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Binuclear Complexes with an Aminocarbene−Cyclopropenylidene Unit as Bridging Ligand: Facile Migration of Carbonylmetal Fragments in Carbene Complexes[†]

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The sequential reaction of the (dimethylamino)ethynylcarbene complexes $[(CO)_5M{=}C(NMe_2)C{\equiv}CH]$ (**1a**−**c**: M = W (**a**), Mo (**b**), Cr (**c**)) with BuLi, $[M(CO)_6]$, and $CF_3SO_3CH_3$ affords homobinuclear complexes with an aminocarbene−cyclopropenylidene bridging ligand, $[(CO)_5M{=}C(NMe_2)\overline{C{=}C(OMe)C}{\equiv}M(CO)_5]$ (**3a**−**c**). Two isomeric heterobinuclear complexes (**4xy** and **4yx**) are formed in the reaction of $[(CO)_5M{=}C(NMe_2)C{\equiv}CH]$ (**1**) with BuLi, $[M'(CO)_6]$ ($M \neq M'$: W, Mo, Cr), and $CF_3SO_3CH_3$. **4xy** and **4yx** differ in the relative distribution of the metals M and M′: $[(CO)_5M{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}M'(CO)_5]$ (**4xy**) and $[(CO)_5M'{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}M(CO)_5]$ (**4yx**). The **4xy**/**4yx** ratios obtained by the two different possible reaction sequences are similar. Complexes **4xy** and **4yx** do not interconvert. The reaction of *cis*-$[(CO)_4(Me_3P)W{=}C(NMe_2)C{\equiv}CH]$ with BuLi, $[W(CO)_6]$, and $CF_3SO_3CH_3$ likewise gives two isomers, *cis*-$[(CO)_4(Me_3P)W{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}W(CO)_5]$ (**7**) and $[(CO)_5W{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}M(PMe_3)(CO)_4]$ (**8**). These results demonstrate the facile migration of carbonylmetal fragments along a carbon chain. The structures of the complexes **3b**,**c** and **7** have been established by X-ray structural analyses.

Introduction

Bi- and polynuclear organometallic complexes containing π-unsaturated conjugated bridging ligands are expected to exhibit potentially useful physical and chemical properties.[1] Developing synthetic routes to such complexes has therefore been an attractive goal in recent years. Electronic communication between metal centers in bi- and polynuclear complexes can be mediated in different ways.[2] Various types of bridging ligands have been proposed. Recently, attention has focused on complexes with linear carbon-rich bridges, $[L_nM(C)_xM'L'_m]$.[3] Binuclear complexes with up to 20 carbon atoms linking the metals[4] as well as linear polynuclear complexes with all-carbon units linking the metals[5] have been synthesized. Linear[6] and L-shaped trinuclear[7] and cyclic tetra- and octanuclear butadiynediyl complexes[8] have also been reported. Rigid-rod organometallic polymers $(-L_nMC_x-)_y$ have also been studied theoretically by extended Hückel MO calculations.[9]

In addition to linear carbon-only bridges, other bridging ligands are likewise conceivable. Structural alternatives for binuclear complexes with one C(sp^2) and one C(sp) atom linking the conjugated bridge to transition metals are shown in Chart 1.

Several routes to complexes of type **I** have been developed recently. Binuclear complexes **I** with various combinations of the metals M and M′ have been synthesized by reaction of deprotonated alkynyl complexes with metal carbonyls and subsequent alkylation

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[†] Dedicated to Prof. Gottfried Huttner on the occasion of his 65th birthday.

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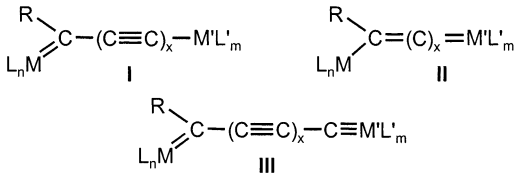
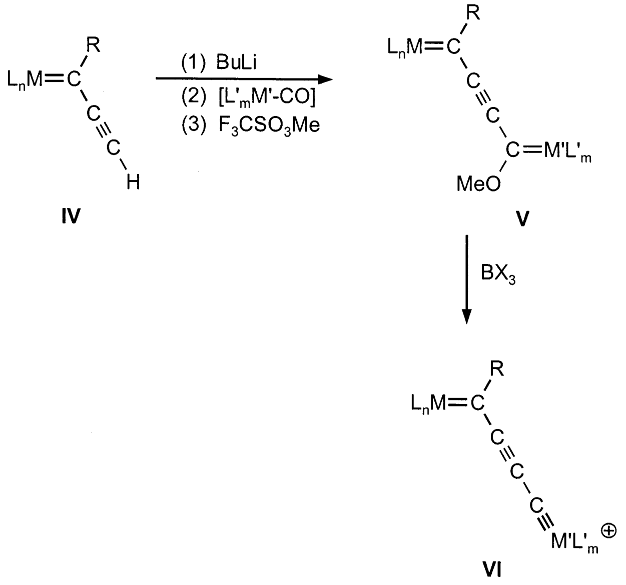
Chart 1



of the resulting metalates,[3d,10] by substitution of alkynylcarbene anions for the halide in metal halides, or by Pd-catalyzed coupling of C-stannylated carbene complexes with metal halides. By means of the last method, in addition to a series of heterobinuclear complexes,[11,12] “linear” trinuclear (M′ = Fe, Ni, Pd, Pt, Hg),[12,13] L-shaped trinuclear (M′ = Ti),[13] star-shaped tetranuclear (M′ = B, P),[13] and pentanuclear complexes (M′ = Ge; Sn)[13] were accessible. Complexes of type **II** (R = H; x = 1) have also been reported.[14] For the homobinuclear complex with $L_nM = M'L'_n = Fe(CO)_2Cp^*$ a dynamic process was observed which equilibrates the two metal centers. To the best of our knowledge, complexes of type **III** have not been prepared until now. However, complexes of type **III** should be accessible by a rather straightforward approach (x = 1; Scheme 1).

Scheme 1



Deprotonation of **IV**, followed by reaction with a metal carbonyl and subsequent alkylation of the resulting metalate should give complex **V**. Reaction of **V** with Lewis acids such as boron trihalides should transform **V** into the carbene−carbyne complex **VI**.

