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Bimetallic Complexes with Conjugated C_4, C_6, C_{10}, and C_{14} Bridges: Synthetic Routes to Alkynediyl-Bridged Bis(carbene) Complexes[†]

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The reaction of $[(CO)_5W{=}C(Ph)H]$ with $Me_2NC{\equiv}CNMe_2$ affords two complexes: the binuclear complex $[(CO)_5W{=}C(NMe_2)(Me_2N)C{=}W(CO)_5]$ (**2**) and the insertion product $[(CO)_5W{=}C(NMe_2)C(NMe_2){=}C(Ph)H]$ (**3**). Sequential reaction of the (dimethylamino)ethynylcarbene complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CH]$ (**4a**) with *n*BuLi, $W(CO)_6$, and F_3CSO_3Me yields the new ethynediyl-bridged binuclear alkoxycarbene−aminocarbene complex $[(CO)_5W{=}C(NMe_2)C{\equiv}C(MeO)C{=}W(CO)_5]$ (**5**). Treatment of **4a** and of $[(CO)_5Cr{=}C(NMe_2)C{\equiv}CH]$ (**4b**) with *n*BuLi and iodine gives the new iodine-substituted complexes $[(CO)_5M{=}C(NMe_2)C{\equiv}CI]$ (M = W (**6a**), M = Cr (**6b**)). By Pd-catalyzed coupling of **6a**,**b** with the C-stannylated ethynylcarbene complexes $[(CO)_5M{=}C(NMe_2)C{\equiv}CSn(nBu)_3]$ (**7a**,**b**) the butadiynediyl-bridged bis(carbene) complexes $[(CO)_5M{=}C(NMe_2)(C{\equiv}C)_2(Me_2N)C{=}M(CO)_5]$ (**8a**,**b**) are obtained. Analogously, from $[(CO)_5W{=}C(NMe_2)(C{\equiv}C)_xH]$ ($x = 2, 3$) and *n*BuLi/I_2 amino(iodobutadiynyl)carbene and amino(iodohexatriynyl)carbene complexes $[(CO)_5W{=}C(NMe_2)(C{\equiv}C)_xI]$ (x = 2 (**10**), 3 (**14**)) are obtained. Pd-catalyzed coupling with the corresponding C-stannylated alkynylcarbene complexes finally affords the binuclear $C_{10}(NMe_2)_2$- and $C_{14}(NMe_2)_2$-bridged complexes $[(CO)_5W{=}C(NMe_2)(C{\equiv}C)_x(Me_2N)C{=}W(CO)_5]$ (x = 4 (**12**), 6 (**16**)). All alkynediyl-bridged bis(carbene) complexes are stable at room temperature. The spectroscopic data of **5** indicate that it is best described as a hybrid of a dipolar allenyl-type compound and an alkynylcarbene complex. In contrast, the $C{\equiv}C$ units in the binuclear complexes **8a**,**b**, **12**, and **16** are essentially localized.

Introduction

Electronic communication between metal centers in bi- and polynuclear complexes can be mediated in different ways.[1] Various types of bridging ligands have been proposed. In recent years attention has focused on carbon-rich bridges.[2] Bi- and polynuclear transition-metal complexes containing unsaturated conjugated carbon bridges are expected to exhibit potentially useful physical and chemical properties such as liquid crystalline properties[3] and second-order or third-order nonlinear optical properties.[4]

For C_n (carbon-only) bridges several structural motifs are conceivable and have been realized (Chart 1, **A**−**D**).

Binuclear complexes of types **A** and **B**/**C** with various lengths of the carbon chain C_x (x up to 20)[5] have been prepared.[2] In addition, linear polynuclear complexes with all-carbon units linking the metals[6] as well as linear[7] and L-shaped trinuclear[8] and cyclic tetra- and octanuclear butadiynediyl complexes[9] have been reported. Rigid-rod organometallic polymers $(-L_nMC_x-)_y$ have also been studied theoretically by extended-Hückel MO calculations.[10] Only very few complexes of structural type **D** are known. Schrock et al. reported on $[(tBuO)_3W{\equiv}CC{\equiv}W(OtBu)_3]$,[11] and Templeton et al. recently synthesized $[Tp'(CO)_2M{\equiv}C{-}C{\equiv}W(CO)(PhC{\equiv}CPh)Tp]$ (M = Mo, W).[12]

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[†] Dedicated to Prof. Helmut Werner on the occasion of his 65th birthday.

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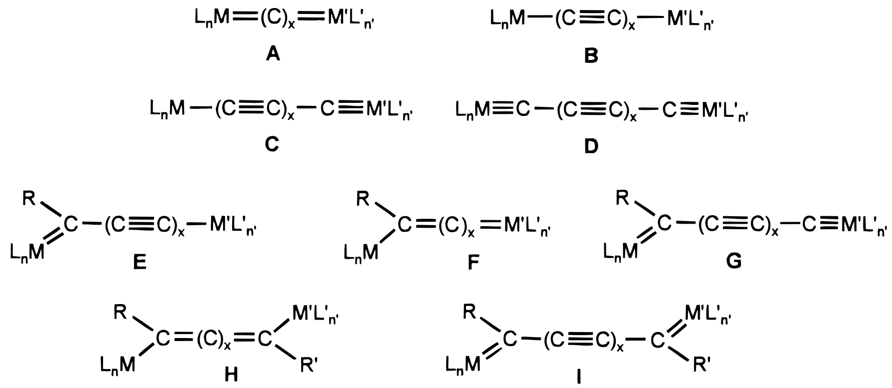
Chart 1



A feature common to all of these complexes is the M−C(sp) linkage of the bridge to both L_nM fragments. Binuclear complexes with an M−C(sp^2) and an M−C(sp) linkage are likewise known. Several structural alternatives are possible (Chart 1, **E**−**G**). Three different routes to complexes of type **E** have been developed recently. Gladysz et al. synthesized several heterobimetallic complexes by reaction of $[Cp^*(NO)(PPh_3)Re(C\equiv C)_x]^-$ with $[Mn(CO)_3Cp]$, $[Fe(CO)_5]$, $[W(CO)_6]$, or $[Re_2(CO)_{10}]$ and subsequent alkylation of the resulting metalate with $[Me_3O]BF_4$.[2d,13] Other approaches are the substitution of alkynylcarbene anions for the halide in metal halides and the Pd-catalyzed coupling of C-stannylated carbene complexes with $[XML_n]$. Recently, we reported the synthesis of a series of heterobinuclear complexes $[(CO)_5M{=}C(NR_2)(C\equiv C)_xM'L'_n]$ (M = Cr, W; NR_2 = NMe_2, NHMe; $x = 1-3$; M′ = Sn, Mn, Re, Fe, Ru, Rh, Ni, Pd) by the latter methods.[14,15] “Linear” trinuclear (M′ = Fe, Ni, Pd, Pt, Hg),[15,16] L-shaped (M′ = Ti) trinuclear,[16] and star-shaped tetra- (M′ = B, P)[16] and pentanuclear complexes (M′ = Ge, Sn)[16] were also accessible. Complexes of type **F** (R = H; $x = 1$) have also been studied.[17] For $L_nM = M'L'_n$ (= $Fe(CO)_2Cp^*$) a dynamic process was observed which equilibrates the two metal centers. To the best of our knowledge, complexes of type **G** are unknown.

Two types of homo- and heterobinuclear complexes with a $C(R)(C)_xC(R)$ bridge (two terminal M−C(sp^2) bonds) are conceivable (Chart 1, **H** and **I**). Complexes of type **H** have been known for a long time. The first one ($x = 0$), $[(CN)_5CoC(COOMe){=}C(COOMe)Co(CN)_5]^{6-}$, was already prepared in 1967.[18] Since then several others have been synthesized.[1b,2a] Only two complexes of type **I** have been reported until now. Both compounds, $[(CO)_5M{=}C(NEt_2)(Et_2N)C{=}M(CO)_5]$ (M = Cr,[19] W[20]), were obtained by reductive dimerization of the cationic carbyne complexes $[(CO)_5M\equiv CNEt_2]BF_4$. However, several complexes with unsaturated cyclic π-conjugated carbon bridges linking two metal−carbene fragments $L_nM{=}C(R)$ are known. These include phenyl-,[21,22] biphenyl-,[23] binaphthyl-,[22] anthracenyl-,[24] or 1.6-methanol-[10]annulen-2,7-diyl-bridged[25] symmetrical bis(carbene) complexes as well as derivatives with an ammonium pentadienide bridge.[26] Symmetrical bis(carbene) complexes with a noncyclic alkenyl bridge are scarce.[27] Carbon-only bridged bis(carbene) complexes are unknown.

