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Organic Syntheses via Transition Metal Complexes. 89.[1] 5-Aza-1-metalla-1,3,5,7-octatetraenes and 2*H*-Pyrrole and 2*H*-Dihydroazete Complexes from (1-Alkynyl)carbene Complexes (M = Cr, W) and Alkenyl *N*-H Imidates

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Addition of alkenyl *N*-H imidates $RCH{=}CR^1C(OEt){=}NH$ (**8a**−**d**; R, R^1 = Ph, Me, H) to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**6a**,**b**; M = Cr, W) affords novel 5-aza-1-metalla-1,3,5,7-octatetraenes $(CO)_5M{=}C(OEt)CH{=}C(Ph)N{=}C(OEt)CR^1{=}CHR$ ((*Z*)-**9a**−**h**; by Michael addition) together with 2,5-diethoxy-2*H*-pyrrole complexes **10a**−**h** (by 3 + 2 cycloaddition) as well as 2,4-diethoxy-2*H*-dihydroazete complexes **11e**−**h** (by 2 + 2 cycloaddition) in good overall yields. The product ratio **9**:**10**:**11** is strongly influenced by the nature of the metal (chromium or tungsten). Thus, formation of 5-aza-1-metalla-1,3,5,7-octatetraenes **9** is favored in the case of M = W, while 2*H*-dihydroazete complexes **11** are major products in the case of M = Cr. Compounds **9a**−**d** undergo smooth cyclization at 80−90 °C to give 2,3-diethoxy-2*H*-pyrrole complexes **12a**−**d** (which are regioisomers of **10a**−**d**) in 86−93% yields, from which (metal-free) 2*H*-pyrroles **13a**−**d** are generated on thermolysis at 110 °C. X-ray structure analyses are reported for the 5-aza-1-metalla-1,3,5,7-octatetraene **9b**, the (regioisomeric) 2*H*-pyrrole complexes **10b** and **12b**, and the 2*H*-dihydroazete complex **11e**.

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ of chromium and tungsten have been utilized in a broad array of organic transformations.[2] Recently, a highly regioselective 3 + 2 cyclopentadiene annulation method was reported, which is based on the addition of (1-alkynyl)carbene complexes (=C3 unit) to cycloalkenyl amines **C$=$C(NR_2)*** (=C2 unit).[3] The key step of this reaction involves formation of 1-metalla-1,3,5-hexatrienes[4] $(CO)_5M{=}C(OEt)CH{=}C(Ph)$(**)C$=$C($NR_2$)*** by Michael-type addition of the enamine to the C≡C bond of the (1-alkynyl)carbene complex,[5] which subsequently undergoes cyclization to cyclopentadiene complexes. Formation of cyclopentadienes in a 3 + 2 fashion is achieved also by reaction of alkynes $R^1C{\equiv}CH$ (=C2 unit) with 4-amino 1-chroma 1,3-dienes [=(enamino)carbene complexes] $(CO)_5Cr{=}C(OEt)CH{=}C(NR_2)R$ (=C3 unit),[6] but the regiochemistry of the "alkyne route" is different from that of the "enamine route", since 1-metalla-1,3,5-hexatriene key intermediates $(CO)_5M{=}CR^1CH{=}C(OEt)$-$CH{=}C(NR_2)R$ are generated with different regiochemistry by insertion of the alkyne $R^1C{\equiv}CH$ into the M=C bond of the 1-metalla-1,3-diene.[7]

We have extended studies on 1-metalla-1,3,5-hexatrienes to the nitrogen analogues 5-aza-1-metalla-1,3,5-hexatrienes and also to 5-aza-1-metalla-1,3,5,7-octatetraenes $(CO)_5M{=}C(OEt)CH{=}C(Ph)N{=}C(OEt)CR^1{=}CHR$ (M = Cr, W; R, R^1 = Me, Ph, H) and now wish to report on the generation and thermal cyclization of the last group of compounds.

5-Aza-1-metalla-1,3,5-hexatrienes and Iminium Carbonylmetalates

5-Aza-1-tungsta-1,3,5-hexatriene $(CO)_5W{=}C(NEt_2)$-$CMe{=}C(Ph)N{=}CHPh$ (**3**) represents the first (fully characterized) example of this class of carbene complexes. Compound **3** was generated through chain extension by addition of the electron-rich alkyne $Et_2NC{\equiv}CMe$ (**2**) to 3-aza-1-tungsta-1,3-butadiene $(CO)_5W{=}C(OEt)N{=}CHPh$ (**1a**). The isomer (*Z*)-**3** was shown to cyclize spontaneously and uniformly regiochemically to the 2*H*-pyrrole complex **4** (Scheme 1), from which the corresponding 1*H*-pyrrole is generated by ligand disengagement.[8]

The electron-rich alkyne **2** is assumed to add as a nucleophile directly to the carbene carbon atom of compound **1a**, thus generating the zwitterionic (nonconjugated) iminium carbonylmetalate **A**, in which the negative charge is stabilized by five oxygen atoms of the $(CO)_5M$ moiety. The 5-aza-1-tungsta-1,3,5-hexatriene **3** is obtained from the zwitterion **A** by 1,3-migration of the $(CO)_5M$ moiety. It should be noted that formation

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† X-ray structure analyses.

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(2) For a review see: Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.*, in press.

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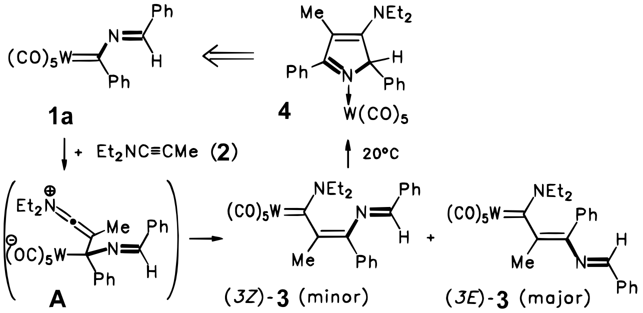
Scheme 1. Pyrrole Formation via a 5-Aza-1-tungsta-1,3,5-hexatriene Generated by Addition of an Electron-Rich Alkyne to a 3-Aza-1-metalla-1,3-butadiene



of compound **3** is assumed to follow a route significantly different from the initial steps of a Dötz reaction, which involve loss of a *cis* carbon monoxide ligand and coordination of the alkyne to the metal atom prior to insertion into the M═C bond.[9] In principle, both the carbene carbon atom and the terminal carbon atom of the M═CN═CR$_2$ unit are susceptible to nucleophilic attack by an electron-rich alkyne. The regiochemistry of addition of alkyne **2** to a 3-aza-1-metalla-1,3-butadiene is strongly influenced by the nature of the metal (M = Cr, W) as well as by the substituents R on the terminal carbon atom of the ═CN═CR$_2$ ligand. An example for the latter case is represented by the highly regioselective addition of alkyne **2** to the terminal carbon atom of the *chromium imidato* compound (CO)$_5$Cr═C(Ph)N═C(OEt)Ph.[10]

Reactions of the 3-aza-1-chroma-1,3-butadiene (CO)$_5$Cr═C(Ph)N═CHPh with nonpolarized or electron-poor alkynes RC≡CR^1 (R = Ph, Tol, *n*-Bu, SiMe$_3$, CH$_2$OMe, CO$_2$Me, Me; R^1 = H, Me, Ph) follow a route different from that outlined above for an electron-rich alkyne. Such reactions seem to be initiated by exchange of a *cis* carbon monoxide ligand for an alkyne and subsequent insertion of the alkyne ligand into the M═C bond to produce a chelated (3,4-η^2)-5-aza-1-metalla-1,3,5-hexatriene instead of an open-chain 5-aza-1-metalla-1,3,5-hexatriene. Accordingly, 1*H*-pyrroles as well as 3-hydroxypyridines are formed by insertion of carbon monoxide, as in the Dötz reaction.[9,11,12] Interestingly, 2-aza-1-chroma-1,3-butadienes exhibit reversed but highly selective heteroannulations with electron-rich and electron-poor alkynes, respectively.[13]

An efficient approach to the formation of 5-aza-1-metalla-1,3,5-hexatrienes other than by chain extension of 3-aza 1-metalla 1,3-dienes through addition of alkynes is based on addition of *N*-lithio imines LiN═CR^{1}R^2 (R^1, R^2 = Ph, c-Pr, anisyl) to the C≡C bond of chromium (1-alkynyl)carbene complexes (CO)$_5$Cr═C(OEt)C≡CR (R = Ph, *n*-Pr, c-Pr, *t*-Bu). 5-Aza-1-chroma-1,3,5-hexatrienes (CO)$_5$Cr═C(OEt)CH═C(R)N═CR^{1}R^2 thus generated were reported to cyclize to 2*H*-pyrroles and (quite unexpectedly) also to 3*(2H)*-pyridinones by insertion of carbon monoxide.[14]

Factors governing the regiochemistry of addition of nitrogen nucleophiles to (1-alkynyl)carbene complexes (CO)$_5$M═C(OEt)C≡CR (M = Cr, W) are of current interest, since they are crucial to the structure of the organic product finally derived from such a reaction. Strong influence on the regioselectivity is encountered not only with different types of nitrogen nucleophiles but also with different metals (chromium instead of tungsten), different solvents, and different reaction temperatures. Addition of *N*-lithio imines LiN═CR$_2$ was found to occur exclusively at the C≡C bond of the chromium (1-alkynyl)carbene complex (CO)$_5$Cr═C(OEt)C≡CR. The regioselectivity of this (fast) addition could be explained by the assumption of an early transition state leading to preferential formation of the lithium allenylmetalate Li[(OC)$_5$CrC(OEt)═C═C(R)N═CR$_2$] rather than the lithium metalate Li[(OC)$_5$CrC(OEt)(N═CR$_2$)C≡CR]. On the other hand, addition of alkenyl *N*-alkyl imines R^{1}N═CHCH═CHR^2 (R^1, R^2 = Me, *n*-Pr, Bn, *n*-Pr, Ph) to chromium (1-alkynyl)carbene complexes (CO)$_5$Cr═C(OEt)C≡CR (R = Ph, SiMe$_3$, *t*-Bu) occurs exclusively at the Cr═C bond and leads to production of chromium azepine complexes in 60−90% yields.[15] The regioselectivity of this (slow) reaction seems could be controlled by a late transition state and thus would be governed by the ease with which the iminium metalate $^-$(OC)$_5$CrC(OEt)(R^{1}N$^+$═CHCH═CHR^2)C≡CR is produced, which (on the basis of estimates of spacial charge separation) could be energetically favored over the iminium metalate $^-$(OC)$_5$CrC(OEt)═C═CR(R^{1}N$^+$═CH-CH═CHR^2). It is interesting to note that 4 + 2 cycloadducts of alkenyl *N*-alkyl imines to the C≡C bond of (1-alkynyl)carbene complexes are minor byproducts only in case of chromium but become major products with the corresponding tungsten complexes, which is in line with the trend expected for the higher steric demand of a tungsten compared to a chromium atom.[16]

2- vs 4-Addition of Alkenyl *N*-H Imidates to (1-Alkynyl)carbene Complexes

In an attempt to gain more information on the factors governing the regiochemistry of the addition of nitrogen nucleophiles to (1-alkynyl)carbene complexes **6a**,**b** (M = Cr, W), we have extended the above-mentioned studies on cycloadditions of alkenyl *N*-alkyl imides to the addition of alkenyl *N*-H imid*ates* **8**. *N*-H Imid*ates* were chosen as substrates under the assumption that structures of primary adducts might be traced back from structures of the rearrangement products resulting from N/C migration of a hydrogen atom.

