

# Organic Syntheses via Transition Metal Complexes. 96.<sup>1</sup> 1-Azacycloalkene and 2-Azabicycloalkene Derivatives of 4-Amino-1-metalla-1,3-dienes by Reaction of Saturated Lactims with (1-Alkynyl)carbene Complexes of Chromium and Tungsten

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Reaction of five- and six-membered *O*-alkyl lactims  $\sim(\text{CH}_2)_n\text{-N}=\text{C}(\text{OR})\sim$  **5** ( $n = 3$ ) and **7** ( $n = 4$ ) with (1-alkynyl)carbene complexes  $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$  **1** (**a**,  $\text{M} = \text{Cr}$ ; **b**,  $\text{W}$ ) gives binuclear 1-alkoxy-2-azabicyclo[ $n.2.0$ ]alkene derivatives (*E*)-**6** and (*E*)-**8**, respectively, in 90–94% yields. Reaction of seven- and eight-membered *O*-alkyl lactims  $\sim(\text{CH}_2)_n\text{-N}=\text{C}(\text{OR})\sim$  **9** ( $n = 5$ ) and **11** ( $n = 6$ ) with compounds **1** affords mononuclear 4-(1-aza-cyclo-2-alken-1-yl) 1-metalla-1,3-butadienes (*E*)-**10** and (*E*)-**11**, respectively, but no binuclear derivatives. Both mono- and binuclear metal compounds undergo fast transformations on contact with silica gel. Chromatography of the binuclear tungsten compound (*E*)-**6b** on silica gel results in fragmentation of the (cyclobutenyl)carbene unit to give 1,11-bis(tungsta)-5-azaundeca-1,3,6,8,10-pentaene (**13**) as well as in hydrolysis of the 2-alkoxy pyrrolidine unit with formation of a bis(carbene) derivative **15** of an amino acid. Compound **13**, on extended contact with silica gel, undergoes cyclization and subsequent hydrolysis to 2-azabicyclo[3.3.0]octenone **14**. Thermal fragmentation of the mononuclear dihydroazepine compound (*E*)-**10c** affords dihydro- and tetrahydropyrrolo[1,2-*a*]azepines **17** and **18**, respectively. X-ray crystal structural data are reported for the binuclear compound (*E*)-**6b** as well as for mononuclear compounds (*E*)-**10c** and **14**.

The usefulness of Fischer carbene complexes to organic synthesis has been amply demonstrated over the past decades. Most prominently, reactions of (1-alkenyl)carbene with *alkynes* have found wide application to organic synthesis. Much less attention has been paid, so far, to the inherent synthetic potential of reactions of (1-alkynyl)carbene complexes with *alkenes*.<sup>2</sup> We have recently reported on the formation of aminocyclopentadienes in an overall [3 + 2] cycloaddition induced by addition of (1-alkynyl)carbene complexes to the  $\text{C}=\text{C}(\text{N})$  bond of an enamine.<sup>3</sup> As a logical consequence of these findings, our investigation has been extended to studies on reactions of (1-alkynyl)carbene complexes with compounds containing a  $\text{C}=\text{N}$  bond. We now wish to report on successful generation of 1-azacycloalken-1-yl and 2-azabicycloalken-2-yl derivatives of

4-amino-1-metalla-1,3-dienes from saturated lactims and of organic ring compounds derived by disengagement of the metal unit.

**2-Azabicyclo[ $n.0.2$ ]alkenes.** A manifold of reactions of (1-alkynyl)carbene complexes  $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{-C}\equiv\text{CPh}$  **1** ( $\text{M} = \text{Cr}, \text{W}$ ) with nitrogen bases **N** are initiated by addition of the nitrogen atom to the strongly electrophilic  $\text{C}\equiv\text{C}$  bond of **1** with formation of a zwitterionic carbiminium carbonylmetalate  $^-(\text{OC})_5\text{M}-\text{C}(\text{OEt})=\text{C}(\text{Ph})\text{N}^+$ .<sup>2b</sup> It was anticipated that addition of saturated cyclic imidates (lactimes) **A** to a (1-alkynyl)carbene complex **1** might possibly generate enamino derivatives **B** by migration of an  $\alpha$ -hydrogen atom in the zwitterionic adducts initially formed (Scheme 1). Since binuclear carbene complexes **4** of 2-azabicyclo[4.2.0]octadiene ring systems have recently been generated from alkenyl imidates **2** and (1-alkynyl)carbene tungsten complex **1** via metal-activated di(alkenyl)amino intermediates **3** (Scheme 1),<sup>1</sup> it was assumed that monocyclic enamino derivatives **B** might possibly be further metalated to give bicyclic derivatives **C** (Scheme 1). Compounds **B** and **C** are multifunctional and were envisaged as potential building blocks for organic synthesis. Compounds **B**, which contain a di(alkenyl)amino functionality activated by a  $(\text{CO})_5\text{M}=\text{C}$  unit, have gained our attention as candidates for ring-annulation and fragmentation reactions.<sup>4</sup> It should be noted that even though a number of reports dealing with the

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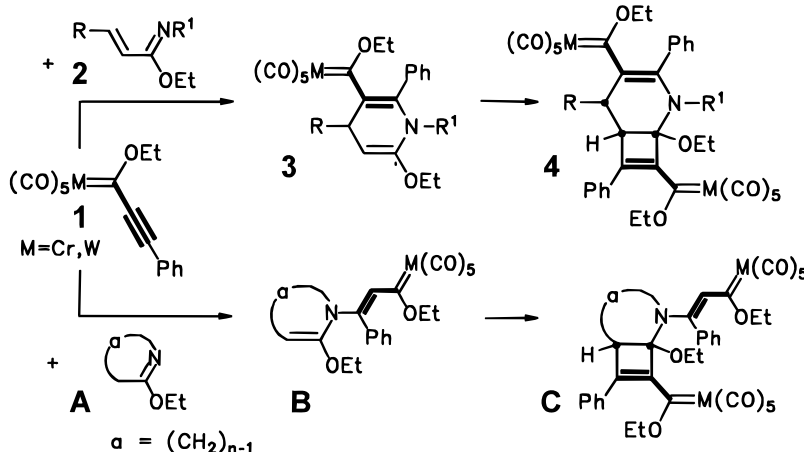
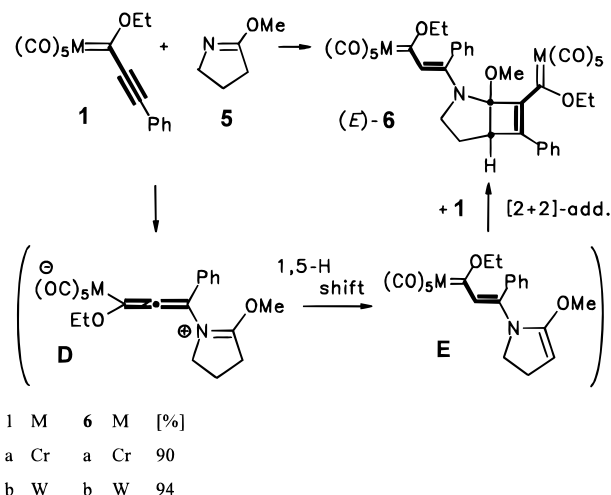
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<sup>‡</sup> X-ray crystal structure analyses.

(1) For part 95 of this series see: Aumann, R.; Hildmann, B.; Fröhlich, R. *Organometallics* **1998**, *17*, 1197.

(2) Recent reviews: (a) de Meijere, A. *Pure Appl. Chem.* **1996**, *68*, 61. (b) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163.

(3) (a) Aumann, R.; Heinen, H.; Hinterding, P.; Sträter, N.; Krebs, B. *Chem. Ber.* **1991**, *124*, 1229. (b) Aumann, R.; Kössmeier, M.; Roths, K.; Fröhlich, R. *Synlett* **1994**, 1041. (c) Meyer, A. G.; Aumann, R. *Synlett* **1995**, 1011. (d) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018. (e) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343. (f) Aumann, R.; Kössmeier, M.; Zippel, F. *Synlett* **1997**, 621.

**Scheme 1. Approaches to 1-Alkoxy-2-azabicyclo[*n*.2.0]alkenes **4** with Endo-, and **C** with Exocyclic 4-Amino-1-metalla-1,3-diene Units, Respectively****Scheme 2. Binuclear 2-Azabicyclo[3.2.0]heptenyl Carbene Complexes (*E*)-**6a,b****

preparation of 2-azabicyclo[3.2.0]heptenes have appeared in the literature, most of which are based on photocyclization of dihydroazepines,<sup>5</sup> to date only a few reports have focused on the synthesis of higher homologues of such compounds.<sup>6</sup>

Cyclic imidates (*O*-alkyl lactimes) **A** (Scheme 1) are accessible by *O*-alkylation of the corresponding *NH*-lactames. For example, 5-methoxy-3,4-dihydro-2*H*-pyrrole (**5**) (Scheme 2) is obtained by reaction of *NH*-pyrrolidone with dimethyl sulfate. Since the ring size of a cyclic imidate **A** has a marked influence on its ability to add to a (1-alkynyl)carbene complex **1**, compounds of different ring sizes will subsequently be described in separate chapters.

**Binuclear 1-Alkoxy-2-azabicyclo[3.2.0]heptene Derivatives 6.** Reaction of five-membered *O*-methyl lactim **5** (5-methoxy-3,4-dihydro-2*H*-pyrrole) with (1-alkynyl)carbene complexes  $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$  (**1a**,

$\text{M} = \text{Cr}$ ; **1b**,  $\text{W}$ ) in a 1:2 molar ratio affords binuclear carbene complexes (*E*)-**6a,b** in 90–94% yields (Scheme 2). The reaction is most conveniently performed in pentane at 20 °C, a solvent in which the products are only sparsely soluble and, therefore, precipitate rapidly once they are formed. Mononuclear carbene complexes of type **E** could not be detected as intermediates. If the molar ratio of the starting compounds is changed to 1:1, 0.5 equiv of lactim **5** remains unchanged, indicating that the second step, the [2 + 2] cycloaddition, is faster than the first one. The reaction is assumed to proceed via a carbiminium carbonylmetalate **D**, which undergoes a spontaneous 1,5-hydrogen shift to give an enamine derivative **E**. Binuclear compounds (*E*)-**6a,b** appear to be generated from mononuclear enamine derivatives **E** by [2 + 2] cycloaddition of the (electron-deficient)  $\text{C}\equiv\text{C}$  bond of complex **1** to the (electron-rich)  $\text{C}=\text{C}(\text{OMe})\text{N}$  bond. A reversed reaction sequence, involving initial formation of a cyclobutene derivative by [2 + 2] cycloaddition of the  $\text{C}=\text{C}$  bond of the (1-alkynyl)carbene complex **1** to the  $\text{C}=\text{C}(\text{OMe})\text{N}$  bond of an enamine obtained by isomerization of compound **5**, appears to be less probable, particularly since mononuclear compounds of type **E** could indeed be trapped and isolated from addition of seven- and eight-membered lactims to compounds **1** (vide infra).

