Organic Syntheses via Transition Metal Complexes. 95.[1] Rearrangement of (Cyclobutenyl)carbene Tungsten Complexes to 1-Tungsta-1,3,5-hexatrienes

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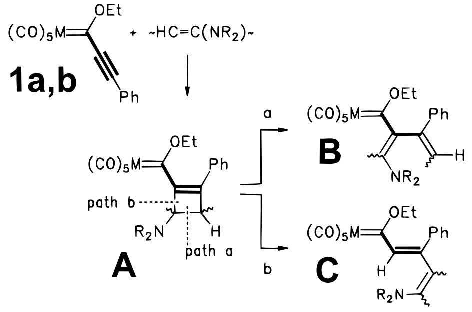
(Cyclobutenyl)carbene tungsten complexes are shown to rearrange to 1-tungsta-1,3,5-hexatrienes. Azabicyclo[4.2.0]octadiene (bis)carbene tungsten complexes **3a**−**c**, which served as model compounds in these studies, were generated by [4 + 2]- and [2 + 2] domino cycloaddition of 2 equiv of (1-alkynyl)carbene complex $(CO)_5W{=}C(OEt)C{\equiv}CPh$ (**1**) to alkenyl imidates $RCH{=}CHC(OEt){=}NR^1$ (**2a**−**c**) (R = Ph, Me; R^1 = Me, *i*-Pr). Compounds **3** are stable in the solid state at 20 °C but rearrange in solution to 1-metalla-1,3,5-hexatrienes **7a**−**c** by ring opening of the cyclobutene ring and subsequent 1,3 hydrogen migration. Compounds **3a** and **7b** were characterized by crystal structure analyses.

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (**1a**,**b**) (M = W, Cr) have been applied as building blocks in a manifold of reactions, which are potentially useful for organic synthesis.[2] It was found only recently that, for example, amino cyclopentadienes,[2a,3,4,6,7c] 2,3-homopyrroles,[7b] and pyran-2-ylidene complexes[5−7] are generated in high yields by addition of (1-alkynyl)carbene complexes **1** to tertiary enamines $-CH{=}C(NR_2)-$ and secondary enaminones, respectively.[7] Conjugated 6-amino-1-metalla-1,3,5-hexatrienes $(CO)_5M{=}C(OEt)$-$CH{=}C(Ph)C(-){=}C(NR_2)-$ (**C**) (Scheme 1, path b), resulting from addition of the enamine to the $C{\equiv}C$ bond of compound **1**, were shown to be key intermediates in these reactions. Other than tertiary enamines, reactions of tertiary enaminones with compounds **1** led to production of cross-conjugated metallahexatrienes $(CO)_5M{=}C(OEt)C[{=}C(NR_2){-}]C(Ph){=}CH{-}$(**B**) instead of conjugated 1-metalla-1,3,5-hexatrienes **C** by dichotomy of the $-CH{=}C(NR_2)-$ unit at the $C{\equiv}C$ bond of compound **1** involving (cyclobutenyl)carbene complexes **A** as intermeditates (Scheme 1, path a).[8]

We now report that (cyclobutenyl)carbene complexes of type **A** are precursors not only to cross-conjugated metallahexatrienes **B** but also to conjugated 1-metalla-1,3,5-hexatrienes **C**. While the former reaction mode (path a, Scheme 1) could easily be traced back from the stereochemistry of compounds **B**,[8] a more sophisticated molecular framework was required to prove existence of the latter reaction mode (path b). We finally considered bicyclic compounds **3**, in which a six-membered-ring tether is attached to the cyclobutene ring in order to suppress formation of the corresponding cross-conjugated metallatrienes **B** (by conrotatory ring opening) for reasons of ring strain, to be reasonable model compounds for the generation of conjugated 1-metalla-1,3,5-hexatrienes via reaction path b.

Scheme 1. Generation of Conjugated and Cross-Conjugated Metallatrienes via (Cyclobutenyl)carbene Complexes A (M = Cr, W)



Compounds **3** are readily available from reaction of alkenyl *N*-alkylimidates $RCH{=}CHC(OEt){=}NR^1$ (**2**) with 2 equiv of (1-alkynyl)carbene tungsten complex **1** (Scheme 2). Though the reaction principle leading to formation of a 2-azabicyclo[4.2.0]octa-3,7-diene bridge in compound **3** appears to be straightforward, to the best of our knowledge, addition of 2 equiv of an alkyne to an alkenyl imidate in this manner has not been reported before.