Alkenyl *N*-H imidates **8a**−**d** are most conveniently prepared by alkylation of alkenyl *N*-H amides **5** with triethyloxonium tetrafluoroborate.[17] The iminium salt **7** which is generated in the first reaction step is very

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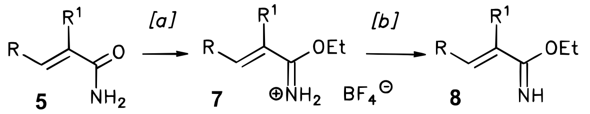
Table 1. Product Ratios of Compounds 9−11, Selected ^{13}C NMR Shifts (δ Values, C_6D_6) and IR Frequencies (cm^{-1}) of 5-Aza-1-metalla-1,3,5,7-octatetraenes (*Z*)-9

9−11	M	R	R^1	ratio[a]	yield[b]	δ(C2)	δ(C4)	δ(C6)	δ(C8)	ν(C=N)	ν(C=C)
a	W	H	H	12:1:0	80	295.4	147.7	154.7	126.3	1677	1612
b	W	Me	H	10:1:0	87	296.8	147.8	154.7	128.2	1678	1635
c	W	Ph	H	9:1:0	75	297.1	147.3	155.3	128.6	1680	1638
d	W	H	Me	8:1:0	86	293.9	147.9	154.9	126.2	1695	1624
e	Cr	H	H	2:2:3	78	322.8	143.2	154.9	126.0	1674	1611
f	Cr	Me	H	2:1:2	79	322.6	143.9	155.2	125.3	1675	1634
g	Cr	Ph	H	4:1:8	78	322.9	143.4	155.7	125.0	1660	1620
h	Cr	H	Me	1:2:2	75	318.9	143.7	155.1	122.9	1689	1614

[a] Product ratio **9**:**10**:**11**. [b] Total yield of complexes in percent.

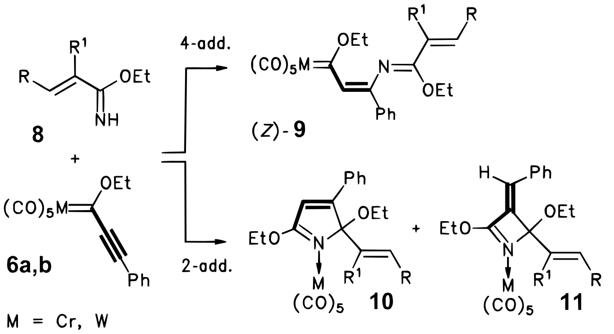
Scheme 2. Alkenyl *N*-H Imidates from Alkenyl Amides



[a] + $[Et_3O]BF_4$ [b] +Et_3N, $-[Et_3NH]BF_4$

5, 7, 8	R	R^1
a	H	H
b	Me	H
c	Ph	H
d	H	Me

Scheme 3. Adducts of Alkenyl *N*-H Imidates to (1-Alkynyl)carbene Complexes

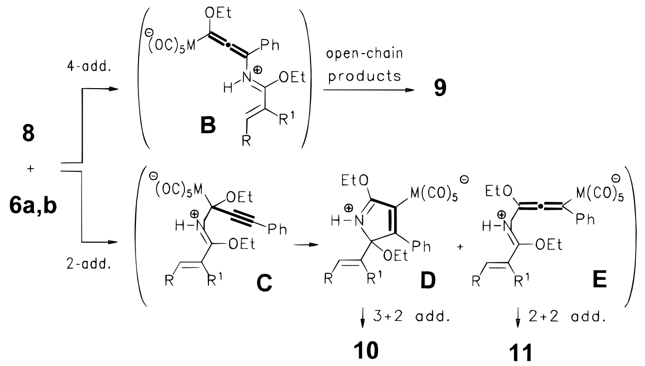


sensitive to aqueous base but is readily transformed into the imidate **8** with triethylamine in diethyl ether (Scheme 2).

Reaction of alkenyl *N*-H imidates **8a**−**d** with (1-alkynyl)carbene complexes **6a**,**b** is complete within *ca.* 2 h at 20 °C and affords a mixture of three compounds in good overall yields: red nonpolar 5-aza-1-metalla-1,3,5,7-octatetraenes (*Z*)-**9a**−**h** by Michael addition, yellow polar 2*H*-pyrrole complexes **10a**−**h** by [3 + 2] cycloaddition, and yellow polar dihydroazete complexes **11e**−**h** by [2 + 2] cycloaddition (Scheme 3, Table 1). Dihydroazete complexes **11** are obtained with chromium but not with tungsten compounds (Table 1), while 5-aza-1-metalla-1,3,5,7-octatetraenes **9** constitute the major products in the case of tungsten compounds.

On the basis of the substitution pattern of the products **9**−**11** two major reaction paths must be distinguished in order to explain the formation of these compounds. It appears that iminium carbonylmetalates **B** and **C**, respectively, would play pivotal roles and must be considered primary adducts of alkenyl imidates **8** to (1-alkynyl)carbene complexes **6a**,**b** (Scheme 4). Compounds **B** seem to act as precursors to 5-aza-1-metalla-1,3,5-hexatrienes **9**, which are generated therefrom by 1,3-hydrogen migration. Compounds **C**, on the other hand, may either produce 2*H*-pyrrole complexes **10** by 1,2-migration of the $(CO)_5M$ moiety to initially give an intermediate **D** which subsequently undergoes a 1,3-hydrogen migration, or they may form dihydroazete complexes **11** via allene-type intermediates **E** generated by 1,3-migration of the $(CO)_5M$ moiety, a subsequent [2 + 2] cycloaddition, and a 1,4-hydrogen migration.

Scheme 4. Mechanistic Consideration of the Imidate Addition to (1-Alkynyl)carbene Complexes



According to the product ratio summarized in Table 1, addition of alkenyl *N*-H imidates to the M=C bond of (1-alkynyl)carbene compounds is favored for M = Cr, while addition to the C≡C bond is preferred for M = W.

Our results are in line with the regiochemistry observed for cycloaddition reactions of alkenyl *N*-alkyl im*ines* to compounds **6a**,**b**. Nevertheless, it should be strictly noted that the products **9**−**11** resulting from addition of alkenyl *N*-H imi*dates* **8** to compounds **6** have structures completely different from those resulting from addition of alkenyl *N*-alkyl imines to compounds **6a**,**b**. Interestingly, open-chain products **9** as well as four- and five-membered *N*-heterocyclic rings **10** and **11** are obtained only with alkenyl *N*-H imidates, while six- and seven-membered rings are generated only with alkenyl *N*-alkyl imines.

Spectroscopy

The spectroscopic data most characteristic of 5-aza-1-metalla-1,3,5-hexatrienes **9** include ^{13}C NMR chemical shifts of the carbene carbon atom C2 (W, δ *ca.* 295; Cr, δ *ca.* 322), C4 (W, δ *ca.* 147; Cr, δ *ca.* 143), C6 and C8, as well as ν(C=N) and ν(C=C) frequencies in the IR spectra in a narrow range (Table 1). Chromium and tungsten compounds are easily distinguished by the ^{13}C NMR shifts of C2 and C4 as well as by the ν(C≡O) pattern in the IR spectra (hexane solution), which exhibits small but characteristic frequency differences for the A1 band (e.g., tungsten complex **9a** 2062 (20%), 1973 (5), 1938 cm^{-1}(100) and chromium complex **9e**

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9b

W−C(4)	2.215(5)	N(7)−C(8)	1.269(6)
O(3)−C(4)	1.325(6)	C(8)−O(9)	1.346(6)
C(4)−C(5)	1.436(6)	C(8)−C(12)	1.452(7)
C(5)−C(6)	1.374(6)	C(12)−C(13)	1.312(8)
C(6)−N(7)	1.375(6)		
C(4)−O(3)−C(2)	122.2(4)	N(7)−C(8)−O(9)	120.0(4)
O(3)−C(4)−C(5)	110.0(4)	N(7)−C(8)−C(12)	126.9(5)
O(3)−C(4)−W	129.8(4)	O(9)−C(8)−C(12)	113.1(4)
C(5)−C(4)−W	120.3(3)	C(8)−O(9)−C(10)	118.4(4)
C(6)−C(5)−C(4)	129.7(4)	O(9)−C(10)−C(11)	108.1(5)
C(5)−C(6)−N(7)	125.4(4)	C(13)−C(12)−C(8)	124.4(5)
C(8)−N(7)−C(6)	125.7(4)	C(12)−C(13)−C(14)	125.6(6)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 10b

W−N(1)	2.249(4)	C(2)−C(3)	1.534(6)
N(1)−C(5)	1.304(5)	C(21)−C(22)	1.268(7)
N(1)−C(2)	1.497(5)	C(3)−C(4)	1.330(6)
C(2)−O(24)	1.397(5)	C(4)−C(5)	1.436(7)
C(2)−C(21)	1.502(7)	C(5)−O(51)	1.322(5)
C(5)−N(1)−C(2)	105.6(4)	C(3)−C(4)−C(5)	108.5(4)
C(5)−N(1)−W	129.1(3)	N(1)−C(5)−O(51)	119.1(4)
C(2)−N(1)−W	125.3(3)	N(1)−C(5)−C(4)	114.3(4)
N(1)−C(2)−C(3)	104.6(3)	O(51)−C(5)−C(4)	126.6(4)
C(4)−C(3)−C(2)	106.8(4)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 11e

Cr−N(1)	2.091(8)	C(3)−C(4)	1.577(14)
N(1)−C(2)	1.261(10)	C(4)−O(4)	1.325(11)
N(1)−C(4)	1.540(12)	C(4)−C(5)	1.54(2)
C(2)−O(2)	1.303(10)	C(3)−C(30)	1.284(13)
C(2)−C(3)	1.507(13)		
C(2)−N(1)−C(4)	93.1(7)	C(2)−C(3)−C(4)	82.9(7)
C(2)−N(1)−Cr	137.0(6)	C(3)−C(30)−C(31)	129.0(9)
C(4)−N(1)−Cr	129.7(6)	O(4)−C(4)−N(1)	115.6(8)
N(1)−C(2)−O(2)	126.0(8)	O(4)−C(4)−C(5)	109.3(9)
N(1)−C(2)−C(3)	98.5(8)	N(1)−C(4)−C(5)	111.3(8)
O(2)−C(2)−C(3)	135.5(8)	O(4)−C(4)−C(3)	120.9(9)
C(30)−C(3)−C(2)	137.8(9)	N(1)−C(4)−C(3)	84.8(7)
C(30)−C(3)−C(4)	139.3(9)	C(5)−C(4)−C(3)	113.0(8)

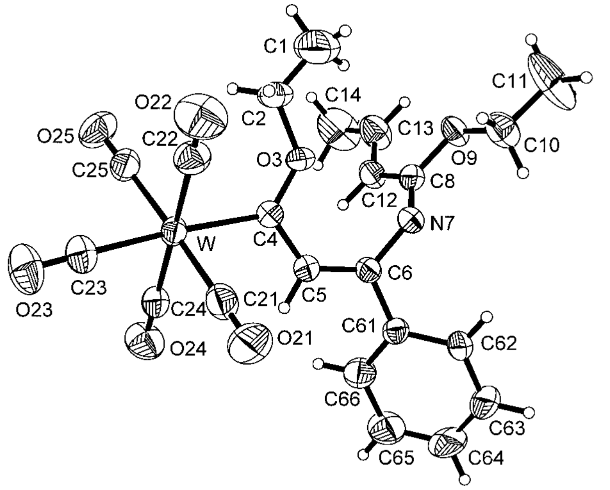


Figure 1. Molecular structure of the 5-aza-1-tungsta-1,3,5,7-tetraene **9b**.