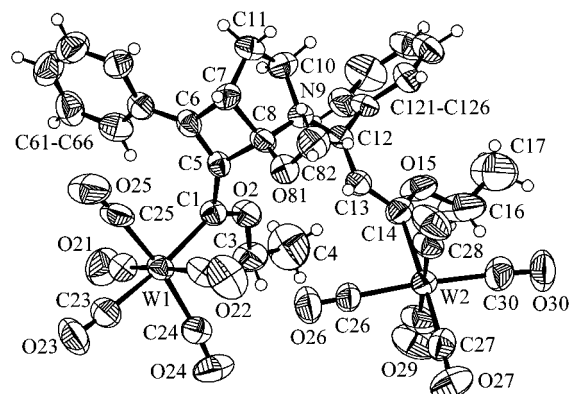
The structures of compounds (*E*)-**6a,b** could be assigned on the basis that two different  $\text{M}=\text{C}$  moieties are detected in the  $^{13}\text{C}$  NMR spectra (**6a**,  $\delta$  346.2 and 307.9; **6b**,  $\delta$  317.6 and 280.9) and also that two  $[\nu(\text{C}=\text{O})]$   $\text{A}^1$  bands are observed in the IR spectra, which are attributed to different  $\text{M}(\text{CO})_5$  groups (**6a**, 2063.6  $\text{cm}^{-1}$  and 2048.1; **6b**, 2071.3  $\text{cm}^{-1}$  and 2056.1). An NOE enhancement of the  $\text{OCH}_3$  signal on irradiation of the bridgehead hydrogen atom, and vice versa, indicates that the four-membered ring is attached to the five-membered ring in a *cis* fashion, in line with what is expected.

Structural details of compound (*E*)-**6b** were obtained from an X-ray crystal structure analysis, Figure 1. Both metal units were found to be arranged *exo* with respect to the envelope-shaped 2-azabicyclo[3.2.0]heptene ligand. The  $\text{W1}-\text{C1}-\text{C5}-\text{C6}$  metalladiene unit is twisted by  $-64.7(14)^\circ$ , and the  $\text{W2}-\text{C14}-\text{C13}-\text{C12}$  unit adopts an *s-trans* conformation with an interplanar angle of  $174.2(9)^\circ$  (Table 1).

(4) Aumann, R.; Fröhlich, R.; Kotila, S. *Organometallics* **1996**, *15*, 4842.

(5) (a) Paquette, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 500. (b) Chapman, O. L.; Hoganson, E. D. *J. Am. Chem. Soc.* **1964**, *86*, 498. (c) Paquette, L. A.; Barret, J. H. *J. Am. Chem. Soc.* **1966**, *88*, 1718. (d) Jones, G.; Turbini, L. J. *J. Org. Chem.* **1976**, *41*, 2362. (e) Satake, K.; Saitoh, H.; Kimura, M.; Morosawa, S. *Heterocycles* **1994**, *38*, 769.

(6) Review: Chan, T.-L. Cyclobutenes *Houben-Weyl*; de Meijere, A., Ed.; 1997; Vol. E17, pp 615.

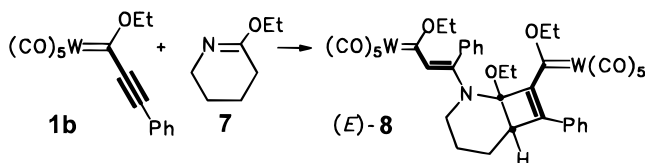


**Figure 1.** Molecular structure of the binuclear carbene complex (*E*)-6b.

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for Complex (*E*)-6b

W(1)–C(1)	2.170(10)	C(8)–N(9)	1.498(12)
C(1)–O(2)	1.306(12)	O(81)–C(82)	1.393(13)
C(1)–C(5)	1.465(13)	N(9)–C(12)	1.337(13)
O(2)–C(3)	1.446(13)	N(9)–C(10)	1.469(14)
C(3)–C(4)	1.46(2)	C(10)–C(11)	1.53(2)
C(5)–C(6)	1.367(14)	C(12)–C(13)	1.357(14)
C(5)–C(8)	1.520(13)	C(13)–C(14)	1.417(14)
C(6)–C(7)	1.522(14)	C(14)–O(15)	1.319(12)
C(7)–C(11)	1.51(2)	C(14)–W(2)	2.237(11)
C(7)–C(8)	1.545(14)	O(15)–C(16)	1.44(2)
C(8)–O(81)	1.394(14)	C(16)–C(17)	1.45(2)
O(2)–C(1)–C(5)	106.8(8)	N(9)–C(8)–C(7)	103.3(8)
O(2)–C(1)–W(1)	132.9(7)	C(5)–C(8)–C(7)	87.8(8)
C(5)–C(1)–W(1)	120.3(6)	C(82)–O(81)–C(8)	115.1(9)
C(1)–O(2)–C(3)	120.4(9)	C(12)–N(9)–C(10)	122.8(9)
O(2)–C(3)–C(4)	108.5(12)	C(12)–N(9)–C(8)	127.1(8)
C(6)–C(5)–C(1)	136.2(9)	C(10)–N(9)–C(8)	109.4(8)
C(1)–C(5)–C(8)	132.0(9)	N(9)–C(10)–C(11)	105.8(11)
C(5)–C(6)–C(61)	135.1(9)	C(7)–C(11)–C(10)	101.8(9)
C(5)–C(6)–C(7)	94.6(8)	N(9)–C(12)–C(13)	123.7(9)
C(61)–C(6)–C(7)	130.0(9)	N(9)–C(12)–C(121)	113.6(9)
C(11)–C(7)–C(6)	118.9(10)	C(13)–C(12)–C(121)	122.7(9)
C(11)–C(7)–C(8)	109.1(9)	C(12)–C(13)–C(14)	130.5(10)
C(6)–C(7)–C(8)	85.2(7)	O(15)–C(14)–C(13)	110.7(9)
O(81)–C(8)–N(9)	114.0(8)	O(15)–C(14)–W(2)	127.8(7)
O(81)–C(8)–C(5)	115.3(8)	C(13)–C(14)–W(2)	121.6(7)
N(9)–C(8)–C(5)	114.1(8)	C(14)–O(15)–C(16)	122.9(10)
O(81)–C(8)–C(7)	119.3(8)	C(17)–C(16)–O(15)	113.0(13)
C(6)–C(5)–C(8)	91.8(7)		

**Scheme 3.** Binuclear 2-Azabicyclo[4.2.0]octene Derivative (*E*)-8

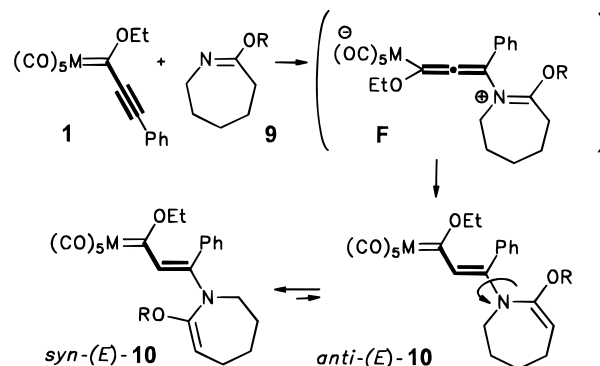


**Binuclear 1-Alkoxy-2-azabicyclo[4.2.0]octene Derivative 8.** The reaction of complex **1b** with the six-membered *O*-alkyl lactim **7** (6-ethoxy-2,3,4,5-tetrahydropyridine) proceeds in close analogy to that of **5** and leads to precipitation of the binuclear compound (*E*)-**8** in 89% yield in pentane at 20 °C (Scheme 3). Since only binuclear compounds (*E*)-**6** and (*E*)-**8**, but no mononuclear precursors, have been obtained from five- and six-membered lactims **5** and **7**, respectively, independent of the molar ratio of the starting compounds, it has been concluded that the first metalation step [i.e., the formation of an (enamino)carbene complex of type **B** (Scheme 1)] must be slower than the second metalation

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Complex *syn*-(*E*)-10c

W–C(1)	2.248(9)	N(7)–C(8)	1.47(2)
C(1)–O(2)	1.338(10)	C(8)–C(9)	1.51(2)
C(1)–C(5)	1.396(12)	C(9)–C(10)	1.54(2)
O(2)–C(3)	1.443(12)	C(10)–C(11)	1.53(2)
C(3)–C(4)	1.48(2)	C(11)–C(12)	1.46(2)
C(5)–C(6)	1.384(12)	C(12)–C(13)	1.35(2)
C(6)–N(7)	1.353(11)	C(13)–O(14)	1.355(13)
C(6)–C(61)	1.483(13)	O(14)–C(15)	1.454(13)
N(7)–C(13)	1.422(12)	C(15)–C(16)	1.48(2)
O(2)–C(1)–C(5)	111.5(8)	C(13)–N(7)–C(8)	114.1(8)
O(2)–C(1)–W	129.5(6)	N(7)–C(8)–C(9)	113.9(10)
C(5)–C(1)–W	119.0(6)	C(8)–C(9)–C(10)	115.4(13)
C(1)–O(2)–C(3)	121.5(8)	C(11)–C(10)–C(9)	114.1(10)
O(2)–C(3)–C(4)	106.4(10)	C(12)–C(11)–C(10)	112.1(13)
C(6)–C(5)–C(1)	128.8(8)	C(13)–C(12)–C(11)	122.8(11)
N(7)–C(6)–C(5)	119.5(8)	O(14)–C(13)–C(12)	129.4(10)
N(7)–C(6)–C(61)	117.2(8)	O(14)–C(13)–N(7)	110.1(8)
C(5)–C(6)–C(61)	123.2(8)	C(12)–C(13)–N(7)	120.5(11)
C(6)–N(7)–C(13)	120.7(8)	C(13)–O(14)–C(15)	116.2(9)
C(6)–N(7)–C(8)	123.4(8)	O(14)–C(15)–C(16)	106.9(11)