We now report on a new route to binuclear bis(carbene) complexes, on the synthesis of the first amino(iodoalkynyl)carbene complexes, and on the synthesis and properties of the first series of homobinuclear bis(carbene) complexes of the type $[(CO)_5W{=}C(NMe_2)(C\equiv C)_x(Me_2N)C{=}W(CO)_5]$ (x = 0, 2, 4, 6).

Results and Discussion

The first member of the series ($x = 0$), $[(CO)_5W{=}C(NMe_2)(Me_2N)C{=}W(CO)_5]$ (**2**), was obtained as a byproduct from the reaction of $[(CO)_5W{=}C(Ph)H]$ (**1**)[28,29] with $Me_2NC\equiv CNMe_2$. When the alkyne was added at −50 °C to a solution of **1** in dichloromethane, the solution immediately changed from red to orange. Chromatographic workup afforded two fractions. The first fraction contained the binuclear complex **2** and the second fraction the mononuclear complex **3** (Scheme 1).

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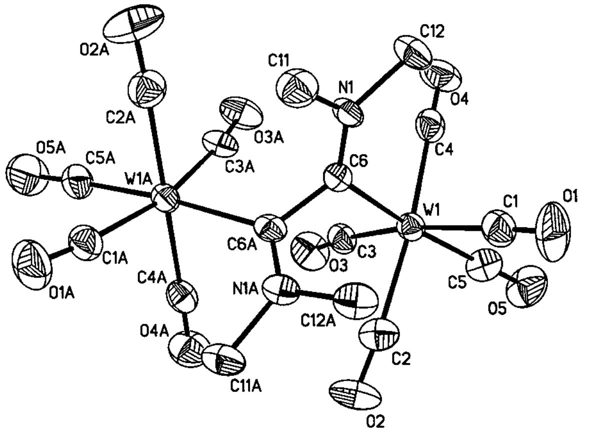
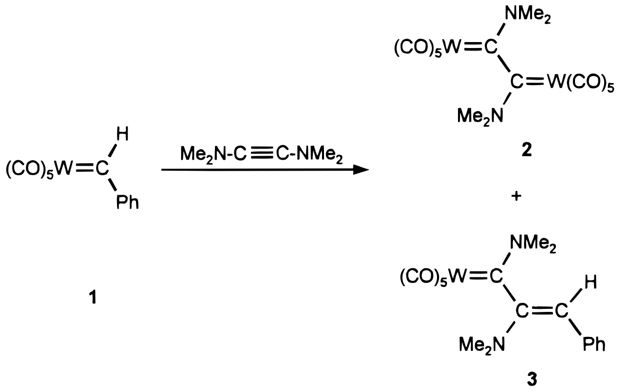


Figure 1. ORTEP plot of complex **2** (hydrogens omitted).

Scheme 1



Complex **3** was the expected reaction product. It was formed by insertion of the C≡C bond of the alkyne into the W=C bond of **1**. The insertion of electron-rich alkynes into the metal−carbene bond is a typical reaction of electrophilic carbene complexes.[30] Complex **2** presumably was either formed by addition of two $(CO)_5W$ fragments to the alkyne or, more likely, by substitution of the alkyne for the bridging carbene ligand in $[(CO)_5W\{\mu\text{-}C(Ph)H\}W(CO)_5]$ and subsequent rearrangement. $[(CO)_5W\{\mu\text{-}C(Ph)H\}W(CO)_5]$ usually is formed in addition to stilbene on thermolysis of **1**.[29,31]

Both complexes were characterized by spectroscopic means. The ^{1}H NMR spectrum of **2** exhibits only two singlets for the two inequivalent *N*-Me groups; the ^{13}C NMR spectrum shows signals for the two *N*-Me groups, signals at δ 198.3 and 201.0 for the CO substituents, and the carbene resonance at δ 241.4 in the range typical for aminocarbene complexes.[32] Although this complex could not be obtained in an analytically pure form, it was possible to grow a few crystals of **2** suitable for X-ray analysis (Figure 1 and Table 1).

The $(CO)_5W$ fragments are connected by a $C_2(NMe_2)_2$ bridge. The central C−C distance (1.463(9) Å) corresponds to a C(sp^2)−C(sp^2) single bond and agrees well with that in the related chromium complex $[(CO)_5Cr{=}C(NEt_2)(Et_2N)C{=}Cr(CO)_5]$ (1.480(9) Å).[19] To prevent unfavorable steric interactions, the W=C distances (2.281(7) and 2.295(7) Å) are rather long and are significantly longer than in typical aminocarbene complexes such as $[(CO)_5W{=}C(NHMe)Ph]$ (2.186(22) Å)[33] and $[(CO)_5W{=}C(NMe_2)C{\equiv}CSiMe_3]$ (2.224 Å).[34] Compared to a C(sp^2)−N(sp^2) single bond,[35] the C(carbene)−N bonds are rather short. This indicates considerable double-bond character of the C(carbene)−N bonds, which is consistent with the observation of two distinct NMR resonances for the NMe_2 groups in the ^{1}H and ^{13}C NMR spectra. Both carbene atoms are planar coordinated (sums of angles 359.7 and 359.9°). These carbene planes are almost orthogonal (torsion angle W1−C6−C6A−W1A = −93.9°), which excludes the presence of a bridging delocalized π-system.

Table 1. Selected Bond Distances, Bond Angles, and Torsion Angles for Complex 2

Bond Distances (Å)			
W(1)−C(6)	2.295(7)	W(1A)−C(6A)	2.281(7)
W(1)−C(5)	1.991(8)	W(1A)−C(5A)	1.978(8)
C(6)−N(1)	1.310(8)	C(6A)−N(1A)	1.314(9)
C(6)−C(6A)	1.463(9)		
Bond Angles (deg)			
W(1)−C(6)−N(1)	130.4(5)	W(1A)−C(6A)−N(1A)	128.8(5)
W(1)−C(6)−C(6A)	112.7(4)	W(1A)−C(6A)−C(6)	114.5(5)
N(1)−C(6)−C(6A)	116.6(6)	N(1A)−C(6A)−C(6)	116.6(6)
Torsion Angles (deg)			
N(1)−C(6)−C(6A)−N(1A)	−89.7		
W(1)−C(6)−C(6A)−W(1A)	−93.9		

Complex **2** exhibits in the IR spectrum two distinct sets of $(CO)_5W$ ν(CO) vibrations. This indicates that in solution two conformers are present. Two sets of ν(CO) vibrations have also been reported for the related (diethylamino)carbene complexes, $[(CO)_5M{=}C(NEt_2)(Et_2N)C{=}M(CO)_5]$ (M = Cr, W), prepared earlier by Fischer et al.[9,20] The interconversion of the conformers must be rapid on the NMR time scale, since the ^{1}H and ^{13}C NMR spectra show only two NMe signals as expected on the basis of restricted rotation around the C(carbene)−N bond.

The π-conjugated, ethyne-bridged bis(carbene) complex was prepared via the classical route to Fischer carbene complexes starting from the ethynylcarbene complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CH]$[34] (**4a**). Addition of *n*BuLi to **4a** in Et_2O at −80 °C afforded the lithiated derivative $[(CO)_5W{=}C(NMe_2)C{\equiv}CLi]$,[34] which was then used as the nucleophile in the in situ reaction with $[W(CO)_6]$. The resulting $[(CO)_5W{=}C(NMe_2)C{\equiv}C(LiO)C{=}W(CO)_5]$ was alkylated with F_3CSO_3Me to give the new unsymmetrical C_2-bridged alkoxycarbene−aminocarbene complex $[(CO)_5W{=}C(NMe_2)\text{-}C{\equiv}C(MeO)C{=}W(CO)_5]$ (**5**) in 31% yield, after chromatography and recrystallization (Scheme 2).