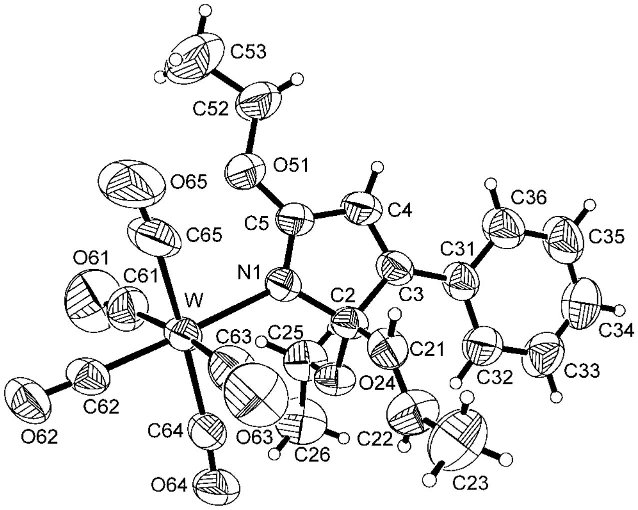


Figure 2. Molecular structure of tungsten 2,5-diethoxy-2*H*-pyrrole complex **10b**.

2053 (20%), 1974 (5), 1939 cm^{-1} (100)). Typical ν(C≡O) patterns are found also for 2*H*-pyrrole complexes (e.g. tungsten compound **10a** 2065 (10%), 1928 (100), 1903 cm^{-1} (30); chromium compound **10e** 2062 (10%), 1934 (100), 1906 cm^{-1} (30)) and for dihydroazete complexes **11** (e.g. chromium complex **11e** 2063 (10%), 1973 (5), 1939 (100), 1913 cm^{-1} (30); ν(C=N) 1671 cm^{-1}).

Crystal Structure Analyses of the 5-Aza-1-metallaoctatetraene 9b, 2,5-Diethoxy-2*H*-Pyrrole Complex 10b, and 2,4-Diethoxy-2*H*-Dihydroazete Complex 11e

Unambiguous structural assignment of the reaction products is based on X-ray structure analyses of compounds **9b**, **10b**, and **11e**. For crystal data see the Experimental Section. Selected bond lengths and angles are given in Tables 2−4.

The plane defined by the atoms attached to the carbene carbon atom of **9b** bisects the angle between two neighboring *cis* carbonyl groups, C(21)−W−C(4)−C(5) = 49.4(0.4)°. The W=CC=CN=CC=C backbone of the ligand displays the alternating bond pattern W−C(4) = 2.215(5) Å, C(4)−C(5) = 1.436(6) Å, C(5)−C(6) = 1.374(6) Å, C(6)−N(7) = 1.375(6) Å, N(7)−C(8) = 1.269(6) Å, C(8)−C(12) = 1.452(7) Å, and C(12)−C(13) = 1.312(8) Å, similar to that found for 2-alkoxy-1-tungsta-1,3,5-hexatrienes.[18] The W=CC=C and N=CC=C portions of the ligand are essentially planar (W−C(4)−C(5)−C(6) = −165.2(0.4)°, N(7)−C(8)−C(12)−C(13) = 179.6(0.6)°) but strongly distorted against each other (C(5)−C(6)−N(7)−C(8) = −83.7(0.7)°).

The 2*H*-pyrrole ring of compound **10b** is planar by ±0.003 Å within standard deviations. Bond distances within the ring are alternating and correlate with the distances found for a chromium 4-(diethylamino)-2-ethoxy-3-methyl-2,5-diphenyl-2*H*-pyrrole complex.[10]

The four-membered ring of compound **11e** is almost planar (deviation from plane ±0.03 Å), as has been found also for the metal-free 1-azetine.[19] The distance N(1)−C(2) = 1.261(10) Å is somewhat shorter than in 1-azetine (1.307 Å), and the distance C(3)−C(4) = 1.577(14) Å is somewhat elongated, leading to a trapezoidal ring. The Cr−N(1) distance 2.091(8) Å is similar to

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(18) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3510−3516.

(19) (a) Gieren, A.; Burger, K.; Thenn, W. *Z. Naturforsch., B* **1974**, *29*, 399. (b) Review on 1-azetines (2,3-dihydroazetes): Moore, J. A. In *The Chemistry of Heterocyclic Compounds*; Hassner, A., Ed.; Wiley-Interscience: New York, 1983; Vol. 42/2, pp 1−218.

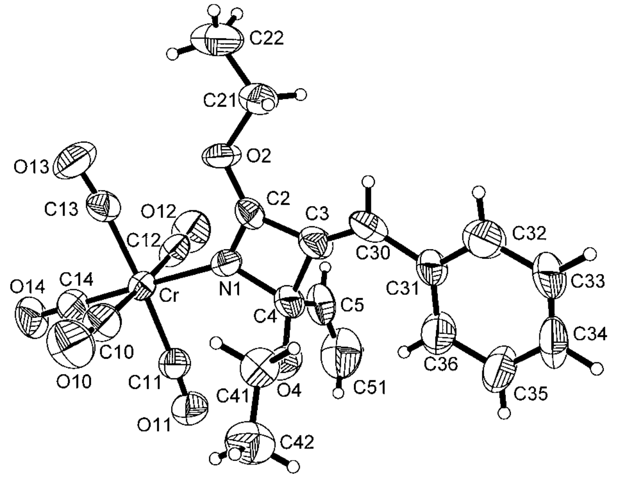
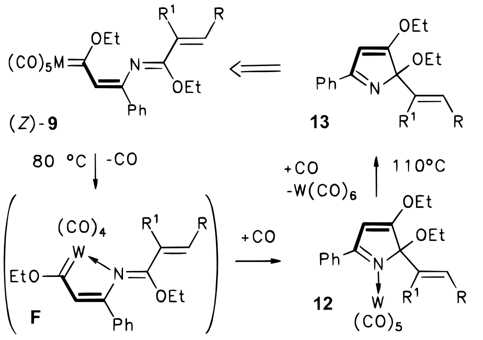


Figure 3. Molecular structure of tungsten dihydroazete complex **11e**.

Scheme 5. Thermal Cyclization of 5-Aza-1-tungsta-1,3,5,7-octatetraenes 9



those in $(CO)_5Cr(NC_5H_5)$ (2.204(3) Å)[20] and {4-[2-(diethylamino)-1-methylethenyl]-3-ethoxy-2,3-dihydrophenylazete}$Cr(CO)_5$.[21]

Cyclization of 5-Aza-1-metalla-1,3,5,7-octatetraenes

Formation of pyrroles *via* cyclization of 5-aza-1-metalla-1,3,5-hexatrienes has been achieved previously by the "alkyne route" (e.g. Scheme 1),[8,11,12] and the "imine route" (Scheme 4).[14] Cyclization of 5-aza-1-metalla-1,3,5,7-octatetraenes (*Z*)-**9** might in principle lead to formation of 2-alkenyl-2*H*-pyrrole complexes as well as of 4*H*-azepine complexes. It has been found that 5-aza-1-tungsta-1,3,5,7-octatetraenes **9a**−**d** undergo smooth rearrangement at 80−90 °C to give 2-alkenyl-2*H*-pyrrole complexes **12a**−**d** in 86−93% yields. The latter compounds afford (metal-free) 2-alkenyl-2*H*-pyrroles **13a**−**d** at 110 °C by disengagement of $W(CO)_6$ (Scheme 5). Formation of azepine derivatives has not been observed under these conditions.

It should be noted that the 2-alkenyl-2*H*-pyrrole complexes **12a**−**d** (Scheme 5) are regioisomers of the 2-alkenyl-2*H*-pyrrole complexes **10a**−**d** (Scheme 3). The regioisomeric compounds can be easily distinguished by NMR chemical shifts of C3, C4, C5, and 4-H. Structural proof is based also on a X-ray analysis of the 2,3-diethoxy-2*H*-pyrrole compound **12b**.

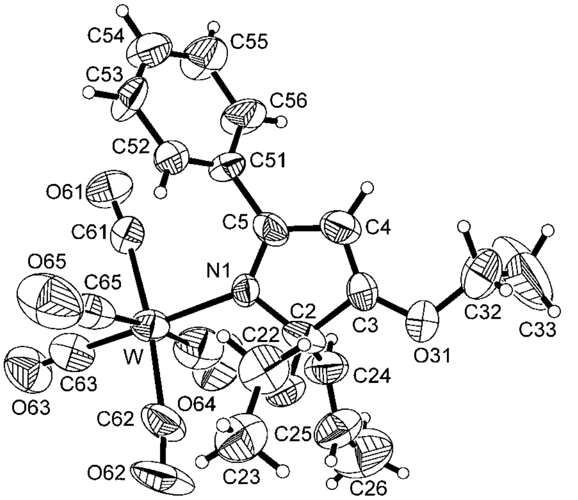


Figure 4. Molecular structure of tungsten 2,3-diethoxy-2*H*-pyrrole complex **12b**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 12b

W−N(1)	2.238(10)	C(2)−C(3)	1.51(2)
N(1)−C(5)	1.333(14)	C(3)−C(4)	1.32(2)
N(1)−C(2)	1.50(2)	C(3)−O(31)	1.32(2)
C(2)−O(21)	1.38(2)	C(4)−C(5)	1.41(2)
C(2)−C(24)	1.50(2)	C(5)−C(51)	1.50(2)
C(5)−N(1)−C(2)	102.8(11)	C(4)−C(3)−C(2)	107.6(14)
C(5)−N(1)−W	134.0(10)	O(31)−C(3)−C(2)	118.2(14)
C(2)−N(1)−W	123.0(8)	C(3)−C(4)−C(5)	107.9(14)
N(1)−C(2)−C(3)	105.6(12)	N(1)−C(5)−C(4)	115.8(13)
C(4)−C(3)−O(31)	134(2)		

Crystal Structure Analysis of 2,3-Diethoxy-2*H*-Pyrrole Complex 12b

The molecular structural of compound **12b** was determined also by an X-ray structure analysis. For crystal data, see the Experimental Section. Selected bond lengths and angles are given in Table 5.

The bond distances and bond angles of compound **12b** are very similar to those of compound **10b**, except for the longer distance N(1)−W = 2.238(10) Å.

Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. In particular, dichloromethane was dried, distilled from P_2O_5, and stored over 4 Å molecular sieves. Pentane refers to that fraction boiling between 40 and 60 °C. All ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker ARX 300 instrument in $CDCl_3$, unless otherwise indicated, and all chemical shift values refer to δ_{TMS} 0.00. ^{13}C NMR multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60_{F240}, were viewed by UV light (254 nm) and stained by a 5% aqueous acidic ammonium molybdate solution. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100.

2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-octatetraene (9a) and Pentacarbonyl(2,5-diethoxy-2-ethenyl-3-phenyl-2*H*-pyrrole-*N*)tungsten (10a). Acrylamide **5a** (92 mg, 1.30 mmol) and triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol) are reacted in 2 mL of dry dichloromethane at 20 °C for 15 h with careful mixing by efficient stirring (and/or ultrasonic radiation) and then added

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[20] Cotton, F. A.; Darensbourg, D. J.: Fang, A.; Kolthammer, B. W. S.; Reed, D.; Thompson, J. L. *Inorg. Chem.* **1981**, *20*, 4090.