**Scheme 4.** Mononuclear Tetrahydroazepine Derivatives (*E*)-10

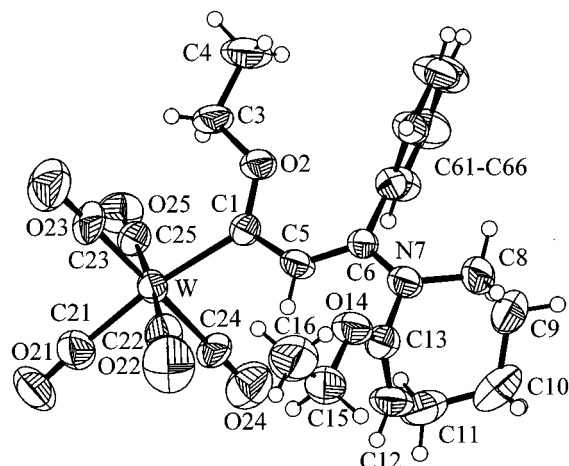


<b>1</b>	M	<b>10</b>	M	R	<i>syn/anti</i> <sup>a</sup>
<b>a</b>	Cr	<b>a</b>	Cr	Et	<sup>b</sup>
<b>b</b>	W	<b>b</b>	W	Me	4:1
		<b>c</b>	W	Et	2:1

step (i.e., the annelation of the four-membered ring to the electron-rich C=C(OR)N bond of compound **B**).

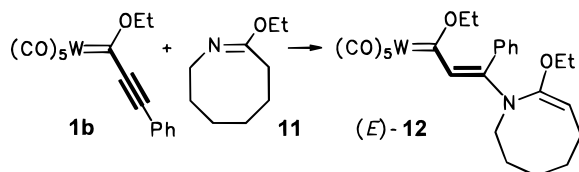
**Mononuclear Tetrahydroazepine Derivatives 10.** The reactivity pattern outlined in Schemes 2 and 3 is remarkably changed if seven-membered lactims (7-alkoxy-3,4,5,6-tetrahydro-2*H*-azepines) **9a,b** are reacted with (1-alkynyl)carbene complexes **1a,b**. In this case, mononuclear carbene complexes **10** are obtained as the only products. They form yellow precipitates from pentane in 89–94% yields (Scheme 4). Further [2 + 2] cycloaddition onto the C=C(OR)N bond of compounds **10a,b** by addition of excess (1-alkynyl)carbene complex **1** could not be achieved within 2 days at 20 °C.

<sup>1</sup>H NMR spectra of compounds **10** exhibit broadened signals at 20 °C resulting from rapid interconversion of different conformers. Two sets of signals are observed at –5 °C, which have been assigned to compounds *syn*-(*E*)-**10** and *anti*-(*E*)-**10**. An X-ray crystal structure analysis was performed of compound *syn*-(*E*)-**10c** (Table 2). In contrast to the dihydropyrrole ring in compound **E** (Scheme 2), the tetrahydroazepine ring in *syn*-(*E*)-**10c** is puckered and the C=C(N) bond is sterically shielded from both endo- as well as exo-attack on the



**Figure 2.** Molecular structure of mononuclear carbene complex *syn*-(*E*)-**10c**.

**Scheme 5. Mononuclear Pentahydroazocine Derivative (*E*)-**12****



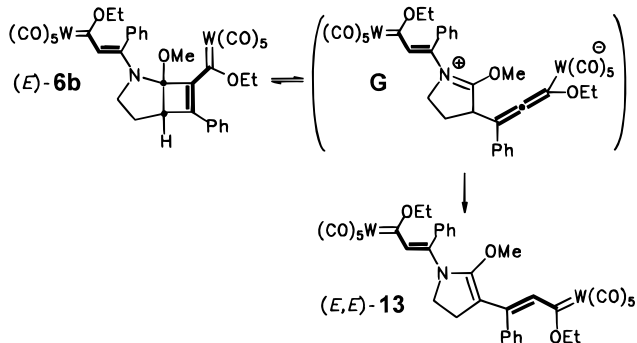
seven-membered ring (Figure 2). Since the interplanar angle of C6–N7–C13–O14 = 82.5(11)° indicates little (if no)  $\pi$ -interaction between the nitrogen atom and the adjacent C=C bond and, therefore, little "enamine character" of this unit, formation of a binuclear carbene complex by addition of compound **1** to this bond is expected to be slow, in line with the observation that mononuclear compounds **10** are isolated as the only products at 20 °C. It should be noted that the W=C–C=C metalladiene unit of compound (*E*)-**10c** adopts an *s-trans* conformation and the C1–C5–C6–N7 unit exhibits an (*E*)-configuration (dihedral angle 172.9°). On the basis of the long bond distance W–C1 2.248(9) Å and the short distances C6–N7 1.353(11) Å, C1–C5 1.392(12) Å, and C5–C6 1.384(12) Å, *syn*-(*E*)-**10c** should be considered a carbinium carbonylmetalate (–OC)<sub>5</sub>W–C=C–C=N<sup>+</sup> rather than a (2-aminoalkenyl)carbene structure (OC)<sub>5</sub>W=C–C=C–N.<sup>7</sup>

**Mononuclear Pentahydroazocine Derivatives**

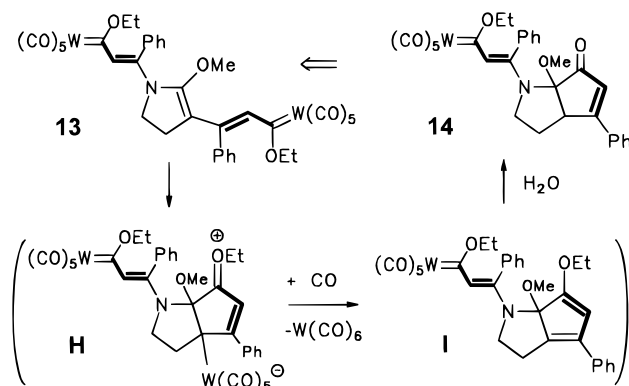
**12.** Reaction of the eight-membered lactim (8-ethoxy-2,3,4,5,6,7-hexahydroazocine) **11** with the (1-alkynyl)carbene tungsten complex **1b** in pentane takes a course similar to that observed with seven-membered ring compounds and, thus, affords a mononuclear carbene complex **12** (Scheme 5), which exhibits spectroscopic features similar to those of compounds **10b,c**.

**Rearrangement and Hydrolysis of Binuclear Compound 6b.** Binuclear compounds **6** and **8** are not stable in solution and undergo fast transformations, especially under chromatography on silica gel. For example, attempted chromatography of (orange) compound **6b** leads to elution of three products: a dark blue fraction of (highly reactive) binuclear compound (*E,E*)-**13** containing a 1,11-bis(tungsta)-5-aza-undeca-1,3,6,8,-

**Scheme 6. (Cyclobutenyl)carbene/1-Metalla-1,3,5-triene Rearrangement of Compound 6b**



**Scheme 7. Cyclopentenone Annellation by Cyclization of Metallatriene 13 and Subsequent Hydrolysis**

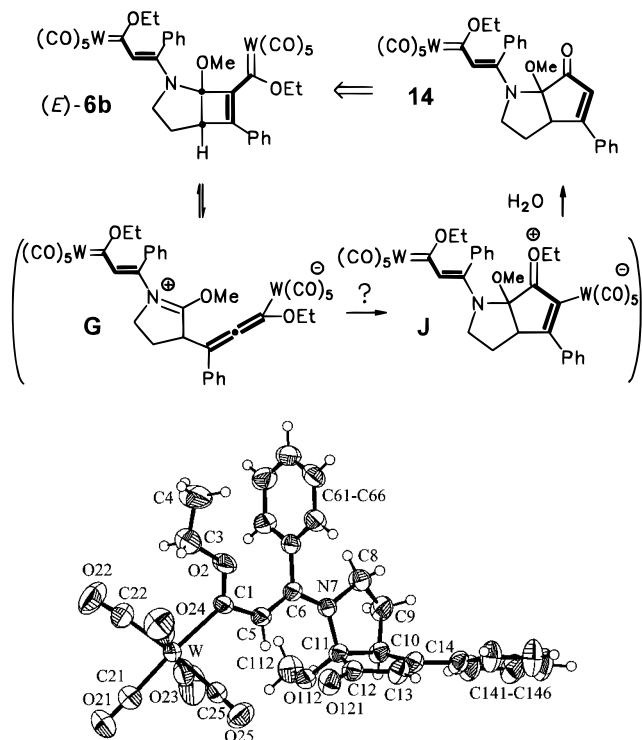


10-pentaene backbone, a yellow polar fraction of mononuclear 2-azabicyclo[3.3.0]octene derivative **14**, and an orange polar fraction of the binuclear amino acid derivative **15**. Compound (*E,E*)-**13** is generated from complex (*E*)-**6b**, obviously by a (1-cyclobutenyl)carbene/metallatriene rearrangement<sup>1</sup> involving a 1,3-hydrogen migration of a zwitterionic intermediate **G** (Scheme 6).