Alkenyl *N*-alkylimidates **2a**−**c** required as starting compounds for our investigation are most conveniently available by alkylation of alkenyl *N*-alkylamides **5** with triethyloxonium tetrafluoroborate.[9] The iminium salts

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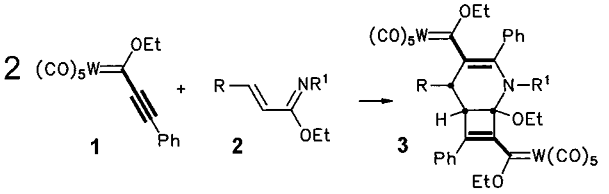
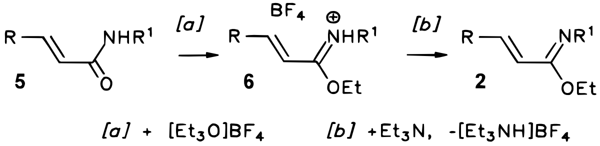
Scheme 2. Azabicyclo[4.2.0]octa-3,7-diene (Bis)carbene Complexes 3 by Domino [4 + 2] and [2 + 2] Cycloaddition

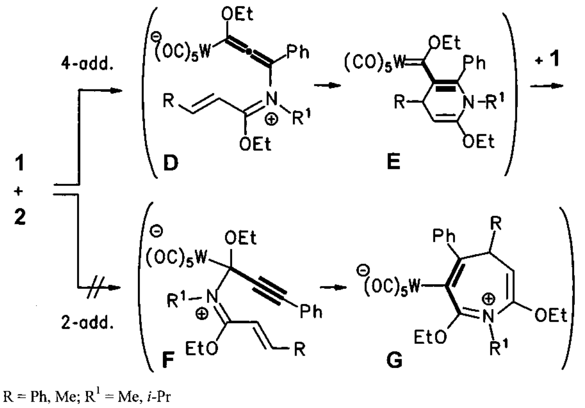


2,3	R	R1
a	Ph	Me
b	Ph	*i*-Pr
c	Me	Me

Scheme 3. Alkenyl Imidates 2 by Alkylation of Alkenyl Amides 5



Scheme 4. Iminium Carbonylmetalates as Precursors to Compounds 3



R = Ph, Me; R^1 = Me, *i*-Pr

6 which are generated in the first reaction step could be readily transformed into imidates **2** with triethylamine in dry diethyl ether (Scheme 3).

Formation of Azabicyclo[4.2.0]octadiene (Bis)carbene Complexes 3

On the basis of earlier reports, addition of an alkenyl imidate RCH=CHC(OEt)=NR^1 (**2**) to (1-alkynyl)carbene complex **1** is expected to form an iminium carbonyltungstate **A** in the first reaction step,[10] which readily undergoes cyclization to a dihydropyridinyl carbene complex **E** (Scheme 4). While dihydropyridinyl carbene complexes derived from addition of alkenyl imines RCH=CHCH=NR^1 to compound **1** are stable under the reaction conditions,[11,12] compounds **E** undergo fast [2 + 2] addition of the electron-rich C=C(OEt)N bond to the C≡C bond of compound **1** to give (cyclobutenyl)carbene tungsten complexes **3**. It should be noted that addition of the nitrogen atom of an imidate **2** to the W=C bond of compound **1** to give an iminium carbonyltungstate **F** and, subsequently, a zwitterionic 1-azonia-5*H*-cycloheptatrien-3-yl carbonyltungstate **G** has not been observed in this case, even though cycloadducts of type **G** were isolated as stable byproducts from addition of alkenyl imines to tungsten compound **1**.[12b,13]

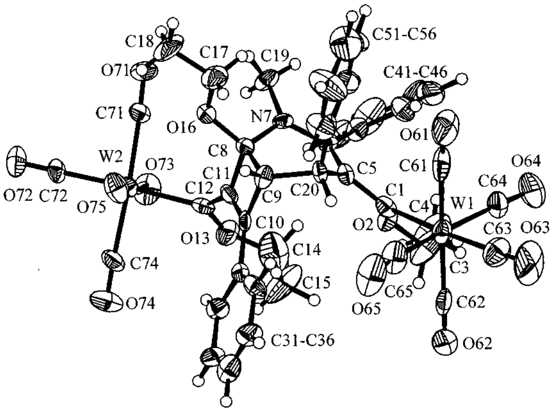


Figure 1. Molecular structure of azabicyclo[4.2.0]octadiene (bis)carbene complex **3a**.