[21] Aumann, R.; Kuckert, E.; Krüger, C.; Goddard, R.; Angermund, K. *Chem. Ber.* **1988**, *121*, 1475−1478.

to pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**6b**; 482 mg, 1.00 mmol) in a 5 mL screw-top vessel. The mixture is stirred for 2 min, and then triethylamine (202 mg, 2.00 mmol) in 2 mL of dichloromethane is added slowly with stirring at 0 °C. Reaction progress is followed by TLC. After the starting material is consumed completely (*ca.* 12 h at 20 °C), the solvent is removed in vacuo and the residue is dissolved in 3 mL of toluene. Chromatography on silica gel with pentane/diethyl ether (20:1) affords red **9a** (429 mg, 74%, R_f 0.5 in pentane, dark red crystals from pentane at −15 °C, mp 79 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction with **10a** (35 mg, 6%, R_f 0.6 in pentane/diethyl ether (1:1), yellow crystals from diethyl ether/pentane (1:5), mp 126 °C).

9a: ^{1}H NMR (C_6D_6) δ 7.82 (1 H, s, 3-H), 7.66 and 7.05 (2:3 H, m each, Ph), 5.80 and 5.00 (2:1 H, m each, $H_2C{=}CH$), 4.52 (2 H, q, 2-OCH_2), 3.98 (2 H, q, 6-OCH_2), 1.05 (6 H, t, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 295.4 (W═C), 204.3 and 199.4 [*trans*- and *cis*-CO, W(CO)$_5$], 154.7 (C_q, N═C, C6), 147.7 [C_q, C═*C*(N), C4], 138.0 (C_q, *i*-C Ph), 131.1, 129.2, and 127.9 (1:2:2, CH each, Ph), 128.0 (CH, C7), 125.0 (CH, C3), 126.3 (CH_2, C8), 79.5 (2-OCH_2), 63.0 (6-OCH_2), 14.5 and 14.4 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2061.5 (20), 1973.0 (5), 1938.1 (100) [ν(C≡O)], 1677.3 [ν(C═N)], 1612.4 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 581 (5) [M$^+$], 553 (15), 525 (60), 497 (40), 469 (30), 441 (50) [M$^+$ − 5 CO], 412 (100). Anal. Calcd for $C_{21}H_{19}NO_7W$ (581.2): C, 43.40; H, 3.29; N, 2.41. Found: C, 43.60; H, 3.37; N, 2.36.

10a: ^{1}H NMR (C_6D_6) δ 7.80 and 7.45 (2:3 H, m each, Ph), 5.92 (1 H, s, 4-H), 5.82 and 5.25 (1:2 H, m each, $H_2C{=}CH$), 3.45 (2 H, m, diastereotopic 5-OCH_2), 3.30 and 2.80 (1 H each, diastereotopic 2-OCH_2), 1.16 (3 H, t, 5-OCH_2CH_3), 1.05 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 203.4 and 198.8 [*trans*- and *cis*-CO, W(CO)$_5$], 174.1 (C_q, C═N, C5), 166.8 [C_q, C3], 135.8 (2-*C*H═CH_2), 131.2, 128.9, and 127.2 (1:2:2, CH each, Ph), 129.9 (C_q, *i*-C Ph), 120.1 (═CH_2), 111.7 (CH, C4), 103.0 (C_q, C2), 68.2 (5-OCH_2), 59.4 (2-OCH_2), 14.8 and 14.5 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2065.2 (10), 1928.3 (100), 1903.2 (30) [ν(C≡O)], 1615.0 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 581 (25) [M$^+$], 553 (10), 525 (5), 497 (20), 469 (5), 441 (100) [M$^+$ − 5 CO], 257 (60) [ligand$^+$], 228 (60), 200 (100). Anal. Calcd for $C_{21}H_{19}NO_7W$ (581.2): C, 43.40; H, 3.29; N, 2.41. Found: C, 43.40; H, 3.33; N, 2.51.

2,6-Diethoxy-4-phenyl-1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-nonatetraene (9b) and Pentacarbonyl[2,5-diethoxy-2-(1-propenyl)-3-phenyl-2*H*-pyrrole-*N*]tungsten (10b). Crotonamide **5b** (111 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**6b**; 482 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9b** (470 mg, 79%, R_f 0.7 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C, mp 101 °C), elution with pentane/diethyl ether (5:1) yields a yellow fraction with **10b** (48 mg, 8%, R_f 0.8 in diethyl ether, yellow crystals from diethyl ether/pentane (1:5), mp 121 °C).

9b: ^{1}H NMR (C_6D_6) δ 7.96 (1 H, s, 3-H), 7.80 and 7.03 (2:3 H, m each, Ph), 6.50 (1 H, dq, ^3J = 15 and 6 Hz, ═C*H*Me), 5.68 (1 H, d, ^3J = 15 Hz, C*H*═CHMe), 4.58 (2 H, q, 2-OCH_2), 4.05 (2 H, q, 6-OCH_2), 1.30 (3 H, d, ^3J = 6 Hz, ═CHCH_3), 1.05 (6 H, t, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 296.8 (W═C), 204.0 and 199.0 [*trans*- and *cis*-CO, W(CO)$_5$], 154.7 (C_q, N═C, C6), 147.8 [C_q, C═*C*(N), C4], 140.1 (CH, C7), 137.9 (C_q, *i*-C Ph), 130.8, 129.1, and 127.8 (1:2:2, CH each, Ph), 128.2 (CH, C8), 119.0 (CH, C3), 79.1 (2-OCH_2), 62.7 (6-OCH_2), 17.7 (═CH*C*H_3), 14.6 and 14.1 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2060.8 (20), 1972.3 (5), 1938.5 (100) [ν(C≡O)], 1677.8 [ν(C═N)], 1635.2 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (5) [M$^+$], 567 (25), 539 (60), 511 (10), 483 (30), 455 (100) [M$^+$ − 5 CO], 426 (60). Anal. Calcd for $C_{22}H_{21}NO_7W$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.60; H, 3.55; N, 2.27.

X-ray crystal structure analysis of **9b**: formula $C_{22}H_{21}NO_7W$, M_r = 595.25, 1.2 × 0.7 × 0.7 mm, a = 9.209(1) Å, b = 9.731(1) Å, c = 26.710(2) Å, V = 2393.6(2) Å^3, ρ_{calc} = 1.652 g cm^{-3}, μ = 48.65 cm^{-1}, T = 223 K, empirical absorption correction via ψ-scan data (0.761 ≤ C ≤ 0.999), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.710 73 Å, $\omega/2\theta$ scans, 5519 reflections collected (+h,±k,−l), (sin θ)/λ = 0.62 Å^{-1}, 4791 independent and 4545 observed reflections (I ≤ 2$\sigma(I)$), 283 refined parameters, R = 0.025, wR2 = 0.063, maximum (minimum) residual electron density 0.30 (−0.74) e Å^{-3}, Flack parameter −0.02(1), hydrogens calculated and riding. All data were collected on a Enraf-Nonius MACH3 diffractometer. Programs used: MolEN, SHELXS-86, SHELXL-93, XP.

10b: ^{1}H NMR (C_6D_6) δ 7.60 and 7.05 (2:3 H, m each, Ph), 6.22 (1 H, dq, ^3J = 15.5 and 6.5 Hz, ═CHMe), 6.05 (1 H, s, 4-H), 5.05 (1 H, d, ^3J = 15.5 Hz, *H*C═CHMe), 3.50 (2 H, q, 5-OCH_2), 3.30 and 2.80 (1 H each, diastereotopic 2-OCH_2), 1.55 (3 H, d, ^3J = 6.5 Hz, ═CHCH_3), 1.15 (3 H, t, 5-OCH_2CH_3), 1.05 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 203.4 and 199.4 [*trans*- and *cis*-CO, W(CO)$_5$], 173.9 (C_q, C═N, C5), 166.9 (C_q, C3), 131.2 and 129.6 (*C*H═*C*HMe), 131.2, 129.0, and 127.3 (1:2:2, CH each, Ph), 130.5 (C_q, *i*-C Ph), 111.5 (CH, C4), 103.3 (C_q, C2), 67.8 (5-OCH_2), 59.4 (2-OCH_2), 17.8 (═CH*C*H_3), 14.5 and 14.4 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2064.3 (10), 1925.5 (100), 1903.1 (30) [ν(C≡O)], 1614.2 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (25) [M$^+$], 567 (10), 511 (20), 455 (100) [M$^+$ − 5 CO], 426 (60), 271 (60) [ligand$^+$], 256 (70), 241 (60), 214 (60), 198 (60), 69 (100). Anal. Calcd for $C_{22}H_{21}NO_7W$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.54; H, 3.58; N, 2.54.

X-ray crystal structure analysis of **10b**: formula $C_{22}H_{21}NO_7W$, M_r = 595.25, 0.7 × 0.7 × 0.3 mm, a = 11.894(1) Å, b = 17.050(2) Å, c = 12.033(1) Å, β = 101.60(1)°, V = 2390.4(4) Å^3, ρ_{calc} = 1.654 g cm^{-3}, μ = 48.72 cm^{-1}, T = 293 K, empirical absorption correction via ψ-scan data (0.682 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, $\omega/2\theta$ scans, 5069 reflections collected (−h,+k,±l), (sin θ)/λ = 0.62 Å^{-1}, 4835 independent and 3605 observed reflections (I ≤ 2 $\sigma(I)$), 283 refined parameters, R = 0.029, wR2 = 0.069, maximum (minimum) residual electron density 1.13 (−0.78) e Å^{-3}, hydrogens calculated and riding. All data were collected on a Enraf-Nonius MACH3 diffractometer. Programs used: MolEN, SHELXS-86, SHELXL-93, XP.

2,6-Diethoxy-4,8-diphenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-octatetraene (9c) and Pentacarbonyl[2,5-diethoxy-2-(2-phenyl-1-ethenyl)-3-phenyl-2*H*-pyrrole-*N*]tungsten (10c). Cinnamamide **5c** (191 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**6b**; 482 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9c** (443 mg, 67%, R_f 0.6 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C, mp 126 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction with **10c** (50 mg, 8%, R_f 0.8 in diethyl ether, yellow crystals from diethyl ether/pentane (1:5)).

9c: ^{1}H NMR (C_6D_6) δ 7.96 (1 H, s, 3-H), 7.80 and 7.03 (2:3 H, m each, 4-Ph), 7.50 (1 H, d, ^3J = 16 Hz, ═C*H*Ph), 7.10 and 6.90 (2:3 H, m each, 8-Ph), 6.45 (1 H, d, ^3J = 16 Hz, C*H*═CHPh), 4.55 (2 H, q, 2-OCH_2), 4.15 (2 H, q, 6-OCH_2), 1.20 and 1.05 (3 H each, t each, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 297.1 (W═C), 204.0 and 198.9 [*trans*- and *cis*-CO, W(CO)$_5$], 155.3 (C_q, N═C, C6), 147.3 [C_q, C═*C*(N), C4], 140.8 (CH, C7), 138.0 (C_q, *i*-C 4-Ph), 135.0 (C_q, *i*-C 8-Ph); 131.0, 129.3, and 127.9 (1:2:2, CH each, 4-Ph), 130.3, 129.1, and 128.0 (1:2:2, CH each, 8-Ph), 128.6 (CH, C8), 114.3 (CH, C3), 79.2 (2-OCH_2), 63.0 (6-OCH_2), 14.7 and 14.2 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2061.2 (10), 1972.3 (1), 1940.6 (100) [ν(C≡O)], 1680.4 [ν(C═N)], 1638.1 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 657 (10) [M$^+$], 629 (15), 601 (60), 573 (10), 545 (30), 517 (100) [M$^+$ − 5 CO], 488 (60), 333 (30) [ligand$^+$], 304 (80), 289 (100). Anal. Calcd for $C_{27}H_{23}NO_7W$ (657.3): C, 49.34; H, 3.53; N, 2.13. Found: C, 48.99; H, 3.45; N, 2.14.