Compound (*E,E*)-**13** is unstable on extended contact with silica gel and forms the mononuclear 2-azabicyclo[3.3.0]octene derivative **14** by cyclization of the metallatriene moiety (Scheme 7). There is ample precedence for reactions in which a 1-metallatriene unit is cyclized to a cyclopentadiene complex.<sup>3</sup> Cyclization of compound (*E,E*)-**13** involves an (*E/Z*) configurational change of the central C=C bond of the metallatriene unit in order to meet the geometric requirements for a ring closure. On the basis of model reactions carried out previously, it is assumed that complex **14** would result from hydrolysis of a cyclopentadiene derivative **I**, which is generated by demetalation of an initially formed zwitterionic  $\eta^1$ -cyclopentadiene complex **H**.<sup>3a</sup>

Two mechanistic suggestions, path a and path b, markedly different from that outlined in Scheme 7, should be mentioned. Path a would involve an *E* to *Z* isomerization of compound **13**, subsequent 6 $\pi$  cyclization, and finally reductive elimination of the six-membered ring species. Path b is based on the assumption that a five-membered species **J** might be generated by cyclization of **G** involving a 1,2-migration of the metal unit (Scheme 8 and Scheme 6) and subsequently afford compound **14** by hydrolysis. Even though both path a and path b might be considered as reasonable alterna-

(7) Aumann, R.; Roths, K.; Fröhlich, R. *Organometallics* **1997**, *16*, 5893.

**Scheme 8. Consideration of an Alternate Mechanism for the Cyclopentenone Annelation Product 14****Figure 3.** Molecular structure of cyclopentenone annelation product **14**.

tives, it should be pointed out that any experimental evidence for these mechanisms is lacking to date, while the mechanism outlined in Scheme 7 has gained support by the fact that species of type **H** could be isolated crystalline and have been studied by X-ray crystal structure analysis.<sup>3a</sup>

Independent of mechanistic details, it should be noted that the overall transformation of compound (*E*)-**6b** to compound **14** involves a novel-type ring-expansion of a (cyclobutenyl)carbene unit by insertion of the carbon atom of the W=C unit into the cyclobutene ring.

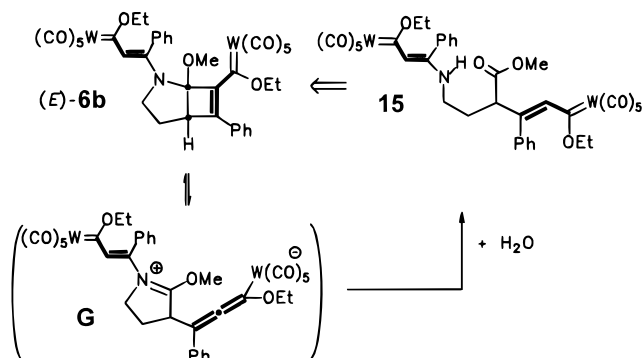
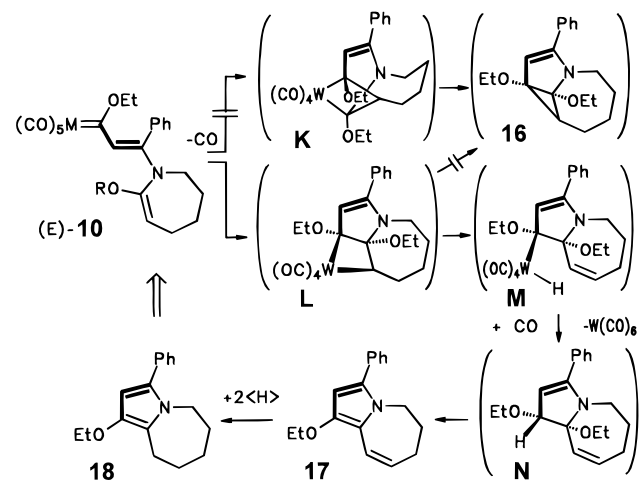
The structure of compound **14** was derived from spectroscopic measurements, but more details could be obtained from an X-ray crystal structure analysis (Figure 3, Table 3). Bond distances and bond angles of the tungsta-1,3-diene unit of **14** are similar to those of its precursor compound **6b**, with minor changes in the geometry of the metalladiene portion of the molecule. The most striking structural difference, of course, is the presence of a cyclopentenone unit in compound **14**.

The bis(carbene) complex **15**, in which two 1-metalladiene units are connected by a  $\gamma$ -amino acid bridge, is the third product derived from chromatography of compound **6b** on silica gel (vide supra). This compound quite obviously results from addition of water to the zwitterionic species **G** (Scheme 9), which has been assumed to be an intermediate also en route to compounds **13** (Scheme 6).

**Fragmentation of Mononuclear Compound (*E*)-10a.** Heating of the mononuclear compound (*E*)-**10a** to 90 °C for 2 h results in formation of a 1:1 mixture of dihydro- and tetrahydropyrrolo[1,2-*a*]azepines **17** and **18** along with W(CO)<sub>6</sub> (Scheme 10). The reaction is

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 14**

W-C(1)	2.233(6)	C(10)-C(14)	1.512(8)
C(1)-O(2)	1.336(7)	C(10)-C(11)	1.546(7)
C(1)-C(5)	1.413(8)	C(11)-O(111)	1.397(7)
O(2)-C(3)	1.449(8)	C(11)-C(12)	1.541(8)
C(3)-C(4)	1.408(12)	O(111)-C(112)	1.433(8)
C(5)-C(6)	1.379(8)	C(12)-O(121)	1.210(7)
C(6)-N(7)	1.364(7)	C(12)-C(13)	1.461(9)
C(6)-C(61)	1.491(7)	C(13)-C(14)	1.340(9)
N(7)-C(11)	1.487(7)	C(14)-C(141)	1.473(8)
N(7)-C(8)	1.476(7)	C(100)-Cl(3)	1.730(12)
C(8)-C(9)	1.512(9)	C(100)-Cl(1)	1.725(12)
C(9)-C(10)	1.522(8)	C(100)-Cl(2)	1.725(11)
C(6)-N(7)-C(8)	123.2(5)	C(6)-C(5)-C(1)	129.1(5)
C(11)-N(7)-C(8)	110.7(4)	N(7)-C(6)-C(5)	123.5(5)
N(7)-C(8)-C(9)	104.4(5)	N(7)-C(6)-C(61)	113.4(4)
C(8)-C(9)-C(10)	103.8(5)	C(5)-C(6)-C(61)	123.0(5)
C(14)-C(10)-C(9)	114.5(5)	C(6)-N(7)-C(11)	126.1(4)
C(14)-C(10)-C(11)	104.2(4)	O(111)-C(11)-C(10)	116.4(5)
C(9)-C(10)-C(11)	106.2(4)	N(7)-C(11)-C(10)	104.0(4)
O(111)-C(11)-N(7)	114.1(4)	C(12)-C(11)-C(10)	104.6(4)
O(111)-C(11)-C(12)	107.4(4)	C(11)-O(111)-C(112)	115.5(5)
N(7)-C(11)-C(12)	110.0(4)	O(121)-C(12)-C(13)	127.6(6)
O(2)-C(1)-C(5)	111.0(5)	O(121)-C(12)-C(11)	125.8(5)
O(2)-C(1)-W	128.4(4)	C(13)-C(12)-C(11)	106.7(5)
C(5)-C(1)-W	120.6(4)	C(14)-C(13)-C(12)	111.5(6)
C(1)-O(2)-C(3)	122.4(5)	C(13)-C(14)-C(141)	127.2(6)
C(4)-C(3)-O(2)	111.6(7)	C(13)-C(14)-C(10)	111.9(5)

**Scheme 9. Hydrolysis of Compound 6b on Silica Gel****Scheme 10. Pyrrolo[1,2-*a*]azepines 17 and 18 by Thermal Fragmentation of Compound (*E*)-10a**

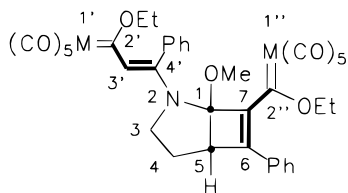
assumed to be initiated by elimination of CO and formation of a tungstacyclobutane **L**, which apparently undergoes  $\beta$ -elimination to give a metal hydride **M** faster than formation of a cyclopropane derivative **16** by reductive elimination. Even though a tungsta-

clobutane **K**, which is a regioisomer of compound **L**, could be considered a precursor to compound **16**, since  $\beta$ -elimination would not be possible in this compound, there is no indication that this compound is actually formed. Dihydropyrrolo[1,2-*a*]azepine **17** seems to be derived by trans elimination of ethanol from an intermediate **N**. Tetrahydropyrrolo[1,2-*a*]azepine **18** is assumed to be generated by hydrogenation of compound **17**.

### 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 and distilled from  $P_2O_5$  and stored over 4 Å molecular sieves. Pentane refers to that fraction boiling between 40 and 60 °C.  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker ARX 300 unless otherwise indicated, and all chemical shift values refer to  $\delta_{TMS} = 0.00$ .  $^{13}C$  NMR multiplicities were determined by DEPT measurements. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analysis were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kieselgel 60<sub>F240</sub>, were viewed by UV light (254 nm) and/or stained by a 5% aqueous acidic ammonium molybdate solution.  $R_f$  values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. The *O*-alkyl lactams were generated by alkylation of the corresponding lactams with dimethyl sulfate,<sup>8</sup> and triethyl oxonium<sup>9</sup> tetrafluoroborate, respectively.

