Organic Syntheses via Transition Metal Complexes. 96.[1] 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

Rudolf Aumann,* Zhengkun Yu,† and Roland Fröhlich‡

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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Reaction of five- and six-membered *O*-alkyl lactims ∼$(CH_2)_n$−N=C(OR)∼ **5** (n = 3) and **7** (n = 4) with (1-alkynyl)carbene complexes $(CO)_5$M=C(OEt)C≡CPh **1** (**a**, M = Cr; **b**, 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 ∼$(CH_2)_n$−N=C(OR)∼ **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*.[2] 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 C=C(N) bond of an enamine.[3] 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 C=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 $(CO)_5$M=C(OEt)−C≡CPh **1** (M = Cr, W) with nitrogen bases N are initiated by addition of the nitrogen atom to the strongly electrophilic C≡C bond of **1** with formation of a zwitterionic carbiminium carbonylmetalate $^-(OC)_5$M−C(OEt)=C=C(Ph)N^+.[2b] 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 α-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),[1] 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 $(CO)_5$M=C unit, have gained our attention as candidates for ring-annelation and fragmentation reactions.[4] It should be noted that even though a number of reports dealing with the

* To whom correspondence should be addressed.
† On leave of absence from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, 116023 Dalian, China.
‡ X-ray crystal structure analyses.

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

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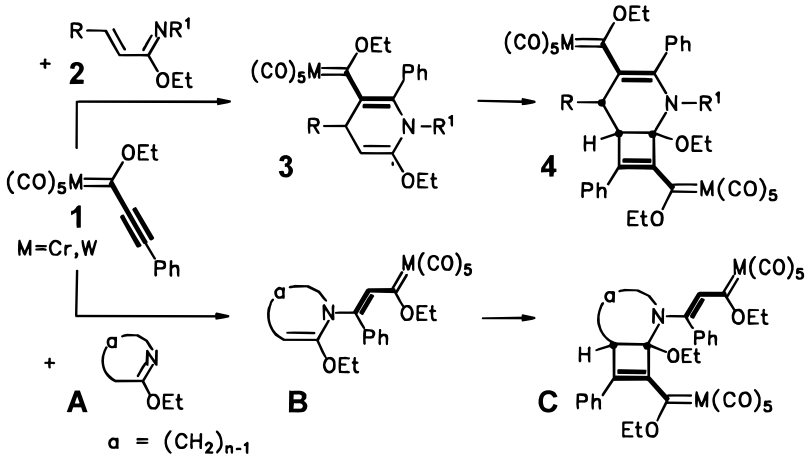
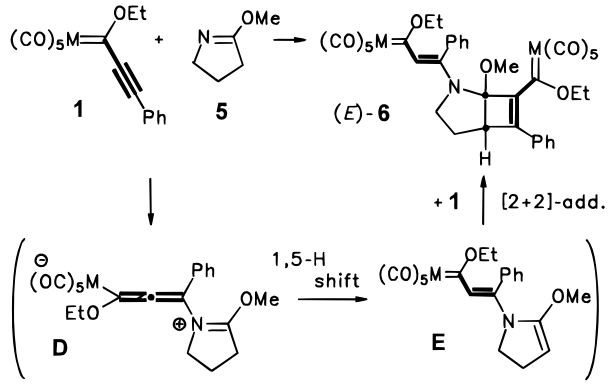
Scheme 1. Approaches to 1-Alkoxy-2-azabicyclo[*n*.2.0]alkenes 4 with Endo-, and C with Exocyclic 4-Amino-1-metalla-1,3-diene Units, Respectively



Scheme 2. Binuclear 2-Azabicyclo[3.2.0]heptenyl Carbene Complexes (*E*)-6a,b



1	M	6	M	[%]
a	Cr	a	Cr	90
b	W	b	W	94

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

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 $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**1a**, M = Cr; **1b**, 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, preciptate 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) C≡C bond of complex **1** to the (electron-rich) C=C(OMe)N bond. A reversed reaction sequence, involving initial formation of a cyclobutene derivative by [2 + 2] cycloaddition of the C≡C bond of the (1-alkynyl)carbene complex **1** to the C=C(OMe)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 M=C moieties are detected in the ^{13}C NMR spectra (**6a**, δ 346.2 and 307.9; **6b**, δ 317.6 and 280.9) and also that two [ν(C≡O)] A^1 bands are observed in the IR spectra, which are attributed to different $M(CO)_5$ groups (**6a**, 2063.6 cm^{-1} and 2048.1; **6b**, 2071.3 cm^{-1} and 2056.1). An NOE enhancement of the 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 W1−C1−C5−C6 metalladiene unit is twisted by −64.7(14)°, and the W2−C14−C13−C12 unit adopts an s-trans conformation with an interplanar angle of 174.2-(9)° (Table 1).

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(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.