We recently reported the synthesis of a series of binuclear alkynediyl-bridged bis(aminocarbene) complexes $[(CO)_5W{=}C(NMe_2)(C{\equiv}C)_y(Me_2N)C{=}W(CO)_5]$ (y = 0, 2, 4, 6).[15] In the course of these investigations we also briefly studied the sequential reaction of $[(CO)_5W{=}C(NMe_2)C{\equiv}CH]$ with nBuLi, $[W(CO)_6]$, and F_3CSO_3Me and tentatively assigned an aminocarbene−methoxycarbene structure, $[(CO)_5W{=}C(NMe_2)C{\equiv}C(MeO)C{=}W(CO)_5]$, to the resulting binuclear complex.[15] In subsequent studies of its reactivity we observed that, rather unexpectedly, this complex did not react with $HNMe_2$ to form the corresponding bis(aminocarbene) complex $[(CO)_5W{=}C(NMe_2)C{\equiv}C(Me_2N)C{=}W(CO)_5]$. Follow-up investigation and the results of an X-ray structural analysis revealed that the major reaction product is an unusual aminocarbene−cyclopropenylidene complex and that the expected aminocarbene−methoxycarbene complex is at best a minor product. We now report (a) the synthesis of several homo- and heterobinuclear aminocarbene−cyclopropenylidene complexes, (b) their detailed structures, and (c) the obviously fast reversible rearrangement of intermediates in the course of the formation of these aminocarbene−cyclopropenylidene complexes.

Results and Discussion

Deprotonation of the ethynylcarbene tungsten complex **1a** with nBuLi in diethyl ether gave the lithiated complex **2a**. When subsequently an equimolar amount of tungsten hexacarbonyl in a few milliliters of THF was added to the solution, the slow formation of an anionic binuclear complex at room temperature was observed by IR spectroscopy. The spectrum was in accord with that of the acyl tungstate $[(CO)_5W{=}C(NMe_2)C{\equiv}CC(OLi){=}W(CO)_5]$, whose formation was expected on the basis of previous results. The new complex was only modestly stable. Its decomposition to an as yet unidentified product competed with its formation. After 45 min at room temperature the decomposition reaction dominated. Therefore, the reactions were stopped after 45 min by addition of CF_3SO_3Me, although the reaction of **2a** with $[W(CO)_6]$ was still incomplete. The alkylation also proceeded only slowly, requiring approximately 1 h. Chromatography on silica and recrystallization afforded the novel homobinuclear aminocarbene−cyclopropenylidene complex **3a** as yellow crystals (Scheme 2).

Complex **3a** exhibited ν(CO) absorptions for two different pentacarbonylmetal fragments in the IR spectrum and three singlets of equal intensity in the ^{1}H NMR spectrum. In addition to six resonances for groups bonded to tungsten (for two trans CO ligands, two cis CO ligands, and two carbene ligands) and three peaks for methyl groups, two resonances at rather low field (at δ 169.2 and 174.3) were observed in the ^{13}C NMR spectrum. The carbene resonance at lower field (δ 235.9) was in the range characteristic for aminocarbene complexes; however, the second carbene resonance at δ 181.7 was at unusually high field and did not agree with the position expected for an alkoxycarbene carbon atom.

The reactions of the molybdenum complex **1b** with nBuLi, $[Mo(CO)_6]$, and F_3CSO_3Me and that of the chromium complex **1c** with nBuLi, $[Mo(CO)_6]$, and F_3CSO_3Me proceeded analogously and afforded the ho-

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Scheme 2

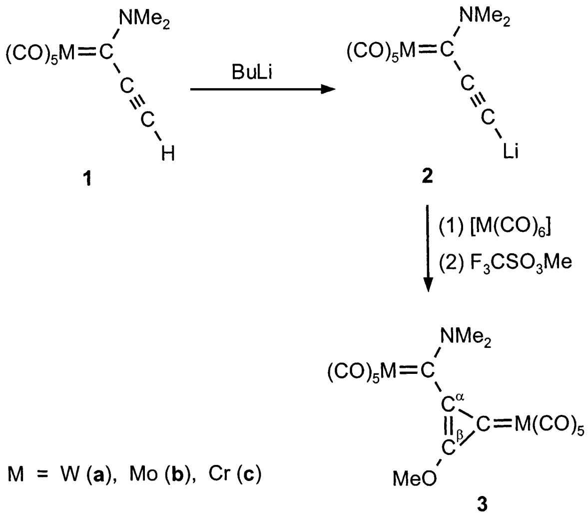

Table 1. Selected Bond Distances, Bond Angles, and Torsion Angles in 3b and 3c

	3b (M = Mo)	**3c** (M = Cr)
Bond Distances (Å)		
M(1)−C(6)	2.258(3)	2.120(4)
M(1A)−C(8)	2.192(3)	2.057(4)
C(6)−N(1)	1.316(4)	1.313(5)
C(6)−C(7)	1.462(4)	1.460(6)
C(7)−C(9)	1.348(4)	1.348(6)
C(7)−C(8)	1.435(4)	1.427(6)
C(8)−C(9)	1.385(4)	1.385(6)
C(9)−O(9)	1.318(4)	1.314(5)
O(9)−C(10)	1.473(4)	1.472(6)
N(1)−C(11)	1.481(4)	1.477(6)
N(1)−C(12)	1.483(4)	1.484(6)
Bond Angles (deg)		
N(1)−C(6)−C(7)	114.9(3)	115.1(4)
N(1)−C(6)−M(1)	134.6(2)	133.7(3)
C(7)−C(6)−M(1)	110.6(2)	111.2(3)
C(9)−C(7)−C(8)	59.6(2)	−59.8(3)
C(9)−C(7)−C(6)	153.3(3)	152.4(4)
C(8)−C(7)−C(6)	145.5(3)	146.5(4)
C(9)−C(8)−C(7)	57.1(2)	−57.2(3)
C(9)−C(8)−M(1A)	153.8(2)	153.1(3)
C(7)−C(8)−M(1A)	148.9(2)	149.5(3)
O(9)−C(9)−C(7)	145.6(3)	145.8(4)
O(9)−C(9)−C(8)	151.1(3)	151.2(4)
C(7)−C(9)−C(8)	63.3(2)	62.9(3)
Torsion Angles (deg)		
C(1)−M(1)−C(6)−N(1)	116.9(3)	−115.9(4)
N(1)−C(6)−C(7)−C(8)	78.3(5)	−77.8(7)
C(4A)−M(1A)−C(8)−C(7)	36.5(4)	−35.4(6)
M(1)−C(6)−C(7)−C(9)	53.5(7)	−54.4(9)

mobinuclear complexes **3b** and **3c** (Scheme 2), respectively. From the IR and NMR data it followed that the structures of **3b** and **3c** are similar to that of **3a**.

The structures of **3** were finally established by X-ray analyses of **3b**,**c**. Selected bond distances, bond angles, and torsion angles are compiled in Table 1. Analogous bond distances and bond angles in both complexes differ only slightly. Therefore, only the structure of **3b** is shown in Figure 1.

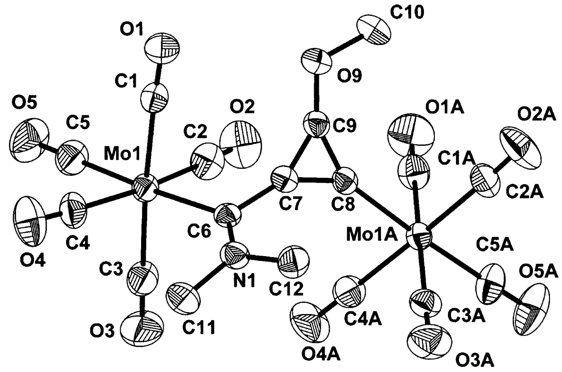

Figure 1. Structure of complex **3b**.