**7-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-1-chroma-1-ethen-2-yl)-2-(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dienyl)-1-methoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene (6a).** To pentacarbonyl(1-ethoxy-3-phenyl-



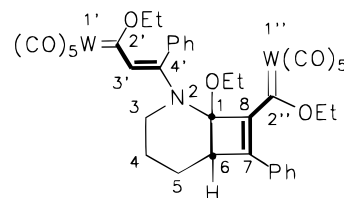
2-propyn-1-ylidene)chromium (**1a**) (350 mg, 1.00 mmol) and 1.5 mL of pentane in a 5-mL screwtop vessel was added at 20 °C a solution of 5-methoxy-3,4-dihydro-2*H*-pyrrole (**5**) (50 mg, 0.50 mmol) in 2 mL of pentane. The reaction was followed by TLC. After ca. 2.5 h, the orange precipitate is collected by centrifugation and washed with pentane (357 mg, 90%, orange crystals from 5:1 dichloromethane/pentane at -5 °C, mp 130 °C).  $^1H$  NMR ( $C_6D_6/CS_2$  5:1):  $\delta$  7.18–7.14 and 7.09–6.87 (10 H, m, br, 2 Ph), 6.81 (1 H, s, 3'-H), 4.70 (2 H, m, br, diastereotopic 2''-OCH<sub>2</sub>), 4.34 and 4.14 (1:1 H, m, 2'-OCH<sub>2</sub>), 3.29 (1 H, d, 5-H), 3.11 (3 H, s, OCH<sub>3</sub>), 2.73 (2 H, m br, 3-H<sub>2</sub>), 1.28 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>), 1.11 (2 H, m br, 4-H<sub>2</sub>), 0.44 (3 H, t, 2''-OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}C$  NMR ( $CDCl_3/CS_2$  5:1):  $\delta$  346.2 ( $C_q$ , Cr<sup>I</sup>=C), 307.9 ( $C_q$ , Cr<sup>I</sup>=C), 224.2 and 215.4 ( $C_q$ , 1:4, *trans*- and *cis*-CO, Cr<sup>I</sup>(CO)<sub>5</sub>), 223.9 and 218.5 ( $C_q$ , 1:4, *trans*- and *cis*-CO, Cr<sup>I</sup>(CO)<sub>5</sub>), 148.9 and 147.3 ( $C_q$ , C4' and C7), 139.2 ( $C_q$ , C3'), 136.0 and 135.1 ( $C_q$ , *i*-C, 2 Ph), 121.1 ( $C_q$ , C6), 131.1, 129.4, 128.7, 128.4, 128.2, 127.9, 127.8, 127.6, 127.1, 126.5 (1 C, 2 Ph), 99.5 ( $C_q$ , C1), 73.3 (2''-OCH<sub>2</sub>), 70.0 (2'-OCH<sub>2</sub>), 48.4 (OCH<sub>3</sub>), 44.1 (CH<sub>2</sub>, C3), 41.0 (CH, C5), 18.9 (CH<sub>2</sub>, C4), 11.0 (2'-OCH<sub>2</sub>CH<sub>3</sub>), 10.2 (2''-OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether),  $cm^{-1}$ : 2063.6 (40), 2048.1 (30), 1997.5 (15), 1916.2 (100) [ $\nu(C\equiv O)$ ]. MS (70 eV),  $m/e$ : 551 (12) [ $M^+ - Cr(CO)_5 - 2CO$ ], 467 (32)

[ $M^+ - Cr(CO)_5 - 5CO$ ], 415 (50) [ $M^+ - 2Cr(CO)_5$ ], 386 (100) [ $M^+ - 2Cr(CO)_5 - Et$ ], 358 (10) [ $M^+ - 2Cr(CO)_5 - Et - CO$ ], 339 (12), 310 (16), 282 (10), 149 (14), 111 (12), 97 (17), 85 (25), 71 (36), 57 (54). Anal. Calcd for  $C_{37}H_{29}Cr_2NO_{13}$  (799.6): C, 55.58; H, 3.66; N, 1.75. Found: C, 55.68; H, 3.81; N, 1.84.

**7-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-1-tungsta-1-ethen-2-yl)-2-(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dienyl)-1-methoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene (6b).** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene) tungsten(**1b**) (482 mg, 1.00 mmol) and 5-methoxy-3,4-dihydro-2*H*-pyrrole (**5**) (50 mg, 0.50 mmol) in 2 mL of pentane were reacted as described above for 2.5 h at 20 °C to give compound **6b** (497 mg, 94%, crystals from 4:1 dichloromethane/pentane at -5 °C, mp 138 °C).  $^1H$  NMR ( $CDCl_3$ , 268 K):  $\delta$  7.67 (1 H, s, dynamically broadened, 3'-H), 7.41, 7.26, and 7.09 (6:2:2 H, m each, 2 Ph), 4.92 (2 H, m br, 2''-OCH<sub>2</sub>), 4.19 and 3.99 (1:1 H, m, 2'-OCH<sub>2</sub>), 3.89 (1 H, d, 5-H), 3.58 (3 H, s, OCH<sub>3</sub>), 3.09 (2 H, m br, 3-H<sub>2</sub>), 1.78 (2 H, m br, 4-H<sub>2</sub>), 1.69 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>), 0.59 (3 H, t, 2''-OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  317.6 ( $C_q$ , W<sup>I</sup>=C), 280.9 ( $C_q$ , W<sup>I</sup>=C), 203.9, 203.8, 199.0, and 196.2 ( $C_q$ , 2 W(CO)<sub>5</sub>), 153.5 ( $C_q$ , 4'-C), 150.6 ( $C_q$ , C7), 139.5 (CH, C3'), 134.9 and 133.8 ( $C_q$ , *i*-C, 2 Ph), 130.5, 129.3, 128.5, 128.2, 127.9, 127.7, 126.1, and 125.5 (1:1:2:2:1:1:1:1, CH, 2 Ph), 122.4 ( $C_q$ , C6), 98.1 ( $C_q$ , C1), 79.5 (2''-OCH<sub>2</sub>), 76.1 (2'-OCH<sub>2</sub>), 52.4 (OCH<sub>3</sub>), 50.3 (CH<sub>2</sub>, C3), 47.9 (CH, C5), 22.4 (CH<sub>2</sub>, C4), 14.6 (2'-OCH<sub>2</sub>CH<sub>3</sub>), 13.6 (2''-OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether),  $cm^{-1}$ : 2071.3 (33), 2056.1 (24), 1993.9 (14), 1909 (100) [ $\nu(C\equiv O)$ ]. MS (70 eV),  $^{184}W$ ,  $m/e$ : 415 (36) [ $M^+ - 2W(CO)_5$ ], 386 (100), 354 (34), 296 (37), 268 (83), 239 (32), 214 (42), 184 (31), 123 (40), 57 (31). MALDI-TOF-MS<sup>10</sup> ( $N_2$ -laser 337 nm, pulse length 3 ns, path 1 m, accuracy  $\pm 0.1\%$ ),  $m/e$ : 1064 ( $M^+ + 1$ ). Anal. Calcd for  $C_{37}H_{29}NO_{13}W_2$  (1063.1): C, 41.77; H, 2.75; N, 1.32. Found: C, 42.02; H, 2.83; N, 1.36.

X-ray crystal structure analysis of **6b**: formula  $C_{37}H_{29}NO_{13}W_2$ ,  $0.60 \times 0.40 \times 0.30$  mm,  $a = 20.751(2)$  Å,  $b = 10.943(1)$  Å,  $c = 18.829(2)$  Å,  $\beta = 115.30(1)^\circ$ ,  $V = 3865.5(7)$  Å<sup>3</sup>,  $\rho_{calc} = 1.827$  g cm<sup>-3</sup>,  $\mu = 60.11$  cm<sup>-1</sup>, empirical absorption correction via  $\varphi$  scan data ( $0.798 \leq C \leq 0.999$ ),  $Z = 4$ , monoclinic, space group  $P2_1/c$  (No. 14),  $\lambda = 0.710$  73 Å,  $T = 293$  K,  $\omega$  scans, 8095 reflections collected ( $\pm h, -k, -l$ ),  $[(\sin \theta)/\lambda] = 0.62$  Å<sup>-1</sup>, 7841 independent and 5313 observed reflections [ $I \geq 2\sigma(I)$ ], 479 refined parameters,  $R = 0.061$ ,  $wR2 = 0.157$ , max (min) residual electron density 2.12 (-1.34) e Å<sup>-3</sup>, hydrogens calculated and refined as riding atoms. All data sets were collected with an Enraf-Nonius CAD4 diffractometer, radiation source rotating anode FR591. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics DIAMOND.

**8-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-1-tungsta-2-ethen-yl)-2-(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dienyl)-1-ethoxy-7-phenyl-2-azabicyclo[4.2.0]oct-7-ene [(E)-8].** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-



1-ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) and 6-ethoxy-2,3,4,5-tetrahydropyridine (**7**) (64 mg, 0.50 mmol) in 2 mL of pentane were reacted as described above for 3 h at 20 °C to give compound (**8**) (484 mg, 89%, orange crystals, mp 80 °C).  $^1H$

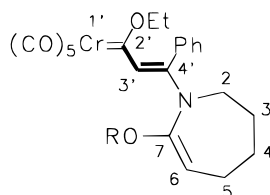
(8) Etienne, A.; Correia, Y. *Bull. Soc. Chim. Fr.* **1969**, 3704. (b) Benson, R. E.; Cairns, T. L. *J. Am. Chem. Soc.* **1948**, 70, 2115.

(9) (a) Meerwein, H. *Org. Synth.* **1966**, 46, 113. (b) Menezes, R.; Smith, M. B. *Synth. Commun.* **1988**, 18, 1625.

(10) MALDI-TOF-MS: Instrument "Lazarus II", constructed by Dr. H. Luftmann, Organisch-Chemisches Institut der Universität Münster, Orleans-Ring 23, D-48149 Münster, Germany.

NMR ( $\text{CDCl}_3$ , solution freshly prepared at 233 K and immediately measured at 233 K):  $\delta$  7.69 (1 H, s, 3'-H), 7.46 (6 H, m, *m*- and *p*-H of 2 Ph), 7.29, 7.19, and 7.09 (1:2:1 H, "d", *o*-H of 2 Ph), 5.12 and 4.43 (1 H, m, diastereotopic 2''-OCH<sub>2</sub>), 4.29 and 3.88 (1 H, m, diastereotopic 2'-OCH<sub>2</sub>), 3.85 and 3.66 (1 H, diastereotopic 1-OCH<sub>2</sub>), 3.80 (1 H, d, 6-H), 3.33, 2.82, 2.20, 1.85, 1.82, and 1.55 (1 H, 3-H<sub>2</sub>, 4-H<sub>2</sub>, and 5-H<sub>2</sub>), 1.68, 1.40, and 0.70 (3 H, t, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 268 °C):  $\delta$  318.0 (C<sub>q</sub>, W<sup>1</sup>=C), 292.8 (C<sub>q</sub>, W<sup>1</sup>=C) 204.1 and 203.9 (*trans*-CO, W(CO)<sub>5</sub>), 198.5 and 196.3 (*cis*-CO, W(CO)<sub>5</sub>), 154.8, 154.3, and 154.0 (C<sub>q</sub>, C4', C7, and C8), 143.0 (CH, m br, C3'), 137.4 and 137.2 (C<sub>q</sub>, *i*-C Ph); 132.9, 131.3, 131.1, 129.6, 129.4, 129.2, 129.0, 128.8, 128.1, and 126.9 (CH, 2 Ph), 90.8 (C<sub>q</sub>, C1), 79.0 (2''-OCH<sub>2</sub>), 77.8 (2'-OCH<sub>2</sub>), 61.2 (1-OCH<sub>2</sub>), 50.3 (NCH<sub>2</sub>), 46.7 (CH<sub>2</sub>, C5), 24.6 (CH<sub>2</sub>, C4), 21.2 (CH<sub>2</sub>, C5), 15.1, 14.8, and 13.8 (CH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether), cm<sup>-1</sup> (%): 2070.8 (42), 2059.3 (32), 1926.2 (100) [ $\nu(\text{C}=\text{O})$ ]. MALDI-TOF-MS:<sup>10</sup> 1093 (M<sup>+</sup> + 2), 1067, 1042, 610, 582, 521, 502, 436, 387. Anal. Calcd for C<sub>38</sub>H<sub>33</sub>NO<sub>13</sub>W<sub>2</sub> (1091.4): C, 42.92; H, 3.05; N, 1.28. Found: C, 43.01; H, 3.12; N, 1.39.