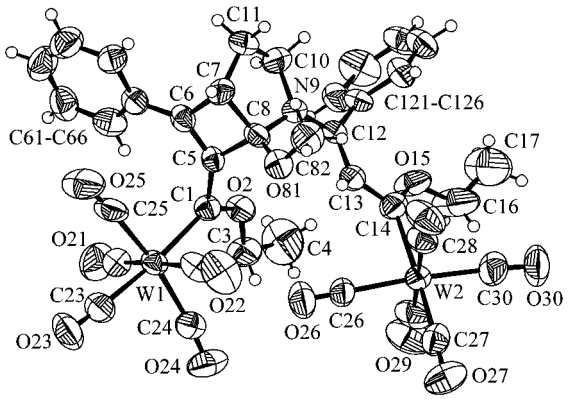
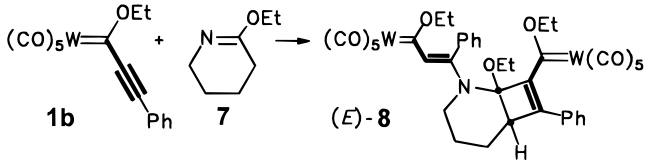


Figure 1. Molecular structure of the binuclear carbene complex (*E*)-**6b**.

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

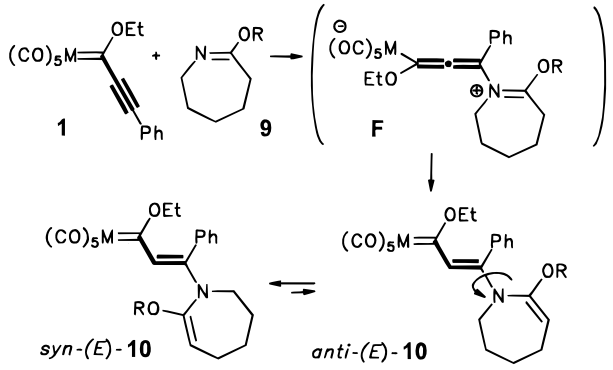


Binuclear 1-Alkoxy-2-azabicyclo[4.2.0]octene Derivative 8. The reaction of complex **1b** with the six-membered *O*-alkyl lactim **7** (6-ethoxy-2,3,4,5-tetrahydropyridine) proceeds in close analogy to that of **5** and leads to precipitation of the binuclear compound (*E*)-**8** in 89% yield in pentane 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 step (i.e., the annelation of the four-membered ring to the electron-rich C═C(OR)N bond of compound **B**).

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



1	M	10	M	R	*syn/anti*[a]
a	Cr	**a**	Cr	Et	-[b]
b	W	**b**	W	Me	4:1
		c	W	Et	2:1

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.

^{1}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

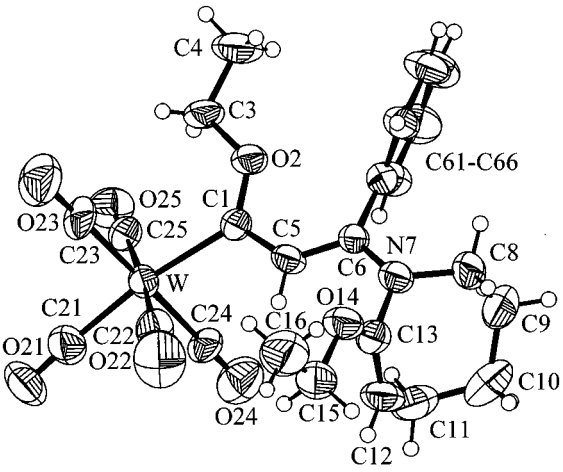
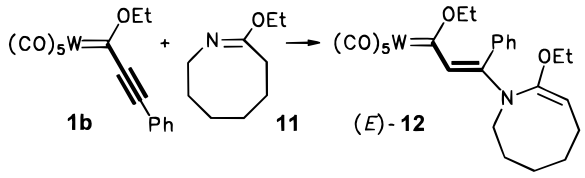


Figure 2. Molecular structure of mononuclear carbene complex *syn*-(*E*)-**10c**.

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



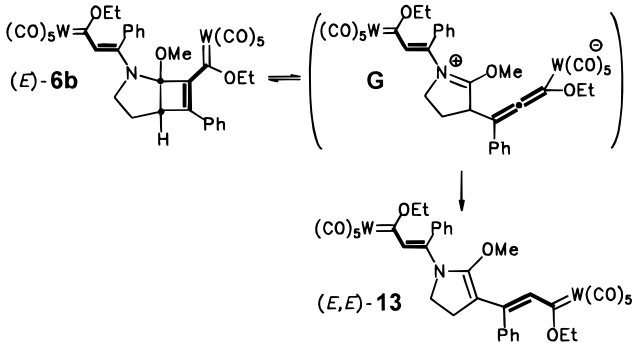
seven-membered ring (Figure 2). Since the interplanar angle of C6−N7−C13−O14 = 82.5(11)° indicates little (if no) π-interaction between the nitrogen atom and the adjacent C=C bond and, therefore, little "enamine character" of this unit, formation of a binuclear carbene complex by addition of compound **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 carbiminium carbonylmetalate $(^{-}OC)_5W-C=C-C=N^{+}$ rather than a (2-aminoalkenyl)carbene structure $(OC)_5W=C-C=C-N$.[7]

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**.