Structure of Azabicyclo[4.2.0]octadiene (Bis)carbene Complexes 3

Compounds **3** exhibit ^{13}C NMR signals of two different carbene carbon atoms (e.g., **3a**: δ 316.4 and 315.2), both in a range observed with nonconjugated carbene tungsten complexes [e.g., $(CO)_5W{=}C(OEt)Ph$: δ 319.6]. It should be noted that the ^{13}C NMR signal of the W=C group in planar [(2-amino)ethenyl]carbene complexes, for example, (*Z*)-$(CO)_5W{=}C(OEt)CH{=}CPh(NHCH_2Ph)$, is appreciably shifted upfield (δ 270.8)[8] by capto-dative interaction according to the contribution of a polarized structure ($^{-}OC)_5WC(OEt){=}CHCPh({=}N^{+}HCH_3Ph)$. A polarization of this type is not possible in compounds **3** since the 1-tungsta-1,3-diene unit W=CC=C(N) is strongly distorted from planarity.[12] Structural details are based on the X-ray structure analysis of compound **3a** (Figure 1, Table 1). Due to steric constraint, both $(CO)_5W$ units are arranged exo with respect to the vaulted azabicyclo[4.2.0]octadiene moiety. The dihedral angle W2=C12–C11=C10 = 107.2(12)° of the 1-tungsta-1,3-diene unit as well as the pattern of alternating bond distances W2=C12 = 2.132(10) Å, C11–C12 = 1.463(13) Å, C10–C11 = 1.344(13) Å indicates that only little (or even no) π-conjugation is expected to operate within the (cyclobutenyl)carbene tungsten unit. On the basis of an essentially planar “enamine unit” C1–C5=C6–N7 = 166.3(9)°, delocalization of the lone pair on the nitrogen atom into the adjacent C=C(N) could be possible, but delocalization should be small as indicated by the relatively short distance C5=C6 = 1.390(13) Å and the long distance C6–N7 = 1.406(11) Å as well as by the dihedral angle W1=C1–C5=C6 = −149.1(8)°.

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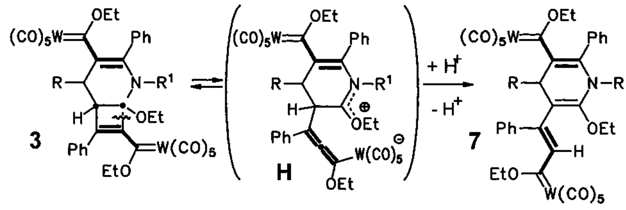
Table 1. Bond Lengths (Å) and Angles (deg) for Compound 3a

W1−C1	2.262(10)	C8−C11	1.513(13)
W2−C12	2.132(10)	C8−C9	1.528(13)
C4−C3	1.400(18)	C9−C10	1.507(13)
C3−O2	1.440(12)	C9−C20	1.564(12)
O2−C1	1.347(11)	C20−C51	1.541(13)
C1−C5	1.418(14)	C15−C14	1.521(18)
C5−C6	1.390(13)	C14−O13	1.361(16)
C5−C20	1.514(12)	O13−C12	1.337(11)
C6−N7	1.406(11)	C12−C11	1.463(13)
C6−C41	1.469(14)	C11−C10	1.344(13)
N7−C19	1.466(11)	C10−C31	1.468(13)
N7−C8	1.486(12)	O16−C17	1.430(11)
C8−O16	1.399(11)	C17−C18	1.499(14)

C4−C3−O2	111.7(11)	C10−C9−C8	86.0(7)
C1−O2−C3	124.9(8)	C10−C9−C20	119.0(8)
O2−C1−C5	108.2(8)	C8−C9−C20	113.1(8)
O2−C1−W1	124.2(7)	C5−C20−C51	116.1(8)
C5−C1−W1	127.5(7)	C5−C20−C9	108.9(7)
C6−C5−C1	121.7(9)	C51−C20−C9	108.6(8)
C6−C5−C20	117.7(9)	O13−C14−C15	108.7(13)
C1−C5−C20	120.6(9)	C12−O13−C14	128.8(11)
C5−C6−N7	119.3(9)	O13−C12−C11	116.3(9)
C5−C6−C41	124.6(9)	O13−C12−W2	120.3(7)
N7−C6−C41	115.7(8)	C11−C12−W2	123.2(7)
C6−N7−C19	123.2(8)	C10−C11−C12	134.5(9)
C6−N7−C8	117.9(8)	C10−C11−C8	92.7(8)
C19−N7−C8	117.2(8)	C12−C11−C8	132.7(9)
O16−C8−N7	109.1(7)	C11−C10−C31	136.4(9)
O16−C8−C11	113.4(8)	C11−C10−C9	94.3(8)
N7−C8−C11	112.2(8)	C31−C10−C9	128.6(9)
O16−C8−C9	117.5(8)	C8−O16−C17	116.1(8)
N7−C8−C9	116.1(8)	O16−C17−C18	107.7(9)
C11−C8−C9	87.0(7)		

Scheme 5. (Cyclobutenyl)carbene Tungsten to 1-Tungsta-1,3,5-hexatriene Rearrangement