As expected, complex **5** exhibits in the IR spectrum two partly overlapping sets of $(CO)_5W$ ν(CO) absorptions and two resonances each for the cis and the trans CO ligands in the ^{13}C NMR spectrum. However, the ^{13}C NMR spectrum shows some peculiarities. In comparison with C-substituted alkynes and alkynylcarbene com-

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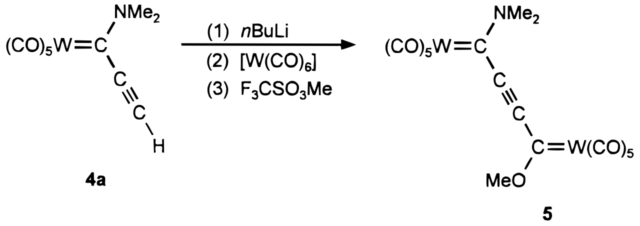
Scheme 2



plexes, the resonances of the alkynediyl unit appear at unusually low field (δ 169.2 and 174.3). In contrast, the resonances of both carbene carbon atoms are observed at unusually high field. The carbene resonance of $[(CO)_5W{=}C(NR_2)C{\equiv}CR']$ complexes is usually found between δ 220 and 235 (e.g. δ 231.1 in **4a**[34]). In contrast, that of **5** is at δ 181.7 ($^1J_{W,C} = 99.0$ Hz). The $W{=}C(OMe)$ resonance is expected in the range δ 270 and 300 (e.g. δ 290.8 in $[(CO)_5W{=}C(OMe)C{\equiv}CSiMe_3]$); however, that in **5** is at δ 235.9 ($^1J_{W,C} = 86.6$ Hz). These data indicate that there is considerable π delocalization in the bridge and that **5** is best represented by several mesomeric structures (Scheme 3, **a**−**f**). The dipolar allenyl-type resonance forms **b** and **c** significantly contribute to the overall bonding description.

Usually, the alkoxy group in alkoxycarbene complexes can be replaced by NH_2, $N(R)H$, or NR_2 by aminolysis with ammonia or primary or secondary amines.[36] However, attempts to transform **5** into the symmetrical C≡C-bridged bis(aminocarbene) complex $[(CO)_5W{=}C(NMe_2)C{\equiv}C(Me_2N)C{=}W(CO)_5]$ failed. When $HNMe_2$ was added to a solution of **5** in diethyl ether at −100 °C,[37] a mixture of many compounds rapidly formed which were inseparable by thin-layer chromatography. Presumably, the first reaction step involves nucleophilic attack of the amine at the C≡C bond (see mesomeric forms **b** and **c**) instead of addition to the carbene carbon atom.[38]

Since **5** could not be transformed into a bis(aminocarbene) complex, attempts to synthesize a π-conjugated, $(-C{\equiv}C-)_x$-bridged bis(aminocarbene) complex via the classical Fischer route followed by aminolysis were abandoned. Instead, a different approach to symmetrical alkynediyl-linked bis(aminocarbene) complexes $[(CO)_5M{=}C(NMe_2)(C{\equiv}C)_x(Me_2N)C{=}M(CO)_5]$ was developed. Coupling of two mononuclear alkynylcarbene complexes should afford binuclear complexes in a straightforward way. The coupling could be achieved by Pd-catalyzed reaction of mononuclear stannylated alkynylcarbene complexes with (iodoalkynyl)carbene complexes.

Deprotonation of the (dimethylamino)ethynylcarbene complexes **4a**,**b** with *n*BuLi in Et_2O at −78 °C followed by in situ reaction with an equimolar amount of iodine afforded the novel (dimethylamino)(iodoethynyl)carbene complexes **6a**,**b** in ca. 50% yield (Scheme 4). Essentially the same route was used for the preparation of organic iodine-substituted alkynes $RC{\equiv}CI$.[39] The IR and NMR spectra of **6a**,**b** are similar to those of the starting complexes **4a**,**b** except for a considerable shift of the C≡C resonances to higher field. At room temperature in solution **4a**,**b** decompose within several days.

The stannylated alkynylcarbene complexes **7a**,**b** were obtained from **4a**,**b**, *n*BuLi and $ClSn\textit{n}Bu_3$.[14] Coupling of **6a**,**b** with **7a**,**b** was achieved by stirring 1:1 mixtures of these complexes in toluene for 1 day in the presence of 10 mol % $[PdCl_2(NCMe)_2]$. The butadiynediyl-bridged bis(aminocarbene) complexes **8a**,**b** were obtained after purification by column chromatography and recrystallization in approximately 40% yield (Scheme 4).

As expected and in contrast to **5**, the IR spectra of **8a**,**b** show only one set of $(CO)_5M$ $\nu(CO)$ absorptions. The ^{13}C NMR spectra of **5** and **8a**,**b** also differ considerably. The C≡C resonances of **8a**,**b** (δ 100.3 and 109.4 (**8a**); δ 100.1 and 113.3 (**8b**)) are shifted upfield by more than 60 ppm compared to those of **5**. For **8a**,**b** only one carbene resonance each is observed which is in the range characteristic for aminocarbene complexes. From these spectroscopic data it follows that the bis(carbene) form dominates and that dipolar allenylalkynylcarbene and pentatetraenylcarbene resonance forms such as **h** and **i** (Scheme 5) at best only slightly contribute to the overall bonding description.

The coupling route could be extended to the synthesis of the corresponding octatetraynediyl- and dodecahexaynediyl-bridged complexes. Reaction of **9**[15a] with *n*BuLi/I_2 gave the new amino(iodobutadiynyl)carbene complex **10**. The Pd-catalyzed coupling of **10** with **11**[15a] afforded **12** with a naked C_8 unit linking two (aminocarbene)pentacarbonyltungsten fragments (Scheme 6). Analogously, the reaction of **13**[15b] with *n*BuLi and I_2 yielded the amino(iodohexatriynyl)carbene complex **14**. Subsequent coupling of **14** with **15**[15b] gave the dodecahexaynediyl-bridged bis(aminocarbene)tungsten complex **16** (Scheme 7).

All new alkynediyl-bridged bis(carbene) complexes **5**, **8a**,**b**, **12**, and **16** are stable at room temperature in the solid state and in solution. In contrast, the (iodobutadiynyl)carbene complex **10** and the (iodohexatriynyl)carbene complex **14** slowly decompose in solution at room temperature but are stable in the solid state below −30 °C.

The $\nu(CO)$ spectra and the ^1H and ^{13}C NMR spectra of the $(CO)_5W{=}C(NMe_2)$ part of **8a**, **12**, and **16** are almost identical. This indicates that the σ-donor/π-acceptor properties of the bridging alkynylaminocarbene ligand in the ground state is nearly independent of the number of (C≡C) units forming the chain. Obviously, insertion of a C_2 or a C_4 unit into the $(Me_2N)CC{\equiv}CC{\equiv}CC(NMe_2)$ fragment does not significantly modify the bonding situation. The spectra of **8a**, **12**, and **16** also differ only slightly from those of **4a**, **9**, and **13** and of **6**,

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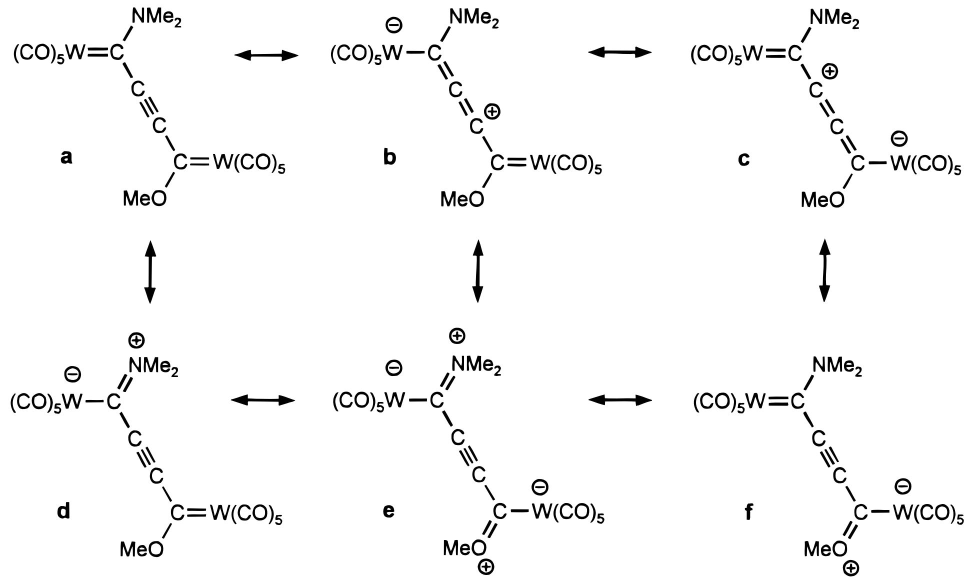
[36] See e.g.: (a) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141. (b) Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

[37] The aminolysis of the typical Fischer carbene complex with primary amines was studied in detail by kinetic methods, and a fourth-order rate law was observed. The activation entropy is strongly negative, giving rise to a negative Arrhenius activation energy. As a consequence the reaction rate increases with decreasing temperature. See: Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.