10c: ^1H NMR (C_6D_6): δ 7.70 and 7.05 (2:3 H, m each, 3-Ph), 7.25 and 7.00 (2:3 H, m each, $CH{=}CHC_6H_5$), 7.42 (1 H, d, ^3J = 15.5, $=CHPh$), 6.09 (1 H, s, 4-H), 5.80 (1 H, d, ^3J = 15.5 Hz, $HC{=}CHPh$), 3.50 (2 H, q, 5-OCH_2), 3.28 and 2.85 (1 H each, diastereotopic 2-OCH_2), 1.12 (3 H, t, 5-OCH_2CH_3), 1.03 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 203.3 and 199.3 [*trans*- and *cis*-CO, $W(CO)_5$], 174.3 (C_q, C=N, C5), 166.8 (C_q, C3), 136.0 (C_q, *i*-C, $=CHC_6H_5$), 134.9 and 128.3 ($CH{=}CHPh$), 131.3, 129.1, and 127.3 (1:2:2, CH each, 5-Ph), 130.4 (C_q, *i*-C 5-Ph), 129.0, 128.0, and 127.8 (1:2:2, CH each, $=CHC_6H_5$), 111.9 (CH, C4), 103.6 (C_q, C2), 68.0 (5-OCH_2), 59.6 (2-OCH_2), 14.6 and 14.5 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2064.7 (10), 1925.3 (100), 1902.4 (30) [$\nu(C{\equiv}O)$], 1614.8 [$\nu(C{=}C)$]; MS (70 eV, *m/e* (%)) ^{184}W, 657 (15) [M$^+$], 629 (10), 601 (5), 517 (100) [M$^+$ − 5 CO], 488 (60), 333 (60) [ligand$^+$], 304 (100), 276 (60). Anal. Calcd for $C_{27}H_{23}NO_7W$ (657.3): C, 49.34; H, 3.53; N, 2.13. Found: C, 49.32; H, 3.65; N, 2.26.

2,6-Diethoxy-7-methyl-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-octatetraene (9d) and Pentacarbonyl[2,5-diethoxy-2-(2-propenyl)-3-phenyl-2*H*-pyrrole-*N*]tungsten (10d). Methacrylamide **5d** (111 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**6b**; 482 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9d** (452 mg, 76%, R_f 0.7 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C, mp 91 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction with **10d** (60 mg, 10%, R_f 0.8 in diethyl ether, yellow crystals from diethyl ether/pentane (1:5), mp 132 °C).

9d: ^1H NMR (C_6D_6) δ 7.65 (1 H, s, 3-H), 7.60 and 7.03 (2:3 H, m each, Ph), 5.40 and 4.90 (1 H each, s each, $=CH_2$), 4.60 (2 H, q, 2-OCH_2), 3.90 (2 H, q, 6-OCH_2), 1.59 (3 H, s, $=CCH_3$), 1.10 and 1.05 (3 H each, t each, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 293.9 (W=C), 204.3 and 199.3 [*trans*- and *cis*-CO, $W(CO)_5$], 154.9 (C_q, N=C, C6), 147.9 [C_q, C=*C*(N), C4], 137.9 (C_q, *i*-C Ph), 136.1 (C_q, $=CMe$), 131.1, 129.3, and 127.8 (1:2:2, CH each, Ph), 126.2 (CH_2, C8), 122.8 (CH, C3), 79.1 (2-OCH_2), 63.6 (6-OCH_2), 19.5 ($=CCH_3$), 14.9 and 14.2 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2060.5 (20), 1971.8 (5), 1938.1 (100) [$\nu(C{\equiv}O)$], 1695.0 [$\nu(C{=}N)$], 1624.2 [$\nu(C{=}C)$]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (5) [M$^+$], 567 (25), 539 (60), 511 (10), 483 (30), 455 (100) [M$^+$ − 5 CO], 426 (100). Anal. Calcd for $C_{22}H_{21}NO_7W$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.66; H, 3.66; N, 2.56.

10d: ^1H NMR (C_6D_6) δ 7.65 and 7.05 (2:3 H, m each, Ph), 6.20 and 5.30 (1 H each, s each, $=CH_2$), 6.12 (1 H, s, 4-H), 3.60 (2 H, q, 5-OCH_2), 3.30 and 2.85 (1 H each, diastereotopic 2-OCH_2), 1.22 (3 H, s, $=CCH_3$), 1.15 and 1.05 (3 H each, t each, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 203.2 and 199.3 [*trans*- and *cis*-CO, $W(CO)_5$], 174.9 (C_q, C=N, C5), 166.5 (C_q, C3), 139.9 ($=CMe$), 131.4, 129.1, and 127.0 (1:2:2, CH each, Ph), 130.5 (C_q, *i*-C Ph), 119.0 ($=CH_2$), 112.8 (CH, C4), 104.5 (C_q, C2), 68.0 (5-OCH_2), 59.5 (2-OCH_2), 17.5 ($=CCH_3$), 14.5 and 14.4 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2064.7 (10), 1926.3 (100), 1904.7 (30) [$\nu(C{\equiv}O)$], 1612.2 [$\nu(C{=}C)$]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (20) [M$^+$], 567 (10), 511 (15), 455 (100) [M$^+$ − 5 CO], 426 (60), 271 (60) [ligand$^+$], 256 (70), 241 (60), 214 (60), 198 (60), 69 (100). Anal. Calcd for $C_{22}H_{21}NO_7W$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.42; H, 3.67; N, 2.62.

2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-chroma-1,3,5,7-octatetraene (9e), Pentacarbonyl(2,5-diethoxy-2-ethenyl-3-phenyl-2*H*-pyrrole-*N*)chromium (10e), and Pentacarbonyl(3-benzylidene-2-ethenyl-2,4-diethoxy-2,3-dihydroazete-*N*)chromium (11e). Acrylamide **5a** (92 mg, 1.30 mmol), triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**6a**; 350 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) are successively reacted as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel with pentane/diethyl ether (20:1) affords red **9e** (103 mg, 23%, R_f 0.3 in pentane, dark red crystals from pentane at −15 °C, mp 74 °C); elution with pentane/diethyl ether (10:1) yields a yellow fraction with **11e** (157 mg, 35%, R_f 0.6 in pentane/diethyl ether (1:1), pale yellow crystals from pentane, mp 123 °C) and **10e** (90 mg, 20%, R_f 0.5 in pentane/diethyl ether (1:1), dark yellow crystals from pentane).

9e: ^1H NMR (C_6D_6) δ 7.82 (1 H, s, 3-H), 7.62 and 7.03 (2:3 H, m each, Ph), 5.80 and 5.00 (2:1 H, m each, $H_2C{=}CH$), 4.60 (2 H, q, 2-OCH_2), 3.99 (2 H, q, 6-OCH_2), 1.05 (6 H, t, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 322.8 (Cr=C), 224.5 and 218.1 [*trans*- and *cis*-CO, $Cr(CO)_5$], 154.9 (C_q, N=C, C6), 143.2 [C_q, C=*C*(N), C4], 137.8 (C_q, *i*-C Ph), 130.7, 129.0, and 128.3 (1:2:2, CH each, Ph), 126.0 (CH_2, C8), 125.3 (CH, C7), 125.0 (CH, C3), 76.4 (2-OCH_2), 62.7 (6-OCH_2), 14.7 and 14.0 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2052.7 (20), 1974.0 (5), 1939.2 (100) [$\nu(C{\equiv}O)$], 1673.9 [$\nu(C{=}N)$], 1611.1 [$\nu(C{=}C)$]; MS (70 eV, *m/e* (%)) 449 (10) [M$^+$], 431 (5), 393 (20), 365 (20), 337 (30), 309 (80) [M$^+$ − 5 CO], 280 (60), 242 (70), 228 (100). Anal. Calcd for $C_{21}H_{19}CrNO_7$ (449.4): C, 56.13; H, 4.26; N, 3.12. Found: C, 55.99; H, 4.33; N, 2.98.

10e: ^1H NMR (C_6D_6) δ 7.70 and 7.15 (2:3 H, m each, Ph), 6.05 (1 H, s, 4-H), 5.80 and 5.20 (1:2 H, m each, $H_2C{=}CH$), 3.50 (2 H, m, diastereotopic 5-OCH_2), 3.30 and 2.80 (1 H each, diastereotopic 2-OCH_2), 1.16 (3 H, t, 5-OCH_2CH_3), 1.05 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 222.6 and 216.6 [*trans*- and *cis*-CO, $Cr(CO)_5$], 174.6 (C_q, C=N, C5), 167.2 [C_q, C3], 136.2 (2-$CH{=}CH_2$); 131.0, 128.9, and 127.2 (1:2:2, CH each, Ph), 129.9 (C_q, *i*-C Ph), 119.9 ($=CH_2$), 112.4 (CH, C4), 103.0 (C_q, C2), 67.6 (5-OCH_2), 59.3 (2-OCH_2), 14.7 and 14.5 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2062.1 (10), 1934.0 (100), 1905.7 (30) [$\nu(C{\equiv}O)$], 1614.2 [$\nu(C{=}C)$].

11e: ^1H NMR (C_6D_6) δ 7.32, 7.10, and 7.05 (2:2:1 H, m each, Ph), 6.02 (1 H, s, =CH), 5.86 (1 H, d, ^3J = 17 Hz, *trans*-$HC{=}CH$), 5.64 (1 H, dd, ^3J = 17 and 10 Hz, $HC{=}CH_2$), 5.29 (1 H, d, ^3J = 10 Hz, *cis*-$HC{=}CH$), 3.79 (2 H, m, 4-OCH_2), 3.50 and 3.10 (1 H each, diastereotopic 2-OCH_2), 1.18 and 1.03 (3 H each, t each, OCH_2CH_3 each); ^{13}C NMR (C_6D_6) δ 222.1 and 215.9 [*trans*- and *cis*-CO, $Cr(CO)_5$], 177.7 (C_q, C=N, C4), 136.1 (2-$CH{=}CH_2$), 133.0 and 132.9 (C_q each, *i*-C Ph and C3), 131.0, 130.5, and 129.0 (2:1:2, CH each, Ph), 121.1 ($=CH_2$), 120.2 ($=CHPh$), 95.1 (C_q, C2), 67.4 (4-OCH_2), 59.3 (2-OCH_2), 14.8 and 14.6 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2063.0 (10), 1973.4 (5), 1938.9 (100), 1913.0 (30) [$\nu(C{\equiv}O)$], 1671.4 [$\nu(C{=}N)$]; MS (70 eV, *m/e* (%)) 449 (85) [M$^+$], 421 (20), 365 (40), 337 (85), 309 (80) [M$^+$ − 5 CO], 265 (80), 257 (60) [ligand$^+$], 183 (60), 142 (80), 96 (100). Anal. Calcd for $C_{21}H_{19}CrNO_7$ (449.4): C, 56.13; H, 4.26; N, 3.12. Found: C, 56.23; H, 4.35; N, 3.20.

X-ray crystal structure analysis of **11e**: formula $C_{21}H_{19}CrNO_7$, M_r = 449.37, 0.3 × 0.2 × 0.1 mm, a = 9.533(2) Å, b = 10.768(3) Å, c = 12.614(3) Å, α = 110.20(2)°, β = 96.37(2)°, γ = 110.12(2)°, V = 1101.6(5) Å^3, ρ_{calc} = 1.355 g cm^{-3}, μ = 5.59 cm^{-1}, T = 223 K, empirical absorption correction via ψ-scan data (0.981 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$, (No. 2), λ = 0.710 73 Å, $\omega/2\theta$ scans, 2193 reflections collected ($\pm h,+k,\pm l$), $(\sin\theta)/\lambda$ = 0.48 Å^{-1}, 2046 independent and 1347 observed reflections ($I \le 2\sigma(I)$), 273 refined parameters, R = 0.071, wR2 = 0.192, maximum (minimum) residual electron density 0.64 (−0.63) e Å^{-3}, hydrogens calculated and riding. All data were collected on a Enraf-Nonius MACH3 diffractometer. Programs used: MolEN, SHELXS-86, SHELXL-93, XP.