A novel aminocarbene−cyclopropenylidene bridge connects the two $(CO)_5M$ fragments in **3**. The M=C(NEt$_2$) and M=C(8) distances agree well with those usually observed for aminocarbene complexes.[16] The Cr=C(cyclopropenylidene) bond is likewise in the range reported earlier for (cyclopropenylidene)chromium complexes.[17,18] In both complexes the M=C(aminocarbene) bond is significantly longer than the M=C(cyclopropenylidene) bond, due to the more pronounced acceptor properties of the cyclopropenylidene ligand. Both carbene carbon atoms are coordinated in a trigonal-planar fashion (sum of angles 359.8−360.1°). To avoid steric congestion, the aminocarbene plane is strongly tilted against the cyclopropenylidene plane (torsion angle N(1)−C(6)−C(7)−C(8) = 78.3(5)° (**3b**), −77.8(7)° (**3c**)). This arrangement prevents π-interaction of the ring π-electrons with the p_z orbital at the aminocarbene carbon atom in the solid state. Consequently, the C(6)−C(7) bond (1.462(4) Å (**3b**), 1.460(6) Å (**3c**)) corresponds to a C(sp^2)−C(sp^2) single bond.[19] Related bond lengths and bond angles of the bridging ligands of **3b** and **3c** are almost identical; however, the bond lengths within each C_3 ring differ considerably. The C(7)−C(9) bond is comparable to the corresponding bond in mononuclear cyclopropenylidene complexes[17] and to the C=C bond in diphenylcyclopropenone (1.349 Å)[20] or its hydrate (1.354 Å).[21] The two single bonds C(8)−C(7) and C(8)−C(9) differ significantly, C(8)−C(7) being longer and C(8)−C(9) being shorter than the C−C bond in diphenylcyclopropenone hydrate (1.409 Å).[21]

Deprotonation of the ethynylcarbene tungsten complex **1a** with *n*BuLi followed by addition of [Cr(CO)$_6$] and subsequently of F_3CSO_3Me surprisingly afforded *two* isomeric heterobinuclear complexes, **4ac** and **4ca** (Scheme 3). It was not possible to separate the compounds. The ^{1}H NMR spectrum of the isomeric mixture exhibited two sets of OMe and NMe resonances in a ratio of 1.8/1. An analogous mixture was obtained when, instead of the tungsten complex **1a**, the (ethynylcarbene)chromium complex **1c** was used as the starting carbene complex and [W(CO)$_6$] instead of [Cr(CO)$_6$] as

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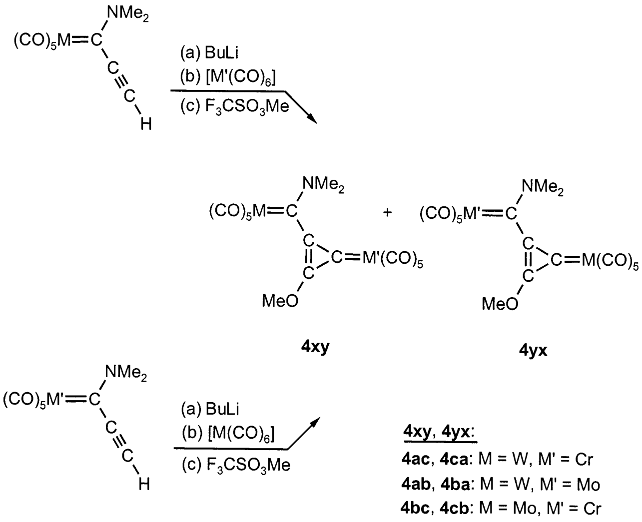
Scheme 3



4xy **4yx**

4xy, 4yx:
4ac, 4ca: M = W, M' = Cr
4ab, 4ba: M = W, M' = Mo
4bc, 4cb: M = Mo, M' = Cr

the hexacarbonyl substrate. The reaction of **1c** with *n*BuLi, [W(CO)$_6$], and F$_3$CSO$_3$Me gave **4ac** and **4ca** in a 2.0/1 ratio (Scheme 3). Thus, within error limits the **4ac**/**4ca** ratios were identical and independent of the preparative route. The formation of homobinuclear complexes (**3a** and **3c**) in addition to **4ac** and **4ca** was not observed.

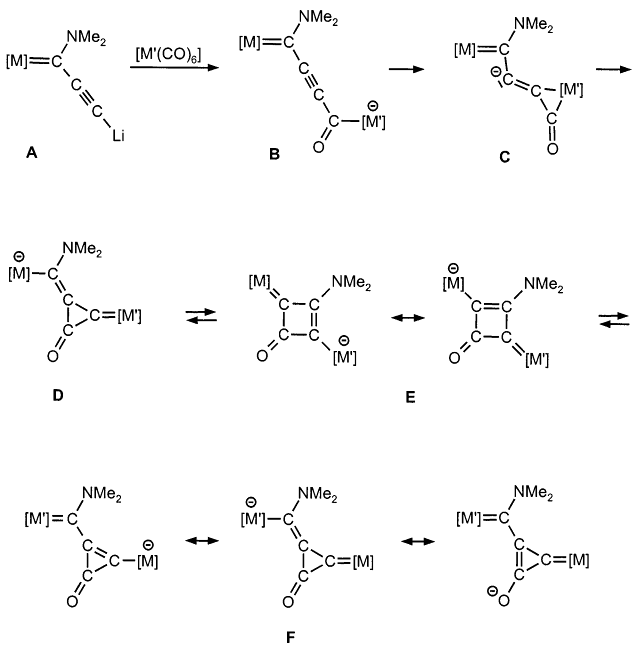
Through comparison of the ^{1}H NMR spectra of the mixtures with those of the homobinuclear complexes **3a** and **3c** it was possible to assign the structures of the isomers. The preferentially formed complex was **4ac**, in which the more electron-rich fragment is bonded to the aminocarbene moiety.

Complex **4ac** could not be transformed into **4ca** and vice versa. However, when solutions of **4ac**/**4ca** in toluene were heated to 105 °C, the ratio irreversibly changed. Both complexes slowly decomposed and the ratio **4ac**/**4ca** increased due to the faster decomposition of the minor, less stable isomer **4ca**.

The reactions of deprotonated **1a** with [Mo(CO)$_6$] and **1b** with [W(CO)$_6$] as well as those of **1b** with [Cr(CO)$_6$] and **1c** with [Mo(CO)$_6$] likewise yielded mixtures of two isomers (**4ab**/**4ba** and **4bc**/**4cb**, respectively). Again, homobinuclear complexes (**3a**–**c**) in addition to heterobinuclear complexes were not detected. The ratios of isomers as determined by integration of the NMe resonances were similar for the two alternative reaction sequences (**4ab**/**4ba** = 0.45 and 0.50, **4bc**/**4cb** = 4.3 and 6.2, respectively). With both mixtures that isomer dominated in which the Mo(CO)$_5$ fragment is bonded to the aminocarbene carbon. The preference for occupying the aminocarbene site decreased in the series Mo > W > Cr.