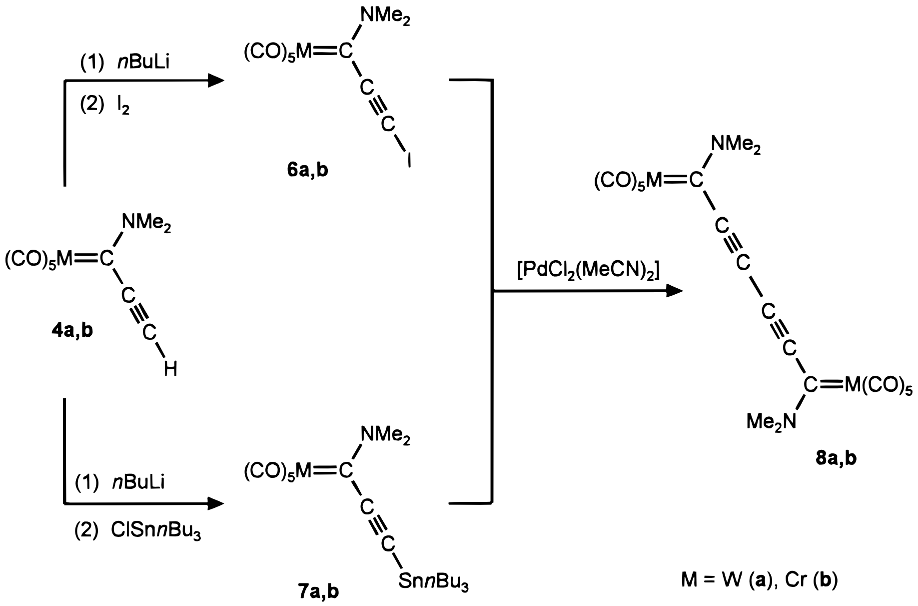
[38] Michael addition of amines to the C≡C bond competes with aminolysis. Due to the large negative activation entropy[37] aminolysis is favored at low temperature. For instance, the reaction of $[(CO)_5W{=}C(OEt)C{\equiv}CPh]$ with $HNMe_2$ affords at −60 °C $[(CO)_5W{=}C(NMe_2)C{\equiv}CPh]$ and EtOH and at −20 °C the Michael adduct $[(CO)_5W{=}C(OEt)CH{=}C(NMe_2)Ph]$. In the temperature range −60 to −20 °C mixtures of both complexes are obtained. See: (a) Fischer; E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57. (b) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163.

[39] (a) de Graaf, W.; Smits, A.; Boersma, J.; van Koten, G.; Hoekstra, W. P. M. *Tetrahedron* **1988**, *44*, 6699. (b) Kloster-Jenson, E. *Tetrahedron* **1971**, *27*, 33.

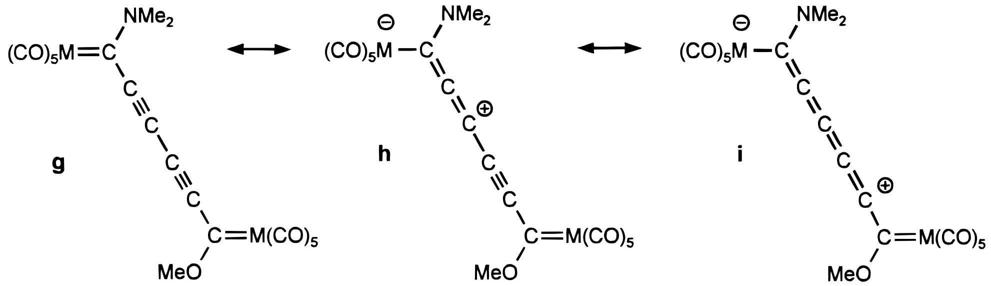
Scheme 3



Scheme 4



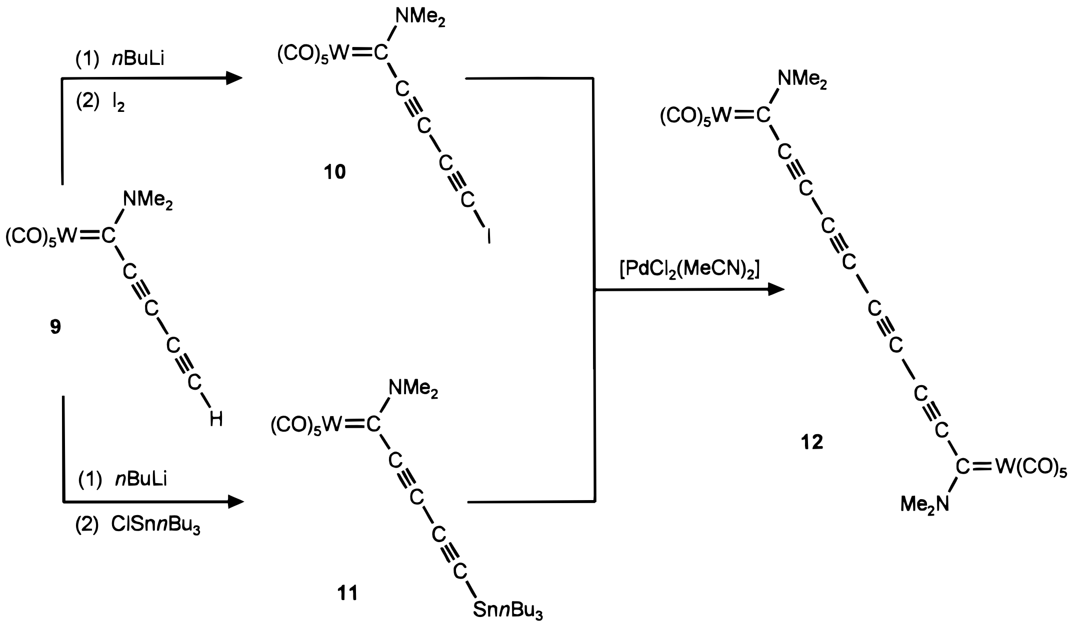
Scheme 5



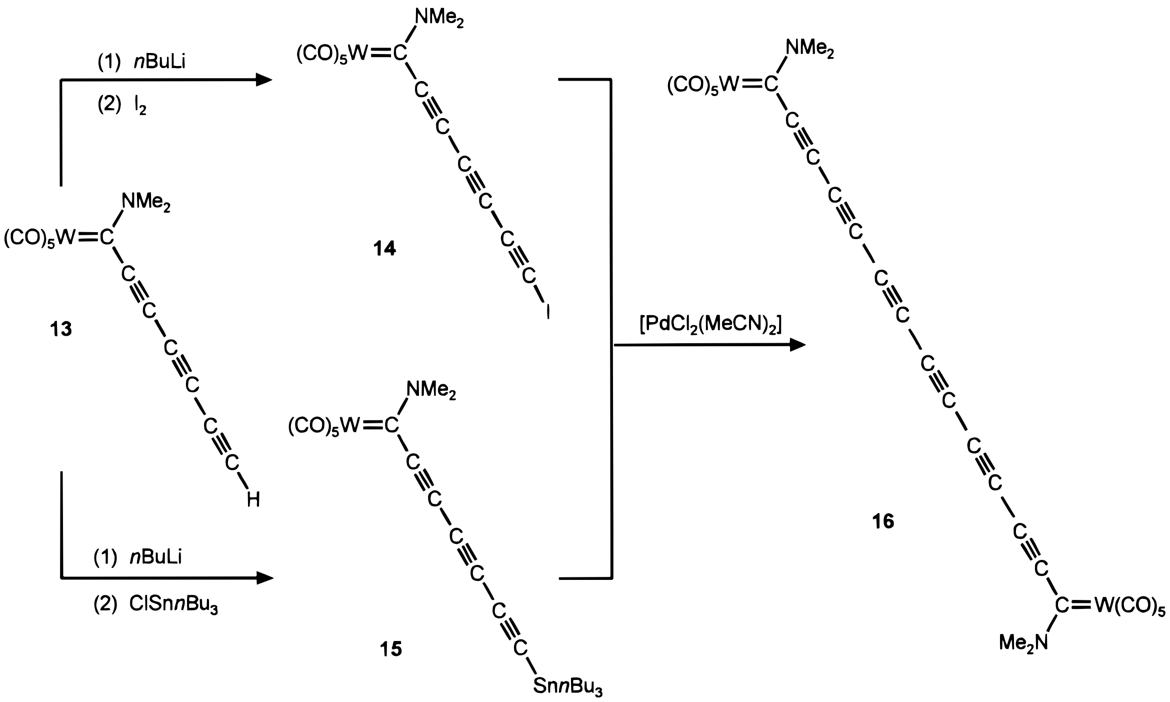
10, and **14**. An alternation of the ^{13}C NMR resonances along the $(C{\equiv}C)_x$ chain is observed. The alternation decreases along the chain with increasing distance from the carbene carbon atom: $\Delta\delta(C_\beta{-}C_\alpha) > \Delta\delta(C_\delta{-}C_\gamma) > \Delta\delta(C_\xi{-}C_\epsilon)$. In general, the alternation is less pronounced than in the corresponding unsubstituted, π-acceptor-substituted ($SiMe_3$, $Sn(nBu)_3$), and π-donor-substituted (I) mononuclear alkynylaminocarbene complexes. This may be interpreted as a sign for a weak interaction of both $(CO)_5W$ groups.