The (Cyclobutenyl)carbene Tungsten to 1-Tungsta-1,3,5-hexatriene Rearrangement

Compounds **3** are a generated in a domino reaction by a [4 + 2] and a subsequent [2 + 2] cycloaddition (Scheme 2) under exceedingly mild conditions at 20 °C and are isolated by crystallization directly from the reaction mixture. They are stable in the solid state, but an attempt to separate compounds **3** from the reaction mixture by chromatography on silica gel results in fast isomerization of the azabicyclo[4.2.0]octadiene (bis)-carbene complexes **3** to 1-metalla-1,3,5-hexatrienes **7** (Scheme 5). This rearrangement, which can be followed by NMR spectra (e.g., in $CDCl_3$ at 20 °C: $t_{1/2}$ = ca. 4 h), is assumed to proceed either by protonation/deprotonation of the (cyclobutenyl)carbene unit of compound **3** or by protonation/deprotonation of an intermediate **H** derived thereof. Generation of a zwitterionic species **H** from compound **3** might be favored by the ability of a $W(CO)_5$ unit to powerfully stabilize negative charge. Since (aminocyclobutenyl)carbene intermediates could be structurally characterized, light is now shed on the mechanism by which 1-metalla-1,3,5-hexatrienes are formed on addition of enamines −HC=C(N)− to (1-alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W).[7] On the basis of results outlined in Scheme 5, it appears that a wide variety of other 1-metalla-1,3,5-hexatrienes, which have been obtained previously by addition of enamines −HC=C(N)− to the C≡C bond of (1-alkynyl)carbene complexes, might be generated similarly via cyclobutene precursors.

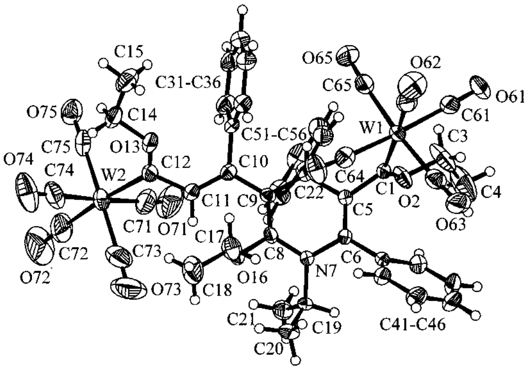


Figure 2. Molecular structure of the 1-metalla-1,3,5-hexatriene **7b**.

Table 2. Bond Lengths (Å) and Angles (deg) for Compound 7b

W1−C1	2.167(5)	C10−C31	1.503(6)
W2−C12	2.181(5)	C11−C12	1.482(7)
C1−O2	1.311(6)	C12−O13	1.306(6)
C1−C5	1.492(6)	O13−C14	1.447(6)
O2−C3	1.458(6)	C14−C15	1.477(8)
C3−C4	1.508(10)	O16−C17	1.450(6)
C5−C6	1.334(6)	C17−C18	1.498(7)
C5−C22	1.538(6)	C19−C21	1.501(7)
C6−N7	1.423(5)	C19−C20	1.523(7)
C6−C41	1.487(6)	C22−C51	1.525(6)
N7−C8	1.385(6)	C31−C32	1.380(7)
N7−C19	1.498(5)	C31−C36	1.382(7)
C8−C9	1.358(6)	C32−C33	1.375(7)
C8−O16	1.368(5)	C33−C34	1.361(9)
C9−C10	1.470(6)	C34−C35	1.375(9)
C9−C22	1.507(6)	C35−C36	1.394(8)
C10−C11	1.361(6)		

O2−C1−C5	106.1(4)	C10−C11−C12	126.5(5)
O2−C1−W1	133.8(3)	O13−C12−C11	109.1(4)
C5−C1−W1	120.1(3)	O13−C12−W2	132.5(4)
C1−O2−C3	121.4(4)	C11−C12−W2	118.4(4)
O2−C3−C4	106.8(5)	C12−O13−C14	121.6(4)
C6−C5−C1	122.5(4)	O13−C14−C15	106.6(5)
C6−C5−C22	122.1(4)	C8−O16−C17	112.3(4)
C1−C5−C22	115.1(4)	O16−C17−C18	108.0(5)
C5−C6−N7	121.5(4)	N7−C19−C21	111.0(4)
C5−C6−C41	123.7(4)	N7−C19−C20	114.0(4)
N7−C6−C41	114.2(4)	C21−C19−C20	112.7(4)
C8−N7−C6	117.1(4)	C9−C22−C51	113.2(4)
C8−N7−C19	118.3(4)	C9−C22−C5	110.8(4)
C6−N7−C19	117.5(3)	C51−C22−C5	113.2(4)
C9−C8−O16	122.2(4)	C32−C31−C36	119.0(5)
C9−C8−N7	125.2(4)	C32−C31−C10	122.2(4)
O16−C8−N7	112.6(4)	C36−C31−C10	118.7(4)
C8−C9−C10	122.0(4)	C33−C32−C31	120.6(5)
C8−C9−C22	119.3(4)	C34−C33−C32	120.5(6)
C10−C9−C22	118.7(4)	C33−C34−C35	120.1(6)
C11−C10−C9	121.3(4)	C34−C35−C36	119.7(6)
C11−C10−C31	122.3(4)	C31−C36−C35	120.1(5)
C9−C10−C31	116.0(4)		