2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-chroma-1,3,5,7-nonatetraene (9f), Pentacarbonyl[2,5-diethoxy-2-(1-propenyl)-3-phenyl-2*H*-pyrrole-*N*]chromium (10f), and Pentacarbonyl[3-benzylidene-2,4-diethoxy-2-(1-propenyl)-2,3-dihydroazete-*N*)chromium (11f). Crotonamide **5b** (111 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**6a**; 350 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9f** (144 mg, 31%, R_f 0.7 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C, mp 85 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction consisting of a 1:2 mixture of isomeric compounds **10f** and **11f** (222 mg, 48%, R_f 0.2 in pentane/diethyl ether (10:1), fractional crystallization from diethyl ether affords **11f** in bright yellow crystals, while **10f** is accumulated in the supernatant).

9f: ^{1}H NMR (C_6D_6) δ 7.82 (1 H, s, 3-H), 7.70 and 7.03 (2:3 H, m each, Ph), 6.45 (1 H, dq, ^3J = 15 and 6 Hz, $=CHMe$), 5.69 (1 H, d, ^3J = 15 Hz, $CH=CHMe$), 4.80 (2 H, q, 2-OCH_2), 4.03 (2 H, q, 6-OCH_2), 1.30 (3 H, d, ^3J = 6 Hz, $=CHCH_3$), 1.05 (6 H, t, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 322.6 (Cr=C), 224.6 and 218.4 [*trans*- and *cis*-CO, $Cr(CO)_5$], 155.2 (C_q, N=C, C6), 143.9 [C_q, C=*C*(N), C4], 140.1 (CH, C7), 138.0 (C_q, *i*-C Ph), 130.7, 129.4, and 128.4 (1:2:2, CH each, Ph), 125.3 (CH, C8), 119.2 (CH, C3), 76.8 (2-OCH_2), 62.7 (6-OCH_2), 17.7 ($=CHCH_3$), 14.8 and 14.2 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2052.5 (20), 1974.5 (5), 1938.6 (100) [ν(C≡O)], 1674.7 [ν(C=N)], 1633.9 [ν(C=C)]; MS (70 eV, *m*/*e* (%)) 463 (10) [M$^+$], 435 (5), 407 (10), 379 (10), 351 (30), 323 (100) [M$^+$ − 5 CO], 294 (40), 279 (60). Anal. Calcd for $C_{22}H_{21}CrNO_7$ (463.4): C, 57.02; H, 4.57; N, 3.02. Found: C, 57.26; H, 4.68; N, 3.14.

10f: ^{1}H NMR (C_6D_6) δ 7.60 and 7.03 (2:3 H, m each, Ph), 6.23 (1 H, dq, ^3J = 15 and 6 Hz, $=CHMe$), 5.84 (1 H, s, 4-H), 5.05 (1 H, d, ^3J = 15.5 Hz, $HC=CHMe$), 3.50 (2 H, q, 5-OCH_2), 3.30 and 2.60 (1 H each, diastereotopic 2-OCH_2), 1.65 (3 H, d, ^3J = 6.5 Hz, $=CHCH_3$), 1.25 (3 H, t, 5-OCH_2CH_3), 1.05 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 222.5 and 216.4 [*trans*- and *cis*-CO, $Cr(CO)_5$], 174.7 (C_q, C=N, C5), 167.4 (C_q, C3), 132.6 and 129.6 (*C*H=*C*HMe), 131.2, 129.0, and 127.3 (1:2:2, CH each, Ph), 130.5 (C_q, *i*-C Ph), 111.5 (CH, C4), 103.3 (C_q, C2), 67.5 (5-OCH_2), 59.5 (2-OCH_2), 17.9 ($=CHCH_3$), 14.5 and 14.4 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2061.9 (10), 1934.8 (100), 1907.2 (30) [ν(C≡O)].

11f: ^{1}H NMR (C_6D_6) δ 7.35, 7.12, and 7.00 (2:2:1 H, m each, Ph), 6.23 (1 H, dq, ^3J = 15 and 6 Hz, $=CHMe$), 5.95 (1 H, s, $=CHPh$), 5.23 (1 H, d, ^3J = 15 Hz, $CH=CHMe$), 3.70 (2 H, q, 4-OCH_2), 3.50 and 3.10 (1 H each, diastereotopic 2-OCH_2), 1.57 (3 H, d, $=CCH_3$), 1.19 and 1.00 (3 H each, t each, 2 OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 222.1 and 216.0 [*trans*- and *cis*-CO, $Cr(CO)_5$], 177.4 (C_q, C=N, C4), 133.8 and 133.2 (C_q each, *i*-C Ph and C3), 132.8 (CH=), 130.5, 129.7, and 129.0 (2:1:2, CH each, Ph), 128.6 (=CHMe), 119.5 (=CHPh), 95.2 (C_q, C2), 67.2 (4-OCH_2), 59.2 (2-OCH_2), 17.7 ($=CCH_3$), 14.9 and 14.7 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2061.8 (10), 1937.5 (100), 1912.4 (30) [ν(C≡O)], 1670.5 [ν(C=N)]; MS (70 eV, *m*/*e* (%)) 463 (25) [M$^+$], 435 (10), 407 (10), 379 (5), 351 (60), 323 (100) [M$^+$ − 5 CO], 271 (50) [ligand$^+$], 242 (60). 228 (100). Anal. Calcd for $C_{22}H_{21}CrNO_7$ (463.4): C, 57.02; H, 4.57; N, 3.02. Found: C, 56.88; H, 4.70; N, 3.17.

2,6-Diethoxy-4,8-diphenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-chroma-1,3,5,7-octatetraene (9g), Pentacarbonyl[2,5-diethoxy-2-(2-phenyl-1-ethenyl)-3-phenyl-2*H*-pyrrole-*N*]chromium (10g), and Pentacarbonyl[3-benzylidene-2,4-diethoxy-2-(2-propenyl)-2,3-dihydroazete-*N*)chromium (11g). Cinnamamide **5c** (191 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**6a**; 350 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as decribed above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9g** (126 mg, 24%, R_f 0.6 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C, mp 121 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction of a 1:8 mixture of **10g** and **11g** (284 mg, 54%, R_f 0.2 in diethyl ether/pentane (10:1), from which yellow crystals of **11g** are obtained by fractional crystallization).

9g: ^{1}H NMR (C_6D_6) δ 7.98 (1 H, s, 3-H), 7.79 and 6.85 (2:3 H, m each, 4-Ph), 7.55 (1 H, d, ^3J = 16 Hz, $=CHPh$), 7.20 and 7.10 (2:3 H, m each, 8-Ph), 6.45 (1 H, d, ^3J = 16 Hz, $CH=CHPh$), 4.70 (2 H, q, 2-OCH_2), 4.12 (2 H, q, 6-OCH_2), 1.20 and 1.15 (3 H each, t each, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 322.9 (Cr=C), 224.5 and 218.0 [*trans*- and *cis*-CO, $Cr(CO)_5$], 155.7 (C_q, N=C, C6), 143.4 [C_q, C=*C*(N), C4], 140.7 (CH, C7), 138.0 (C_q, *i*-C 4-Ph), 135.0 (C_q, *i*-C 8-Ph); 130.7, 129.0, and 127.9 (1:2:2, CH each, 4-Ph); 130.1, 129.1, and 128.0 (1:2:2, CH each, 8-Ph), 125.0 (CH, C8), 114.0 (CH, C3), 76.4 (2-OCH_2), 62.0 (6-OCH_2), 14.8 and 14.2 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2052.5 (10), 1974.6 (1), 1940.7 (100) [ν(C≡O)], 1659.9 [ν(C=N)], 1619.8 [ν(C=C)]; MS (70 eV, *m*/*e* (%)) 525 (5) [M$^+$], 497 (5), 469 (10), 441 (10), 413 (30), 385 (50) [M$^+$ − 5 CO], 333 (30) [ligand$^+$], 304 (80), 289 (60), 228 (100). Anal. Calcd for $C_{27}H_{23}CrNO_7$ (525.5): C, 61.71; H, 4.41; N, 2.67. Found: C, 62.19; H, 4.23; N, 2.82.

10g: ^{1}H NMR (C_6D_6) δ 7.70 and 7.05 (2:3 H, m each, 3-Ph), 7.23 and 7.03 (2:3 H, m each, $CH=CHC_6H_5$), 7.42 and 6.98 (1 H each, d each, ^3J = 15.5 Hz, $CH=CHPh$), 6.20 (1 H, s, 4-H), 3.50 (2 H, q, 5-OCH_2), 3.20 and 3.00 (1 H each, diastereotopic 2-OCH_2), 1.35 (3 H, t, 5-OCH_2CH_3), 0.95 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR (C_6D_6) δ 222.3 and 214.5 [*trans*- and *cis*-CO, $Cr(CO)_5$], 176.0 (C_q, C=N, C5), 167.8 (C_q, C3), 136.0 (C_q, *i*-C, $=CH-C_6H_5$), 134.8 and 128.4 (*C*H=*C*HPh), 131.3, 129.1, and 127.2 (1:2:2, CH each, 5-Ph), 130.4 (C_q, *i*-C 5-Ph), 129.0, 128.0, and 127.8 (1:2:2, CH each, $=CHC_6H_5$), 117.2 (CH, C4), 103.6 (C_q, C2), 67.0 (5-OCH_2), 61.5 (2-OCH_2), 14.6 and 14.5 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2062.1 (10), 1934.0 (100), 1905.7 (30) [ν(C≡O)], 1614.2 [ν(C=C)].

11g: ^{1}H NMR (C_6D_6) δ 7.50−7.20 (10 H, m, 2 Ph), 7.11 (1 H, d, ^3J = 15.5 Hz, =CHPh), 6.50 (1 H, s, =CHPh), 6.12 (1 H, d, ^3J = 15.5 Hz, $HC=CHPh$), 4.68 (2 H, m, 4-OCH_2), 3.58 and 3.30 (1 H each, diastereotopic 2-OCH_2), 1.56 (3 H, t, 4-OCH_2CH_3), 1.30 (3 H, t, 2-OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 221.9 and 215.1 [*trans*- and *cis*-CO, $Cr(CO)_5$], 174.3 (C_q, C=N, C4), 135.9, 134.5, and 133.2 (C_q each, 2 *i*-C Ph and C3), 135.2 and 127.8 (*C*H=*C*HPh), 130.2, 129.7, 128.8, 128.5, 126.9, and 128.8 (2:1:2:2:2:1, CH each, 2 Ph), 119.9 (=CHPh), 95.1 (C_q, C2), 57.5 (4-OCH_2), 59.2 (2-OCH_2), 15.1 and 14.6 (2 CH_2CH_3); IR (hexane, cm^{-1}) 2062.8 (10), 1938.4 (100), 1913.9 (30) [ν(C≡O)], 1671.0 [ν(C=N)]; MS (70 eV, *m*/*e* (%)) 525 (5) [M$^+$], 413 (30), 385 (50) [M$^+$ − 5 CO], 333 (90) [ligand$^+$], 304 (100). Anal. Calcd for $C_{27}H_{23}CrNO_7$ (525.5): C, 61.71; H, 4.41; N, 2.67. Found: C, 62.06; H, 4.56; N, 2.87.