The formation of two isomers independent of the reaction sequence indicates that either the product complexes or an intermediate of the reactions rapidly rearranges by M(CO)$_5$ migration. Since the aminocarbene–cyclopropenylidene complexes do not interconvert, the isomerization must occur during the course of the reactions and before the final alkylation step of the reaction sequence. Homobinuclear complexes are not formed when complexes with different central metals M and M′ are employed. Therefore, the rearrangement must proceed by an intramolecular process. The results are best explained by assuming a pseudosymmetric intermediate. A possible mechanism involving migration of (CO)$_5$M and (CO)$_5$M′ fragments along the carbon chain, ring formation, ring enlargement,[22] and ring contraction steps is shown in Scheme 4.

Scheme 4



Addition of the lithiated complex **1** (**A** in Scheme 4) to the carbonyl carbon atom of a metal hexacarbonyl yields the binuclear complexes **B**. Intramolecular migration of M′(CO)$_5$ and, via **C**, formation of the three-membered ring gives the anionic aminocarbene–cyclopropenylidene complex **D**. A similar sequence has been proposed to explain the formation of (cyclopropenone)-chromium complexes from [Cr(CO)$_6$], Li[C≡COEt], and [Me$_3$O]BF$_4$.[17b] Complex **D** presumably is in equilibrium with its isomer **F** through the pseudosymmetric cyclobutenonylidene intermediate **E**. Alkylation of **D** with F$_3$CSO$_3$Me finally affords the complexes **4xy**; alkylation of **F** affords the complexes **4yx**. The ratio of isomers obtained then primarily depends on the relative stabilities of **D** and **F**, favoring the isomer in which the less electron rich M(CO)$_5$ fragment is bonded to the cyclopropenylidene group.

When **1a** was replaced by the more electron rich *cis*-(amino)ethynylcarbene trimethylphosphine complex **6**, the sequential reaction with BuLi, [W(CO)$_6$], and F$_3$CSO$_3$Me gave an isomeric mixture of phosphine-substituted derivatives of **3a** (Scheme 5). Complex **6** was obtained by irradiation of [(CO)$_5$W=C(NMe$_2$)-C≡CSiMe$_3$] in the presence of PMe$_3$ and subsequent desilylation with KF. As expected, the reaction proceeded more selectively. A strong preference for the formation of that

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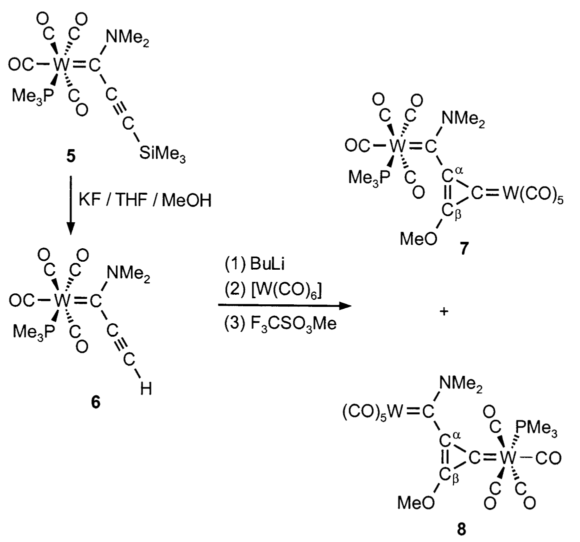
[22] A reviewer suggested a mechanism involving formation of a dimetalated amino dimethylene ketene from **D** and migration of the amino group instead of a metal carbonyl fragment. Although such a mechanism cannot be completely discarded, it seems rather unlikely for two reasons. (a) A cyclobutenonylidene complex is isolated after chromatography when the reaction in Scheme 2 is carried out in tetrahydrofuran instead of diethyl ether. (b) The migration of metal carbonyl fragments in unsaturated carbene complexes is often proposed to explain experimental results. In contrast and to the best of our knowledge, migration of an amino group bonded to a carbene carbon atom has not been observed.

Scheme 5



isomer (**7**) was observed in which the trimethylphosphine ligand resides at the aminocarbene tungsten atom. The isomeric ratio **7**/**8** was approximately 12.

In accord with the presence of two isomers, the ^{1}H and ^{13}C NMR spectra of **7**/**8** exhibited two sets of OMe and NMe resonances. One of the NMe signals of **7** is split into a doublet, presumably due to a through-space interaction with the adjacent PMe$_3$ ligand.

As for the **4xy**/**4yx** complexes, **7** and **8** could not not be separated by chromatography. However, due to the large excess of **7** it was possible to get a few crystals of the major isomer **7** by slowly removing the solvent from a saturated solution of **7**/**8** in CH$_2$Cl$_2$. The results of the X-ray analysis confirmed the presence of (CO)$_4$(PMe$_3$)W−aminocarbene and (CO)$_5$W−cyclopropenylidene units (Figure 2).

The phosphine and the aminocarbene ligand are mutually cis. Bond lengths and angles within the aminocarbene−cyclopropenylidene bridge in **7** (Table 3) are similar to those of **3b** and **3c**. The cyclopropenylidene and the aminocarbene planes are also strongly tilted with respect to each other (torsion angle W(1)−C(5)−C(6)−C(7) = 96.9(11)°). The arrangement of ligands around W(1) is a compromise between destabilizing steric interactions and maximizing π-back-bonding. For steric reasons the carbene plane in carbene−carbonyl complexes is usually staggered with respect to the cis carbonyl ligands. However, for electronic reasons the torsion angle C(1)−W(1)−C(5)−C(6) in **7** is reduced to −21.4(5)° and the P(1)−W(1) axis is almost perpendicular to the carbene plane (torsion angle P(1)−W(1)−C(5)−C(6) = 68.3(5)°), thus increasing overlap of the empty p$_z$ orbital at the carbene carbon with the energetically higher lying back-bonding d orbital at tungsten. To minimize steric congestion, the two bulky group (PMe$_3$ at tungsten and W(CO)$_5$ at the C$_3$ ring) are transoid. One of the NMe groups is significantly closer to the phosphine ligand, thus readily explaining the splitting of its NMe resonance into a doublet.

Our results demonstrate that under suitable conditions carbonylmetal fragments readily and reversibly can migrate along carbon chains. 1,2- and 1,3-migrations of (CO)$_5$M fragments have frequently been proposed recently to explain the structures of products formed in the reaction of unsaturated carbene complexes with nucleophilic substrates.[23]

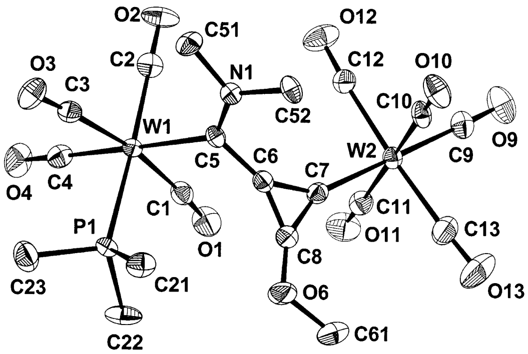


Figure 2. Structure of complex **7**.