Structure of 1-Tungsta-1,3,5-hexatrienes 7

Isomerization of a (cyclobutenyl)carbene tungsten compound **3** to a 1-metalla-1,3,5-hexatriene **7** results in an upfield shift of the W=C signal in the ^{13}C NMR spectrum of the 1-metalla-1,3,5-hexatriene (e.g., **7b**: δ

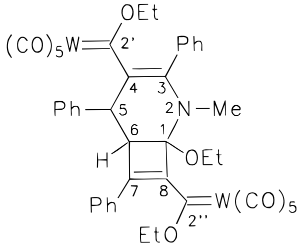
302.1) compared to the corresponding (cyclobutenyl)carbene tungsten complex **3** (e.g., **3b**: δ 315.2). Unambiguous structural proof of compound **7b** is given by an X-ray structure analysis (Figure 2, Table 2). The pattern of alternating bond distances W1═C1 = 2.167(5) Å, C1−C5 = 1.492(6) Å, C5═C6 = 1.334(6) Å, and C6−N7 = 1.423(5) Å and the dihedral angles W1═C1−C5═C6 = −88.4(5)° and C1−C5═C6−N7 = 166.4(4)° are similar to those of compound **3a**. Furthermore, the carbon skeleton of the newly formed 1-metalla-1,3,5-hexatriene unit of compound **7b** exhibits the expected pattern of alternating bond distances: W2═C12 = 2.181(5) Å, C12−C11 = 1.482(7) Å, C10═C11 = 1.361(6) Å, C9−C10 = 1.470(6) Å, C8═C9 = 1.358(6) Å, and N7−C8 = 1.385(6) Å. Except for the unit W2═C12−C11═C10 [dihedral angle 146.5(4)°], the 1-metalla-1,3,5-hexatriene skeleton is almost planar: C12−C11═C10−C9 = 176.9(5)°, C11−C10−C9−C8 = −32.5(7)°, C10−C9−C8−N7 = −178.2(4)° (Figure 2).

Experimental Section

All operations were performed under an atmosphere of dry argon. Solvents were dried prior to use. Melting points are not corrected. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were obtainend with Bruker ARX 300, Bruker AM 360, and Varian U 600 spectrometers [C,H ^1J, ^2J, and ^3J coupling). Chemical shifts refer to $\delta_{TMS} = 0.00$ ppm). Other analyses: IR Digilab FTS 45; MS Finnigan MAT 312; elemental analysis; Perkin-Elmer 240 elemental analyzer; TLC, 3Merck DC-Alufolien Kieselgel 60 F_{254}. R_f values refer to TLC tests. Column chromatographic purification was achieved with Merck Kieselgel 100.

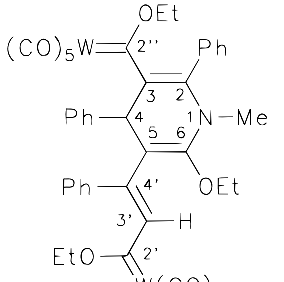
4,8-Bis(2-ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-1-ethoxy-2-methyl-3,5,7-triphenylazabicyclo[4.2.0]-octa-3,7-diene (3a) and 3-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-5-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadien-4-yl)-6-ethoxy-1-methyl-4-phenyl-1,4-dihydropyridine (7a). *N*-Methyl cinnamamide (**5a**) (209 mg, 1.30 mmol) is reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol) in 2 mL of dry dichloromethane in a 5-mL screwtop vessel with stirring at 20 °C. Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (964 mg, 2.00 mmol) is added to the mixture after 3 h, and stirring is continued for 2 min. Triethylamine (202 mg, 2.00 mmol) in 2 mL of dichloromethane is added dropwise with stirring at 0 °C, and the reaction progress is followed by TLC. After compound **1** has been consumed completely (ca. 4 h), the mixture is cooled to −15 °C to give dark-red crystals of compound **3a** (530 mg, 46%, $R_f = 0.6$ in pentane/dichloromethane, 2:1). Chromatography of **3a** on silica gel with pentane/diethyl ether (20:1) affords violet compound **7a** as the only detectable product ($R_f = 0.6$ in pentane/dichloromethane, 2:1, violet crystals, mp 145 °C). According to the ^{1}H NMR spectrum, a smooth conversion of **3a** to **7a** is observed in $CDCl_3$ solution ($t_{1/2}$ = ca. 4 h at 20 °C).