2,6-Diethoxy-7-methyl-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-chroma-1,3,5,7-octatetraene (9h), Pentacarbonyl[2,5-diethoxy-2-(2-propenyl)-3-phenyl-2*H*-pyrrole-*N*]chromium (10h), and Pentacarbonyl[3-benzylidene-2,4-diethoxy-2-(2-propenyl)-2,3-dihydroazete-*N*)chromium (11h). Methacrylamide **5d** (111 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)chromium (**6a**; 350 mg, 1.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above until the reaction is complete (*ca.* 2 h at 20 °C). Chromatography on silica gel (column 20 × 2 cm) with pentane/diethyl ether affords the red compound **9h** (69 mg, 15%, R_f 0.7 in pentane/diethyl ether (10:1), dark red crystals from pentane at −15 °C); elution with pentane/diethyl ether (5:1) yields a yellow fraction consisting of a 1:1 mixture of isomeric compounds **10h** and **11h** (278 mg, 60%, R_f 0.2 in pentane/diethyl ether (10:1), fractional crystallization from diethyl ether affords **11h** as bright yellow crystals, while **10h** is accumulated in the supernatant).

9h: ^{1}H NMR (C_6D_6) δ 7.68 (1 H, s, 3-H), 7.60 and 7.00 (2:3 H, m each, Ph), 5.30 and 4.92 (1 H each, s each, $=CH_2$), 4.70 (2 H, q, 2-OCH_2), 3.88 (2 H, q, 6-OCH_2), 1.58 (3 H, s, $=CCH_3$), 1.20 and 1.02 (3 H each, t each, 2 CH_2CH_3); ^{13}C NMR (C_6D_6) δ 318.9 (Cr=C), 224.6 and 218.4 [*trans*- and *cis*-CO, $Cr(CO)_5$], 155.1 (C$_q$, N═C, C6), 143.7 [C$_q$, C═*C*(N), C4], 137.9 (C$_q$, *i*-C Ph), 136.0 (C$_q$, ═*C*Me), 130.8, 129.1, and 127.7 (1:2:2, CH each, Ph), 122.9 (CH$_2$, C8), 122.5 (CH, C3), 76.2 (2-OCH$_2$), 63.2 (6-OCH$_2$), 19.3 (═C*C*H$_3$), 14.9 and 14.0 (2 CH$_2$*C*H$_3$); IR (hexane, cm^{-1}) 2052.2 (20), 1974.1 (5), 1938.0 (100) [ν(C≡O)], 1689.0 [ν(C═N)], 1613.7 [ν(C═C)]; MS (70 eV, *m/e* (%)) 463 (10) [M$^+$], 435 (5), 407 (10), 379 (10), 351 (30), 323 (100) [M$^+$ − 5 CO], 294 (40), 279 (60). Anal. Calcd for C$_{22}$H$_{21}$CrNO$_7$ (463.4): C, 57.02; H, 4.57; N, 3.02. Found: C, 57.22; H, 4.63; N, 2.88.

10h: ^{1}H NMR (C$_6$D$_6$) δ 7.55 and 7.03 (2:3 H, m each, Ph), 6.10 and 5.25 (1 H each, s each, ═CH$_2$), 5.97 (1 H, s, 4-H), 3.42 (2 H, q, 5-OCH$_2$), 3.23 and 2.77 (1 H each, diastereotopic 2-OCH$_2$), 1.18 (3 H, s, ═CC*H*$_3$), 1.16 and 1.12 (3 H each, t each, 2-OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 222.5 and 216.4 [*trans*- and *cis*-CO, Cr(CO)$_5$], 174.9 (C$_q$, C═N, C5), 167.4 (C$_q$, C3), 139.9 (═*C*Me), 131.5, 129.5, and 127.2 (1:2:2, CH each, Ph), 130.5 (C$_q$, *i*-C Ph), 118.8 (═CH$_2$), 113.1 (CH, C4), 104.2 (C$_q$, C2), 67.5 (5-OCH$_2$), 59.5 (2-OCH$_2$), 17.5 (═C*C*H$_3$), 14.6 and 14.4 (2 CH$_2$*C*H$_3$); IR (hexane, cm^{-1}) 2061.9 (10), 1934.8 (100), 1907.2 (30) [ν(C≡O)]; MS (70 eV, *m/e* (%)) MS (70 eV, *m/e* (%)) 463 (15) [M$^+$], 435 (10), 407 (10), 379 (5), 351 (5), 323 (100) [M$^+$ − 5 CO], 271 (90) [ligand$^+$], 242 (100). Anal. Calcd for C$_{22}$H$_{21}$CrNO$_7$ (463.4): C, 57.02; H, 4.57; N, 3.02. Found: C, 57.26; H, 4.62; N, 3.14.

11h: ^{1}H NMR (C$_6$D$_6$) δ 7.25, 7.07, and 6.95 (2:2:1 H, m each, Ph), 6.23 and 5.25 (1 H each, s each, ═CH$_2$), 5.86 (1 H, s, ═CHPh), 3.65 (2 H, q, 4-OCH$_2$), 3.50 and 3.12 (1 H each, diastereotopic 2-OCH$_2$), 1.47 (3 H, s, ═CC*H*$_3$), 1.03 and 0.91 (3 H each, t each, 2 OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 221.9 and 215.8 [*trans*- and *cis*-CO, Cr(CO)$_5$], 177.9 (C$_q$, C═N, C4), 140.0 (═*C*Me), 133.2 and 132.8 (C$_q$ each, *i*-C Ph and C3), 130.3, 130.7, and 129.4 (1:2:2, CH each, Ph), 119.6 (═CH$_2$), 119.8 (CH, ═CHPh), 96.4 (C$_q$, C2), 67.3 (4-OCH$_2$), 59.2 (2-OCH$_2$), 18.4 (═C*C*H$_3$), 14.9 and 14.4 (2 CH$_2$*C*H$_3$); IR (hexane, cm^{-1}) 2061.9 (10), 1934.8 (100), 1907.2 (30) [ν(C≡O)], 1670.5 [ν(C═N)]; MS (70 eV, *m/e* (%)) 463 (25) [M$^+$], 435 (10), 407 (10), 379 (5), 351 (60), 323 (100) [M$^+$ − 5 CO], 271 (50) [ligand$^+$], 242 (60). Anal. Calcd for C$_{22}$H$_{21}$CrNO$_7$ (463.4): C, 57.02; H, 4.57; N, 3.02. Found: C, 57.17; H, 4.72; N, 2.98.

Pentacarbonyl(2,3-diethoxy-2-ethenyl-5-phenyl-2*H*-pyrrole-*N*)tungsten (12a) and 2,3-Diethoxy-2-ethenyl-5-phenyl-2*H*-pyrrole (13a). 2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-octatetraene (**9a**; 290 mg, 0.50 mmol) in 2 mL of toluene is heated to 80 °C for 6 h. Reaction progress is followed by TLC. Chromatography on silica gel with pentane/diethyl ether affords the pale yellow compound **12a** (270 mg, 93%, R_f 0.3 in pentane/diethyl ether (10:1), yellow crystals from pentane at −15 °C, mp 110 °C). Thermolysis of compound **9a** at 110 °C for 6 h affords the metal-free pyrrole **13a** together with W(CO)$_6$.

12a: ^{1}H NMR (C$_6$D$_6$) δ 7.20 and 7.18 (3:2 H, m each, Ph), 5.96 and 5.42 (1:2 H, m each, H$_2$C═CH), 4.75 (1 H, s, 4-H), 3.22 (2 H, m, diastereotopic 3-OCH$_2$), 3.40 and 3.05 (1 H each, diastereotopic 2-OCH$_2$), 1.30 (3 H, t, 3-CH$_2$C*H*$_3$), 0.90 (3 H, t, 2-CH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 202.1 and 199.1 [*trans*- and *cis*-CO, W(CO)$_5$], 184.4 (C$_q$, C═N, C5), 180.0 (C$_q$, C3), 137.4 (C$_q$, *i*-C Ph), 134.2 (2-*C*H═CH$_2$), 130.8, 128.1, and 126.9 (1:2:2, CH each, Ph), 120.8 (═CH$_2$), 104.7 (C$_q$, C2), 100.5 (C$_q$, C4), 68.4 (3-OCH$_2$), 60.1 (2-OCH$_2$), 14.8 and 13.7 (2 CH$_2$*C*H$_3$); IR (hexane, cm^{-1}) 2065.6 (10), 1932.4 (100), 1906.9 (30) [ν(C≡O)], 1628.0 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 581 (25) [M$^+$], 553 (10), 525 (1), 497 (10), 469 (5), 441 (100) [M$^+$ − 5 CO], 257 (30) [ligand$^+$], 228 (80), 213 (60). Anal. Calcd for C$_{21}$H$_{19}$NO$_7$W (581.2): C, 43.40; H, 3.29; N, 2.41. Found: C, 43.10; H, 3.21; N, 2.60.

13a: ^{1}H NMR (C$_6$D$_6$) δ 8.10 and 7.21 (2:3 H, m each, Ph), 6.15 (1 H, dd, ^3J = 17.5 and 10.5 Hz, *H*C═CH$_2$), 5.88 (1 H, d, ^3J = 17.5 Hz, *trans* ═CH$_2$), 5.42 (1 H, s, 4-H), 5.20 (1 H, d, ^3J = 10.5, *cis* ═CH$_2$), 3.55 (2 H, m, diastereotopic 3-OCH$_2$), 3.70 and 3.20 (1 H each, diastereotopic 2-OCH$_2$), 1.20 (3 H, t, 3-OCH$_2$C*H*$_3$), 1.00 (3 H, t, 2-OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 181.1 (C$_q$, C═N, C5), 172.4 (C$_q$, C3), 136.5 (2-*C*H═CH$_2$), 135.0 (C$_q$, *i*-C Ph), 130.9, 128.6, and 126.9 (1:2:2, CH each, Ph), 116.5 (═CH$_2$), 94.1 (C$_q$, C4), 100.5 (C$_q$, C2), 67.5 (3-OCH$_2$), 59.7 (2-OCH$_2$), 15.9 and 14.1 (2 CH$_2$*C*H$_3$).

Pentacarbonyl[2,3-diethoxy-2-(1-propenyl)-5-phenyl-2*H*-pyrrole-*N*]tungsten (12b) and 2,3-Diethoxy-2-(1-propenyl)-5-phenyl-2*H*-pyrrole (13b). 2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-nonatetraene (**9b**; 297 mg, 0.50 mmol) in 2 mL of toluene is heated to 90 °C for 5.5 h. Reaction progress is followed by TLC. Chromatography on silica gel with pentane/diethyl ether affords the pale yellow compound **12b** (267 mg, 90%, R_f 0.2 in pentane/diethyl ether (10:1), yellow crystals from pentane at −15 °C, mp 110 °C). Thermolysis of compound **9b** at 110 °C for 6 h affords the metal-free pyrrole **13b** together with W(CO)$_6$.

12b: ^{1}H NMR (C$_6$D$_6$) δ 7.23 (5 H, m, Ph), 6.38 (1 H, dq, ^3J = 15.5 and 6.5 Hz, ═CHMe), 5.19 (1 H, d, ^3J = 15.5 Hz, *H*C═CHMe), 4.80 (1 H, s, 4-H), 3.40 and 3.10 (1 H each, diastereotopic 2-OCH$_2$), 3.35 (2 H, q, 3-OCH$_2$), 1.80 (3 H, d, ^3J = 6.5 Hz, ═CHC*H*$_3$), 1.30 (3 H, t, 3-OCH$_2$C*H*$_3$), 0.90 (3 H, t, 2-OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 202.3 and 199.2 [*trans*- and *cis*-CO, W(CO)$_5$], 184.0 (C$_q$, C═N, C5), 180.2 (C$_q$, C3), 137.6 (C$_q$, *i*-C Ph), 132.2 and 127.6 (*C*H═*C*HMe), 130.9, 129.6, and 127.0 (1:2:2, CH each, Ph), 104.7 (C$_q$, C2), 100.1 (CH, C4), 68.4 (3-OCH$_2$), 60.0 (2-OCH$_2$), 17.9 (═CH*C*H$_3$), 14.9 and 13.7 (2 CH$_2$*C*H$_3$); IR (hexane, cm^{-1}) 2064.5 (10), 1931.2 (100), 1905.8 (30) [ν(C≡O)], 1625.5 [ν(C═C)]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (25) [M$^+$], 567 (10), 511 (20), 455 (100) [M$^+$ − 5 CO], 426 (60), 271 (20) [ligand$^+$], 241 (70), 227 (90), 198 (100). Anal. Calcd for C$_{22}$H$_{21}$NO$_7$W (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.60; H, 3.56; N, 2.48.