Experimental Section

General Procedures. All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over CaH$_2$ (CH$_2$Cl$_2$) or sodium/benzophenone ketyl (pentane, Et$_2$O, THF) and were freshly distilled prior to use. The silica gel used for chromatography (J. T. Baker, silica gel for flash chromatography) was dried in vacuo and saturated with argon. The yields refer to analytically pure substances and were not optimized. The complexes **1a** and **1b** were prepared by a slight modification[24] of the procedure reported in ref 25. Complex **1c** was synthesized analogously. All other reagents, *n*BuLi and CF$_3$SO$_3$Me, were used as obtained from commercial sources. IR spectra were obtained on a Bio-Rad FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX 600 instrument. All spectra were recorded at room temperature in CDCl$_3$. Unless specifically mentioned, chemical shifts are reported relative to the residual solvent peaks (^{1}H NMR, δ 7.24 ppm; ^{13}C NMR, δ 77.0 ppm). The mass spectra were obtained on a Finnigan MAT 312 instrument (EI). Elemental analyses were carried on a Heraeus CHN-O-Rapid instrument.

General Procedure for the Synthesis of Complexes 3x and 4xy. At −80 °C 1.0 mmol of BuLi (0.63 mL of a 1.6 M solution in hexane) was added to a solution of 1.0 mmol of **1a** (0.27 g), **1b** (0.32 g), or **1c** (0.41 g) in 20 mL of Et$_2$O. When it was stirred for 30 min at −60 °C, the yellow solution turned cloudy. A mixture of 1.0 mmol of [Cr(CO)$_6$] (0.22 g), [Mo(CO)$_6$] (0.26 g), or [W(CO)$_6$] (0.35 g) and 5 mL of THF was added. The resulting red suspension was stirred for 45 min at room temperature and then cooled to −5 °C. A 1.25 mmol portion (0.21 g, 0.14 mL) of F$_3$CSO$_3$Me was added. The red-brown suspension was stirred for 15 min at −5 °C and for 45 min at room temperature. The solvent was removed in vacuo. The residue was dissolved in 8 mL of CH$_2$Cl$_2$ and the solution chromatographed at −40 °C on silica. With pentane/CH$_2$Cl$_2$ (7/3) a light yellow band was eluted. Removal of the solvent in vacuo and recrystallization of the residue from CH$_2$Cl$_2$ afforded the complexes **3x (4xy)** as light yellow crystals.

[(CO)$_5$W=C(NMe$_2$)$\overline{\text{C=C(OMe)C}}$=W(CO)$_5$] (3a). Yield: 34%. Mp: 147 °C dec. IR (Et$_2$O): ν(CO) 2073 w, 2063 m, 1982 vw, 1976 vw, 1945 vs, 1926 vs cm^{-1}. ^{1}H NMR: δ 3.38 (s, 3 H, NMe), 3.84 (s, 3 H, NMe), 4.52 (s, 3 H, OMe). ^{13}C NMR: δ 48.4, 51.9 (NMe), 63.2 (OMe), 169.2 (C$_\alpha$), 174.3 (C$_\beta$), 181.7 (^1J(WC) = 98.4 Hz, W=*C*(C$_2$)), 196.3 (^1J(WC) = 127.5 Hz, cis CO), 197.0

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[23] For recent reviews see e.g.: (a) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (b) Barluenga, J.; Flórez, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5.

[24] Hartbaum, C.; Roth, G.; Fischer, H. *Eur. J. Inorg. Chem.* **1998**, 191.

[25] Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1993**, *12*, 597.

Table 2. Crystal Data and Summary of X-ray Data Collection

	3b	**3c**	**7**
formula	$C_{17}H_9Mo_2NO_{11}$	$C_{17}H_9Cr_2NO_{11}$	$C_{19}H_{18}NO_{10}PW_2$
fw	595.13	507.25	819.0
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.026(4)	6.859(5)	6.8803(18)
b, Å	16.347(9)	15.909(11)	25.097(3)
c, Å	19.801(11)	19.559(14)	14.682(2)
α, deg	90	90	90
β, deg	92.20(9)	92.31(9)	95.035(16)
γ, deg	90	90	90
V, Å^3	2272.6(21)	2132.4(26)	2525.4(8)
Z	4	4	4
T, K	262	241	188
D_c, g cm^{-3}	1.739	1.580	2.154
F(000)	1160	1016	1528
cryst size, mm	0.4 × 0.35 × 0.3	0.4 × 0.4 × 0.6	0.4 × 0.35 × 0.3
μ, mm^{-1}	1.158	1.076	9.216
θ range, deg	2.06−27.00	2.06−27.00	2.14−27.00
max/min transmissn	0.5835/0.4746	0.4912/0.4201	0.0787/0.0463
no of rflns measd	7376	9549	7207
no of indep rflns (R_{int})	4942 (0.0330)	4635 (0.0500)	5519 (0.0265)
no. of params	280	280	298
goodness of fit on F^2	1.058	1.093	1.150
R1/wR2 ($I > 2\sigma(I)$)	0.0318/0.0754	0.0648/0.1580	0.0387/0.0993
R1/wR2 (all data)	0.0427/0.0803	0.0931/0.1934	0.0459/0.1037
largest diff peak/hole (e Å^{-3})	0.491/−0.476	1.733/−0.599	2.260/−1.996

Table 3. Selected Bond Distances, Bond Angles, and Torsion Angles in 7

Bond Distances (Å)			
W(1)−C(5)	2.225(7)	W(2)−C(7)	2.194(7)
C(5)−C(6)	1.467(10)	C(6)−C(7)	1.416(10)
C(6)−C(8)	1.325(10)	C(7)−C(8)	1.366(10)
C(5)−N(1)	1.312(9)	C(8)−O(6)	1.304(9)
W(1)−P(1)	2.5161(18)		
Bond Angles (deg)			
W(1)−C(5)−C(6)	112.6(5)	C(5)−C(6)−C(7)	146.0(7)
C(5)−C(6)−C(8)	153.9(7)	C(6)−C(7)−C(8)	56.9(6)
C(6)−C(8)−C(7)	63.5(5)	C(6)−C(7)−W(2)	148.3(5)
Torsion Angles (deg)			
P(1)−W(1)−C(5)−N(1)	−119.8(6)		
P(1)−W(1)−C(5)−C(6)	68.3(5)		
C(1)−W(1)−C(5)−C(6)	−21.4(5)		
N(1)−C(5)−C(6)−C(7)	−76.4(13)		
C(6)−C(7)−W(2)−C(12)	−20.8(10)		
W(1)−C(5)−C(6)−C(7)	96.6(11)		
W(1)−C(5)−C(6)−C(8)	−69.6(17)		

(^1J(WC) = 125.7 Hz, cis CO), 201.5 (^1J(WC) = 127.4 Hz, trans CO), 202.3 (^1J(WC) = 132.9 Hz, trans CO), 235.9 (^1J(WC) = 86.7 Hz, W=*C*(NMe$_2$)). MS/EI (70 eV, 220 °C), *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 $C_{17}H_9NO_{11}W_2$ (771.0): C, 26.48; H, 1.18; N, 1.82. Found: C, 26.37; H, 1.34; N, 1.82.