3a. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43−7.32 (15 H, m, 3 Ph), 5.12 (1 H, s, dynamically broadened, 5-H), 4.95 and 4.90 (1 H each, dynamically broadened signals, 2″-OCH_2), 4.03 and 3.90 (1 H each, dynamically broadened signals, 2′-OCH_2), 3.92 (1 H, s, 6-H), 2.90 and 2.70 (1 H each, dynamically broadened signals, 1-OCH_2), 2.60 (3 H, s, NCH_3), 1.76 (3 H, t broad, CH_3, 1-OEt), 1.00 and 0.76 (3 H each, t each, CH_3 each, 2′-OEt and 2″-OEt). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 316.4 and 315.2 (Cq each, W═*C* each), 204.2 and 201.7 [*trans*-CO, $W(CO)_5$], 197.9 and 196.6 [*cis*-CO, $W(CO)_5$], 157.4 [Cq, C═*C*(N), C3], 143.9, 143.5, 142.3, 141.6, 133.9, and 131.9 (Cq each, C4, C7, C8, 3 *i*-C Ph), 129.0−127.6 (CH each, 3 Ph), 100.7 (Cq, C1), 79.4 (2″-OCH_2), 77.8 (2′-OCH_2 broad), 61.8 (1-OCH_2), 56.2 (CH, C5), 45.2 (CH, C6), 33.4 (NCH_3), 14.9, 14.8, and 14.3 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2061.5 (20), 1973.0 (5), 1938.1 (100) [ν(C≡O)]. Anal. Calcd for $C_{44}H_{35}NO_{13}W_2$ (1153.4): C, 45.82; H, 3.06; N, 1.21. Found: C, 45.90; H, 3.36; N, 1.40.



X-ray crystal structure analysis of **3a**: formula $C_{44}H_{35}NO_{13}W_2$, $M = 1153.43$, $0.25 \times 0.20 \times 0.20$ mm, $a = 19.316(2)$ Å, $b = 37.348(5)$ Å, $c = 11.996(2)$ Å, $V = 8654(2)$ Å^3, $\rho_{calc} = 1.771$ g cm^{-3}, $\mu = 53.77$ cm^{-1}, empirical absorption correction via φ scan data ($0.973 \leq C \leq 0.999$), $Z = 8$, orthorhombic, space group *Pccn* (No. 56), $\lambda = 0.710\ 73$ Å, $T = 223$ K, ω scans, 7609 reflections collected ($-h$, $-k$, $-l$), [(sin θ)/λ] = 0.59 Å^{-1}, 7609 independent and 4243 observed reflections [$I \geq 2\sigma(I)$], 545 refined parameters, R1 = 0.042, wR2 = 0.093, maximum residual electron density 1.12 (−1.56) e Å^{-3} close to W, hydrogens calculated and riding. All data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, DIAMOND.

7a. ^{1}H NMR (C_6D_6): δ 7.68 (1 H, s, 3′-H), 7.36−6.90 (15 H, m, 3 Ph), 7.12 and 7.00 (1 H each, “t” each, *p*-H Ph each), 7.14−7.04 (5 H, dynamically broadened signal of 4′-Ph), 4.90 (1 H, s, 4-H), 4.30−4.10 (4 H, m, 2′-OCH_2 and 2″-OCH_2), 3.65 and 3.25 (1 H each, m each, diastereotopic 6-OCH_2), 2.38 (3 H, NCH_3), 0.86, 0.65, and 0.48 (3 H each, CH_2CH_3 each). ^{13}C NMR (C_6D_6): δ 319.3 and 302.1 (Cq each, W═*C* each), 204.4 and 202.6 [*trans*-CO, $W(CO)_5$], 198.5 and 197.0 [*cis*-CO, $W(CO)_5$], 176.4 (Cq, C6), 157.7 [Cq, C═*C*(N), C2], 144.3 (CH, C3′), 143.1, 142.0, 140.1, 134.2, and 131.8 (Cq each, C3, C4′, and 3 *i*-C Ph), 129.4−127.3 (CH each, 3 Ph), 100.8 (Cq, C5), 79.6 and 78.3 (CH_2 each, 2″-OCH_2 and 2′-OCH_2), 69.0 (6-OCH_2), 47.2 (CH, C4), 34.5 (NCH_3), 14.5, 14.3, and 13.6 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2070.8 (20), 2060.1 (20), 1982.4 (5), 1958.5 (80), 1932.2 (100) [ν(C≡O)]. Anal. Calcd for $C_{44}H_{35}NO_{13}W_2$ (1153.4): C, 45.82; H, 3.06; N, 1.21. Found: C, 45.65; H, 3.12; N, 1.33.



4,8-Bis(2-ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-1-ethoxy-2-isopropyl-3,5,7-triphenylazabicyclo[4.2.0]-octa-3,7-diene (3b) and 3-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-5-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadien-4-yl)-6-ethoxy-1-isopropyl-4-phenyl-1,4-dihydropyridine (7b). *N*-Isopropyl cinnamamide (**5b**) (248 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (964 mg, 2.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above to give compound **3b** (649 mg, 55%, $R_f = 0.6$ in pentane/dichloromethane, 2:1, red crystals, mp 145

°C), which on isomerization affords compound **7b** (633 mg, 98%, $R_f = 0.6$ in pentane/dichloromethane, 2:1, violet crystals, mp 123 °C).