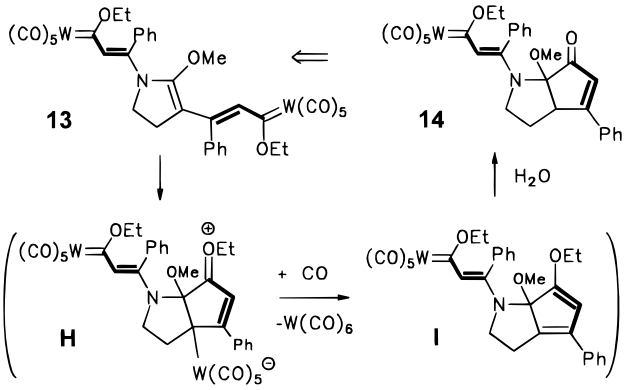
Rearrangement and Hydrolysis of Binuclear Compound 6b. Binuclear compounds **6** and **8** are not stable in solution and undergo fast transformations, especially under chromatography on silica gel. For example, attempted chromatography of (orange) compound **6b** leads to elution of three products: 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,-

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

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



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

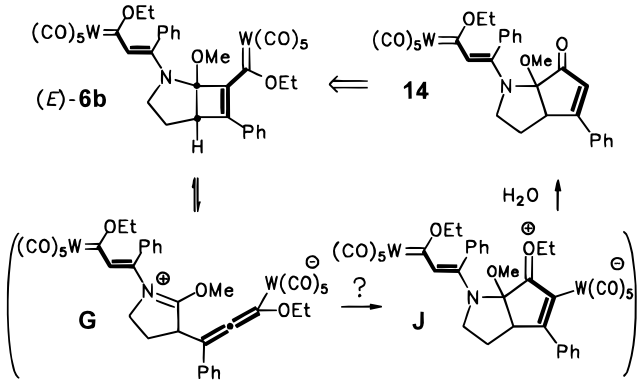


10-pentaene backbone, a yellow polar fraction of mononuclear 2-azabicyclo[3.3.0]octene derivative **14**, and an orange polar fraction of the binuclear amino acid derivative **15**. Compound (*E*,*E*)-**13** is generated from complex (*E*)-**6b**, obviously by a (1-cyclobutenyl)carbene/metallatriene rearrangement[1] 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.[3] 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 η^1-cyclopentadiene complex **H**.[3a]

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 6π 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-

Scheme 8. Consideration of an Alternate Mechanism for the Cyclopentenone Annelation Product 14



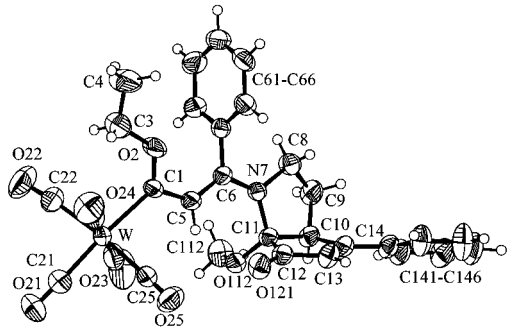


Figure 3. Molecular structure of cyclopentenone annelation product **14**.

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.[3a]

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 γ-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).

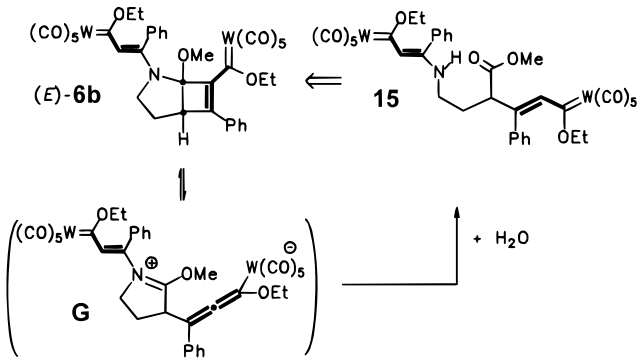
Fragmentation of Mononuclear Compound (*E*)-10a. Heating of the mononuclear compound (*E*)-**10a** to 90 °C for 2 h results in formation of a 1:1 mixture of dihydro- and tetrahydropyrrolo[1,2-*a*]azepines **17** and **18** along with $W(CO)_6$ (Scheme 10). The reaction is