[(CO)$_5$Mo=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=Mo(CO)$_5$] (3b). Yield: 18%. Mp: 121 °C dec. IR (Et$_2$O): ν(CO) 2073 w, 2064 m, 1986 vw, 1958 sh, 1951 vs, 1934 vs cm^{-1}. ^{1}H NMR: δ 3.37 (s, 3 H, NMe), 3.88 (s, 3 H, NMe), 4.51 (s, 3 H, OMe). ^{13}C NMR: δ 48.6, 51.3 (NMe), 63.1 (OMe), 170.0 (C$_\alpha$), 176.5 (C$_\beta$), 194.6 (Mo=*C*(C$_2$)), 204.6, 205.9 (cis CO), 211.9, 212.0 (trans CO), 248.0 (Mo=*C*(NMe$_2$)). MS/EI (70 eV, 220 °C): *m/z* (%) 595 (36) [M$^+$], 567 (4), 539 (6), 511 (17) [M$^+$ − *n*CO, *n* = 1−3], 484 (20) [MH$^+$ − 4CO], 455 (47), 427 (100), 399 (89), 371 (71), 343 (34), 315 (60) [M$^+$ − *n*CO, *n* = 5−10]. Anal. Calcd for $C_{17}H_9Mo_2NO_{11}$ (595.1): C, 34.31; H, 1.52; N, 2.35. Found: C, 34.49; H, 1.67; N, 2.20.

[(CO)$_5$Cr=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=Cr(CO)$_5$] (3c). Yield: 21%. Mp: 130 °C dec. IR (Et$_2$O): ν(CO) 2067 w, 2056 m, 1986 vw, 1955 sh, 1948 vs, 1930 vs cm^{-1}. ^{1}H NMR: δ 3.38 (s, 3 H, NMe), 3.93 (s, 3 H, NMe), 4.53 (s, 3 H, OMe). ^{13}C NMR: δ 49.7, 49.9 (NMe), 63.6 (OMe), 170.5 (C$_\alpha$), 178.3 (C$_\beta$), 203.5 (Cr=C(sp^2)), 215.5, 217.1 (cis CO), 222.0, 222.1 (trans CO), 255.7 (Cr=C(NMe$_2$)). MS/EI (70 eV, 20 °C): *m/z* (%) 507 (28) [M$^+$], 423 (3), 395 (19), 367 (31), 339 (19), 311 (67), 283 (69), 255 (45), 227 (100) [M$^+$ − *n*CO, *n* = 3−10]. Anal. Calcd for $C_{17}H_9Cr_2NO_{11}$ (507.3): C, 40.25; H, 1.79; N, 2.76. Found: C, 40.22; H, 1.80; N, 2.38.

[(CO)$_5$W=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=Cr(CO)$_5$] (4ac) and [(CO)$_5$Cr=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=W(CO)$_5$] (4ca). Yield: 38% (from **1a** and [Cr(CO)$_6$]), 25% (from **1c** and [W(CO)$_6$]). **4ac/4ca** ratio: 1.8 (from **1a** and [Cr(CO)$_6$]); 2.0 (from **1c** and [W(CO)$_6$]). Mp: 151 °C dec. IR (Et$_2$O): ν(CO) 2071 w, 2058 m, 1984 vw, 1947 vs, 1929 vs cm^{-1}. ^{1}H NMR: **4ac**, δ 3.36 (s, 3 H, NMe), 3.85 (s, 3 H, NMe), 4.53 (s, 3 H, OMe); **4ca**, δ 3.40 (s, 3 H, NMe), 3.92 (s, 3 H, NMe), 4.53 (s, 3 H, OMe). ^{13}C NMR: **4ac**, δ 48.3, 51.8 (NMe), 63.7 (OMe), 173.0 (C$_\alpha$), 178.1 (C$_\beta$), 204.9 (Cr=*C*(sp^2)), 196.4 (^1J(WC) = 127.4 Hz, cis CO, W−CO), 201.5 (trans CO, W−CO), 217.1 (*cis*-CO, Cr−CO), 222.1 (trans CO, Cr−CO), 236.3 (W=*C*(sp^2)); **4ca**, δ 49.7, 49.8 (NMe), 63.2 (OMe), 166.8 (C$_\alpha$), 174.5 (C$_\beta$), 180.6 (W=*C*(sp^2)), 196.8 (^1J(WC) = 126.0 Hz, cis CO, W−CO), 202.3 (trans CO, W−CO), 215.4 (*cis*-CO, Cr−CO), 221.9 (trans CO, Cr−CO), 255.4 (Cr=*C*(sp^2)). MS/EI (70 eV, 200 °C): *m/z* (%) 639 (33) [M$^+$], 527 (17), 499 (53), 471 (20), 443 (41), 415 (100), 387 (15), 359 (40) [M$^+$ − *n*CO, *n* = 4−10], 316 (26) [MH$^+$ − 10CO − NMe$_2$]. Anal. Calcd for $C_{17}H_9CrNO_{11}W$ (639.10): C, 31.95; H. 1.42; N, 2.19. Found: C, 32.03; H, 1.45; N, 1.94.

[(CO)$_5$W=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=Mo(CO)$_5$] (4ab) and [(CO)$_5$Mo=C(NMe$_2$)$\overline{\mathrm{C{=}C(OMe)C}}$=W(CO)$_5$] (4ba). Yield: 19% (from **1a** and [Mo(CO)$_6$]), 20% (from **1b** and [W(CO)$_6$]). **4ab/4ba** ratio: 0.45 (from **1a** and [Mo(CO)$_6$]), 0.50 (from **1b** and [W(CO)$_6$]). Mp: 125 °C dec. IR (Et$_2$O): ν(CO) 2073 w, 2064 m, 1987 vw, 1978 vw, 1949 vs, 1941 sh, 1930 vs cm^{-1}. ^{1}H NMR: **4ab**, δ 3.36 (s, 3 H, NMe), 3.84 (s, 3 H, NMe), 4.52 (s, 3 H, OMe); **4ba**, δ 3.39 (s, 3 H, NMe), 3.87 (s, 3 H, NMe), 4.51 (s, 3 H, OMe). ^{13}C NMR: **4ab**, δ 48.2, 51.9 (NMe), 63.2 (OMe), 171.8 (C$_\alpha$), 176.4 (C$_\beta$), 196.3 (^1J(WC) = 124.1 Hz, *cis*-CO, W−CO), 201.6 (^1J(WC) = 127.4 Hz, trans CO, W−CO), 205.9 (cis CO, Mo−CO), 211.9 (trans CO, Mo−CO), 236.1 (W=*C*(sp^2)); **4ba**, δ 48.8, 51.3 (NMe), 63.2 (OMe), 167.4 (C$_\alpha$), 174.4 (C$_\beta$), 180.5 (^1J(WC) = 78.2 Hz, W=*C*(sp^2)), 197.0 (^1J(WC) = 125.9 Hz, *cis*-CO, W−CO), 202.4 (^1J(WC) = 133.3 Hz, trans CO, W−CO), 204.5 (cis CO, Mo−CO), 211.9 (trans CO, Mo−CO), 247.9 (Mo=*C*(sp^2)). MS/EI (70 eV, 200 °C): *m/z* (%) 683 (31) [M$^+$], 655 (5), 627 (5), 599 (30), 571 (30), 543 (69), 515