**1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dien-4-yl)-7-ethoxy-2,3,4,5-tetrahydro-1H-azepine (10a).** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-



ylidene)chromium (**1a**) (350 mg, 1.00 mmol) and 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine (**9b**) (141 mg, 1.00 mmol) in 2.0 mL of pentane were reacted as described above to give compound **10a** (420 mg, 89%, yellow crystals from 4:1 pentane/dichloromethane at -5 °C, mp > 90 °C, dec). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6/\text{CS}_2$  5:1):  $\delta$  7.01–6.91 (5 H, m, Ph), 4.44 (1 H, m, 6-H), 4.23 (2 H, q, 2'-OCH<sub>2</sub>), 3.30 (2 H, m br, 2-H<sub>2</sub>), 3.00 (2 H, m br, 7-OCH<sub>2</sub>), 1.93 (2 H, m br, 5-H<sub>2</sub>), 1.14 (4 H, m br, 3-H<sub>2</sub> and 4-H<sub>2</sub>), 0.87 (3 H, m br, 7-OCH<sub>2</sub>CH<sub>3</sub>), 0.42 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR ( $\text{CDCl}_3/\text{CS}_2$  5:1):  $\delta$  304.3 (C<sub>q</sub>, Cr=C), 224.0 and 218.4 (C<sub>q</sub>, 1:4, *trans*- and *cis*-CO, Cr(CO)<sub>5</sub>), 154.4 (C<sub>q</sub>, C7), 149.3 (C<sub>q</sub>, C4'), 147.8 (CH, C3'), 136.4 (C<sub>q</sub>, *i*-C Ph), 128.1, 127.9, and 122.2 (2:2:1, CH, Ph), 95.3 (CH, C6), 73.7 (2'-OCH<sub>2</sub>), 63.9 (7-OCH<sub>2</sub>), 49.6 (CH<sub>2</sub>, C2), 29.3 (CH<sub>2</sub>, br, C5), 24.8 and 24.1 (CH<sub>2</sub> each, C3 and C4), 14.0 (7-OCH<sub>2</sub>CH<sub>3</sub>), 13.9 (2'-OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether), cm<sup>-1</sup>: 2047.2 (70), 1968.3 (40), 1920.5 (95), 1902.6 (100) [ $\nu(\text{C}=\text{O})$ ]. MS (70 eV), *m/e*: 491 (10) [M<sup>+</sup>], 463 (8) [M<sup>+</sup> - CO], 407 (60) [M<sup>+</sup> - 3CO], 379 (20) [M<sup>+</sup> - 4CO], 351 (75) [M<sup>+</sup> - 5CO], 305 (65) [M<sup>+</sup> - 5CO - EtOH], 299 (5) [M<sup>+</sup> - Cr(CO)<sub>5</sub>], 277 (64), 254 (70), 226 (65), 220 (65) [Cr(CO)<sub>6</sub>], 180 (55), 146 (72), 129 (58), 115 (65), 94 (65), 67 (78), 55 (100). Anal. Calcd for C<sub>24</sub>H<sub>25</sub>CrNO<sub>7</sub> (491.5): C, 58.65; H, 5.13; 2.85. Found: C, 58.46; H, 5.43; N, 2.89.

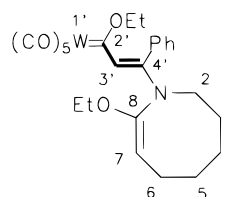
**1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dien-4-yl)-7-methoxy-2,3,4,5-tetrahydro-1H-azepine (10b).** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) was reacted with 7-methoxy-3,4,5,6-tetrahydro-2H-azepine (**9a**) (127 mg, 1.00 mmol) as described above. Complex **1b** was completely consumed after ca. 12 h at 20 °C. Yellow crystals of compound **10b** were obtained at -15 °C (470 mg, 94%, mp 61–63 °C). Two sets of signals were observed in the NMR spectra due to the presence of (interconverting) isomers *syn*-(*E*)-**10b**/*anti*-(*E*)-**10b** in a 4:1 molar ratio. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 268 K):  $\delta$  7.85 [6.77] (1 H, 3'-H), 7.61–7.24 (5 H, m each, Ph, both isomers), 4.32 [4.93] (2 H, t, 6-H), 4.00 [4.12] (2 H, q, OCH<sub>2</sub>), 3.52 [3.66] (3 H, s, OCH<sub>3</sub>), 3.41 [3.21] (2 H, t, 2-H), 2.82 [2.20] (2 H, m br, 5-H), 1.83 [1.54] (4 H, m, 3-H and 4-H), 1.15 [0.62] (3 H, t, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 268 K):  $\delta$  279.7 [275.1] (C<sub>q</sub>,

W=C), 204.5 [208.2] and 199.1 [200.3] [C<sub>q</sub>, W(CO)<sub>5</sub>], 177.1 [161.5] (C<sub>q</sub>, C7), 153.2 [154.9] (C<sub>q</sub>, C4'), 141.2 [143.9] (CH, C3'), 135.7 [134.6] (C<sub>q</sub>, *i*-C Ph), 132.3 [130.9], 129.6 [129.4], 128.5 [128.8], 127.2 [127.5], and 125.7 [126.6] (CH, Ph), 95.2 [95.6] (CH, C6), 76.4 [70.6] (OCH<sub>2</sub>), 55.8 [57.3] (OCH<sub>3</sub>), 49.5 [49.9] (CH<sub>2</sub>, C2), 32.2 [30.6] (CH<sub>2</sub>, C5), 23.6 and 23.2 [25.9 and 25.6] (CH<sub>2</sub>, C3 and C4), 13.8 [14.8] (OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether), cm<sup>-1</sup>: 2055.7 (80), 1966.0 (70), 1921.6 (97), 1905.9 (100) [ $\nu(\text{C}=\text{O})$ ]. MS (70 eV), <sup>184</sup>W, *m/e*: 609 (12) [M<sup>+</sup>], 525 (32), 497 (8), 469 (26), 440 (48), 351 (8), 253 (46), 224 (68), 119 (80), 91 (80), 68 (100). Anal. Calcd for C<sub>23</sub>H<sub>23</sub>NO<sub>7</sub>W (609.3): C, 45.34; H, 3.80; N, 2.30. Found: C, 45.62; H, 3.77; N, 2.45.

**1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dien-4-yl)-7-ethoxy-2,3,4,5-tetrahydro-1H-azepine (10c).** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) was reacted with 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine (**9b**) (141 mg, 1.00 mmol) as described above. Precipitation of yellow compound **10c** started after 1 h at 20 °C and was complete after 3–4 h (563 mg, 91%, single crystals from 1:5 dichloromethane/pentane at -5 °C, mp 98 °C). Two sets of resonance signals were observed in the NMR spectra due to the presence of isomers *syn*-(*E*)-**10c**/*anti*-(*E*)-**10c** in a 2:1 ratio. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 268 K):  $\delta$  7.39–7.12 (5 H, m br, Ph of both isomers), 6.77 [6.88] (1 H, s, 3'-H), 4.89 [4.39] (1 H, t, 6-H), 4.10 (2 H, q, 2'-OCH<sub>2</sub>), 3.81 (2 H, m, 7-OCH<sub>2</sub> of both isomers), 3.18 [2.94] (2 H, m br, 2-H<sub>2</sub>), 2.14 [2.01] (2 H, m br, 5-H<sub>2</sub>), 1.48 [1.61] (2 H, m br, 3-H<sub>2</sub>), 1.48 [0.87] (2 H, m br, 4-H<sub>2</sub>), 1.34 (3 H, t, 7-OCH<sub>2</sub>CH<sub>3</sub>), 0.60 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 268 K):  $\delta$  279.1 [280.0] (C<sub>q</sub>, W=C), 204.5 [204.3] and 199.2 [199.1] [C<sub>q</sub>, W(CO)<sub>5</sub>], 154.2 (C<sub>q</sub>, C4'), 153.1 [153.0] (C<sub>q</sub>, C7), 135.8 [136.8] (C<sub>q</sub>, *i*-C Ph both isomers), 128.4, 127.9, 127.5, 127.1, and 125.3 (CH, Ph both isomers), 121.2 [113.1] (CH, C3'), 95.5 [95.2] (CH, C6), 76.3 [76.4] (2'-OCH<sub>2</sub>), 64.2 [63.5] (7-OCH<sub>2</sub>), 49.4 [50.2] (CH<sub>2</sub>, C2), 30.7 [26.5] (CH<sub>2</sub>, C5), 25.0 [25.9] (CH<sub>2</sub>, C4), 23.7 [24.1] (CH<sub>2</sub>, C3), 14.2 (7-OCH<sub>2</sub>CH<sub>3</sub>), 13.7 [13.8] (2'-OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether), cm<sup>-1</sup>: 2056.0 (38), 1966.5 (19), 1903.7 (100) [ $\nu(\text{C}=\text{O})$ ]. MS (70 eV), <sup>184</sup>W, *m/e*: 623 (10) [M<sup>+</sup>], 595 (5), 539 (35), 483 (15), 455 (32), 422 (8), 351 (9), 270 (16), 254 (22), 224 (26), 69 (86), 57 (100). Anal. Calcd for C<sub>24</sub>H<sub>25</sub>NO<sub>7</sub>W (623.1): C, 46.22; H, 4.04; N, 2.25. Found: C, 46.21; H, 4.06; N, 2.22.