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

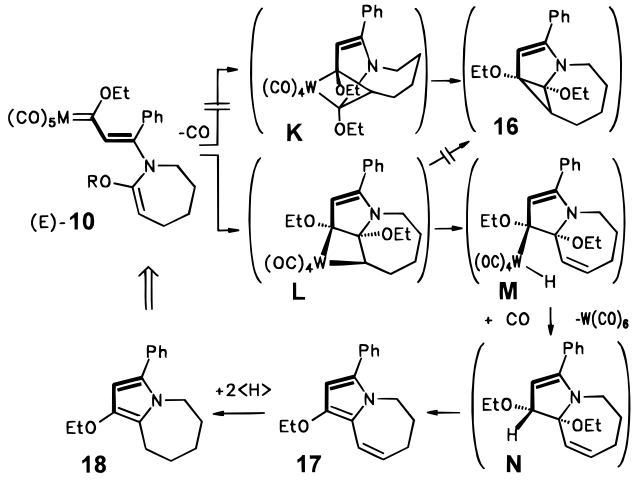
W−C(1)	2.233(6)	C(10)−C(14)	1.512(8)
C(1)−O(2)	1.336(7)	C(10)−C(11)	1.546(7)
C(1)−C(5)	1.413(8)	C(11)−O(111)	1.397(7)
O(2)−C(3)	1.449(8)	C(11)−C(12)	1.541(8)
C(3)−C(4)	1.408(12)	O(111)−C(112)	1.433(8)
C(5)−C(6)	1.379(8)	C(12)−O(121)	1.210(7)
C(6)−N(7)	1.364(7)	C(12)−C(13)	1.461(9)
C(6)−C(61)	1.491(7)	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



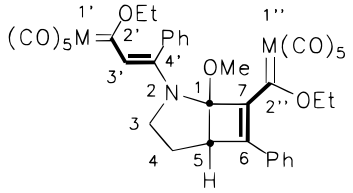
assumed to be initiated by elimination of CO and formation of a tungstacyclobutane **L**, which apparently undergoes β-elimination to give a metal hydride **M** faster than formation of a cyclopropane derivative **16** by reductive elimination. Even though a tungstacy-

clobutane **K**, which is a regioisomer of compound **L**, could be considered a precursor to compound **16**, since β-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. ^{1}H 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$_{F240}$, 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 lactims were generated by alkylation of the corresponding lactams with dimethyl sulfate,[8] and triethyl oxonium[9] tetrafluoborate, 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-

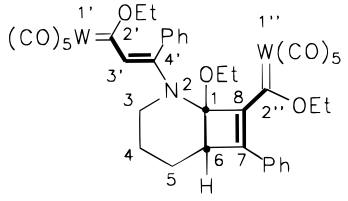


2-propyn-1-ylidene)chromium (**1a**) (350 mg, 1.00 mmol) and 1.5 mL of pentane in a 5-mL screwtop vessel was added at 20 °C a solution of 5-methoxy-3,4-dihydro-2*H*-pyrrole (**5**) (50 mg, 0.50 mmol) in 2 mL of pentane. The reaction was followed by TLC. After ca. 2.5 h, the orange precipitate is collected by centrifugation and washed with pentane (357 mg, 90%, orange crystals from 5:1 dichloromethane/pentane at −5 °C, mp 130 °C). ^{1}H NMR (C_6D_6/CS_2 5:1): δ 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_2), 4.34 and 4.14 (1:1 H, m, 2′-OCH_2), 3.29 (1 H, d, 5-H), 3.11 (3 H, s, OCH_3), 2.73 (2 H, m br, 3-H_2), 1.28 (3 H, t, 2′-OCH_2CH_3), 1.11 (2 H, m br, 4-H_2), 0.44 (3 H, t, 2″-OCH_2CH_3). ^{13}C NMR ($CDCl_3$/CS_2 5:1): δ 346.2 (C_q, $Cr^{1''}$=C), 307.9 (C_q, $Cr^{1'}$=C), 224.2 and 215.4 (C_q, 1:4, *trans*- and *cis*-CO, $Cr^{1'}(CO)_5$), 223.9 and 218.5 (C_q, 1:4, *trans*- and *cis*-CO,-$Cr^{1''}(CO)_5$), 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_2), 70.0 (2′-OCH_2), 48.4 (OCH_3), 44.1 (CH_2, C3), 41.0 (CH, C5), 18.9 (CH_2, C4), 11.0 (2′-OCH_2CH_3), 10.2 (2″-OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2063.6 (40), 2048.1 (30), 1997.5 (15), 1916.2 (100) [ν(C≡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). ^{1}H NMR ($CDCl_3$, 268 K): δ 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_2), 4.19 and 3.99 (1:1 H, m, 2′-OCH_2), 3.89 (1 H, d, 5-H), 3.58 (3 H, s, OCH_3), 3.09 (2 H, m br, 3-H_2), 1.78 (2 H, m br, 4-H_2), 1.69 (3 H, t, 2′-OCH_2CH_3), 0.59 (3 H, t, 2″-OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 317.6 (C_q, $W^{1''}$=C), 280.9 (C_q, $W^{1'}$=C), 203.9, 203.8, 199.0, and 196.2 (C_q, 2 $W(CO)_5$), 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_2), 76.1 (2′-OCH_2), 52.4 (OCH_3), 50.3 (CH_2, C3), 47.9 (CH, C5), 22.4 (CH_2, C4), 14.6 (2′-OCH_2CH_3), 13.6 (2″-OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2071.3 (33), 2056.1 (24), 1993.9 (14), 1909 (100) [ν(C≡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[10] (N_2-laser 337 nm, pulse length 3 ns, path 1 m, accuracy ± 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 × 0.40 × 0.30 mm, $a = 20.751(2)$ Å, $b = 10.943(1)$ Å, $c = 18.829(2)$ Å, $\beta = 115.30(1)°$, $V = 3865.5(7)$ Å^3, $\rho_{calc} = 1.827$ g cm^{-3}, $\mu = 60.11$ cm^{-1}, empirical absorption correction via φ scan data ($0.798 \le C \le 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 293$ K, ω scans, 8095 reflections collected ($\pm h$, $-k$, $-l$), [(sin θ)/λ] = 0.62 Å^{-1}, 7841 independent and 5313 observed reflections [$I \ge 2\sigma(I)$], 479 refined parameters, $R = 0.061$, w*R2* = 0.157, max (min) residual electron density 2.12 (−1.34) e Å^{-3}, 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-ethenyl)-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 (484 mg, 89%, orange crystals, mp 80 °C). ^{1}H