(100), 487 (94), 459 (73), 431 (35), 403 (52) [$M^+ - n$CO, n = 1−10], 316 (26). Anal. Calcd for $C_{17}H_9MoNO_{11}W$ (683.05): C, 29.85; H, 1.33; N, 2.05. Found: C, 30.14; H, 1.56; N, 1.76.

$[(CO)_5Mo{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}Cr(CO)_5]$ (4bc) and $[(CO)_5Cr{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}Mo(CO)_5]$ (4cb). Yield: 22% (from **1b** and [$Cr(CO)_6$]), 38% (from **1c** and [$Mo(CO)_6$]). **4bc/4cb** ratio: 4.3 (from **1b** and [$Cr(CO)_6$]), 6.2 (from **1c** and [$Mo(CO)_6$]). Mp: 143 °C dec. IR (Et_2O): ν(CO) 2071 w, 2059 m, 1989 vw,1981 vw, 1956 sh, 1949 vs, 1935 sh, 1932 vs cm^{-1}. ^{1}H NMR: **4bc**, δ 3.37 (s, 3 H, NMe), 3.88 (s, 3 H, NMe), 4.52 (s, 3 H, OMe); **4cb**, δ 3.38 (s, 3 H, NMe), 3.93 (s, 3 H, NMe), 4.52 (s, 3 H, OMe). ^{13}C NMR: **4bc**, δ 48.8, 51.3 (NMe), 63.6 (OMe), 171.1 (C_α), 178.2 (C_β), 205.9 (Cr=C(sp^2)), 204.6 (cis Mo−CO), 211.9 (trans Mo−CO), 217.1 (cis Cr−CO), 222.2 (trans Cr−CO), 248.1 (Mo=C(sp^2)); **4cb**, δ 49.5, 49.9 (NMe), 63.1 (OMe), 169.3 (C_α), 176.5 (C_β), 194.6 (Mo=C(sp^2)), 203.4 (cis Mo−CO), 211.9 (trans Mo−CO), 215.4 (cis Cr−CO), 221.9 (trans Cr−CO), 255.4 (Cr=C(sp^2)). MS/EI (70 eV, 330 °C): m/z (%) 553 (39) [M$^+$], 569 (14), 441 (19), 413 (65), 385 (42), 357 (100), 329 (78), 301 (74), 273 (39) [$M^+ - n$CO, n = 3−10]. Anal. Calcd for $C_{17}H_9CrMoNO_{11}$ (551.19): C, 37.04; H, 1.65; N, 2.54. Found: C, 37.09; H, 1.61; N, 2.21.

***cis*-$[(CO)_4(PMe_3)W{=}C(NMe_2)C{\equiv}CSiMe_3]$ (5).** An orange solution of 8.6 g (18 mmol) of **1a** and 1.52 g (2.07 mL, 20 mmol) of PMe_3 in 30 mL of CH_2Cl_2 was irradiated at ca. 12 °C for 10 h. The solution turned red. The solvent was removed in vacuo. The red residue was dissolved in 15 mL of CH_2Cl_2, and at −40 °C the solution was chromatographed on silica. First, with pentane/CH_2Cl_2 (7/3) an orange-red zone (**1a**) was eluted and then, with pentane/CH_2Cl_2 (3/2), a red band. Removal of the solvent in vacuo gave complex **5** as a red solid. Yield: 4.5 g (47% based on **1a**). Mp: 115 °C. IR (Et_2O): ν(CO) 2006 m, 1908 s, 1883 vs cm^{-1}; ν(C≡C) = 2116 vw cm^{-1}. ^{1}H NMR: δ 0.22 (s, 9 H, SiMe), 1.50 (d, ^2J(PH) = 7.4 Hz, 9 H, PMe), 3.47 (d, J(PH) = 0.9 Hz, 3 H, NMe), 3.71 (s, 3 H, NMe). ^{13}C NMR: δ −0.54 (SiMe), 19.5 (d, J(PC) = 26.1 Hz, PMe), 45.9 (NCH_3), 51.5 (dd, J(PC) = 2.6 and 6.1 Hz, NMe), 107.3 (C_α), 128.3 (C_β), 204.0 (J(WC) = 127.6 Hz, ^2J(PC) = 8.3 Hz, apic cis CO), 209.6 (d, ^2J(PC) = 23.3 Hz, eq cis CO), 211.9 (J(WC) = 127.0 Hz, ^2J(PC) = 5.9 Hz, trans CO), 236.97 (J(WC) = 87.4 Hz, ^2J(PC) = 6.7 Hz, W=C). ^{31}P NMR: δ −32.9 (J(PW) = 226.1 Hz). MS/EI (70 eV, 115 °C): m/z (%) 525 (47) [M$^+$], 469 (72), 441 (100), 413 (64) [$M^+ - n$CO, n = 2−4], 452 (10), 396 (27) [$M^+ - n$CO − $SiMe_3$, n = 0, 2], 320 (20), 264 (11) [$M^+ - n$CO − PMe_3 − $SiMe_3$, n = 2, 4], 369 (18) [M^+ − 4CO − NMe_2], 349 (18) [M^+ − 2CO − PMe_3 − NMe_2], 293 (14) [M^+ − 4CO − PMe_3 − NMe_2]. Anal. Calcd for $C_{15}H_{24}NO_4PSiW$ (525.3): C, 34.30, H, 4.61, N, 2.67. Found: C, 34.22, H, 4.62, N, 2.30.