In the series **8a**, **12**, and **16** the absorption at lowest energy in the UV/vis spectra is shifted toward longer wavelengths (Figure 2). The absorption is assigned to a MLCT transition. The HOMO in these complexes is essentially metal d in character. Conversely, the LUMO is predominantly localized at the bridging ligand. From

Scheme 6



Scheme 7



the IR and NMR spectra it follows that the energy of the HOMO is only marginally influenced by the length of the bridge. Therefore, the bathochromic shift reflects the decreasing energy of the LUMO. The insertion of a (C≡CC≡C) fragment lowers the energy of the LUMO by about 15−20 kJ/mol. Although **8a**, **12**, and **16** are symmetric, the MLCT transition is solvent-dependent and is shifted toward shorter wavelengths when nonpolar solvents are replaced by polar ones. However, the solvatochromic effect is small and decreases with increasing length of the chain ($\tilde{\nu}$(pentane−CH$_2$Cl$_2$) 2830 (**8a**), 1240 (**12**), 900 (**16**) cm^{-1}).

Conclusions

Novel binuclear bis(carbene) complexes with an alkynediyl fragment linking two (CO)$_5$M=C(R) units are accessible by two different CC-coupling routes. The reaction of the lithiated (dimethylamino)ethynylcarbene complex [(CO)$_5$W=C(NMe$_2$)C≡CLi] with [W(CO)$_6$] followed by alkylation with methyl triflate affords the unsymmetrically bridged alkoxycarbene−aminocarbene complex [(CO)$_5$W=C(NMe$_2$)C≡C(MeO)C=W(CO)$_5$] (**5**). This route should also be applicable to other "electron-poor" metal carbonyls such as [Cr(CO)$_6$] and [Mo(CO)$_6$]. Presumably, the method can also be extended to the synthesis of binuclear complexes with longer alkynediyl linking groups such as [(CO)$_5$M=C(NR$_2$)(C≡C)$_x$(R′O)C=M(CO)$_5$] (x = 2, 3, ...). However, the yields are expected to be much lower due to the reduced nucleophilicity of the lithiated alkynylcarbene complexes [(CO)$_5$W=C(NMe$_2$)(C≡C)$_x$Li] required as the starting compounds.

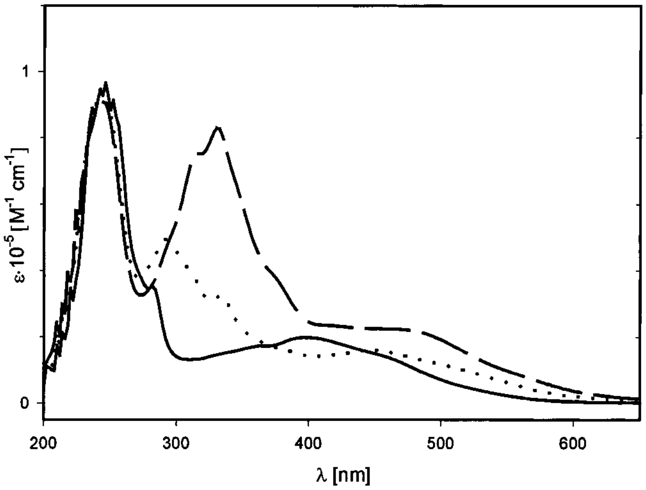


Figure 2. UV/vis spectra of [(CO)$_5$W═C(NMe$_2$)(C≡C)$_x$-(Me$_2$N)C═W(CO)$_5$] in dichloromethane at room temperature: (—) $n = 2$; (···) $n = 4$; (---) $n = 6$.

Symmetrically substituted alkynediylbis(aminocarbene) complexes are obtained by Pd-catalyzed coupling of two (CO)$_5$M═C(NR$_2$)(C≡C)$_x$ units. Thus, C(NMe$_2$)(C≡C)$_x$(Me$_2$N)C-bridged binuclear complexes with $x = 2$, 4, and 6 are readily accessible. This route is not restricted to the synthesis of complexes with an even number of C≡C units. Since two different precursors, [(CO)$_5$M═C(NR$_2$)(C≡C)$_x$I] and [(CO)$_5$M═C(NR$_2$)(C≡C)$_y$SnR$_3$], are involved, complexes with an odd number of C≡C linking units can likewise be prepared. The same applies to binuclear complexes with an even larger number of bridging C≡C units. In the series **8**, **12**, **16** the thermal stability of the complexes is not significantly reduced by elongation of the bridging ligand. Therefore, complexes with even longer bridging chains should also be stable. Limitations may arise from the availability of the unsubstituted alkynylcarbene complexes [(CO)$_5$M═C(NR$_2$)(C≡C)$_x$H], which are the precursors for both the iodo- and the SnR$_3$-substituted complexes. Until now, two different routes to alkynylcarbene complexes [(CO)$_5$M═C(NR$_2$)(C≡C)$_x$H] ($x > 1$) have been developed: (a) Cu-catalyzed coupling of [(CO)$_5$W═C(NMe$_2$)C≡CLi] with I(C≡C)$_x$SiMe$_3$ followed by desilylation of the resulting product with KF in MeOH/THF and (b) Pd-catalyzed coupling of [(CO)$_5$W═C(NMe$_2$)C≡CSn(nBu)$_3$] with I(C≡C)$_x$SiMe$_3$ and subsequent desilylation. Both routes suffer from rather poor yields.[15]

Crucial intermediates in these syntheses are unsubstituted alkynylcarbene complexes [(CO)$_5$M═C(R)(C≡C)$_x$H]. For R = NR$_2$ these compounds are stable at room temperature. However, the corresponding alkoxyalkynylcarbene complexes are very labile. [(CO)$_5$W═C(OMe)C≡CH] has been shown to decompose rapidly even at −78 °C.[34] Therefore, until now it was not possible to synthesize binuclear alkynediyl-bridged bis(alkoxycarbene) complexes related to **5**, **8**, **12**, and **16** (OR instead of NMe$_2$).

From a comparison of the IR and NMR spectra of the symmetrically substituted alkynediyl-bridged complexes **8**, **12**, and **16** with those of **2** it follows that in the ground state there is only weak π-interaction between the (CO)$_5$W═C(NMe$_2$) fragments through the bridge. In complex **2** π-interaction is prevented by the orthogonal arrangement of both carbene planes. However, from the bathochromic shift of the MLCT absorption in the series **8**, **12**, and **16** a decreasing energy of the LUMO with increasing chain length can be deduced. In contrast to **8**, **12**, and **16**, the considerable high-field shift of *both* carbene resonances and the low-field shift of *both* C≡C resonances of the unsymmetrical alkoxycarbene−aminocarbene complex **5** indicate significant π-interaction between both carbene units.