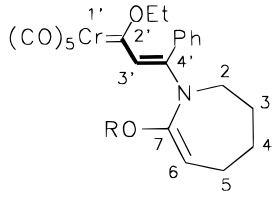
(8) Etienne, A.; Correia, Y. *Bull. Soc. Chim. Fr.* **1969**, 3704. (b) Benson, R. E.; Cairns, T. L. *J. Am. Chem. Soc.* **1948**, 70, 2115.

(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, Orléans-Ring 23, D-48149 Münster, Germany.

NMR ($CDCl_3$, solution freshly prepared at 233 K and immediately measured at 233 K): δ 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_2), 4.29 and 3.88 (1 H, m, diastereotopic 2′-OCH_2), 3.85 and 3.66 (1 H, diastereotopic 1-OCH_2), 3.80 (1 H, d, 6-H), 3.33, 2.82, 2.20, 1.85, 1.82, and 1.55 (1 H, 3-H_2, 4-H_2, and 5-H_2), 1.68, 1.40, and 0.70 (3 H, t, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 268 °C): δ 318.0 (C_q, W$^{1''}$=C), 292.8 (C_q, W$^{1'}$=C) 204.1 and 203.9 (*trans*-CO, $W(CO)_5$), 198.5 and 196.3 (*cis*-CO, $W(CO)_5$), 154.8, 154.3, and 154.0 (C_q, C4′, C7, and C8), 143.0 (CH, m br, C3′), 137.4 and 137.2 (C_q, *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_q, C1), 79.0 (2″-OCH_2), 77.8 (2′-OCH_2), 61.2 (1-OCH_2), 50.3 (NCH_2), 46.7 (CH_2, C5), 24.6 (CH_2, C4), 21.2 (CH_2, C5), 15.1, 14.8, and 13.8 (CH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2070.8 (42), 2059.3 (32), 1926.2 (100) [ν(C≡O)]. MALDI-TOF-MS:[10] 1093 (M^+ + 2), 1067, 1042, 610, 582, 521, 502, 436, 387. Anal. Calcd for $C_{39}H_{33}NO_{13}W_2$ (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-1*H*-azepine (10a). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-