3b. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.52−7.30 (15 H, m, 3 Ph), 5.19 (1 H, s, dynamically broadened, 5-H), 5.00 and 4.84 (1 H each, dynamically broadened signals, 2″-OCH_2), 4.00 and 3.85 (1 H each, dynamically broadened signals, 2′-OCH_2), 3.90 (1 H, s, 6-H), 2.90 and 2.70 (1 H each, dynamically broadened signals, 1-OCH_2), 2.82 (1 H, sept, NCH), 1.70 (3 H, t broad, CH_3, 1-OEt), 1.20 and 0.84 [3 H each, d each, $C(CH_3)_2$], 1.00 and 0.74 (3 H each, t each, CH_3 each, 2′-OEt and 2″-OEt). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 315.2 and 313.2 (Cq each, W═*C* each), 204.1 and 201.7 [*trans*-CO, $W(CO)_5$], 197.8 and 196.6 [*cis*-CO, $W(CO)_5$], 152.3 [Cq, C═*C*(N), C3], 144.8, 142.6, 142.0, 141.3, 134.7, and 130.8 (Cq each, C4, C7, C8, 3 *i*-C Ph), 129.0−127.6 (CH each, 3 Ph), 98.8 (Cq, C1), 79.0 (2″-OCH_2), 78.0 (2′-OCH_2 broad), 61.4 (1-OCH_2), 56.2 (CH, C5), 45.3 ($CHMe_2$), 45.0 (CH, C6), 21.7 and 21.0 [$N(CH_3)_2$]; 14.9, 14.7, and 14.4 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2060.9 (20), 1973.6 (5), 1938.6 (100) [ν(C≡O)]. Anal. Calcd for $C_{46}H_{39}NO_{13}W_2$ (1181.5): C, 46.76; H, 3.33; N, 1.19. Found: C, 46.53; H, 3.36; N, 1.20.

7b. ^{1}H NMR (C_6D_6): δ 7.79 (1 H, s, 3′-H), 7.36 and 7.31 (2 H each, “d” each, *o*-H Ph each), 7.26 and 7.08 (2 H each, “t” each, *m*-H Ph each), 7.12 and 7.00 (1 H each, “t” each, *p*-H Ph each), 7.14−7.04 (5 H, dynamically broadened signal of 4′-Ph), 5.00 (1 H, s, 4-H), 4.18 (2 H, m, 2′-OCH_2), 4.16 (1 H, sept, CHN), 4.03 (2 H, m, 2″-OCH_2), 3.65 and 3.35 (1 H each, m each, diastereotopic 6-OCH_2), 0.95 and 0.85 [3 H each, diastereotopic $C(CH_3)_2$], 0.81, 0.75, and 0.49 (3 H each, CH_2CH_3 each). ^{13}C NMR (C_6D_6): δ 320.4 and 302.8 (Cq each, W═*C* each), 204.3 and 202.4 [*trans*-CO, $W(CO)_5$], 197.0 and 198.4 [*cis*-CO, $W(CO)_5$], 176.2 (Cq, C6), 158.2 [Cq, C═*C*(N), C2], 144.5 (CH, C3′), 144.3, 140.9, 140.3, 135.7, and 133.3 (Cq each, C3, C4′, and 3 *i*-C Ph), 129.6−127.2 (CH each, 3 Ph), 103.2 (Cq, C5), 79.4 and 78.2 (CH_2 each, 2″-OCH_2 and 2′-OCH_2), 69.9 (6-OCH_2), 52.6 (HCN), 46.8 (CH, C4), 23.0 and 21.5 [diastereotopic $C(CH_3)_2$]; 14.6, 14.2, and 13.6 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2064.1 (20, broad), 1981.0 (5), 1938.6 (100, broad) [ν(C≡O)]. Anal. Calcd for $C_{46}H_{39}NO_{13}W_2$: C, 46.76; H, 3.33; N, 1.19. Found: C, 46.60; H, 3.09; N, 1.08.

X-ray crystal structure analysis of **7b**: formula $C_{46}H_{39}NO_{13}W_2$, $M = 1181.47$, 0.40 × 0.30 × 0.20 mm, $a = 11.936(1)$ Å, $b = 12.798(1)$ Å, $c = 15.314(1)$ Å, $\alpha = 93.91(1)°$, $\beta = 94.00(1)°$, $\gamma = 97.24(1)°$, $V = 2308.0(3)$ Å^3, $\rho_{calc} = 1.700$ g cm^{-3}, $\mu = 50.43$ cm^{-1}, empirical absorption correction via φ scan data ($0.829 \leq C \leq 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 9808 reflections collected ($-h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 9341 independent and 6744 observed reflections [$I \geq 2\sigma(I)$], 564 refined parameters, R1 = 0.032, wR2 = 0.073, maximum residual electron density 1.89 (−1.99) e Å^{-3} close to W, hydrogens calculated and riding. All data sets were collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93; graphics, DIAMOND.