Experimental Section

All operations were performed under argon by using standard Schlenk techniques. Solvents were dried by refluxing from CaH$_2$ (CH$_2$Cl$_2$) and sodium benzophenone ketyl (pentane, Et$_2$O, THF) and were freshly distilled prior to use. The yields refer to analytically pure compounds and were not optimized. Silica used for column chromatography (Fa. J. T. Baker, silica for flash chromatography) was argon-saturated. The complexes **1**,[28,29] **4a**,**b**,[16] **7a**,**b**,[3] **9**,[4] **11**,[4] **13**,[5] **15**,[5] NEt$_4$[(CO)$_5$WCPh(OMe)H],[40] and [PdCl$_2$(MeCN)$_2$][23] were prepared according to literature procedures. NMR spectra were determined on Bruker AC 250, Bruker DRX 600, and JEOL JNX 400 instruments; chemical shifts are reported relative to internal TMS (^{1}H and ^{13}C). Unless mentioned otherwise, all NMR spectra were recorded in CDCl$_3$ at room temperature. The labeling scheme for atoms in the chain is as follows: [(CO)$_5$M═C(NMe$_2$)C$_\alpha$≡C$_\beta$C$_\gamma$≡C$_\delta$C$_\epsilon$≡C$_\xi$R]. IR spectra were measured on Biorad FTS 60 and Perkin-Elmer 983G instruments and UV/vis spectra on a Hewlett-Packard 8452A diode-array spectrophotometer. IR and UV/vis spectra were analyzed using the program Peakfit (SPSS Inc.). For UV/vis spectra only the absorption at lowest energy is given. MS determinations were carried out on a Finnigan MAT 312 instrument and elemental analyses on a Heraeus CHN-O-RAPID.

***μ*-Bis[pentacarbonyl((dimethylamino)carbene)-tungsten] (2) and Pentacarbonyl[(dimethylamino)(1-(dimethylamino)-2-phenylethenyl)carbene]tungsten (3).** A 1.0 mL (7.3 mmol) portion of bis(dimethylamino)ethyne was added at −50 °C to a solution of [(CO)$_5$W═C(Ph)H] (**1**) in 10 mL of CH$_2$Cl$_2$ freshly prepared from 0.90 g (1.6 mmol) of NEt$_4$[(CO)$_5$WCH(OMe)Ph] and 0.44 mL (3.2 mmol) of HBF$_4$ (54% in Et$_2$O). The initially red solution immediately changed to orange. The solvent was removed in vacuo and the residue dissolved in CH$_2$Cl$_2$ and chromatographed at −50 °C on silica. The first yellow zone was eluted with hexane/CH$_2$Cl$_2$ (1:1). Subsequently, an orange fraction was eluted with hexane/CH$_2$Cl$_2$ (ratio gradually changing from 1:1 to 0:1). The solvents of both fractions were removed in vacuo. When the residue of the first fraction was dissolved at 0 °C in the least amount of hexane/CH$_2$C1$_2$ (1:1) possible and the temperature slowly reduced to −30 °C, fine orange-brown needles of **2** formed. Similarly, the residue of the second fraction was dissolved in hexane/CH$_2$C1$_2$ (1:1) at ambient temperature and the temperature was reduced to −30 °C to give yellow crystals of **3**.

2: yield 0.10 g (8% based on NEt$_4$[(CO)$_5$WCH(OMe)Ph]); C$_{16}$H$_{12}$N$_2$O$_{10}$W$_2$ (759.96). It was not possible to completely separate **2** from **3** and bis(dimethylamino)ethyne. The sample still contained about 16% of **3** and 9% of bis(dimethylamino)ethyne, as determined by ^{1}H NMR spectroscopy. IR (hexane): ν(CO) 2071 w, 2064 w, 2009 sh, 1956 s, 1937 sh, 1933 sh, 1925 vs cm^{-1}. ^{1}H NMR (−50 °C): δ 3.21 (s, 6 H, NMe), 3.83 (s, 6 H, NMe). ^{13}C NMR (−50 °C): δ 51.2, 46.0 (NMe), 198.3 ($^1J_{W,C}$ = 128 Hz, cis-CO), 201.0 (trans-CO), 241.4 (W═C). EI-MS, m/z (%): 760 (7) [M$^+$], 732 (17), 704 (3), 676 (3), 648 (7), 620 (16) [M$^+$ − n CO, n = 1−5], 592 (34), 564 (18), 536 (27), 504 (18), 480 (18) [M$^+$ − 10 CO], 380 (18), 352 (58) [W(CO)$_6$$^+$], 73 (100).

3: yield 0.21 g (25% based on NEt$_4$[(CO)$_5$WCH(OMe)Ph]); mp 79−80 °C; C$_{18}$H$_{18}$N$_2$O$_5$W (526.18). It was impossible to

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(40) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045.

completely separate **3** from bis(dimethylamino)ethyne, which was used in about 7-fold excess. The sample of **3** still contained about 20% of bis(dimethylamino)ethyne, as determined by ^{1}H NMR spectroscopy. IR (hexane): ν(CO) 2064 w, 1975 vw, 1949 vw, 1938 s, 1925 vs cm^{-1}. ^{1}H NMR (−30 °C): δ 2.75 (s, 6 H, NMe), 3.21 (s, 3 H, W=CNMe), 3.86 (s, 3 H, W=CNMe), 4.88 (s, 1 H, =C(Ph)H), 7.2−6.9 (m, 5 H, Ph). ^{13}C NMR (−30 °C): δ 39.4 (Me), 44.4 (Me), 52.9 (Me), 93.2 (=C), 123.5, 126.3, 128.4, 137.1, 155.9 (Ph), 198.2 ($^1J_{\mathrm{W,C}}$ = 128 Hz, cis-CO), 203.3 (trans-CO), 254.6 (W=C). EI-MS, *m*/*z* (%): 526 (18) [M$^+$], 498 (29), 470 (37), 442 (64), 414 (62), 386 (100) [M$^+$ − *n* CO, *n* = 1−5].

1-[Pentacarbonyl((dimethylamino)carbene)tungsten]-2-[pentacarbonyl(methoxycarbene)tungsten]ethyne (5). A 3.13 mL portion of a 1.6 M solution of *n*BuLi in hexane (5.00 mmol) was added at −78 °C to a solution of 2.03 g (5.00 mmol) of **4a** in 30 mL of Et$_2$O. When the yellow solution was stirred for 30 min at −78 °C, a white precipitate formed. A 1.76 g (5.00 mmol) portion of [W(CO)$_6$] and 10 mL of THF were added, and the mixture was stirred at 0 °C for 1 h. At −30 °C 1.23 g (7.50 mmol) of F$_3$CSO$_3$Me was added and the solution was stirred for another 30 min. A 150 mL amount of Et$_2$O was added, and the yellow solution was extracted three times with 50 mL of a saturated aqueous NaHCO$_3$ solution. The yellow organic layers were combined, and the solvent was evaporated in vacuo. The yellow residue was dissolved in 10 mL of CH$_2$Cl$_2$ and chromatographed at −40 °C on silica with pentane/CH$_2$Cl$_2$ (2:1). First a light yellow fraction containing unreacted [W(CO)$_6$] was eluted. The second yellow fraction contained complex **5**. Removal of the solvent in vacuo gave **5** as a analytically pure yellow powder: yield 1.20 g (31% based on **4a**); mp 147 °C dec. IR (Et$_2$O): ν(CO) 2072 w, 2063 w, 1982 w, 1976 w, 1945 vs, 1927 s cm^{-1}. ^{1}H NMR: δ 3.40 (s, 3 H, NMe), 3.86 (s, 3 H, NMe), 4.54 (s, 3 H, OMe). ^{13}C NMR: δ 48.4 (NMe), 51.9 (NMe), 63.2 (OMe), 169.2, 174.3 (C$_\alpha$, C$_\beta$), 181.7 [$^1J_{\mathrm{W,C}}$ = 99.0 Hz, W=*C*(NMe$_2$)], 196.3 ($^1J_{\mathrm{W,C}}$ = 126.5 Hz), 197.0 ($^1J_{\mathrm{W,C}}$ = 125.0 Hz, trans-CO), 201.5 ($^1J_{\mathrm{W,C}}$ = 126.4 Hz), 202.4 ($^1J_{\mathrm{W,C}}$ = 133.3 Hz, cis-CO), 235.9 [$^1J_{\mathrm{W,C}}$ = 86.6 Hz, W=*C*(OMe)]. UV/vis, $\lambda_{\max}$ (nm) (log ϵ): 396 (2.823) [pentane]; 389 (3.825) [CH$_2$Cl$_2$]. EI-MS, *m*/*z* (%): 771 (53) [M$^+$], 743 (7), 687 (20), 659 (43), 631 (74), 603 (100), 575 (66), 547 (54), 519 (17), 491 (22) [M$^+$ − *n* CO, *n* = 1, 3−10]. Anal. Calcd for C$_{17}$H$_9$NO$_{11}$W$_2$ (771.0): C, 26.48; H, 1.18; N, 1.82. Found: C, 26.37; H, 1.34; N, 1.82.