X-ray crystal structure analysis of compound *syn*-(*E*)-**10c**: formula C<sub>24</sub>H<sub>25</sub>NO<sub>7</sub>W, 0.30 × 0.20 × 0.20 mm, *a* = 28.560(6) Å, *b* = 12.101(2) Å, *c* = 16.584(3) Å,  $\beta$  = 118.80(3)°, *V* = 5023-(2) Å<sup>3</sup>,  $\rho_{\text{calc}}$  = 1.649 g cm<sup>-3</sup>,  $\mu$  = 46.41 cm<sup>-1</sup>, empirical absorption correction via  $\varphi$  scan data (0.865 ≤ *C* ≤ 0.999), *Z* = 8, monoclinic, space group *C2/c* (No. 15),  $\lambda$  = 0.710 73 Å, *T* = 293 K,  $\omega$  scans, 5188 reflections collected (+*h*, -*k*, ±*l*), [(sin  $\theta$ )/ $\lambda$ ] = 0.62 Å<sup>-1</sup>, 5085 independent and 3688 observed reflections [*I* ≥ 2 $\sigma$ (*I*)], 300 refined parameters, *R* = 0.060, *wR*<sup>2</sup> = 0.166, max (min) residual electron density 1.26 (-2.13) e Å<sup>-3</sup>, hydrogens calculated and refined as riding atoms. All data sets were collected with an Enraf-Nonius CAD4 diffractometer, radiation source rotating anode FR591. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics DIAMOND.

**1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dien-4-yl)-8-ethoxy-2,3,4,5,6-pentahydro-1H-azocine (12).** Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-

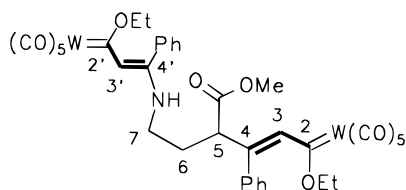


ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) was reacted with 8-methoxy-2,3,4,5,6,7-hexahydroazocine (**11**) (155 mg, 1.00

mmol) as described above for 4 days to give compound **12** (380 mg, 60%, yellow crystals, mp 50–52 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.50–7.10 (5 H, m br, Ph), 6.99 (1 H, s, 3'-H), 4.39 (1 H, m br, 7-H), 4.20 (2 H, q, 2'-OCH<sub>2</sub>), 3.82 (2 H, m br, 2-H<sub>2</sub>), 3.70 (2 H, q, 9-OCH<sub>2</sub>), 2.66 (2 H, m br, 6-H<sub>2</sub>), 1.81 (4 H, m br, 3-H<sub>2</sub> and 4-H<sub>2</sub>), 1.65 (2 H, m br, 5-H<sub>2</sub>), 1.49 (3 H, t, 9-OCH<sub>2</sub>CH<sub>3</sub>), 1.23 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  277.8 ( $\text{C}_q$ , W=C), 203.9 and 199.5 [1:4,  $\text{C}_q$ , *trans*- and *cis*-CO, W(CO)<sub>5</sub>], 162.7 ( $\text{C}_q$ , C8), 154.9 ( $\text{C}_q$ , C4'), 143.8 (CH, C3'), 140.5 ( $\text{C}_q$ , *i*-C Ph), 129.9, 129.5, and 128.6 (1:2:2, CH, Ph), 111.2 (CH, C7), 71.0 (2'-OCH<sub>2</sub>), 59.7 (9-OCH<sub>2</sub>), 55.4 (CH<sub>2</sub>, C2), 30.4 (CH<sub>2</sub>, C6), 26.2 (CH<sub>2</sub>, C3), 24.6 (CH<sub>2</sub>, C4), 23.8 (CH<sub>2</sub>, C5), 14.6 (9-OCH<sub>2</sub>CH<sub>3</sub>), 14.1 (2-OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether),  $\text{cm}^{-1}$ : 2063.6 (47), 1967.9 (64), 1913.7 (100), 1899.1 (98). MS (70 eV),  $^{184}\text{W}$ , *m/e*: 637 (1) [ $\text{M}^+$ ], 553 (3), 469 (3), 421 (3), 365 (5), 268 (5), 126 (25), 83 (40), 57 (100). Anal. Calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_7\text{W}$  (637.3): C, 47.09; H, 4.27; N, 2.20. Found: C, 46.48; H, 4.30; N, 1.97.

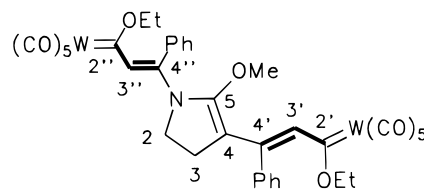
**1,4-Bis(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dien-4-yl)-5-methoxy-2,3-dihydropyrrol (13), 1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dien-4-yl)-6a-methoxy-2,3,3a,6a-tetrahydro-1H-cyclopenta[b]pyrrol-6-one (14), (1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dienyl)-(1,1,1,1,1-pentacarbonyl-2-ethoxy-5-methoxycarbonyl-4-phenyl-1-tungsta-hepta-1,3-dien-4-yl)amine (15).** A column of dry silica gel (20 × 1.5 cm) was charged with a solution of 7-(1,1,1,1,1-pentacarbonyl-2-ethoxy-1-tungsta-2-ethen-2-yl)-2-(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dien-4-yl)-1-methoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene (**6b**) (480 mg, 0.45 mmol) in 2 mL of dichloromethane and then immediately eluted with pentane and afterward with pentane/dichloromethane 4:1 to give a dark-blue fraction of (very air sensitive) compound **13** (102 mg, 21%), followed by an orange fraction of complex **15** (170 mg, 35%,  $R_f$  = 0.5 in pentane/ethyl acetate 2:1, orange crystals from 5:1 pentane/dichloromethane, at -5 °C, mp 31 °C). A yellow fraction of complex **14** was collected with 1:1 pentane/diethyl ether (130 mg, 41%,  $R_f$  = 0.8 in diethyl ether, yellow crystals from pentane/dichloromethane 5:1 at -5 °C, mp > 98 °C, dec).

**15.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.08 (1 H, t, NH), 7.46–7.27, 7.10,



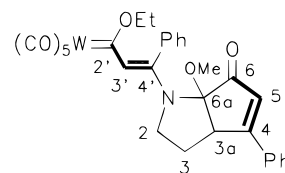
and 6.90 (10 H, m, 2 Ph), 7.08 (1 H, s, 3-H), 6.26 (1 H, s, 3'-H), 4.68 (2 H, m, 2-OCH<sub>2</sub>), 4.42 (2 H, m, 2'-OCH<sub>2</sub>), 3.67 (3 H, s, OCH<sub>3</sub>), 3.22 (3 H, m, 5-H and 7-H<sub>2</sub>), 2.08 and 1.77 (1:1 H, m, 6-H<sub>2</sub>), 1.48 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>), 0.90 (3 H, t, 2-OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  312.5 ( $\text{C}_q$ , W=C), 270.8 ( $\text{C}_q$ , W'=C), 203.7 and 203.4 ( $\text{C}_q$ , *trans*-CO W(CO)<sub>5</sub>), 199.2 and 196.9 ( $\text{C}_q$ , *cis*-CO W(CO)<sub>5</sub>), 171.6 ( $\text{C}_q$ , CO<sub>2</sub>Me), 157.9 and 157.6 ( $\text{C}_q$ , C4 and C4'), 145.2 (CH, C3), 138.8 ( $\text{C}_q$ , C3'), 136.7 and 134.1 ( $\text{C}_q$ , *i*-C Ph), 130.2, 128.7, 128.6, 128.3, 128.0, 127.5, 127.4, 126.9, 126.5, and 122.2 (CH, 2 Ph), 80.8 (2-OCH<sub>2</sub>), 76.6 (2'-OCH<sub>2</sub>), 52.4 (OCH<sub>3</sub>), 50.8 (CH, C5), 43.9 (NCH<sub>2</sub>, C7), 31.9 (CH<sub>2</sub>, C6), 15.6 and 13.5 (OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether),  $\text{cm}^{-1}$ : 3750–3400 (w, br, N-H), 2066.6 (70), 2057.3 (60), 1916.7 (100), 1902.3 (100) [ $\nu(\text{C}\equiv\text{O})$ ], 1737.1 (30) [ $\nu(\text{C}=\text{O})$ ]. MS (70 eV),  $^{184}\text{W}$ , *m/e*: 757 (1) [ $\text{M}^+$  - W(CO)<sub>5</sub>], 644 (1), 589 (2) [ $\text{M}^+$  - W(CO)<sub>5</sub> - 6CO], 433 (17) [ $\text{M}^+$  - 2W(CO)<sub>5</sub>], 404 (97) [ $\text{M}^+$  - 2W(CO)<sub>5</sub> - Et], 352 (42) [W(CO)<sub>6</sub>], 296 (50), 254 (100), 244 (74), 212 (40), 194 (24), 184 (18), 57 (26). Anal. Calcd for  $\text{C}_{37}\text{H}_{31}\text{NO}_{14}\text{W}_2$  (1081.4): C, 41.10; H, 2.89; N, 1.30. Found: C, 40.87; H, 3.03; N, 1.59.