4,8-Bis(2-ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-1-ethoxy-2,5-dimethyl-3,7-diphenylazabicyclo[4.2.0]-octa-3,7-diene (3c) and 3-(2-Ethoxy-1,1,1,1,1-pentacarbonyl-1-tungstaethen-2-yl)-5-(2-ethoxy-4-phenyl-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadien-4-yl)-6-ethoxy-1,4-dimethyl-1,4-dihydropyridine (7c). *N*-Methyl crotonamide (**5c**) (129 mg, 1.30 mmol) is successively reacted with triethyloxonium tetrafluoroborate (285 mg, 1.50 mmol), pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene)tungsten (**1**) (964 mg, 2.00 mmol), and triethylamine (202 mg, 2.00 mmol) as described above to give compound **3c** (424 mg, 39%, $R_f = 0.6$ in pentane/dichloromethane, 2:1, red crystals), which on isomerization affords compound **7c** (400 mg, 94%, $R_f = 0.6$ in pentane/dichloromethane, 2:1, violet crystals).

3c. ^{1}H NMR (C_6D_6): δ 7.25−7.00 (10 H, m, 2 Ph), 4.45 (2 H, q, 2″-OCH_2), 3.95 (3 H, m, 2′-OCH_2 and 5-H), 3.30 (1 H, s, 6-H), 3.20 (2 H, m, 1-OCH_2), 2.29 (3 H, s, NCH_3), 1.29 (3 H, d, ^3J = 7 Hz, 5-CH_3), 1.18, 1.12, and 0.56 (3 H each, t each, CH_2CH_3 each). ^{13}C NMR (C_6D_6): δ 322.8 and 318.8 (Cq each, W═*C* each), 204.2 and 202.9 [*trans*-CO, $W(CO)_5$], 198.9 and 197.3 [*cis*-CO, $W(CO)_5$], 157.4 (Cq, C═*C*(N), C3], 138.4, 138.2, 138.1, 131.4, and 130.0 (Cq each; C4, C7, C8, 2 *i*-C Ph); 129.9, 129.0, 130.3, 129.6, 129.3, and 129.1 (1:1:2:1:2:1, CH each, 2 Ph), 93.1 (Cq, C1), 78.4 (2″-OCH_2 broad), 77.4 (2′-OCH_2), 61.7 (1-OCH_2), 53.9 (CH, C5), 46.6 (CH, C6), 33.4 (NCH_3), 20.5 (5-CH_3), 14.9, 14.5, and 14.2 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2070.6 (20), 2060.7 (20), 1982.7 (5), 1954.4 (80), 1932.1 (100) [ν(C≡O)]. Anal. Calcd for $C_{39}H_{33}NO_{13}W_2$ (1091.4): C, 42.92; H, 3.05; N, 1.28. Found: C, 42.67; H, 3.33; N, 1.36.

7c. ^{1}H NMR (C_6D_6): δ 7.86 (1 H, s, 3′-H), 7.15−6.90 (10 H, m, 2 Ph), 4.30−4.20 (4 H, m, 2′-OCH_2 and 2″-OCH_2), 4.16 (1 H, q, 4-H), 3.60 and 3.35 (1 H each, m each, diastereotopic 6-OCH_2), 2.35 (3 H, s, NCH_3), 1.35 (3 H, d, 4-CH_3), 1.00, 0.90, and 0.51 (3 H each, CH_2CH_3 each). ^{13}C NMR (C_6D_6): δ 319.1 and 298.3 (Cq each, W═*C* each), 204.4 and 202.9 [*trans*-CO, $W(CO)_5$], 198.9 and 196.0 [*cis*-CO, $W(CO)_5$], 169.1 (Cq, C6), 158.2 [Cq, C═*C*(N), C2], 145.3 (CH, C3′), 142.4, 142.1, 134.0, and 132.6 (Cq each, C3, C4′ and 2 *i*-C Ph), 129.5−127.4 (CH each, 3 Ph), 103.5 (Cq, C5), 81.6 and 78.2 (CH_2 each, 2″-OCH_2 and 2′-OCH_2), 68.5 (6-OCH_2), 42.7 (CH, C4), 31.4 (NCH_3), 22.7 (4-CH_3), 15.2, 14.4, and 13.7 (3 CH_2CH_3). IR (hexane), cm^{-1}: 2070.2 (20), 2060.3 (20), 1983.4 (5), 1958.5 (80), 1932.1 (100) [ν(C≡O)]. Anal. Calcd for $C_{39}H_{33}NO_{13}W_2$ (1091.4): C, 42.92; H, 3.05; N, 1.28. Found: C, 42.76; H, 3.16; N, 1.26.

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Supporting Information Available: Tables of positional and displacement parameters, bond distances and angles, and hydrogen coordinates for compounds **3a** and **7b** (21 pages). Ordering information is given on any current masthead page.

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