Pentacarbonyl(1-(dimethylamino)-3-iodopropynylidene)tungsten (6a) and -chromium (6b). A 3.13 mL portion of a 1.6 M solution of *n*BuLi in hexane (5.00 mmol) was added to a solution of 2.03 g of **4a** or 1.37 g of **4b** (5 mmol) in 15 mL of Et$_2$O. When the yellow solution was stirred for 30 min at −78 °C, a white precipitate formed. A 1.27 g (5.00 mmol) amount of I$_2$ in 20 mL of THF was added, and the mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo. The dark residue was dissolved in 10 mL of CH$_2$Cl$_2$ and chromatographed at −40 °C on silica. With pentane/CH$_2$Cl$_2$ (4:1) a yellow fraction containing **6** was eluted. Removal of the solvent in vacuo afforded **6a** or **6b** as a yellow powder.

6a: yield 1.37 g (52% based on **4a**); mp 70 °C dec. IR (pentane): ν(C≡C) 2146 vw; ν(CO) 2065 m, 1978 w, 1943 s, 1934 vs cm^{-1}. ^{1}H NMR (−40 °C): δ 3.62 (s, 3 H, Me), 3.74 (s, 3 H, Me). ^{13}C NMR (−40 °C): δ 46.9 (Me), 50.8 (C$_\beta$), 51.4 (Me), 97.6 (C$_\alpha$), 197.9 ($^1J_{\mathrm{W,C}}$ = 128.4 Hz, cis-CO), 204.5 ($^1J_{\mathrm{W,C}}$ = 131.7 Hz, trans-CO), 229.9 ($^1J_{\mathrm{W,C}}$ = 88.3 Hz, W=C). EI-MS, *m*/*z* (%): 531 (39) [M$^+$], 475 (55), 447 (40), 419 (100), 391 (87) [M$^+$ − *n* CO, *n* = 2−5], 376 (14), 348 (32), 320 (17) [M$^+$ − *n* CO − I, *n* = 1−3]. Anal. Calcd for C$_{10}$H$_6$INO$_5$W (530.9): C, 22.62; H, 1.14; N, 2.64. Found C, 22.69; H, 1.08; N, 2.64.

6b: yield 0.96 g (48% based on **4b**); mp 55 °C dec. IR (pentane): ν(C≡C) 2125 vw; ν(CO) 2058 m, 1983 w, 1946 s, 1938 vs cm^{-1}. ^{1}H NMR (−40 °C): δ 3.65 (s, 3 H, Me), 3.84 (s, 3 H, Me). ^{13}C NMR (−40 °C): δ 48.2 (Me), 49.2 (Me), 54.2 (C$_\beta$), 95.8 (C$_\alpha$), 216.6 (cis-CO), 223.9 (trans-CO), 250.2 (Cr=C). EI-MS, *m*/*z* (%): 399 (16) [M$^+$], 343 (14), 315 (39), 287 (24), 259 (100) [M$^+$ − *n* CO, *n* = 2−5], 244 (83) [M$^+$ − CO − I]. Anal. Calcd for C$_{10}$H$_6$CrINO$_5$ (399.1): C, 30.10; H, 1.52; N, 3.51. Found: C, 29.98; H, 1.67; N, 3.32.

1,4-Bis[pentacarbonyl((dimethylamino)carbene)tungsten]-1,3-butadiyne (8a) and 1,4-Bis[pentacarbonyl((dimethylamino)carbene)chromium]-1,3-butadiyne (8b). A 1.59 or 1.20 g portion of **6a**,**b**, respectively (3.00 mmol), and 2.08 or 1.69 g of **7a**,**b** (3.00 mmol), respectively, along with 0.08 g (0.30 mmol) of [PdCl$_2$(MeCN)$_2$] were dissolved in 15 mL of toluene. The solution was stirred for 1 day at room temperature. The color of the solution changed from yellow to dark brown. Removal of the solvent in vacuo afforded a dark brown residue which was dissolved in 6 mL of CH$_2$Cl$_2$ and chromatographed at −40 °C on silica. With pentane/CH$_2$Cl$_2$ (3:1) the red fraction containing **8** was eluted. Evaporation of the solvent in vacuo afforded **8a**,**b** as a red solid. **8a**: yield 0.96 g (40% based on **7a**); mp 89 °C dec. IR (Et$_2$O): ν(C≡CC≡C) 2066 w; ν(CO) 2061 m, 1977 w, 1936 vs, 1925 m, sh cm^{-1}. ^{1}H NMR: δ 3.56 (s, 6 H, Me), 3.78 (s, 6 H, Me). ^{13}C NMR: δ 47.7 (Me), 51.2 (Me), 100.3 (C$_\alpha$), 109.4 (C$_\beta$), 197.6 ($^1J_{\mathrm{W,C}}$ = 127.1 Hz, cis-CO), 203.5 (trans-CO), 226.4 (W=C). UV/vis, $\lambda_{\max}$, nm (log ϵ): 492 (3.719) [pentane]; 454 (3.958) [CH$_2$Cl$_2$]. EI-MS, *m*/*z* (%): 808 (2) [M$^+$], 780 (4), 752 (1), 696 (3), 668 (5), 640 (11), 612 (5), 584 (8), 556 (6), [M$^+$ − *n* CO, *n* = 1, 2, 4−9], 352 (66) [W(CO)$_6{}^+$]. Anal. Calcd for C$_{20}$H$_{12}$N$_2$O$_{10}$W$_2$ (808.0): C, 29.73; H, 1.50; N, 3.47. Found: C, 29.84; H, 1.50; N, 3.43. **8b**: yield 0.65 g (40% based on **7b**); mp 74 °C dec. IR (Et$_2$O): ν(C≡CC≡C) 2059 w; ν(CO) 2053 m, 1984 w, 1939 vs, 1925 m, sh cm^{-1}. ^{1}H NMR: δ 3.61 (s, 6 H, Me), 3.90 (s, 6 H, Me). ^{13}C NMR: δ 49.1 (Me), 100.1 (C$_\alpha$), 113.3 (C$_\beta$), 216.5 (cis-CO), 223.8 (trans-CO), 246.4 (Cr=C). UV/vis, $\lambda_{\max}$, nm (log ϵ): 521 (3.872) [pentane]; 477 (3.769) [CH$_2$Cl$_2$]. MS (FAB, 3-nitrobenzyl alcohol), *m*/*z* (%): 544 (30) [M$^+$], 488 (85), 460 (6), 432 (87), 376 (27), 348 (40), 320 (13) [M$^+$ − *n* CO, *n* = 2−7]. Anal. Calcd for C$_{20}$H$_{12}$Cr$_2$N$_2$O$_{10}$ (544.1): C, 44.13; H, 2.22; N, 5.15. Found: C, 43.91; H, 2.31; N, 5.32.

