect absorption correction.

Acknowledgment. Support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. Dr. W. Kantlehner, Universität Stuttgart, for authentic samples of HC≡CC(NMe_2)$_3$[25] and (Me_2N)$_3$CCl.[27]

Supporting Information Available: Tables of crystal data and refinement details, complete positional and thermal parameters, and bond distances and angles for compounds **2b**, **3b**, and **4b** (20 pages). Ordering information is given on any current masthead page.

OM950845X