**13.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.30–7.00 (10 H, m, 2 Ph), 7.20 (1 H, s br, 3'-H), 6.80 (1 H, s, 3''-H), 4.60 (2 H, m br, 2'-OCH<sub>2</sub>),



4.20 (2 H, q, 2''-OCH<sub>2</sub>), 3.60, 3.10 and 2.65 (1:1:2 H, 2-H<sub>2</sub> and 3-H<sub>2</sub>), 2.98 (3 H, s, OCH<sub>3</sub>), 1.50 (3 H, t, 2'-OCH<sub>2</sub>CH<sub>3</sub>), 0.60 (3 H, t, 2''-OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  296.1 and 295.3 ( $\text{C}_q$ , W=C), 204.4 and 204.2 ( $\text{C}_q$ , *trans*-CO W(CO)<sub>5</sub>), 198.5 and 198.0 ( $\text{C}_q$ , *cis*-CO W(CO)<sub>5</sub>), 161.3 and 159.6 ( $\text{C}_q$ , C4' and C5), 144.9 ( $\text{C}_q$ , C4'), 141.7 and 138.6 (CH, C3' and C3''), 137.3 and 134.9 ( $\text{C}_q$ , *i*-C Ph), 131.3, 130.0, 129.1, 128.8, 128.1, 127.4, 127.3, 126.4, 126.3, and 126.0 (CH, 2 Ph), 78.2 and 77.8 (OCH<sub>2</sub>), 50.2 (OCH<sub>3</sub>), 50.0 (NCH<sub>2</sub>), 27.2 (NCH<sub>2</sub>CH<sub>2</sub>), 14.8 and 13.6 (OCH<sub>2</sub>-CH<sub>3</sub>). IR (diethyl ether): 2070.1 (43), 2056.7 (80), 1928.0 (96), 1905.6 (100) [ $\nu(\text{C}\equiv\text{O})$ ]. MS (70 eV),  $^{184}\text{W}$ , *m/e*: 1063 (1) [ $\text{M}^+$ ], 654 (1), 598 (2), 570 (6), 415 (30) [ $\text{M}^+$  - 2W(CO)<sub>5</sub>], 386 (60).

**14.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  8.24 (1 H, s, 3'-H), 7.58



and 7.48 (2:3 H, m, 4-Ph), 7.33 and 7.08 (3:2 H, m broad each, 4'-Ph), 6.56 (1 H, d,  $^4J$  = 1.2 Hz, 5-H), 4.19 and 4.11 (1:1 H, m, OCH<sub>2</sub>), 4.02 (1 H, d,  $^3J$  = 8.9 Hz,  $^4J$  = 1.2 Hz, 3a-H), 3.58 (3 H, s, OCH<sub>3</sub>), 3.12 and 2.82 (1 H, m, 2-H<sub>2</sub>), 2.14 and 1.83 (1 H, m, 3-H<sub>2</sub>), 0.59 (3 H, t, OCH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  286.1 ( $\text{C}_q$ , W=C), 204.6 and 199.0 (1:4,  $\text{C}_q$ , *trans*- and *cis*-CO, W(CO)<sub>5</sub>), 193.7 ( $\text{C}_q$ , C=O, C6), 168.4 ( $\text{C}_q$ , C4'), 149.2 ( $\text{C}_q$ , C4), 139.4 ( $\text{C}_q$ , *i*-C 4'-Ph), 131.9 ( $\text{C}_q$ , *i*-C 4-Ph), 131.8 (CH, C3'), 129.2, 128.5, 127.9, 127.4, 126.5 and 126.4 (2:1:2:2:1:2, CH, 2 Ph), 125.6 (CH, C5), 98.3 ( $\text{C}_q$ , C6a), 76.6 (OCH<sub>2</sub>), 52.1 (OCH<sub>3</sub>), 51.3 (CH, C3a), 50.1 (CH<sub>2</sub>, C2), 25.7 (CH<sub>2</sub>, C3), 13.8 (OCH<sub>2</sub>CH<sub>3</sub>). IR (diethyl ether),  $\text{cm}^{-1}$ : 2056.7 (55), 1969.7 (30), 1907.8 (100) [ $\nu(\text{C}\equiv\text{O})$ ], 1715.3 (30) [ $\nu(\text{C}=\text{O})$ ], 1598.2 (8) [ $\nu(\text{C}=\text{C})$ ]. MS (70 eV),  $^{184}\text{W}$ , *m/e*: 711 (1) [ $\text{M}^+$ ], 627 (1) [ $\text{M}^+$  - 3CO], 571 (1) [ $\text{M}^+$  - 5CO], 544 (1), 516 (0.5), 387 (99) [ $\text{M}^+$  - W(CO)<sub>5</sub>], 372 (23), 342 (22), 298 (62), 268 (50), 240 (24), 226 (100), 198 (36), 149 (32), 83 (26), 71 (38), 60 (78). Anal. Calcd for  $\text{C}_{30}\text{H}_{25}\text{NO}_8\text{W}$ · $\text{CDCl}_3$  (831.7) (obtained by recrystallization from  $\text{CDCl}_3$ ): C, 44.82; H, 3.15; N, 1.69. Found: C, 44.96; H, 3.22; N, 1.92.

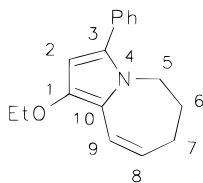
Crystal structure and refinement details of compound **14**: formula  $\text{C}_{30}\text{H}_{25}\text{NO}_8\text{W}\cdot\text{CDCl}_3$ , crystal system triclinic, space group  $P\bar{1}$  (No. 2),  $a$  = 9.815(1) Å,  $b$  = 10.977(2) Å,  $c$  = 16.173(2) Å,  $\alpha$  = 75.54(1)°,  $\beta$  = 79.96(1)°,  $\gamma$  = 85.90(1)°,  $V$  = 1660.7(4) Å<sup>3</sup>, diffractometer CAD4, temperature 293(2) K,  $\lambda$  = 0.710 73 Å, program used SCHAKAL-92,  $Z$  = 2,  $D_c$  = 1.661 g cm<sup>-3</sup>,  $\mu$  = 3.768 mm<sup>-1</sup>,  $F(000)$  = 816, crystal size 0.20 × 0.20 × 0.10 mm,  $\theta$  limits 2.58–26.36°, empirical abs corr  $\varphi$ -scan, no. of data collected 6975, no. of unique data 6725,  $R_{av}$  0.065, no. of data observed with  $I > 2\sigma(I)$  5394, refined parameters 400, goodness-of-fit on  $F^2$  1.029,  $R$  (all data/obsd data) 0.071/0.045,  $wR^2$  (all data/obsd data) 0.118/0.110, residual  $\rho_{\text{max}}$  1.471/–1.838 e Å<sup>-3</sup>.

**1-Ethoxy-3-phenyl-6,7-dihydro-5H-pyrrolo[1,2-*a*]azepine (17) and 1-Ethoxy-3-phenyl-6,7,8,9-tetrahydro-5H-pyrrolo[1,2-*a*]azepine (18).** A 491 mg (1.00 mmol) amount of 1-(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dien-4-yl)-7-ethoxy-2,3,4,5-tetrahydro-1H-azepine (**10a**) in 3 mL of *n*-heptane was heated in a 5-mL screwtop vessel for 2 h at 90 °C. The solid was removed by centrifugation, and the solvent was evaporated at 20 °C to give a 1:1 mixture of compounds **17** and **18** (ca. 180 mg, 71%), which was



separated by chromatography on silica gel (**17**  $R_f$  = 0.5 in pentane/diethyl ether (20:1); **18**, 0.4; colorless crystals each).

**17.**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.30, 7.20, and 7.12 (2:2:1 H, m, Ph),



6.88 (1 H, dt,  $^3J$  = 12 Hz,  $^4J$  = 2, 9-H), 5.90 (1 H, s, 2-H), 5.30 (1 H, dt,  $^3J$  = 12 Hz,  $^3J$  = 4, 8-H), 3.85 (2 H, q,  $\text{OCH}_2$ ), 3.71 (2 H, m br, 5- $\text{H}_2$ ), 2.15 (2 H, m br, 7- $\text{H}_2$ ), 1.55 (2 H, m br, 6- $\text{H}_2$ ), 1.20 (3 H, t,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  146.6 ( $\text{C}_q$ , C1), 134.0 ( $\text{C}_q$ , *i*-C Ph), 132.4 ( $\text{C}_q$ , C3), 129.4, 128.3, and 126.9 (2:2:1, CH, Ph), 119.6 (CH, C8), 119.0 ( $\text{C}_q$ , C10), 117.1 (CH, C9), 97.2 (CH, C2), 66.5 ( $\text{OCH}_2$ ), 48.0 ( $\text{CH}_2$ , C5), 32.0 ( $\text{CH}_2$ , C7), 26.9 ( $\text{CH}_2$ , C6), 15.3 ( $\text{OCH}_2\text{CH}_3$ ). MS (70 eV),  $m/e$ : 253 (60) [ $\text{M}^+$ ], 224 (100) [ $\text{M}^+ - \text{Et}$ ].

**18.**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.35, 7.22, and 7.09 (2:2:1 H, m, Ph), 6.06 (1 H, s, 2-H), 3.90 (2 H, q,  $\text{OCH}_2$ ), 3.59 (2 H, m br, 5- $\text{H}_2$ ), 2.80 (2 H, m br, 9- $\text{H}_2$ ), 1.58 (2 H, m br, 7- $\text{H}_2$ ), 1.31 (2 H, m br, 8- $\text{H}_2$ ), 1.36 (2 H, m br, 6- $\text{H}_2$ ), 1.24 (3 H, t,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  143.0 ( $\text{C}_q$ , C1), 134.7 ( $\text{C}_q$ , *i*-C Ph), 129.8 ( $\text{C}_q$ , C3), 129.2, 128.2, and 126.4 (2:2:1, CH, Ph), 121.8 ( $\text{C}_q$ , C10), 97.5 (CH, C2), 67.1 ( $\text{OCH}_2$ ), 46.5 ( $\text{CH}_2$ , C5), 31.4, 30.1, 28.7, and 24.2 ( $\text{CH}_2$ , C6–C9), 15.6 ( $\text{OCH}_2\text{CH}_3$ ). MS (70 eV),  $m/e$ : 255 (60) [ $\text{M}^+$ ], 226 (100) [ $\text{M}^+ - \text{Et}$ ].

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**Supporting Information Available:** Tables of positional and displacement parameters, bond distances and angles, and hydrogen coordinates for (*E*)-**6b**, (*E*)-**10c**, and **14** (23 pages). Ordering information is given on any current masthead page.

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