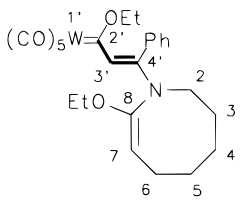
ylidene)chromium (**1a**) (350 mg, 1.00 mmol) and 7-ethoxy-3,4,5,6-tetrahydro-2*H*-azepine (**9b**) (141 mg, 1.00 mmol) in 2.0 mL of pentane were reacted as described above to give compound **10a** (420 mg, 89%, yellow crystals from 4:1 pentane/dichloromethane at −5 °C, mp > 90 °C, dec). ^{1}H NMR (C_6D_6/CS_2 5:1): δ 7.01−6.91 (5 H, m, Ph), 4.44 (1 H, m, 6-H), 4.23 (2 H, q, 2′-OCH_2), 3.30 (2 H, m br, 2-H_2), 3.00 (2 H, m br, 7-OCH_2), 1.93 (2 H, m br, 5-H_2), 1.14 (4 H, m br, 3-H_2 and 4-H_2), 0.87 (3 H, m br, 7-OCH_2CH_3), 0.42 (3 H, t, 2′-OCH_2CH_3). ^{13}C NMR ($CDCl_3$/CS_2 5:1): δ 304.3 (C_q, Cr=C), 224.0 and 218.4 (C_q, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 154.4 (C_q, C7), 149.3 (C_q, C4′), 147.8 (CH, C3′), 136.4 (C_q, *i*-C Ph), 128.1, 127.9, and 122.2 (2:2:1, CH, Ph), 95.3 (CH, C6), 73.7 (2′-OCH_2), 63.9 (7-OCH_2), 49.6 (CH_2, C2), 29.3 (CH_2, br, C5), 24.8 and 24.1 (CH_2 each, C3 and C4), 14.0 (7-OCH_2CH_3), 13.9 (2′-OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2047.2 (70), 1968.3 (40), 1920.5 (95), 1902.6 (100) [ν(C≡O)]. MS (70 eV), *m/e*: 491 (10) [M^+], 463 (8) [M^+ − CO], 407 (60) [M^+ − 3CO], 379 (20) [M^+ − 4CO], 351 (75) [M^+ − 5CO], 305 (65) [M^+ − 5CO − EtOH], 299 (5) [M^+ − $Cr(CO)_5$], 277 (64), 254 (70), 226 (65), 220 (65) [$Cr(CO)_6$], 180 (55), 146 (72), 129 (58), 115 (65), 94 (65), 67 (78), 55 (100). Anal. Calcd for $C_{24}H_{25}CrNO_7$ (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-1*H*-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-2*H*-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. ^{1}H NMR ($CDCl_3$, 268 K): δ 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_2), 3.52 [3.66] (3 H, s, OCH_3), 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_2CH_3). ^{13}C NMR ($CDCl_3$, 268 K): δ 279.7 [275.1] (C_q, W=C), 204.5 [208.2] and 199.1 [200.3] [C_q, $W(CO)_5$], 177.1 [161.5] (C_q, C7), 153.2 [154.9] (C_q, C4′), 141.2 [143.9] (CH, C3′), 135.7 [134.6] (C_q, *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_2), 55.8 [57.3] (OCH_3), 49.5 [49.9] (CH_2, C2), 32.2 [30.6] (CH_2, C5), 23.6 and 23.2 [25.9 and 25.6] (CH_2, C3 and C4), 13.8 [14.8] (OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2055.7 (80), 1966.0 (70), 1921.6 (97), 1905.9 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e*: 609 (12) [M^+], 525 (32), 497 (8), 469 (26), 440 (48), 351 (8), 253 (46), 224 (68), 119 (80), 91 (80), 68 (100). Anal. Calcd for $C_{23}H_{23}NO_7W$ (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-1*H*-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-2*H*-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. ^{1}H NMR ($CDCl_3$, 268 K): δ 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_2), 3.81 (2 H, m, 7-OCH_2 of both isomers), 3.18 [2.94] (2 H, m br, 2-H_2), 2.14 [2.01] (2 H, m br, 5-H_2), 1.48 [1.61] (2 H, m, m br, 3-H_2), 1.48 [0.87] (2 H, m br, 4-H_2), 1.34 (3 H, t, 7-OCH_2CH_3), 0.60 (3 H, t, 2′-OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 268 K): δ 279.1 [280.0] (C_q, W=C), 204.5 [204.3] and 199.2 [199.1] [C_q, $W(CO)_5$], 154.2 (C_q, C4′), 153.1 [153.0] (C_q, C7), 135.8 [136.8] (C_q, *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_2), 64.2 [63.5] (7-OCH_2), 49.4 [50.2] (CH_2, C2), 30.7 [26.5] (CH_2, C5), 25.0 [25.9] (CH_2, C4), 23.7 [24.1] (CH_2, C3), 14.2 (7-OCH_2CH_3), 13.7 [13.8] (2′-OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2056.0 (38), 1966.5 (19), 1903.7 (100) [ν(C≡O)]. MS (70 eV), ^{184}W, *m/e*: 623 (10) [M^+], 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 $C_{24}H_{25}NO_7W$ (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 $C_{24}H_{25}NO_7W$, 0.30 × 0.20 × 0.20 mm, a = 28.560(6) Å, b = 12.101(2) Å, c = 16.584(3) Å, β = 118.80(3)°, V = 5023-(2) Å^3, ρ_{calc} = 1.649 g cm^{-3}, μ = 46.41 cm^{-1}, empirical absorption correction via φ scan data (0.865 ≤ C ≤ 0.999), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.710 73 Å, T = 293 K, ω scans, 5188 reflections collected (+h, −k, ±l), [(sin θ)/λ] = 0.62 Å^{-1}, 5085 independent and 3688 observed reflections [$I \geq 2\sigma(I)$], 300 refined parameters, R = 0.060, wR^2 = 0.166, max (min) residual electron density 1.26 (−2.13) e Å^{-3}, 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-1*H*-azocine (12). Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-

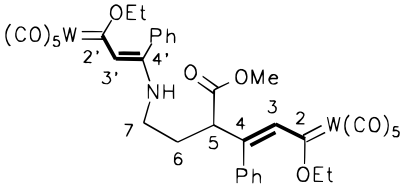


ylidene)tungsten (**1b**) (482 mg, 1.00 mmol) was reacted with 8-methoxy-2,3,4,5,6,7-hexahydroazocine (**11**) (155 mg, 1.00