X-ray crystal structure analysis of **12b**: formula C$_{22}$H$_{21}$NO$_7$W, M_r = 595.25, 0.5 × 0.2 × 0.2 mm, a = 10.440(2) Å, b = 25.870(6) Å, c = 9.203(3) Å, β = 109.47(12)°, V = 2343.4(10) Å^3, ρ_{calc} = 1.687 g cm^{-3}, μ = 49.69 cm^{-1}, T = 293 K, empirical absorption correction via ψ-scan data (0.823 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, $\omega/2\theta$ scans, 4213 reflections collected (±h,+k,+l), (sin θ)/λ = 0.59 Å^{-1}, 3949 independent and 1497 observed reflections (I ≤ 2$\sigma(I)$), 283 refined parameters, R = 0.054, wR2 = 0.067, maximum (minimum) residual electron density 0.74 (−0.89) e Å^{-3}, hydrogens calculated and riding. All data were collected on a Enraf-Nonius MACH3 diffractometer. Programs used: MolEN, SHELXS-86, SHELXL-93, XP.

13b: ^{1}H NMR (C$_6$D$_6$) δ 8.05 and 7.20 (2:3 H, m each, Ph), 6.32 (1 H, dq, ^3J = 15.5 and 6.5 Hz, ═CHMe), 5.88 (1 H, d, ^3J = 15.5 Hz, *H*C═CHMe), 5.42 (1 H, s, 4-H), 3.60 and 3.30 (1 H each, diastereotopic 2-OCH$_2$), 3.55 (2 H, q, 3-OCH$_2$), 1.55 (3 H, d, ^3J = 6.5 Hz, ═CHC*H*$_3$), 1.20 (3 H, t, 3-OCH$_2$C*H*$_3$), 1.05 (3 H, t, 2-OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 181.5 (C$_q$, C═N, C5), 176.1 (C$_q$, C3), 135.2 (C$_q$, *i*-C Ph), 130.9, 129.6, and 127.0 (1:2:2, CH each, Ph), 129.0 (*C*H═*C*HMe), 100.1 (CH, C4), 93.7 (C$_q$, C2), 67.5 (3-OCH$_2$), 59.5 (2-OCH$_2$), 17.9 (═CH*C*H$_3$), 15.9 and 14.2 (2 CH$_2$*C*H$_3$); IR (film, cm^{-1}) 1728.4 (10) [ν(C═N)], 1625.5 (100) [ν(C═C)]; MS (70 eV, *m/e* (%)) 271 (40) [M$^+$], 242 (70), 227 (30), 214 (40), 198 (40), 186 (30), 69 (100).

Pentacarbonyl[2,3-diethoxy-2-(2-phenyl-1-ethenyl)-5-phenyl-2*H*-pyrrole-*N*]tungsten (12c) and 2,3-Diethoxy-2-(2-phenyl-1-ethenyl)-5-phenyl-2*H*-pyrrole (13c). 2,6-Diethoxy-4,8-diphenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-octatetraene (**9c**; 329 mg, 0.50 mmol) in 2 mL of toluene is heated to 90 °C for 5.5 h. Reaction progress is followed by TLC. Chromatography on silica gel with pentane/diethyl ether affords the pale yellow compound **12c** (283 mg, 86%, R_f 0.2 in pentane/diethyl ether (10:1), yellow crystals from pentane at −15 °C). Thermolysis of compound **9c** at 110 °C for 6 h affords the metal-free pyrrole **13c** together with W(CO)$_6$.

12c: ^{1}H NMR (C$_6$D$_6$) δ 7.28 (1 H, d, ^3J = 15.5 Hz, ═C*H*Ph), 7.23 (5 H, m, Ph), 7.20 and 6.90 (2:3 H m each, ═CHC$_6$*H*$_5$), 5.95 (1 H, d, ^3J = 15.5 Hz, *H*C═CHPh), 4.80 (1 H, s, 4-H), 3.55 and 3.10 (1:3 H, 2 diastereotopic OCH$_2$), 1.30 (3 H, t, 3-OCH$_2$C*H*$_3$), 0.75 (3 H, t, 2-OCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$) δ

202.3 and 199.0 [*trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 184.4 ($\mathrm{C_q}$, C$=$N, C5), 180.0 ($\mathrm{C_q}$, C3), 137.4 ($\mathrm{C_q}$, *i*-C 5-Ph), 136.0 ($\mathrm{C_q}$, *i*-C, $=$CH-C_6H_5), 135.8 and 124.5 (*C*H$=$*C*HPh), 131.2, 129.5, and 127.2 (1:2:2, CH each, 5-Ph), 130.9, 128.9, and 128.2 (1:2:2, CH each, $=$CHC_6H$_5$), 104.9 ($\mathrm{C_q}$, C2), 100.3 (CH, C4), 68.4 (3-$\mathrm{OCH_2}$), 60.1 (2-$\mathrm{OCH_2}$), 14.8 and 13.6 (2 $\mathrm{CH_2}$*C*$\mathrm{H_3}$); IR (hexane, cm^{-1}) 2064.7 (10), 1931.2 (100), 1906.7 (30) [ν(C$\equiv$O)], 1624.6 [ν(C$=$C)]; MS (70 eV, *m/e* (%)) ^{184}W, 657 (25) [M$^+$], 573 (10), 517 (100) [M$^+$ $-$ 5 CO], 488 (60), 333 (20) [ligand$^+$], 304 (70), 289 (100), 260 (90). Anal. Calcd for $\mathrm{C_{27}H_{23}NO_7W}$ (657.3): C, 49.34; H, 3.53; N, 2.13. Found: C, 49.26; H, 3.42; N, 1.99.

13c: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 8.15 and 7.20 (2:3 H, m each, Ph), 6.25 (1 H, d, ^3J = 15.5 Hz, $=$CHPh), 7.20 and 6.90 (2:3 H, m each, $=$CHC$_6$*H*$_5$), 6.53 (1 H, d, ^3J = 15.5 Hz, *H*C$=$CHPh), 5.48 (1 H, s, 4-H), 4.15 and 3.40 (1:3 H, 2 diastereotopic $\mathrm{OCH_2}$), 1.20 (3 H, t, 3-$\mathrm{OCH_2C}$*H*$_3$), 1.05 (3 H, t, 2-$\mathrm{OCH_2C}$*H*$_3$).

Pentacarbonyl[2,3-diethoxy-2-(2-propenyl)-5-phenyl-2*H*-pyrrole-*N*]tungsten (12d) and 2,3-Diethoxy-2-(2-propenyl)-5-phenyl-2*H*-pyrrole (13d). 2,6-Diethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-5-aza-1-tungsta-1,3,5,7-nonatetraene (**9e**; 297 mg, 0.50 mmol) in 2 mL of toluene is heated to 90 °C for 5.5 h. Reaction progress is followed by TLC. Chromatography on silica gel with pentane/diethyl ether affords the pale yellow compound **12d** (261 mg, 88%, R_f 0.2 in pentane/diethyl ether (10:1), yellow crystals from pentane at -15 °C, mp 110 °C). Thermolysis of compound **9e** at 110°C for 6 h affords the metal-free pyrrole **13d** together with $\mathrm{W(CO)_6}$.

12d: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.23 (5 H, m, Ph), 6.10 and 5.30 (1 H each, s each, $=$$\mathrm{CH_2}$), 4.80 (1 H, s, 4-H), 3.40 and 3.05 (1 H each, diastereotopic 2-$\mathrm{OCH_2}$), 3.25 (2 H, q, 3-$\mathrm{OCH_2}$), 1.60 (3 H, s, $=$CC*H*$_3$), 1.30 (3 H, t, 3-$\mathrm{OCH_2C}$*H*$_3$), 0.95 (3 H, t, 2-$\mathrm{OCH_2C}$*H*$_3$); ^{13}C NMR ($\mathrm{C_6D_6}$): δ 201.9 and 199.0 [*trans*- and *cis*-CO, $\mathrm{W(CO)_5}$], 185.4 ($\mathrm{C_q}$, C$=$N, C5), 179.7 ($\mathrm{C_q}$, C3), 137.6 ($\mathrm{C_q}$, *i*-C Ph), 137.5 (CH, $=$*C*Me), 130.6, 129.1, and 126.8 (1:2:2, CH each, Ph), 119.0 ($=$$\mathrm{CH_2}$), 105.9 ($\mathrm{C_q}$, C2), 101.5 (CH, C4), 68.5 (3-$\mathrm{OCH_2}$), 60.2 (2-$\mathrm{OCH_2}$), 17.5 ($=$C*C*$\mathrm{H_3}$), 14.8 and 13.7 (2 $\mathrm{CH_2}$*C*$\mathrm{H_3}$); IR (hexane, cm^{-1}) 2064.5 (10), 1931.2 (100), 1908.1 (30) [ν(C$\equiv$O)], 1628.6 [ν(C$=$C)]; MS (70 eV, *m/e* (%)) ^{184}W, 595 (25) [M$^+$], 567 (10), 511 (20), 455 (100) [M$^+$ $-$ 5 CO], 426 (60), 271 (20) [ligand$^+$], 242 (70), 214 (90), 57 (100). Anal. Calcd for $\mathrm{C_{22}H_{21}NO_7W}$ (595.3): C, 44.39; H, 3.56; N, 2.35. Found: C, 44.62; H, 3.43; N, 2.50.

13d: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 8.10 and 7.21 (2:3 H, m each, Ph), 5.80 and 5.00 (1 H each, s each, $=$$\mathrm{CH_2}$), 5.35 (1 H, s, 4-H), 3.70 and 3.45 (1 H each, diastereotopic 2-$\mathrm{OCH_2}$), 3.55 (2 H, q, 3-$\mathrm{OCH_2}$), 1.95 (3 H, s, $=$CC*H*$_3$), 1.20 (3 H, t, 3-$\mathrm{OCH_2C}$*H*$_3$), 1.00 (3 H, t, 2-$\mathrm{OCH_2C}$*H*$_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 181.0 ($\mathrm{C_q}$, C$=$N, C5), 172.6 ($\mathrm{C_q}$, C3), 142.8 ($=$*C*Me), 135.0 ($\mathrm{C_q}$, *i*-C Ph), 130.9, 128.6, and 127.6 (1:2:2, CH each, Ph), 112.9 ($=$$\mathrm{CH_2}$), 104.4 ($\mathrm{C_q}$, C2), 94.8 (CH, C4), 67.4 (3-$\mathrm{OCH_2}$), 59.5 (2-$\mathrm{OCH_2}$), 18.6 ($=$C*C*$\mathrm{H_3}$), 15.9 and 14.1 (2 $\mathrm{CH_2}$*C*$\mathrm{H_3}$); MS (70 eV, *m/e* (%)) 271 (60) [M$^+$], 242 (100), 227 (20), 214 (30), 198 (20), 186 (60).

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and displacement parameters, bond distances and angles, and hydrogen coordinates for **9b**, **10b**, **11e**, and **12b** (24 pages). Ordering information is given on any current masthead page.

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