***cis*-$[(CO)_4(PMe_3)W{=}C(NMe_2)C{\equiv}CH]$ (6).** A 0.10 g portion (1.7 mmol) of KF was added to an orange solution of 4.2 g (8.0 mmol) of **5** in 40 mL of THF/MeOH (1:1). The solution was stirred for 30 min at room temperature. A 150 mL amount of Et_2O was added. The resulting orange-red solution was extracted three times each with 100 mL of a saturated solution of $NaHCO_3$ in water. The organic layer was dried with Na_2SO_4. The solvent was removed in vacuo. The red residue was dissolved in 25 mL of CH_2Cl_2 and the solution chromatographed at −40 °C on silica. Elution of the red band with pentane/CH_2Cl_2 (1/1) and removal of the solvent afforded **6** as a red solid. Yield: 3.3 g (90% based on **5**). Mp: 79 °C dec. IR (Et_2O): ν(CO) 2008 m, 1909 m, 1883 vs, 1843 vw cm^{-1}. ^{1}H NMR: δ 1.49 (d, ^2J(PH) = 7.4 Hz, 9 H, PMe), 3.50 (d, J(PH) = 0.9 Hz, 3 H, NMe), 3.75 (s, 3 H, NMe), 5.52 (s, 1 H, C≡CH). ^{13}C NMR: δ 19.6 (d, J(PC) = 26.5 Hz, PMe), 46.1 (s, NMe), 51.6 (d, J(PC) = 3.2 Hz, NMe), 87.1 (C_α), 109.9 (J(PC) = 12.6 Hz, C_β), 204.0 (J(WC) = 126.7 Hz, ^2J(PC) = 8.6 Hz, apic cis CO), 209.4 (J(WC) = 173.4 Hz, ^2J(PC) = 24.4 Hz, eq cis CO), 211.9 (J(WC) = 127.1 Hz, ^2J(PC) = 4.8 Hz, trans CO), 237.4 (d, ^2J(PC) = 7.1 Hz, W=C). ^{31}P NMR: δ −35.42 (J(PW) = 226.6 Hz). MS/EI (70 eV, 160 °C): m/z (%) 453 (77) [M$^+$], 397 (56), 369 (65), 341 (100) [$M^+ - n$CO, n = 2−4], 321 (38), 293 (52), 265 (36) [$M^+ - n$CO − PMe_3, n = 2−4]. Anal. Calcd for $C_{12}H_{16}NO_4PW$ (453.1): C, 31.81, H, 3.56, N, 3.09. Found: C, 31.69, H, 4.23, N, 2.37.

$[(CO)_4(PMe_3)W{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}W(CO)_5]$ (7) and $[(CO)_5W{=}C(NMe_2)\overline{C{=}C(OMe)C}{=}W(PMe_3)(CO)_4]$ (8). At −78 °C, 1 mmol of nBuLi (0.63 mL of a 1.6 M solution in hexane) was added to a red solution of 0.45 g (1.00 mmol) of **6** in 20 mL of Et_2O. Within 30 min at −60 °C an orange precipitate formed. A 0.35 g portion (1.00 mmol) of [$W(CO)_6$] in 3 mL of THF was added. The solution was warmed to room temperature and stirred for 45 min. A deep red suspension formed. At −5 °C, 0.21 g (0.14 mL, 1.25 mmol) of F_3CSO_3Me was added. After 1.5 h at room temperature, the solvent was removed in vacuo. The deep red residue was dissolved in 15 mL of CH_2Cl_2 and the solution chromatographed at −40 °C on silica. First with pentane/CH_2Cl_2 (3/2) an orange band was eluted and then with CH_2Cl_2 a deep red band containing **7** and **8**. Removal of the solvent in vacuo and recrystallization from 3 mL of CH_2Cl_2 at 4 °C gave **7**/**8** as a deep red mixture of isomers. Yield: 0.46 g (56% based on **6**). **7**/**8** ratio: ∼12. Mp: 102 °C dec. IR (Et_2O): ν(CO) 2067 w, 2011 m, 1980 vw, 1934 vs, 1924 sh, 1890 s, 1843 vw cm^{-1}. ^{1}H NMR ($CDCl_3$): **7**, δ 1.54 (d, ^2J(PH) = 7.5 Hz, 9 H, PMe), 3.28 (s, 3 H, NMe), 3.72 (s, 3 H, NMe), 4.48 (s, 3 H, OMe); **8**, δ 1.65 (d, ^2J(PH) = 7.9 Hz, 9 H, PMe), 3.46 (s, 3 H, NMe), 3.80 (s, 3 H, NMe), 4.46 (s, 3 H, OMe). ^{1}H NMR (CD_2Cl_2): **7**, δ 1.56 (d, ^2J(PH) = 7.5 Hz, 9 H, PMe), 3.30 (d, J(PH) = 1.2 Hz, 3 H, NMe), 3.73 (s, 3 H, NMe), 4.51 (s, 3 H, OMe); **8**, δ 1.43 (d, ^2J(PH) = 7.9 Hz, 9 H, PMe), 3.27 (s, 3 H, NMe), 3.62 (s, 3 H, NMe), 4.37 (s, 3 H, OMe). ^{13}C NMR: **7**, δ 21.3 (d, J(PC) = 27.8 Hz, PMe), 47.6 (NMe), 50.9 (d, J(PC) = 3.5 Hz, NMe), 62.9 (d, J(PC) = 7.4 Hz, OMe), 168.2 (C_α), 174.4 (C_β), 177.8 (C(C_2)), 197.1 (J(WC) = 125.8 Hz, cis CO), 202.3 (trans CO), 202.3 (d, ^2J(PC) = 16.3 Hz, apic cis CO), 204.8 (d, ^2J(PC) = 22.0 Hz, eq cis CO), 209.3 (d, ^2J(PC) = 6.1 Hz, trans CO), 240.5 (d, ^2J(PC) = 8.3 Hz, C(NMe_2)). ^{31}P NMR ($CDCl_3$): **7**, δ −34.47 (J(WC) = 231.2 Hz). MS/EI (70 eV, 190 °C): m/z (%) 820 (12) [MH$^+$], 735 (13), 707 (25), 679 (21), 651 (49), 623 (16), 595 (8), 567 (10) [$M^+ - n$CO, n = 3−9], 344 (45), 316 (100), 288 (36) [$(CO)_nW{=}C{-}C_3$, n = 4−2]. Anal. Calcd for $C_{19}H_{18}NO_{10}PW_2$ (819.0): C, 27.86, H, 2.22, N, 1.71. Found: C, 27.98, H, 2.77, N, 1.47.

X-ray Structural Analyses of 3b, 3c, and 7. Crystal data and data collection and refinement parameter of **3b** (yellow), **3c** (yellow-orange), and **7** (red) are collected in Table 2. Single crystals were grown from CH_2Cl_2 and mounted in a glass capillary. All data were collected on a Siemens P4 diffractometer (adaptive ω scan type) with a graphite monochromator (Mo Kα, λ = 0.710 73 Å). Absorption corrections (ψ-scan with 10 reflections) were performed. The structures were solved with direct methods and refined by full-matrix least-squares techniques (Siemens SHELXL-93 (**3b**, **3c**)[26] and SHELXL-97 (**7**)).[27] The positions of the hydrogen atoms were calculated in ideal geometry and refined in the "riding model". All other atoms were refined anisotropically.

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Supporting Information Available: Tables of atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for complexes **3b**, **3c**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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