mmol) as described above for 4 days to give compound **12** (380 mg, 60%, yellow crystals, mp 50−52 °C). ^{1}H NMR ($CDCl_3$): δ 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_2), 3.82 (2 H, m br, 2-H_2), 3.70 (2 H, q, 9-OCH_2), 2.66 (2 H, m br, 6-H_2), 1.81 (4 H, m br, 3-H_2 and 4-H_2), 1.65 (2 H, m br, 5-H_2), 1.49 (3 H, t, 9-OCH_2CH_3), 1.23 (3 H, t, 2′-OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 277.8 (C_q, W=C), 203.9 and 199.5 [1:4, C_q, *trans*- and *cis*-CO, $W(CO)_5$], 162.7 (C_q, C8), 154.9 (C_q, C4′), 143.8 (CH, C3′), 140.5 (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_2), 59.7 (9-OCH_2), 55.4 (CH_2, C2), 30.4 (CH_2, C6), 26.2 (CH_2, C3), 24.6 (CH_2, C4), 23.8 (CH_2, C5), 14.6 (9-OCH_2CH_3), 14.1 (2-OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2063.6 (47), 1967.9 (64), 1913.7 (100), 1899.1 (98). MS (70 eV), ^{184}W, *m/e*: 637 (1) [M^+], 553 (3), 469 (3), 421 (3), 365 (5), 268 (5), 126 (25), 83 (40), 57 (100). Anal. Calcd for $C_{25}H_{27}NO_7W$ (637.3): C, 47.09; H, 4.27; N, 2.20. Found: C, 46.48; H, 4.30; N, 1.97.

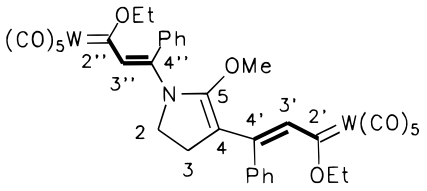
1,4-Bis(1,1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dien-4-yl)-5-methoxy-2,3-dihydropyrrol (13), 1-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dien-4-yl)-6a-methoxy-2,3,3a,6a-tetrahydro-1*H*-cyclopenta[b]pyrrol-6-one (14), (1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-buta-1,3-dienyl)-(1,1,1,1,1-pentacarbonyl-2-ethoxy-5-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}H NMR ($CDCl_3$): δ 9.08 (1 H, t, NH), 7.46−7.27, 7.10,



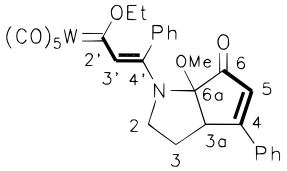
and 6.90 (10 H, m, 2 Ph), 7.08 (1 H, s, 3-H), 6.26 (1 H, s, 3′-H), 4.68 (2 H, m, 2-OCH_2), 4.42 (2 H, m, 2′-OCH_2), 3.67 (3 H, s, OCH_3), 3.22 (3 H, m, 5-H and 7-H_2), 2.08 and 1.77 (1:1 H, m, 6-H_2), 1.48 (3 H, t, 2′-OCH_2CH_3), 0.90 (3 H, t, 2-OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 312.5 (C_q, W=C), 270.8 (C_q, W′=C), 203.7 and 203.4 (C_q, *trans*-CO $W(CO)_5$), 199.2 and 196.9 (C_q, *cis*-CO $W(CO)_5$), 171.6 (C_q, CO_2Me), 157.9 and 157.6 (C_q, C4 and C4′), 145.2 (CH, C3), 138.8 (C_q, C3′), 136.7 and 134.1 (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_2), 76.6 (2′-OCH_2), 52.4 (OCH_3), 50.8 (CH, C5), 43.9 (NCH_2, C7), 31.9 (CH_2, C6), 15.6 and 13.5 (OCH_2CH_3). IR (diethyl ether), cm^{-1}: 3750−3400 (w, br, N−H), 2066.6 (70), 2057.3 (60), 1916.7 (100), 1902.3 (100) [ν(C≡O)], 1737.1 (30) [ν(C=O)]. MS (70 eV), ^{184}W *m/e*: 757 (1) [$M^+ - W(CO)_5$], 644 (1), 589 (2) [$M^+ - W(CO)_5 - 6CO$], 433 (17) [$M^+ - 2W(CO)_5$], 404 (97) [$M^+ - 2W(CO)_5 - Et$], 352 (42) [$W(CO)_6$], 296 (50), 254 (100), 244 (74), 212 (40), 194 (24), 184 (18), 57 (26). Anal. Calcd for $C_{37}H_{31}NO_{14}W_2$ (1081.4): C, 41.10; H, 2.89; N, 1.30. Found: C, 40.87; H, 3.03; N, 1.59.

13. ^{1}H NMR ($CDCl_3$): δ 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_2),



4.20 (2 H, q, 2″-OCH_2), 3.60, 3.10 and 2.65 (1:1:2 H, 2-H_2 and 3-H_2), 2.98 (3 H, s, OCH_3), 1.50 (3 H, t, 2′-OCH_2CH_3), 0.60 (3 H, t, 2″-OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 296.1 and 295.3 (C_q, W=C), 204.4 and 204.2 (C_q, *trans*-CO $W(CO)_5$), 198.5 and 198.0 (C_q, *cis*-CO $W(CO)_5$), 161.3 and 159.6 (C_q, C4′ and C5), 144.9 (C_q, C4′), 141.7 and 138.6 (CH, C3′ and C3″), 137.3 and 134.9 (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_2), 50.2 (OCH_3), 50.0 (NCH_2), 27.2 (NCH_2CH_2), 14.8 and 13.6 (OCH_2CH_3). IR (diethyl ether): 2070.1 (43), 2056.7 (80), 1928.0 (96), 1905.6 (100) [ν(C≡O)]. MS (70 eV), ^{184}W *m/e*: 1063 (1) [M^+], 654 (1), 598 (2), 570 (6), 415 (30) [$M^+ - 2W(CO)_5$], 386 (60).

14. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24 (1 H, s, 3′-H), 7.58



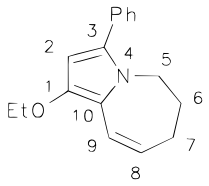
and 7.48 (2:3 H, m, 4-Ph), 7.33 and 7.08 (3:2 H, m broad each, 4′-Ph), 6.56 (1 H, d, ^4J = 1.2 Hz, 5-H), 4.19 and 4.11 (1:1 H, m, OCH_2), 4.02 (1 H, d, ^3J = 8.9 Hz, ^4J = 1.2 Hz, 3a−H), 3.58 (3 H, s, OCH_3), 3.12 and 2.82 (1 H, m, 2-H_2), 2.14 and 1.83 (1 H, m, 3-H_2), 0.59 (3 H, t, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 286.1 (C_q, W=C), 204.6 and 199.0 (1:4, C_q, *trans*- and *cis*-CO, $W(CO)_5$), 193.7 (C_q, C=O, C6), 168.4 (C_q, C4′), 149.2 (C_q, C4), 139.4 (C_q, *i*-C 4′-Ph), 131.9 (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 (C_q, C6a), 76.6 (OCH_2), 52.1 (OCH_3), 51.3 (CH, C3a), 50.1 (CH_2, C2), 25.7 (CH_2, C3), 13.8 (OCH_2CH_3). IR (diethyl ether), cm^{-1}: 2056.7 (55), 1969.7 (30), 1907.8 (100) [ν(C≡O)], 1715.3 (30) [ν(C=O)], 1598.2 (8)[ν(C=C)]. MS (70 eV), ^{184}W, *m/e*: 711 (1) [M^+], 627 (1) [$M^+ - 3CO$], 571 (1) [$M^+ - 5CO$], 544 (1), 516 (0.5), 387 (99) [$M^+ - W(CO)_5$], 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 $C_{30}H_{25}NO_8W \cdot CDCl_3$ (831.7) (obtained by recrystallization from $CDCl_3$): C, 44.82; H, 3.15; N, 1.69. Found: C, 44.96; H, 3.22; N, 1.92.

Crystal data and refinement details of compound **14**: formula $C_{30}H_{25}NO_8W \cdot CDCl_3$, 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, α = 75.54(1)°, β = 79.96(1)°, γ = 85.90(1)°, V = 1660.7(4) Å^3, diffractometer CAD4, temperature 293(2) K, λ = 0.710 73 Å, program used SCHAKAL-92, Z = 2, D_c = 1.661 g cm^{-3}, μ = 3.768 mm^{-1}, $F(000)$ = 816, crystal size 0.20 × 0.20 × 0.10 mm, θ limits 2.58−26.36°, empirical abs corr φ-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 ρ_{max} 1.471/−1.838 e Å^{-3}.

1-Ethoxy-3-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]azepine (17) and 1-Ethoxy-3-phenyl-6,7,8,9-tetrahydro-5*H*-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-1*H*-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}H NMR (C_6D_6): δ 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, OCH_2), 3.71 (2 H, m br, 5-H_2), 2.15 (2 H, m br, 7-H_2), 1.55 (2 H, m br, 6-H_2), 1.20 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 146.6 (C_q, C1), 134.0 (C_q, *i*-C Ph), 132.4 (C_q, C3), 129.4, 128.3, and 126.9 (2:2:1, CH, Ph), 119.6 (CH, C8), 119.0 (C_q, C10), 117.1 (CH, C9), 97.2 (CH, C2), 66.5 (OCH_2), 48.0 (CH_2, C5), 32.0 (CH_2, C7), 26.9 (CH_2, C6), 15.3 (OCH_2CH_3). MS (70 eV), *m*/*e*: 253 (60) [M^+], 224 (100) [$M^+ - Et$].

18. ^{1}H NMR (C_6D_6): δ 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, OCH_2), 3.59 (2 H, m br, 5-H_2), 2.80 (2 H, m br, 9-H_2), 1.58 (2 H, m br, 7-H_2), 1.31 (2 H, m br, 8-H_2), 1.36 (2 H, m br, 6-H_2), 1.24 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 143.0 (C_q, C1), 134.7 (C_q, *i*-C Ph), 129.8 (C_q, C3), 129.2, 128.2, and 126.4 (2:2:1, CH, Ph), 121.8 (C_q, C10), 97.5 (CH, C2), 67.1 (OCH_2), 46.5 (CH_2, C5), 31.4, 30.1, 28.7, and 24.2 (CH_2, C6−C9), 15.6 (OCH_2CH_3). MS (70 eV), *m*/*e*: 255 (60) [M^+], 226 (100) [$M^+ - Et$].

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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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