Pentacarbonyl(1-(dimethylamino)-3-iodo-2,4-pentadiynylidene)tungsten (10). A 1.25 mL portion of a 1.6 M solution of *n*BuLi in hexane (2.00 mmol) was added to a solution of 0.86 g (2.00 mmol) of **9** in 20 mL of Et$_2$O. When the yellow solution was stirred for 30 min at −78 °C, a white precipitate formed. After 2.00 mmol (0.51 g) of I$_2$ in 10 mL of THF was added, the mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo. The dark residue was dissolved in 5 mL of CH$_2$Cl$_2$ and chromatographed at −40 °C on silica. With pentane/CH$_2$Cl$_2$ (5:1) a dark yellow fraction containing **10** was eluted. Removal of the solvent in vacuo afforded **10** as an orange powder: yield 0.14 g (13% based on **9**); mp 88 °C dec; C$_{12}$H$_6$INO$_5$W (554.9). The sample was contaminated with about 15% of the starting complex **9**. We refrained from a rigorous purification of **10** because compound **9** did not significantly influence the reaction of **10** with **11** and because of the rather poor yield of **10**. IR (pentane): ν(CO) 2065 w, 1981 w, 1946 vs, 1937 vs cm^{-1}. ^{1}H NMR (−40 °C): δ 3.60 (s, 3 H, Me), 3.77 (s, 3 H, Me). ^{13}C NMR (−40 °C): δ 27.1 (C$_\delta$), 47.6 (Me), 51.6 (Me), 69.9 (C$_\gamma$), 76.0 (C$_\alpha$), 111.8 (C$_\beta$), 197.7 ($^1J_{\mathrm{W,C}}$ = 128.2 Hz, cis-CO), 204.3 ($^1J_{\mathrm{W,C}}$ = 130.1 Hz, trans-CO), 229.4 (W=C). EI-MS, *m*/*z* (%): 555 (39) [M$^+$], 527 (17), 499 (100), 471 (53), 443 (94), 415 (97) [M$^+$ − *n* CO, *n* = 1−5], 400 (27), 372 (42), 344 (33), 316 (31), 288 (44) [M$^+$ − *n* CO − I, *n* = 1−5].

1,8-Bis[pentacarbonyl((dimethylamino)carbene)tungsten]-1,3,5,7-octatetrayne (12). A 0.05 g (0.20 mmol) portion of [PdCl$_2$(MeCN)$_2$] was added to a solution of 1.11 g (2.00 mmol) of **10** and 1.44 g (2.00 mmol) of **11** in 10 mL of toluene. The solution was stirred for 1 day at room temperature. The solvent was removed in vacuo. The dark brown residue was dissolved in 5 mL of CH$_2$Cl$_2$ and chromatographed at −40 °C on silica. The red fraction containing **12** was eluted with pentane/CH$_2$Cl$_2$ (3:1). Evaporation of the solvent in vacuo afforded **12** as a red powder: yield 0.61 g (36% based on **11**);

mp 97 °C dec. IR (Et_2O): ν(CO) 2063 w, 1980 w, 1938 vs cm^{-1}. ^{1}H NMR: δ 3.56 (s, 6 H, Me), 3.76 (s, 6 H, Me). ^{13}C NMR: δ 48.0 (Me), 51.5 (Me), 70.9 (C_γ), 76.8 (C_α), 88.1 (C_δ), 112.0 (C_β), 197.6 ($^1J_{W,C}$ = 126.9 Hz, cis-CO), 203.5 (trans-CO), 229.5 (W=C). UV/vis, λ_{max}, nm (log ϵ): 538 (due to the poor solubility of **12** in pentane, log ϵ could not exactly be determined) [pentane]; 506 (3.759) [CH_2Cl_2]. MS (FAB, 3-nitrobenzyl alcohol), *m/z* (%): 856 (17) [M^+], 828 (38), 800 (19), 772 (31), 744 (47), 716 (13), 688 (19), 660 (11), 632 (9), 576 (12) [$M^+ - n$ CO, n = 1−8, 10]. Anal. Calcd for $C_{24}H_{12}N_2O_{10}W_2$ (856.1): C, 33.67; H, 1.41; N, 3.27. Found: C, 33.75; H, 1.47; N, 3.44.

Pentacarbonyl(1-(dimethylamino)-3-iodo-2,4,6-heptatriynylidene)tungsten (14). A 1.25 mL portion of a 1.6 M solution of *n*BuLi in hexane (2.00 mmol) was added to a solution of 0.86 g (2.00 mmol) of **13** in 20 mL of Et_2O. When it was stirred for 30 min at −78 °C, the yellow solution turned cloudy. Then 0.51 g (2.00 mmol) of I_2 in 10 mL of THF was added and the mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo. The dark residue was dissolved in 5 mL of CH_2Cl_2 and chromatographed at −40 °C on silica. With pentane/CH_2Cl_2 (5:1) an orange fraction containing **14** was eluted. Removal of the solvent in vacuo afforded **14** as an orange solid: yield 0.13 g (11% based on **13**); mp 97 °C dec; $C_{14}H_6INO_5W$ (579.0). The sample was contaminated with about 5% of the starting complex **13**. We refrained from a rigorous purification of **14** because compound **13** did not significantly influence the reaction of **14** with **15** and because of the rather poor yield of **14**. IR (pentane): ν(CO) 2065 w, 1981 w, 1947 s, 1937 vs cm^{-1}. ^{1}H NMR (−40 °C): δ 3.60 (s, 3 H, Me), 3.77 (s, 3 H, Me). ^{13}C NMR (−40 °C): δ 15.3 (C_ξ), 48.0 (Me), 51.6 (Me), 54.9 (C_γ), 70.1 (C_α), 77.9 (C_ϵ), 88.9 (C_δ), 111.4 (C_β), 197.6 ($^1J_{W,C}$ = 128.5 Hz, cis-CO), 204.2 (trans-CO), 228.7 (W=C). EI-MS, *m/z* (%): 579 (35) [M^+], 551 (9), 523 (59), 495 (35), 467 (41), 439 (32) [$M^+ - n$ CO, n = 1−5], 424 (20), 396 (18) [$M^+ - n$ CO − I, n = 1, 2], 128 (100) [HI^+].

1,12-Bis[pentacarbonyl((dimethylamino)carbene)tungsten]-1,3,5,7,9,11-dodecahexayne (16). A 0.74 g (1 mmol) portion of **15**, 0.58 g (1.00 mmol) of **14**, and 0.03 g (0.10 mmol) of [$PdCl_2(MeCN)_2$] were dissolved in 10 mL of toluene. The solution was stirred for 1 day at room temperature. The solvent was removed in vacuo. The dark brown residue was dissolved in 5 mL of CH_2Cl_2 and chromatographed at −40 °C on silica. The red fraction containing **16** was eluted with pentane/CH_2Cl_2 (5:2). After evaporation of the solvent in vacuo **16** was obtained as a dark red powder (purity at least 95%): yield 0.21 g (23% based on **15**); mp 113 °C dec; $C_{28}H_{12}N_2O_{10}W_2$ (904.1). IR (Et_2O): ν(CO) 2062 w, 1979 w, 1939 vs cm^{-1}. ^{1}H NMR ([D_8]THF): δ 3.94 (s, 6 H, Me), 4.12 (s, 6 H, Me). ^{13}C NMR ([D_8]THF): δ 48.9 (Me), 52.1 (Me), 61.6 (C_γ), 72.3, 74.0 (C_α, C_ξ), 87.3 (C_δ), 109.4 (C_β), 198.4 (cis-CO), 204.1 (trans-CO), 223.5 (W=C); the C_ϵ resonance is presumably obscured by the solvent signal. UV/vis, λ_{max}, nm (log ϵ): 584 (due to the poor solubility of **16** in pentane, log ϵ could not exactly be determined) [pentane]; 565 (3.867) [CH_2Cl_2]. MS (FAB, 3-nitrobenzyl alcohol), *m/z* (%): 904 (5) [M^+], 876 (11), 848 (6), 820 (8), 792 (12) [$M^+ - n$ CO, n = 1−4].

X-ray Structural Analysis of 2. Crystal data: $C_{16}H_{12}N_2O_{10}W_2$, M_r = 760.0, triclinic, space group $P\bar{1}$, a = 8.530(2) Å, b = 9.404(2) Å, c = 15.188(4) Å, α = 78.91(2)°, β = 74.47(2)°, γ = 64.48(2)°, V = 1055.3(4) Å^3, Z = 2, d_c = 2.392 g cm^{-3}, $F(000)$ = 700, μ = 10.947 mm^{-1}, R (R_w) = 0.0331 (0.0746) for 3705 observed reflections ($I > 2.0\sigma(I)$]), largest difference peak/hole +2.283/−1.160 e Å^{-3}. A single crystal was grown from CH_2Cl_2/hexane (1:1) and mounted in a glass capillary. All data were collected on a Siemens R3m/V diffractometer at −39 °C (Wyckoff scan, $5° < 2\theta < 54°$) 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.

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Supporting Information Available: Tables of crystal data and refinement details, complete positional and thermal parameters, and bond distances and angles for complex **5** and NMR spectra of the complexes **2**, **3**, **10**, **14**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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